

Wavelengths, radiation damage and anomalous
dispersion — ways to optimise small-molecule X-ray
crystallography



Dissertation

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Universität Regensburg

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Publications

The content of this thesis was created within the period from November 2022 until June 2026 at the Faculty for Chemistry & Pharmacy at the University of Regensburg under the supervision of Prof. Dr. Nikolaus Korber and Dr. Michael Bodensteiner.

The following is a list of all publications to which the author of this thesis contributed during this time, including the chapters 4, 5, 6, 7, and 9 of this thesis, which have already been published. The chapters 3, and 8 have been submitted for publication. The chapters 1, 3, and 10 put the work into context.

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21. Weissenborn T.*, Hennig C., Leifermann L., Hanemann P., Bright E.L., **Meurer F.**, Lehnert A., Kvashnina K., Walther C. (2026): X-ray diffraction phase analysis of single hot particles from Chornobyl. In: Journal of Hazardous Materials, 505, 141533.
20. **Meurer F.***, Kleemiss F., Br  x D., Hischa B., Koch A.-C., Bodensteiner M.* (2025): SISYPHOS: An automatic procedure for the serial refinement of single-crystal diffraction data in Olex2. In: Structural Dynamics, 12, 5, 054102. (Chapter 9)
19. Rabor J.T., Mangedani Z., Aboonajmi J., Rastegari B., Hosseini F.N., **Meurer F.**, Bodensteiner M., Hoseini S.J., Nabavizadeh S.M.* (2025): Mitochondria-Targeted Benzoxazole-Based Platinum Photosensitizer Complexes: Photophysical Properties and Photocytotoxicity Evaluation Against Breast and Gastric Cancer Cells. In: Journal of Medicinal Chemistry, 68, 16, 17065–17086.

18. Br  x D., **Meurer F.**, Kleemiss F.* (2025): Benchmarking crystal structure refinement: A systematic study on Hirshfeld atom refinement. In: *Structural Dynamics*, 12, 5, 054101.
17. Riesinger C., **Meurer F.**, Zimmermann L., D  tsch L., Scheer M.* (2025): Strain-Release Driven Arsenium Ion Bond Insertion. In: *Angewandte Chemie International Edition*, 64, 35, e202510186.
16. **Meurer F.**, Schimpf M., Kleemiss F., Hischa B., Rehbein J., Hennig C., Bodensteiner M.* (2025): Synthesis and quantum crystallographic evaluation of WYLID: YLID’s red rival. In: *Journal of Applied Crystallography*, 58, 678–687. (Chapter 5)
15. Kleemiss F.*, **Meurer F.**, Shenderovich I.G., Bodensteiner M. (2025): The use of effective core potentials in Hirshfeld atom refinement: making quantum crystallography faster in NoSpherA2. In: *Journal of Applied Crystallography*, 58, 374–382.
14. Hauer S., Bal  zs G., Gliese F., **Meurer F.**, Downie T.M.H., Hennig C., Weigand J.J., Wolf R.* (2024): Functionalization of Tetraphosphido Ligands by Heterocumulenes. In: *Inorganic Chemistry*, 63, 43, 20141–20152.
13. Stanic P., Smokrovi K., Maltar-Strmecki N., Herak M., **Meurer F.**, Bodensteiner M., Hennig C., Molcanov K.* (2024): Structural Variety of Extended Arrays of Pancake-Bonded TCNQ Radicals: Steric Effect of the Bulky Cations. In: *Crystal Growth & Design*, 24, 22, 9365–9378.
12. Williem E.S., Amro A., Ibrahim A.B.M.*, Elkhaliq S.A., **Meurer F.**, Bodensteiner M., Abbas S.M. (2024): Cobalt complexes with bidentate (NO) versus monodentate (N) salicylaldimine ligands: Syntheses, crystal structures, and comparison in bioactivity profile against bacterial, fungal, and cancer cells and activities on wheat germination indices. In: *Applied Organometallic Chemistry*, 38, e7601.
11. **Meurer F.**, Morrison G., Hischa B., zur Loye H.-C., Hennig C.*, Bodensteiner M.* (2024): Improvement of Single-Crystal Structures of Very Heavy Element Compounds by Refining Anomalous Dispersion Parameters. In: *Inorganic Chemistry*, 63, 34, 15784–15790. (Chapter 7)
10. Uhlig F., Stammler M.B., **Meurer F.**, Shenderovich I.G., Blahut J., Wisser F.M.* (2024): Monitoring Structure and Coordination Chemistry of Co₄O₄-Based Oxygen Evolution Catalysts by ^{14/15}N and ⁵⁹Co NMR Spectroscopy. In: *Dalton Transactions*, 53, 8541–8545.
9. **Meurer F.**, Bodensteiner M., Kolev I.* (2024): Redetermination of germacrone type II based on single-crystal X-ray data. In: *IUCrData*, 9, 4, x240346.
8. **Meurer F.***, Moebs J., Nentwich M., Weigel T., Woehrle J.-P. (2024): Young crystallographers’ rejuvenate crystallography in Germany. In: *Acta Crystallographica Section E*, 80, 3, 252–255.
7. **Meurer F.**, Kleemiss F., Riesinger C., Bal  zs G., Vukovi   V., Shenderovich I.G., Jelsch C., Bodensteiner M.* (2024): Probing the Isolobal Relation between Cp^{'''}NiP₃ and White Phosphorus by Experimental Charge Density Analysis. In: *Chemistry - A European Journal*, 30, 19, e202303762. (Chapter 4)

6. **Meurer F.**, Dimova T., Bodensteiner M.*, Kolev I.* (2023): 2,6-Dibromo-3,4,5-trimethoxybenzoic acid. In: Acta Crystallographica Section E, 79, 916–919.
 5. Estevenon P., Amidani L., Bauters S., Tamain C., Bodensteiner M., **Meurer F.**, Hennig C., Vaughan G., Dumas T., Kvashnina K.* (2023): From Molecular Oxo-Hydroxo Ce Clusters to Crystalline CeO₂. In: Chemistry of Materials, 35, 1723–1734.
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Publications Prior to this Thesis

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2. **Meurer F.**, von Essen C., Kühn C., Puschmann H., Bodensteiner M.* (2022): The Benefits of Cu K β Radiation for the Single-Crystal X-ray Structure Determination of Crystalline Sponges. In: IUCrJ, 9, 3, 349–354.
1. Ibrahim A.B.M.*, Mahmoud G.A.E.*, **Meurer F.**, Bodensteiner M. (2021): Preparation and crystallographic studies of a new mercuric salicylaldimine complex for fabrication of microscaled and nanoscaled mercuric sulfide as antimicrobial agents against human pathogenic yeasts and filamentous fungi. In: Applied Organometallic Chemistry, 35, 3, e6134.

To my family, given and chosen

Preface

This thesis investigates the method of X-ray single-crystal structure determination. The work presented here is a collection of publications and manuscripts that have been written during my PhD studies at the University of Regensburg.

Every chapter of this thesis, which is based on a published or submitted publication, is preceded by a separate preface that provides a list of authors and their respective contributions to the publication.

The published and submitted publications were kept in their original form, including the text and its language (British or American English), the images, and the formatting of the references. The titles were adjusted for this thesis to ensure consistency. The supporting information is included as .pdf file in the end of each chapter in its original format and page numbering.

The introduction chapter of this thesis provides a methodological overview of the field of X-ray single-crystal structure determination, including quantum crystallography, bonding indices, anomalous dispersion, and X-ray absorption spectroscopy. The introduction puts the results of this thesis into a broader context and the conclusion chapter summarises the findings comprehensively.

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1 Introduction

1.1 X-ray crystallography

Within only a few years of Wilhelm Conrad Röntgen’s discovery of X-rays [1], their diffraction by ordered materials provided direct evidence for the atomic nature of matter, the periodic arrangement of atoms in crystals, and ionic bonding in salts. X-ray diffraction by crystals was discovered by Walter Friedrich, Paul Knipping, and Max von Laue in 1912 [2], with conceptual guidance from Paul Peter Ewald [3]. William Henry Bragg and William Lawrence Bragg subsequently established X-ray crystallography as a practical method for crystal structure determination in 1913 [4, 5].

The Braggs reported the fundamental relation now known as Bragg’s law (Equation 1.1), which gives the condition for constructive interference of radiation diffracted by a crystal lattice

$$n\lambda = 2d \sin \theta \quad (1.1)$$

where λ is the wavelength of the incident radiation, n is the diffraction order, d is the spacing between lattice planes, and θ is the Bragg angle. The enduring importance of Bragg’s law resides in its mathematical elegance, contemporary indispensability, and cross-disciplinary relevance.

This thesis focuses on X-ray crystallography, which has become the most mature and widely used diffraction technique for determining atomic structures and the corresponding electron density in crystals [6].

When X-rays are diffracted by a single crystal, the positions of the diffraction spots provide information about the symmetry and periodicity of the lattice, whereas their intensities are related to the electron density because X-rays interact primarily with the electrons in the crystal.

The periodic electron density is related to the crystallographic structure factors through the inverse Fourier transform

$$\rho(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{h}} F(\mathbf{h}) e^{-2\pi i \mathbf{h} \cdot \mathbf{r}} \quad (1.2)$$

where $\rho(\mathbf{r})$ is the electron density at position $\mathbf{r}$, V is the unit-cell volume, $F(\mathbf{h})$ is the structure factor for the reflection with Miller indices $\mathbf{h}$, and the sum extends over all reciprocal-lattice points [7].

The structure factors are therefore the Fourier coefficients of the total electron density. Their subsequent decomposition into atom-centred contributions introduces the atomic form factor, which links the measured diffraction intensities to a physically meaningful description of the electron density and underlies modern quantum chemistry and a wavefunction-based descriptions of X-ray scattering.

1.1.1 Quantum mechanics in early X-ray crystallography

The ambition to obtain chemical information from diffraction intensities is almost as old as crystal structure analysis itself. In 1915, only a few years after the discovery of X-ray diffraction, Arthur H. Compton argued that the angular decrease of diffracted intensity could not be understood by treating an atom as a point scatterer. Instead, the atom

had to be considered as a spatial distribution of electrons, so that sufficiently accurate reflection intensities could, in principle, reveal this distribution [8]. This early insight already contains the essential concept of the atomic form factor: the coherent scattering amplitude of an atom is the Fourier transform of its electron density.

The connection between quantum mechanics and crystallographic electron density was recognised with remarkable clarity soon after the emergence of wave mechanics. Already in the 1920s, Linus Pauling emphasised the prospect that X-ray diffraction might provide experimental access to the spatial distribution of electrons and thereby reveal information about the nature of the chemical bond. This idea anticipated the central ambition of modern quantum crystallography [9]. A diffraction experiment does not directly measure a many-electron wavefunction, since the observed intensities are related to the square moduli of the structure factors, which correspond to the total electron density [10]. The wavefunction contains substantially more information and cannot be measured directly. Nevertheless, the electron density derived from a wavefunction and the Fourier coefficients obtained from diffraction are linked through the same spatial distribution of electrons [6, 11]. This early connection between wave mechanics and crystallographic measurements therefore provides a natural historical starting point for the development of experimental charge-density analysis and wavefunction-based refinement [9, 12, 13].

The first crystal structures also demonstrated that diffraction intensities contain information beyond the positions of ideal point scatterers. Rock salt was among the earliest and most consequential examples. Bragg's structural analysis established an alternating arrangement of sodium and chlorine sites rather than discrete NaCl molecules, while subsequent quantitative measurements by Bragg, James, and Bosanquet examined the absolute intensities of reflections from rock salt [14, 15]. The observed scattering could not be understood solely from the nuclear arrangement. It depended on the distribution of electrons assigned to the two sublattices. Describing the sites as approximately Na^+ and Cl^- , rather than as neutral Na and Cl atoms, gave physically more appropriate low-angle form factors because electron transfer decreases the diffuse valence density around sodium and increases that around chlorine. The improvement obtained with ionic form factors provided early diffraction evidence consistent with the ionic description of alkali halides.

Figure 1.1 compares the calculated atomic form factors of Na, Na^+ , Cl, and Cl^- . It is evident that form factors of ions and neutral atoms differ in the low resolution regime. The negatively charged Cl^- possesses one more electron than in its neutral form, increasing the scattering power for forward scattering by one electron. In contrast, the positively charged Na^+ has one fewer electron than neutral Na, reducing its scattering power for forward scattering by one electron. The difference between the form factors of neutral and ionic species is therefore most pronounced at low resolution, where the valence density dominates the scattering. At higher resolution, the core density dominates and the form factors of neutral and ionic species converge.

The quantum mechanical basis of X-ray scattering was developed further during the following years. Waller and Hartree derived a general treatment of the total scattering intensity, including coherent elastic and incoherent contributions, in terms of matrix elements between electronic wavefunctions [17]. Their formalism showed explicitly that X-ray scattering is governed by the quantum-mechanical electronic state rather than by an assembly of classical point electrons. In modern notation, the total scattering contains a sum over possible final electronic states,

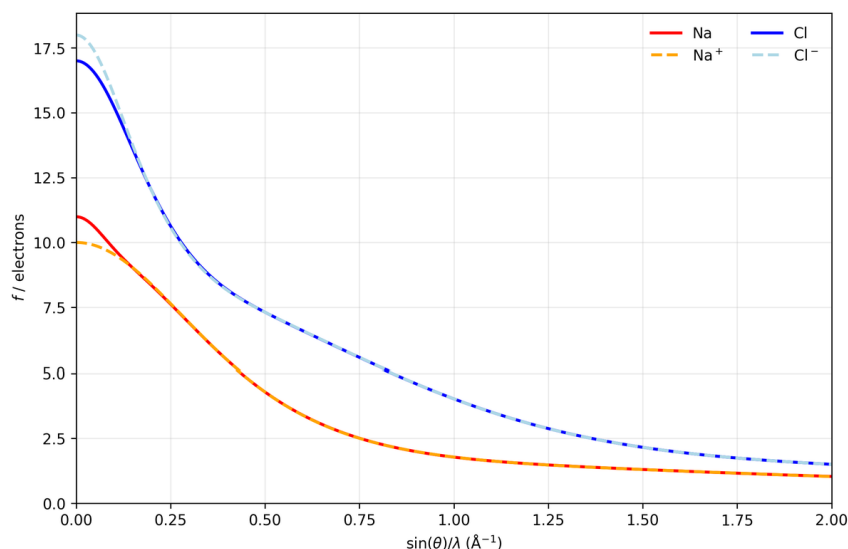


Figure 1.1: Scattering power of neutral and ionic sodium and chlorine as a function of resolution. Neutral and ionic form factors are calculated from the International Tables for Crystallography [16].

$$I_{\text{total}}(\mathbf{q}) \propto \sum_n \left| \left\langle \Psi_n \left| \sum_{j=1}^N \exp(2\pi i \mathbf{q} \cdot \mathbf{r}_j) \right| \Psi_0 \right\rangle \right|^2, \quad (1.3)$$

where Ψ_0 and Ψ_n are the initial and possible final electronic states, respectively, N is the number of electrons, and $\mathbf{q}$ is the scattering vector. The term with $\Psi_n = \Psi_0$ is the coherent elastic contribution that gives the ordinary atomic form factor and, in a periodic crystal, the Bragg reflections. Terms with $\Psi_n \neq \Psi_0$ represent inelastic scattering.

Despite these early developments, routine chemical structure refinement has largely remained geometrical. In the independent-atom model (IAM), atoms of the same element are normally assigned identical spherical reference densities, apart from occupancies and displacement parameters. Valence redistribution caused by ionisation, covalency, polarisation, and intermolecular interactions is therefore omitted from the refined density. This simplification is highly successful for locating atoms, but it deliberately discards much of the electronic information that attracted Compton and Pauling.

Modern quantum crystallography provides several routes for recovering part of this information. Hansen–Coppens multipole refinement represents the density with flexible atom-centred spherical-harmonic functions [12]. Transferable pseudoatom databanks and programs such as MoPro extend this idea to chemically transferable aspherical density parameters [18]. Wavefunction-based approaches generate scattering factors from quantum-chemical densities or allow experimental structure factors to influence a wavefunction directly [9, 13]. Current implementations of the XD and MoPro program packages provide multipolar refinement, topological analysis, and property evaluation for experimental and theoretical structure factors [19, 20]. These methods differ in the extent to which their resulting electronic quantities are experimentally refined or theoretically constrained, but all pursue the objective anticipated by Pauling: using X-ray diffraction not only to determine where atoms are, but also to investigate how their electrons are distributed and how they participate in chemical bonding.

1.1.2 Thermal motion and the Debye–Waller factor

A second early development that remains fundamental to every modern crystal structure refinement was the recognition that atoms are not stationary at their mean lattice positions. Thermal motion changes the phase of the wave scattered by each instantaneous atomic configuration. Averaging over many configurations reduces the coherent Bragg amplitude, particularly at large scattering angles, while transferring intensity into thermal diffuse scattering. Peter Debye first derived a temperature-dependent attenuation of X-ray interference intensities in 1913 [21]. Ivar Waller subsequently developed a more general treatment of the influence of lattice vibrations on X-ray interference and established the form that became the basis of the modern Debye–Waller factor [22].

For an atom with instantaneous displacement $\mathbf{u}_j$ from its mean position $\mathbf{r}_j$, the thermally averaged phase factor is

$$T_j(\mathbf{h}) = \langle \exp(2\pi i \mathbf{h} \cdot \mathbf{u}_j) \rangle, \quad (1.4)$$

where the angle brackets denote an ensemble or time average. If the displacement distribution is Gaussian and harmonic, this average becomes

$$T_j(\mathbf{h}) = \exp[-2\pi^2 \mathbf{h}^T \mathbf{U}_j \mathbf{h}], \quad (1.5)$$

where $\mathbf{U}_j = \langle \mathbf{u}_j \mathbf{u}_j^T \rangle$ is the mean-square displacement tensor. In the isotropic approximation, $\mathbf{U}_j = U_{\text{iso},j} \mathbf{I}$, and the factor is often written as

$$T_j(s) = \exp(-8\pi^2 U_{\text{iso},j} s^2) = \exp(-B_j s^2), \quad B_j = 8\pi^2 U_{\text{iso},j}, \quad (1.6)$$

with $s = \sin \theta / \lambda$. The Debye–Waller factor (see Figure 1.2) therefore attenuates high-angle reflections more strongly than low-angle reflections. This angular dependence is central to crystallographic refinement because it creates correlations between displacement parameters, occupancies, scale factors, and the radial form of the atomic density. An inadequate electron-density model may be partly compensated by distorted anisotropic displacement parameters (ADPs), while unmodelled disorder or anharmonic motion may appear as apparent bonding density. The historical work of Debye and Waller therefore establishes the formal separation between the mean atomic structure and the distribution of instantaneous displacements around it.

The term “Debye–Waller factor” is sometimes used for either the amplitude factor T_j or the corresponding intensity attenuation $|T_j|^2$. The convention should therefore be specified explicitly. In the structure factor equation used below, T_j multiplies the atomic scattering amplitude, so the intensity contains its squared modulus.

1.1.3 The crystallographic structure factor

Equation 1.2 expresses the periodic electron density as a Fourier series. Its coefficients, the complex structure factors $F(\mathbf{h})$, contain the amplitude and phase of each spatial Fourier component. The corresponding forward Fourier transform is

$$F(\mathbf{h}) = \int_V \rho(\mathbf{r}) \exp(2\pi i \mathbf{h} \cdot \mathbf{r}) \, d\mathbf{r}, \quad (1.7)$$

where the integration extends over the unit-cell volume V . The reciprocal-lattice vector is $\mathbf{h} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$, with Miller indices h , k , and l and reciprocal basis vectors $\mathbf{a}^*$, $\mathbf{b}^*$, and $\mathbf{c}^*$ [6, 16].

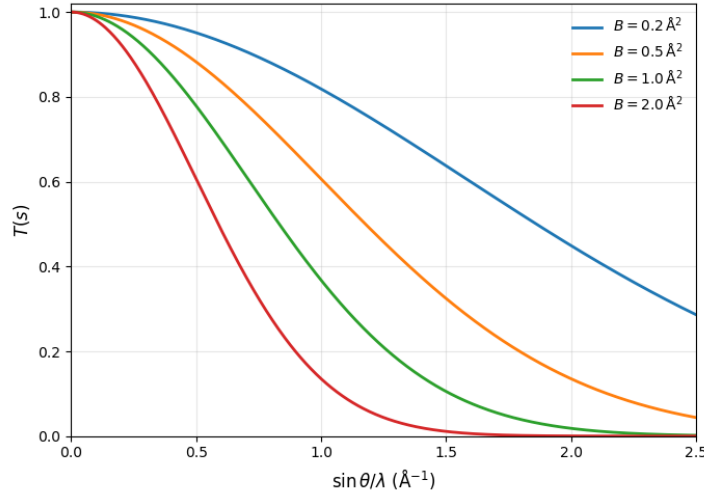


Figure 1.2: Dependence of the isotropic Debye–Waller factor $T(s) = \exp(-Bs^2)$ on $s = \sin \theta / \lambda$ for different values of the displacement parameter B . Adapted from Equation (1.6) using representative values of B .

For a crystal composed of atoms at positions $\mathbf{r}_j$, the total density may be approximated as a sum of atom-centred contributions,

$$\rho(\mathbf{r}) = \sum_j \rho_j(\mathbf{r} - \mathbf{r}_j), \quad (1.8)$$

where ρ_j is the electron density assigned to atom j . The Fourier transform of an isolated atomic contribution is its atomic form factor,

$$f_j(\mathbf{q}) = \int \rho_j(\mathbf{r}) \exp(2\pi i \mathbf{q} \cdot \mathbf{r}) d\mathbf{r}, \quad (1.9)$$

where $\mathbf{q}$ is the scattering vector. At the Bragg condition, $\mathbf{q}$ coincides with a reciprocal-lattice vector. For a spherically symmetric atomic density, the angular part can be integrated analytically,

$$f_j(s) = 4\pi \int_0^\infty \rho_j(r) \frac{\sin(4\pi sr)}{4\pi sr} r^2 dr, \quad s = \frac{\sin \theta}{\lambda}, \quad (1.10)$$

where θ is the Bragg angle and λ the incident wavelength. For a neutral atom, $f_j(0) = Z_j$, with atomic number Z_j . Substitution of Equation 1.8 into Equation 1.7 gives the conventional crystallographic structure factor,

$$F(hkl) = \sum_{j=1}^{N_{\text{at}}} o_j f_j(hkl) T_j(hkl) \exp[2\pi i(hx_j + ky_j + lz_j)]. \quad (1.11)$$

Here, N_{at} is the number of atoms in the unit cell, o_j is the site occupancy, (x_j, y_j, z_j) are fractional coordinates, and T_j is the atomic displacement factor. In the harmonic anisotropic approximation, Equation 1.5 gives the Debye–Waller factor, where $\mathbf{U}_j$ is the symmetric anisotropic displacement tensor. The six independent elements of $\mathbf{U}_j$ describe the mean-square displacement distribution about the average atomic position. They primarily represent thermal motion but can also absorb static disorder and deficiencies of the structural or scattering model.

Within the kinematical approximation, the integrated intensity of a Bragg reflection is proportional to the squared modulus of the structure factor,

$$I(hkl) = K L(hkl) P(hkl) A(hkl) E(hkl) |F(hkl)|^2, \quad (1.12)$$

where K is the overall scale factor, L the Lorentz factor, P the polarisation factor, A an absorption term, and E an extinction correction. Crystallographic data reduction and processing aim to remove these experimental contributions and obtain estimates of $|F_o|^2$ (except for E , which is considered by the refinement software). The phase of F , however, cannot be measured directly, which constitutes the “crystallographic phase problem”. The solution of the phase problem can be approached by a variety of methods, including direct methods [23, 24], the Patterson method [25], charge flipping [26], molecular replacement [27], dual-space methods [28], iterative projection algorithms [29], and, more recently, AI-based [30].

1.1.4 Conventional crystallographic refinement

In routine small-molecule crystallography, the electron density is represented by the IAM [8, 10]. Every atomic position is assigned a spherical atomic form factor calculated for an isolated atom, and the electron density in the crystal is constructed as their superposition. Structural parameters are optimised by minimizing the disagreement between observed and calculated diffraction data. Modern refinements are commonly performed against F_o^2 using a weighted least-squares target,

$$S = \sum_{\mathbf{h}} w_{\mathbf{h}} [F_o^2(\mathbf{h}) - F_c^2(\mathbf{h})]^2, \quad (1.13)$$

where $w_{\mathbf{h}}$ is a reflection weight and the subscripts “o” and “c” denote observed and calculated quantities. The principal refined quantities are atomic coordinates, site occupancies, scale factors, and atomic displacement parameters. Additional parameters may account for disorder, twinning, extinction, or anharmonic motion.

Despite the simplicity of spherical isolated-atom form factors, the IAM routinely yields accurate connectivity, bond lengths, angles, stereochemistry, and crystal packing. This is possible because the phases of the atomic contributions are dominated by the nuclear positions and because much of the core-electron density remains close to spherical.

The IAM is nevertheless not a complete description of a bonded system. Molecular formation redistributes valence density through polarisation, charge transfer, covalency, lone-pair formation, and intermolecular interactions [9]. If these effects are ignored in the model, their signatures can be transferred partly into positional and displacement parameters. The consequences are especially visible for hydrogen atoms, whose only electron participates directly in bonding, and in high-quality data, where systematic residual density around bonds and lone pairs becomes visible. The limitations of spherical-atom refinement motivate more accurate descriptions of both the ordinary elastic form factor and its energy-dependent resonant contribution [10, 12, 31].

1.1.5 Atomic scattering

The term “atomic form factor” suggests that it is a single entity. In reality, the scattering amplitude depends on momentum transfer, photon energy, polarisation, the electronic

state of the atom, and its chemical environment. Within the scalar approximation, the atomic scattering factor is written

$$f_j(\mathbf{q}, E) = f_{0,j}(\mathbf{q}) + f'_j(E) + if''_j(E), \quad (1.14)$$

where $f_{0,j}$ is the non-resonant elastic form factor, while f'_j and f''_j are the real and imaginary anomalous dispersion corrections.

Elastic scattering leaves the internal quantum state of the sample unchanged and preserves the photon energy. Coherent elastic scattering from the periodic density produces Bragg diffraction. Inelastic processes, including Compton scattering, transfer energy to the sample and generally contribute diffuse background rather than coherent Bragg intensity. The imaginary term f'' should therefore not be interpreted simply as an “inelastic form factor”. It represents the absorptive part of the coherent forward-scattering response and is related to photoabsorption through the optical theorem. The terms f' and f'' are more accurately described as resonant or anomalous contributions [11, 16].

A refined physical description of the measured electron density consequently requires two complementary developments. First, the spatial shape of the ground-state elastic density must be improved beyond spherical isolated atoms. Second, the energy dependence and chemical sensitivity of the resonant terms must be treated accurately, particularly near an absorption edge. The first route leads to experimental charge-density and quantum-crystallographic methods, while the second connects anomalous diffraction directly to X-ray absorption spectroscopy.

1.2 Beyond the independent atom model

1.2.1 Multipolar modelling

The most established experimental approach to model the aspherical electron density attributed to chemical effects within the crystal is multipolar refinement. In the Hansen–Coppens formalism, each atomic density is divided into a spherical core, a spherical valence shell, and an aspherical deformation contribution to the valence shell [12]:

$$\begin{aligned} \rho_j(\mathbf{r}) = & P_{c,j}\rho_{\text{core},j}(r) + P_{v,j}\kappa_j^3\rho_{\text{val},j}(\kappa_j r) \\ & + \sum_{l=0}^{l_{\text{max}}} \kappa_j'^3 R_{l,j}(\kappa_j' r) \sum_{m=-l}^l P_{lm,j} Y_{lm}(\theta, \phi). \end{aligned} \quad (1.15)$$

Here, $P_{c,j}$ and $P_{v,j}$ are core and valence populations, κ_j and κ_j' describe radial contraction or expansion, $R_{l,j}$ are radial functions, Y_{lm} are real spherical harmonics, and $P_{lm,j}$ are multipole populations. Fourier transformation of these pseudoatomic densities gives aspherical atomic form factors that can be refined against high-resolution diffraction data. Multipolar refinement provides a compact and chemically flexible description of the static one-electron density. It can describe electron-density accumulation in covalent bonds [32], lone-pair density [33], polarisation of metal–ligand interactions [34], and redistribution associated with intermolecular contacts [35]. A static deformation density is commonly defined as

$$\Delta\rho(\mathbf{r}) = \rho_{\text{multipole}}(\mathbf{r}) - \rho_{\text{IAM}}(\mathbf{r}), \quad (1.16)$$

A dynamic deformation density is obtained by including the atomic displacement factors in the Fourier synthesis of the deformation density.

Multipolar modelling is experimentally demanding. Reliable separation of static density from thermal motion requires accurate, redundant, high-resolution data, usually collected at low temperature. Absorption, extinction, scaling, detector effects, disorder, anharmonic motion, and parameter correlations must be controlled [36]. Multipole populations are also model dependent: truncation of the angular expansion, local coordinate systems, radial functions, chemical constraints, and treatment of core density influence the result. A multipole model is thus not the model-free exact electron density, but a physically informed parametrisation tested against experimental structure factors [9, 10, 37].

1.2.2 Hirshfeld atom refinement

A different strategy is to calculate a tailor-made molecular density quantum mechanically and use it to generate aspherical atomic form factors. Hirshfeld atom refinement (HAR) partitions the molecular density by the Hirshfeld stockholder scheme [31, 38, 39]:

$$\rho_A(\mathbf{r}) = w_A(\mathbf{r})\rho_{\text{mol}}(\mathbf{r}), \quad (1.17)$$

with

$$w_A(\mathbf{r}) = \frac{\rho_A^0(\mathbf{r})}{\sum_B \rho_B^0(\mathbf{r})}, \quad (1.18)$$

where ρ_A^0 is the spherical reference density of atom A . Fourier transformation of each ρ_A yields aspherical atomic scattering factors. In iterative HAR, coordinates and ADPs are refined, a new wavefunction is calculated for the updated geometry and crystal environment, and the form factors are regenerated.

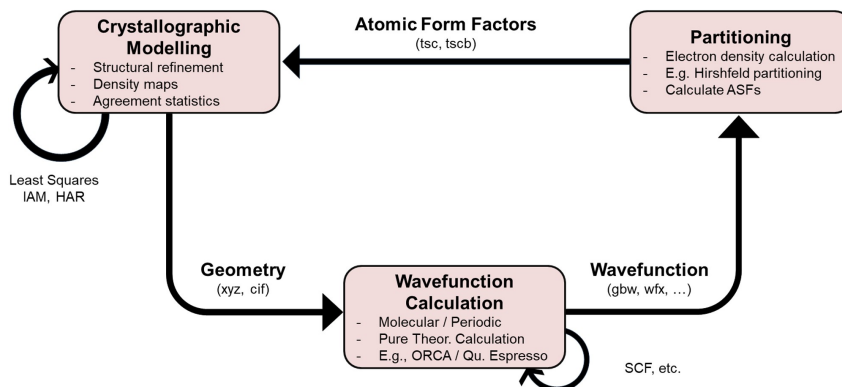


Figure 1.3: Schematic of the Hirshfeld atom refinement procedure.

Figure 1.3 illustrates the HAR workflow. The initial geometry is typically obtained from an IAM. A single-point wavefunction is calculated for the current geometry, the resulting Hirshfeld-partitioned form factors are used in the crystallographic refinement, and the cycle is repeated until convergence is reached.

HAR provides an improved model for structure refinement, but it also yields a theory constrained electron density evaluated at an experimentally refined geometry. The density

depends on the selected quantum-chemical method, basis set, spin state, relativistic treatment, and representation of the crystal environment. A major advantage is that chemically realistic asphericity can be introduced with relatively few additional model parameters. This often reduces chemically structured residual density, improves bond-length precision and quality indicators, and can permit anisotropic refinement of hydrogen atoms. HAR has been shown to yield X–H distances similar to neutron-diffraction values when the diffraction data quality and theoretical model are adequate [31, 40].

HAR yields an experimental electron density on the basis of the experimental geometry. A DFT calculation performed at the exact same geometry would yield exactly the same electron density. Nonetheless, HAR has some key advantages for experimental analysis. First, the geometry is purely experimental and is the best agreement of the non-spherical atomic form factors with the diffraction data. A quantum chemical geometry optimisation could only by chance yield the exact same geometry. Second, the ADPs in the HAR model are included in the dynamic deformation density, giving experimental insights. Lastly, the residual electron density can be analysed to test the improvement of the chemical model over the IAM, giving experimental insights into the accuracy and physicality of the quantum chemical calculation at hand.

1.2.3 X-ray constrained or restrained wavefunction fitting

The X-ray constrained wavefunction approach introduced by Dylan Jayatilaka allows measured structure factors to influence the wavefunction through an additional term in the electronic energy functional [13, 41, 42]. Typically, a Hartree–Fock wavefunction is optimised by striking a balance between electronic energy and the degree of agreement between the quantum crystallographic model and the measured diffraction data. The fitted wavefunction may acquire polarisation and correlation-like features, but these are not automatically or uniquely determined by the diffraction experiment. In general, the functional to be minimised is

$$\mathcal{L}[\Psi] = E[\Psi] + \lambda [\chi^2(\Psi) - \Delta], \quad (1.19)$$

where $E[\Psi]$ is the electronic energy, χ^2 measures disagreement between observed and wavefunction-derived structure-factor amplitudes, λ controls the experimental constraint, and Δ is the target agreement level. A representative crystallographic residual is

$$\chi^2(\Psi) = \frac{1}{N_r - N_p} \sum_{\mathbf{h}} \frac{[\eta |F_{\text{calc}}(\mathbf{h}; \Psi)| - |F_{\text{obs}}(\mathbf{h})|]^2}{\sigma^2(\mathbf{h})}, \quad (1.20)$$

where N_r is the number of reflections, N_p is the number of fitted parameters (usually one or zero), η is a scale factor, and $\sigma(\mathbf{h})$ is the experimental uncertainty.

The terms “X-ray constrained wavefunction” and “X-ray restrained wavefunction” are both used. Recent methodological discussions favour “constrained” when the calculation is driven towards a specified goodness of fit, whereas “restrained” remains common in quantum-crystallographic practice [43]. The combined workflow of HAR and X-ray constrained wavefunction fitting is often termed X-ray wavefunction refinement or fitting.

The conceptual attraction is that the resulting many-electron model is subject to quantum mechanics and diffraction data simultaneously. Its limitations are equally important. Intensities are affected by thermal motion, experimental error, disorder, and intermolecular fields. The fitted wavefunction depends on the Hamiltonian, basis set, embedding

model, relativistic approximation, and stopping criterion. A lower residual does not demonstrate that every orbital or correlated property has been determined experimentally. Reproducibility and information content are therefore central methodological questions [43, 44, 45].

1.3 Bonding analyses

1.3.1 Topological analysis of the electron density

Once a continuous electron density has been obtained, either from multipole refinement or from a quantum-mechanical wavefunction, it can be analysed using Bader’s quantum theory of atoms in molecules (QTAIM) [46, 47]. Critical points satisfy

$$\nabla\rho(\mathbf{r}_c) = \mathbf{0}, \quad (1.21)$$

and are classified by the eigenvalues λ_1 , λ_2 , and λ_3 of the Hessian of ρ . A bond critical point has rank three and signature -1 , conventionally denoted $(3, -1)$. The Laplacian,

$$\nabla^2\rho(\mathbf{r}) = \lambda_1 + \lambda_2 + \lambda_3, \quad (1.22)$$

identifies local valence-shell charge concentration (VSCC) when negative and local valence-shell charge depletion (VSCD) when positive. Atomic basins are bounded by the respective zero-flux surfaces,

$$\nabla\rho(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = 0, \quad (1.23)$$

where $\mathbf{n}$ is the surface normal. Numerical integration over a basin Ω_A gives its electron population and net charge,

$$N_A = \int_{\Omega_A} \rho(\mathbf{r}) d\mathbf{r}, \quad q_A = Z_A - N_A. \quad (1.24)$$

The presence of a bond path and bond critical point is a topological observation, not a complete statement about bond strength, covalency, or energetic stabilisation. Interpretation should consider the density and Laplacian at the critical point, curvature, energy-density descriptors, delocalisation indices where available, and suitable reference compounds. This is especially important for metal–metal bonds, weak interactions, and heavy-element compounds.

The electron-density model determines which chemical analyses are formally available. A multipolar model provides the scalar one-electron density and its derivatives. It therefore supports deformation-density maps, electrostatic properties, QTAIM topology, basin integration, and other density-based descriptors. It does not provide a unique set of molecular orbitals or a many-electron wavefunction. Orbital-dependent analyses cannot be reconstructed uniquely from $\rho(\mathbf{r})$ alone.

1.3.2 Wavefunction-based bonding descriptors

Wavefunction-based approaches provide access to a substantially larger set of bonding descriptors than can be obtained from the electron density alone. Besides the electron density and its derivatives, the molecular orbitals, density matrix, pair density, and

kinetic-energy density become available. Consequently, both real-space and orbital-based bonding analyses can be performed.

One important extension of QTAIM is the calculation of delocalisation indices (DIs), which quantify the number of electron pairs shared between two atomic basins. Within the QTAIM framework, the delocalisation index between atoms A and B can be written as

$$\delta(A, B) = -2 \int_{\Omega_A} \int_{\Omega_B} \rho_{xc}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2, \quad (1.25)$$

where ρ_{xc} is the exchange-correlation density and Ω_A and Ω_B are the atomic basins of atoms A and B , respectively. delocalisation indices often correlate with bond order and are frequently employed for metal-metal bonds and highly delocalised systems [46, 48].

Another important class of real-space descriptors is based on electron localisability. The electron localisation function (ELF), introduced by Becke and Edgecombe, measures the probability of finding same-spin electrons in the vicinity of a reference electron relative to a homogeneous electron gas [49]. In its common form,

$$\text{ELF}(\mathbf{r}) = \frac{1}{1 + \chi^2(\mathbf{r})}, \quad (1.26)$$

where χ is a dimensionless measure of the excess same-spin kinetic-energy density relative to the corresponding homogeneous-electron-gas reference. ELF values close to unity indicate strongly localised electronic regions, whereas values close to zero indicate low localisation.

A related quantity is the electron localisability indicator in its D representation (ELI-D), introduced by Kohout and co-workers [50]. ELI-D is derived from the curvature of the conditional same-spin pair probability and provides a particularly intuitive representation of bonding and lone-pair domains. Maxima of ELI-D define attractors corresponding to localised electron pairs and can therefore be used to identify covalent bonds, lone pairs, multicentre interactions, and metallic bonding domains. Because ELI-D depends on the kinetic-energy density and pair-density information, it is naturally evaluated from a wavefunction or density matrix rather than from an experimental multipole density alone.

An alternative Hilbert-space perspective is provided by the Roby-Gould bond indices. These indices are defined using the one-electron density operator and atomic projection operators and yield separate covalent and ionic contributions to the bond index [51, 52]. They are therefore not equivalent to a Mulliken overlap population and are most appropriately used to compare trends obtained with a consistent computational protocol.

Natural Bond Orbital (NBO) analysis approaches chemical bonding from a localised-orbital perspective [53, 54]. The wavefunction is transformed into a set of localised Lewis-type bonding, antibonding, and lone-pair orbitals. Donor-acceptor interactions are typically quantified through second-order perturbation theory,

$$E^{(2)} = n_i \frac{|\langle \phi_i | \hat{F} | \phi_j \rangle|^2}{\varepsilon_j - \varepsilon_i}, \quad (1.27)$$

where n_i is the occupation number of donor orbital ϕ_i , $\hat{F}$ is the Fock operator, and ε_i and ε_j are the orbital energies. Large stabilisation energies indicate strong donor-acceptor

interactions and are frequently used to describe hyperconjugation, back-bonding, and metal–ligand interactions.

Natural Resonance Theory (NRT) extends NBO analysis by expressing the wavefunction as a weighted combination of resonance structures [55, 56, 57]. The resulting resonance weights provide a quantitative measure of the importance of individual Lewis structures and allow natural bond orders, valencies, and resonance contributions to be evaluated.

1.3.3 Atomic charges

The assignment of atomic charges is not unique because the electron density is a continuous quantity and cannot be partitioned uniquely into atomic contributions. Consequently, a wide variety of charge definitions exist, each emphasizing different physical aspects of bonding.

Within QTAIM, atomic charges are obtained directly from integration over zero-flux basins according to Equation 1.24. These charges are defined directly in real space and do not require an orbital-population partition, although their values still depend on the underlying electron-density model. They are often larger in magnitude than chemically intuitive oxidation-state assignments.

Mulliken population analysis partitions the density matrix according to basis-function overlaps [58]. The gross population of atom A can be written as

$$N_A = \sum_{\mu \in A} \sum_{\nu} P_{\mu\nu} S_{\mu\nu}, \quad (1.28)$$

leading to the Mulliken charge

$$q_A = Z_A - N_A. \quad (1.29)$$

Although computationally inexpensive, Mulliken charges are strongly basis-set dependent and often exhibit poor numerical stability.

Löwdin charges attempt to reduce this basis dependence by orthogonalising the basis functions prior to population analysis [59]. Natural population analysis (NPA), derived from NBO theory, further improves robustness and is widely used in quantum chemistry [54, 60].

Real-space alternatives include Voronoi deformation density (VDD) charges, introduced by Bickelhaupt and co-workers [61]. VDD charges are obtained by integrating the deformation density over Voronoi polyhedra,

$$q_A^{\text{VDD}} = - \int_{\Omega_A^{\text{Vor}}} \Delta\rho(\mathbf{r}) \, \mathrm{d}\mathbf{r}, \quad (1.30)$$

where $\Delta\rho$ is the deformation density relative to neutral atoms. VDD charges are generally less sensitive to basis-set effects and often provide chemically intuitive trends.

Other commonly employed charge schemes include Hirshfeld charges [38], CM5 charges [62], electrostatic-potential-derived charges such as CHELPG [63], and density-derived electrostatic and chemical (DDEC) charges [64]. Each scheme reflects a different partitioning philosophy, and numerical values should therefore only be compared within the same charge framework.

Consequently, no single charge definition can be regarded as the “true” atomic charge. Meaningful interpretation generally relies on comparing trends across related compounds

and combining charge analysis with complementary bonding descriptors such as delocalisation indices, ELI-D, NBO/NRT analyses, and QTAIM topology.

1.4 Anomalous dispersion

1.4.1 Complex scattering factors and Friedel’s law

Near an atomic absorption edge, the dispersive terms in Equation 1.14 vary rapidly with energy. The complete crystal structure factor can be written as

$$F(hkl, E) = \sum_j o_j [f_{0,j}(hkl) + f'_j(E) + if''_j(E)] T_j(hkl) \exp[2\pi i(hx_j + ky_j + lz_j)]. \quad (1.31)$$

For purely real scattering from a real density, Friedel’s law states, that

$$F(-\mathbf{h}) = F^*(\mathbf{h}), \quad I(-\mathbf{h}) = I(\mathbf{h}). \quad (1.32)$$

Complex resonant contributions can make inversion-related intensities unequal. The corresponding Bijvoet difference is

$$\Delta I_{\text{Bijvoet}} = I(\mathbf{h}) - I(-\mathbf{h}). \quad (1.33)$$

Bijvoet, Peerdeman, and van Bommel used this effect in 1951 to determine the absolute configuration of sodium rubidium tartrate and connect molecular stereochemistry experimentally to the Fischer convention [65]. Flack later introduced a refined parameter for estimating enantiomorph polarity and inversion twinning [66]. These developments established anomalous scattering as an essential method for absolute-structure determination. The Templetons broadened the chemical interpretation of resonant diffraction. Their synchrotron experiments demonstrated high-resolution energy dependence and polarisation anisotropy of anomalous scattering. Close to an edge, the response can become tensorial because transitions into directionally anisotropic unoccupied states depend on polarisation and local symmetry [67, 68, 69, 70]. This phenomenon, often termed anisotropic resonant or Templeton–Templeton scattering, shows that resonant diffraction can probe orbital anisotropy and site symmetry in addition to elemental identity.

1.4.2 X-ray crystallography and X-ray absorption

The imaginary dispersion correction used in the crystallographic model is directly related to the photoabsorption, which is experimentally accessible in X-ray absorption spectroscopy (XAS). In a common convention, the atomic absorption cross section $\sigma_{\text{abs}}(E)$ is related to $f''(E)$ by

$$f''(E) = \frac{\sigma_{\text{abs}}(E)}{2r_e\lambda}, \quad (1.34)$$

where r_e is the classical electron radius and λ the photon wavelength. Equivalent expressions may contain unit-dependent constants or use the linear attenuation coefficient rather than an atomic cross section. The essential result is that $f''(E)$ follows the element-specific absorption spectrum, including edge and fine-structure features.

The real and imaginary parts of a causal response are connected through Kramers–Kronig relations, also called Kramers–Kronig transformation (KKT). One expression is

$$f'(E) = f'(\infty) + \frac{2}{\pi} \mathcal{P} \int_0^\infty \frac{E' f''(E')}{E'^2 - E^2} dE', \quad (1.35)$$

where $\mathcal{P}$ denotes the Cauchy principal value. The additive convention depends on the high-energy reference. The equation demonstrates that f' is the dispersive counterpart of absorption over the full energy range. Sharp features in f'' consequently generate characteristic variations in f' .

This connection explains why isolated-atom tabulations can become inadequate directly at an absorption edge. Chemical shifts, multiplet effects, oxidation state, ligand-field splitting, hybridization, and anisotropy alter the absorption spectrum and therefore the site-specific resonant factors. Energy-resolved diffraction can, in principle, recover these chemical differences, especially when inequivalent sites of the same element contribute with different crystallographic phases.

X-ray absorption spectroscopy (XAS) measures energy-dependent attenuation. In transmission geometry, the Lambert-Beer law describes the exponential decay of intensity through a sample [71],

$$I(E) = I_0(E) \exp[-\mu(E)t], \quad (1.36)$$

where $I_0(E)$ and $I(E)$ are incident and transmitted intensities, $\mu(E)$ is the linear absorption coefficient, and t is the sample thickness. Within the electric-dipole approximation, the absorption probability can be written using Fermi’s golden rule [71, 72],

$$\mu(E) \propto \sum_f |\langle f | \boldsymbol{\epsilon} \cdot \mathbf{r} | i \rangle|^2 \delta(E_f - E_i - E), \quad (1.37)$$

where $|i\rangle$ is an initial core state, $|f\rangle$ an unoccupied final state, $\boldsymbol{\epsilon}$ the polarisation vector, E_i and E_f are the energies of the initial and final states, and the delta function enforces energy conservation.

The near-edge region, XANES, is sensitive to oxidation state, local symmetry, orbital hybridization, core-hole effects, and multiple scattering. At higher photoelectron energies, EXAFS oscillations encode local interatomic distances, coordination numbers, and disorder [71, 72, 73]. Diffraction and XAS therefore observe closely related aspects of the same photon–matter interaction. XAS measures the spatially averaged absorption response of the selected element, whereas resonant diffraction weights the same energy-dependent response by crystallographic phase factors. Resonant diffraction can consequently become site selective when crystallographically inequivalent atoms interfere differently in different reflections.

The statement that f'' is an “elemental absorption spectrum” is physically useful but requires qualification. It is element selective because the edge energy identifies a core level of a particular element. It is also site and environment sensitive because the final states depend on oxidation state, coordination, bonding, and symmetry. In anisotropic systems, both XAS and resonant diffraction depend on polarisation, and the anomalous scattering factor is more correctly represented as a tensor.

1.5 Methodological comparison and model selection

The methods described above differ not only in mathematical form but also in the type of information that is allowed to enter the refinement. This distinction is important when the resulting density is interpreted chemically. In the IAM, the scattering factors are fixed before refinement and only structural parameters are adjusted. The refined model is therefore strongly data driven with respect to geometry, but its electron density is predetermined by the library of spherical atoms. In a multipole refinement, additional density parameters are optimised directly against experimental diffraction data. The resulting density may consequently be described as experimental within the limits of the multipole basis, data resolution, thermal-motion model, and applied restraints. In HAR, by contrast, the aspherical density is generated by a quantum-chemical calculation and the crystallographic refinement mainly adjusts geometry and motion. The density is tailor made for the investigated compound but remains theory led. X-ray constrained wavefunction fitting occupies an intermediate position because experimental structure factors modify a quantum-mechanical wavefunction, although the final result remains dependent on the selected Hamiltonian, basis, environment, and statistical constraint.

These distinctions are sometimes obscured by the broad term “quantum crystallography”. The term is useful for methods that combine crystallographic observables with quantum-mechanical models, but it does not imply that all derived quantities possess the same experimental status. Atomic coordinates and ADPs refined against measured intensities are direct model parameters of the crystallographic experiment. A multipole population is also a refined parameter, but it depends on the chosen pseudoatom expansion. An NBO occupation or HOMO–LUMO gap obtained from a HAR wavefunction is a theoretical property evaluated for a geometry constrained by experiment. An analogous quantity derived from an X-ray constrained wavefunction has a more direct dependence on the diffraction data, yet its uncertainty cannot be inferred simply from the crystallographic standard uncertainties of atomic positions.

The choice of model should therefore follow the scientific question. For routine molecular geometry, absolute structure, and crystal packing, the IAM often remains adequate and efficient. Where hydrogen positions, polar bonds, or heavy-element coordination require more realistic scattering, HAR can improve geometry without the very high resolution normally required for a free multipole refinement. Where the objective is an experimental deformation density or topological comparison within a series, a carefully executed multipole analysis remains valuable. Where orbital-based bonding concepts, resonance weights, or localised electron pairs are central, a wavefunction-based model is required. When the aim is to determine whether the diffraction data contain information beyond a chosen theoretical wavefunction, X-ray constrained fitting provides the relevant framework.

Transferable aspherical atom models provide an additional compromise between the IAM and compound-specific quantum calculations. In such approaches, multipole populations or aspherical form factors derived from theoretical calculations or high-quality experimental studies are stored in databanks and transferred according to atom type and chemical environment. They can reduce residual density and improve structural parameters at a computational cost closer to conventional refinement. Their accuracy depends on the transferability of the local electronic environment and on the quality of atom typing. They are therefore especially useful as improved structural models or starting points, while unusual bonding situations may require compound-specific calculations or experimental multipole parameters [9, 10].

The separation of density and thermal motion is a recurring challenge across all approaches. The measured structure factor corresponds to an electron density averaged over nuclear motion and experimental time. If the displacement model is incomplete, density parameters may compensate for anharmonicity or unresolved disorder. Conversely, an inadequate spherical density can distort ADPs. High-order refinement, neutron-derived hydrogen parameters, rigid-bond tests, temperature-dependent measurements, and comparison between independent datasets can help identify such correlations. For heavy atoms, relativistic contraction, core polarisation, absorption, extinction, and insufficient high-angle data introduce further complications. A visually convincing deformation-density map is therefore insufficient by itself. Robustness should be demonstrated against reasonable changes in model, resolution, weighting, and treatment of motion.

The same principle applies to bonding interpretation. Chemical bonds are not quantum-mechanical observables represented by a unique operator, and every bonding analysis introduces a partition or representation. QTAIM partitions real space according to the gradient field of the density. NBO analysis constructs an optimally localised Lewis-like orbital representation. NRT expresses the wavefunction in terms of resonance structures. ELF and ELI-D identify localisation domains using kinetic or pair-density information. Canonical molecular orbitals diagonalize an effective one-electron operator but are generally delocalised and non-unique under transformations within occupied or virtual subspaces. None of these viewpoints is universally superior. Their value lies in producing reproducible descriptors that can be compared across related compounds and connected to chemical behaviour.

For this reason, conclusions should be formulated at a level supported by the data and model. An accumulation of deformation density between two atoms supports redistribution relative to a promolecular reference, but does not alone determine a bond order. A QTAIM bond path identifies a line of maximum density connecting atomic basins, but does not by itself quantify stabilising interaction energy. A donor–acceptor term in NBO analysis depends on the chosen localised representation and perturbative partition. A HOMO–LUMO diagram is useful for rationalising symmetry and qualitative reactivity, but orbital energies and shapes depend on the electronic-structure method. Stronger conclusions emerge from converging evidence: geometry, deformation density, QTAIM descriptors, localised-orbital analyses, spectroscopic signatures, and comparison with chemically meaningful reference systems.

1.5.1 Uncertainty, validation, and reproducibility

Conventional least-squares refinement provides standard uncertainties for parameters under assumptions about the model and reflection errors. Extending this concept to electron-density and wavefunction properties is not straightforward. Derived topological quantities are nonlinear functions of many correlated parameters. Wavefunction analyses additionally depend on theoretical choices that are not represented by the crystallographic covariance matrix. Meaningful validation should therefore combine statistical and chemical tests rather than relying on a single residual factor.

For multipole studies, useful tests include inspection of residual-density maps, resolution-dependent agreement factors, normal probability plots, rigid-bond criteria for ADPs, completeness and redundancy of high-angle data, and stability towards changes in the refinement strategy. Comparison with theoretical structure factors can help distinguish experimental deficiencies from limitations of the pseudoatom model. For HAR, sensitiv-

ity to basis set, density functional, cluster size, point-charge embedding, and relativistic Hamiltonian should be assessed where these choices affect the scientific conclusion. For X-ray constrained wavefunctions, the dependence on the constraint strength and the reproducibility across datasets are central. The target should be agreement with experiment within its credible uncertainty, not unrestricted overfitting of noise [43, 44, 45].

Independent experimental observables provide particularly strong validation. Neutron diffraction can test hydrogen positions and displacement parameters. Electric-field gradients, dipole moments, electrostatic potentials, magnetic measurements, and spectroscopic transitions may test properties derived from a density or wavefunction. XAS can verify oxidation-state and orbital assignments suggested by resonant diffraction or charge-density analysis. Agreement between methods does not eliminate model dependence, but it constrains the range of physically acceptable interpretations.

The increasing automation of aspherical refinement makes explicit validation more rather than less important. Automated HAR and databank methods can now be applied to large numbers of routine datasets, and wavefunction calculations are increasingly embedded in crystallographic software. This widens access to improved scattering models, but also makes it possible to generate sophisticated-looking results without sufficient data quality or understanding of the assumptions. A modern refinement should therefore report the origin of the form factors, electronic-structure level, crystal-environment model, relativistic treatment, reflection resolution and completeness, and criteria used to judge convergence and reliability.

1.6 Implications for modern crystallography

The development of crystallography has often been driven by improved sources, detectors, data reduction, and structure-solution algorithms. The accuracy of a refined structure is also limited, however, by the physical adequacy of the scattering model. Greater photon flux and detector sensitivity do not automatically produce more accurate electron densities if spherical form factors, inappropriate dispersion corrections, unmodelled absorption, radiation damage, or correlated ADPs dominate the error budget.

Improving the elastic scattering model is therefore one major route towards more accurate crystallography. Multipolar refinement can extract an experimental static density when resolution and data quality permit. Transferable aspherical atom models can introduce chemically informed density at moderate computational cost. HAR provides tailor-made quantum-mechanical form factors and improves structural parameters, particularly for hydrogen atoms. X-ray constrained wavefunctions attempt to combine diffraction data with the representability and interpretability of a quantum-mechanical wavefunction. These approaches answer different questions and should not be ranked using a single notion of accuracy. The appropriate model depends on whether the objective is geometry, experimental density, electrostatics, orbital interpretation, or a wavefunction influenced by experiment.

A second route is improved treatment of resonant scattering. Standard tabulations of f' and f'' are indispensable away from strong edge structure, but energy-resolved measurements near an edge require chemically specific values. XAS, Kramers–Kronig transformation, and theoretical XANES calculations can supply more appropriate corrections. Conversely, crystallographic refinement of energy-dependent scattering can provide site-resolved information that conventional XAS cannot separate. This is especially promising

for mixed-valence materials, compounds containing several crystallographically distinct atoms of the same element, transition-metal complexes, and actinide systems.

A third requirement is the joint treatment of density, dynamics, spectroscopy, and radiation damage. ADPs describe averaged nuclear displacements, whereas charge-density and resonant-scattering models describe electrons. These contributions are correlated in measured intensities. Close to absorption edges, absorbed dose rises and element-specific photochemistry can alter oxidation state or coordination during data collection. Small changes in f' , f'' , or bonding density must therefore be distinguished from time-dependent sample damage.

Modern crystallography can consequently be improved not by replacing one conventional model with a universally superior method, but by connecting complementary observables and models. Accurate geometry requires realistic elastic scattering and displacement parameters. Experimental bonding analysis requires high-quality data and explicit density models. Orbital and resonance interpretations require wavefunctions or density matrices. Element- and site-specific electronic information requires anomalous diffraction and XAS. The most reliable conclusions emerge where these approaches agree and where their assumptions and uncertainties are made explicit.

In this perspective, the structure factor is more than a mathematical device for locating atoms. It is the experimental interface between periodic electron density, atomic motion, resonant electronic response, and chemical bonding. Investigating and improving each of these contributions is essential if crystallography is to progress from highly precise structure determination towards a quantitatively accurate experimental description of electronic structure.

1.7 References

- [1] W. C. Röntgen. Ueber eine neue Art von Strahlen (Vorläufige Mittheilung). *Sitzungsberichte der Physikalisch-Medicinischen Gesellschaft zu Würzburg*, 29, 132–141, 1895.
- [2] W. Friedrich, P. Knipping, and M. von Laue. Interferenz-Erscheinungen bei Röntgenstrahlen. *Sitzungsberichte der Königlich Bayerischen Akademie der Wissenschaften, Mathematisch-Physikalische Klasse*, 303–322, 1912.
- [3] P. P. Ewald, editor. *Fifty Years of X-ray Diffraction*. N. V. A. Oosthoek's Uitgeversmaatschappij, Utrecht, 1962. Published for the International Union of Crystallography.
- [4] W. H. Bragg and W. L. Bragg. The reflection of X-rays by crystals. *Proceedings of the Royal Society of London. Series A*, 88, 428–438, 1913.
- [5] W. L. Bragg. The structure of some crystals as indicated by their diffraction of X-rays. *Proceedings of the Royal Society of London. Series A*, 89, 248–277, 1913.
- [6] P. Coppens. The structure factor. In U. Shmueli, editor, *International Tables for Crystallography, Volume B: Reciprocal Space*, chapter 1.2, 10–24. International Union of Crystallography, 2006.
- [7] C. Giacovazzo, editor. *Fundamentals of Crystallography*. Number 15 in IUCr Texts on Crystallography. Oxford University Press, Oxford, 3rd edition, 2011.

-
- [8] A. H. Compton. The distribution of the electrons in atoms. *Nature*, 95, 343–344, 1915.
- [9] S. Grabowsky, A. Genoni, and H.-B. Bürgi. Quantum crystallography. *Chemical Science*, 8, 4159–4176, 2017.
- [10] P. Coppens. *X-ray Charge Densities and Chemical Bonding*. Oxford University Press, Oxford, 1997.
- [11] R. W. James. *The Optical Principles of the Diffraction of X-rays*. G. Bell and Sons, London, 1962.
- [12] N. K. Hansen and P. Coppens. Testing aspherical atom refinements on small-molecule data sets. *Acta Crystallographica Section A*, 34, 909–921, 1978.
- [13] D. Jayatilaka. Wave function for beryllium from X-ray diffraction data. *Physical Review Letters*, 80, 798–801, 1998.
- [14] W. L. Bragg, R. W. James, and C. H. Bosanquet. XXIX. The intensity of reflexion of X-rays by rock-salt. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, 41, 309–337, 1921.
- [15] W. L. Bragg, R. W. James, and C. H. Bosanquet. I. The intensity of reflexion of X-rays by rock-salt—part II. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, 42, 1–17, 1921.
- [16] P. J. Brown, A. G. Fox, E. N. Maslen, M. A. O’Keefe, and B. T. M. Willis. Intensity of diffracted intensities. In E. Prince, editor, *International Tables for Crystallography, Volume C: Mathematical, Physical and Chemical Tables*, chapter 6.1, 554–595. International Union of Crystallography, 2006.
- [17] I. Waller and D. R. Hartree. On the intensity of total scattering of X-rays. *Proceedings of the Royal Society of London. Series A*, 124, 119–142, 1929.
- [18] C. Jelsch, B. Guillot, A. Lagoutte, and C. Lecomte. Advances in protein and small-molecule charge-density refinement methods using MoPro. *Journal of Applied Crystallography*, 38, 38–54, 2005.
- [19] A. Volkov, P. Macchi, L. J. Farrugia, C. Gatti, P. R. Mallinson, T. Richter, and T. Koritsanszky. *XD2024: A Computer Program Package for Multipole Refinement, Topological Analysis of Charge Densities and Evaluation of Intermolecular Energies from Experimental and Theoretical Structure Factors*. University at Buffalo and collaborating institutions, 2024. Program package and documentation.
- [20] B. Guillot, L. Viry, R. Guillot, C. Lecomte, and C. Jelsch. Refinement of proteins at subatomic resolution with MoPro. *Journal of Applied Crystallography*, 34, 214–223, 2001.
- [21] P. Debye. Interferenz von Röntgenstrahlen und Wärmebewegung. *Annalen der Physik*, 348, 49–92, 1913.
- [22] I. Waller. Zur Frage der Einwirkung der Wärmebewegung auf die Interferenz von Röntgenstrahlen. *Zeitschrift für Physik*, 17, 398–408, 1923.

- [23] H. Hauptman and J. Karle. *Solution of the Phase Problem. I. The Centrosymmetric Crystal*. Number 3 in ACA Monograph. Polycrystal Book Service, Pittsburgh, 1953.
- [24] H. Hauptman. The direct methods of X-ray crystallography. *Science*, 233, 178–183, 1986.
- [25] A. L. Patterson. A fourier series method for the determination of the components of interatomic distances in crystals. *Physical Review*, 46, 372–376, 1934.
- [26] G. Oszlányi and A. Sütő. Ab initio structure solution by charge flipping. *Acta Crystallographica Section A*, 60, 134–141, 2004.
- [27] M. G. Rossmann and D. M. Blow. The detection of sub-units within the crystallographic asymmetric unit. *Acta Crystallographica*, 15, 24–31, 1962.
- [28] G. M. Sheldrick. A short history of SHELX. *Acta Crystallographica Section A*, 64, 112–122, 2008.
- [29] S. Marchesini. Invited article: A unified evaluation of iterative projection algorithms for phase retrieval. *Review of Scientific Instruments*, 78, 011301, 2007.
- [30] A. S. Larsen, T. Rekis, and A. Ø. Madsen. PhAI: A deep-learning approach to solve the crystallographic phase problem. *Science*, 385, 522–528, 2024.
- [31] S. C. Capelli, H.-B. Bürgi, B. Dittrich, S. Grabowsky, and D. Jayatilaka. Hirshfeld atom refinement. *IUCrJ*, 1, 361–379, 2014.
- [32] P. Macchi, L. Garlaschelli, and A. Sironi. Electron density of semi-bridging carbonyls. metamorphosis of CO ligands observed via experimental and theoretical investigations on [FeCo(CO)8]-. *Journal of the American Chemical Society*, 124, 14173–14184, 2002.
- [33] H. Birkedal, D. Madsen, R. H. Mathiesen, K. Knudsen, H.-P. Weber, P. Pattison, and D. Schwarzenbach. The charge density of urea from synchrotron diffraction data. *Acta Crystallographica Section A*, 60, 371–381, 2004.
- [34] R. Bianchi, G. Gervasio, and D. Marabello. The experimental charge density in transition metal compounds. *Comptes Rendus Chimie*, 8, 1392–1399, 2005.
- [35] A. Krawczuk and P. Macchi. Charge density analysis for crystal engineering. *Chemistry Central Journal*, 8, 68, 2014.
- [36] L. Krause, B. Niepötter, C. J. Schürmann, D. Stalke, and R. Herbst-Irmer. Validation of experimental charge-density refinement strategies: When do we overfit? *IUCrJ*, 4, 420–430, 2017.
- [37] A. Volkov, P. Macchi, L. J. Farrugia, C. Gatti, P. R. Mallinson, T. Richter, and T. Koritsanszky. *XD2006: A Computer Program Package for Multipole Refinement, Topological Analysis of Charge Densities and Evaluation of Intermolecular Energies from Experimental and Theoretical Structure Factors*. University at Buffalo, 2006.
- [38] F. L. Hirshfeld. Bonded-atom fragments for describing molecular charge densities. *Theoretica Chimica Acta*, 44, 129–138, 1977.

-
- [39] D. Jayatilaka and B. Dittrich. X-ray structure refinement using aspherical atomic density functions obtained from quantum-mechanical calculations. *Acta Crystallographica Section A*, 64, 383–393, 2008.
- [40] M. Woińska, S. Grabowsky, P. M. Dominiak, K. Woźniak, and D. Jayatilaka. Hydrogen atoms can be located accurately and precisely by X-ray crystallography. *Science Advances*, 2, e1600192, 2016.
- [41] D. Jayatilaka and D. J. Grimwood. Wavefunctions derived from experiment. I. motivation and theory. *Acta Crystallographica Section A*, 57, 76–86, 2001.
- [42] D. J. Grimwood and D. Jayatilaka. Wavefunctions derived from experiment. II. a wavefunction for oxalic acid dihydrate. *Acta Crystallographica Section A*, 57, 87–100, 2001.
- [43] M. L. Davidson, S. Grabowsky, and D. Jayatilaka. X-ray constrained wavefunctions based on hirshfeld atoms. I. method and review. *Acta Crystallographica Section B*, 78, 312–332, 2022.
- [44] A. Genoni, L. H. R. Dos Santos, B. Meyer, and P. Macchi. Can X-ray constrained hartree–fock wavefunctions retrieve electron correlation? *IUCrJ*, 4, 136–146, 2017.
- [45] M. L. Davidson, S. Grabowsky, and D. Jayatilaka. X-ray constrained wavefunctions based on hirshfeld atoms. II. reproducibility of electron densities in crystals of α -oxalic acid dihydrate. *Acta Crystallographica Section B*, 78, 397–415, 2022.
- [46] R. F. W. Bader. *Atoms in Molecules: A Quantum Theory*. Oxford University Press, Oxford, 1990.
- [47] R. F. W. Bader. A quantum theory of molecular structure and its applications. *Chemical Reviews*, 91, 893–928, 1991.
- [48] C. F. Matta and R. J. Boyd, editors. *The Quantum Theory of Atoms in Molecules: From Solid State to DNA and Drug Design*. Wiley-VCH, Weinheim, 2007.
- [49] A. D. Becke and K. E. Edgecombe. A simple measure of electron localization in atomic and molecular systems. *The Journal of Chemical Physics*, 92, 5397–5403, 1990.
- [50] M. Kohout. A measure of electron localizability. *International Journal of Quantum Chemistry*, 97, 651–658, 2004.
- [51] K. R. Roby. Quantum theory of chemical valence concepts: I. definition of the charge on an atom in a molecule and of occupation numbers for electron density shared between atoms. *Molecular Physics*, 27, 81–104, 1974.
- [52] M. D. Gould, C. Taylor, S. K. Wolff, G. S. Chandler, and D. Jayatilaka. A definition for the covalent and ionic bond index in a molecule. *Theoretical Chemistry Accounts*, 119, 275–290, 2008.
- [53] F. Weinhold and C. R. Landis. Natural bond orbital analysis: A critical overview of relationships to alternative bonding perspectives. *Journal of Computational Chemistry*, 33, 2363–2379, 2012.

- [54] E. D. Glendening, C. R. Landis, and F. Weinhold. NBO 6.0: Natural bond orbital analysis program. *Journal of Computational Chemistry*, 34, 1429–1437, 2013.
- [55] E. D. Glendening and F. Weinhold. Natural resonance theory: I. general formalism. *Journal of Computational Chemistry*, 19, 593–609, 1998.
- [56] E. D. Glendening and F. Weinhold. Natural resonance theory: II. natural bond order and valency. *Journal of Computational Chemistry*, 19, 610–627, 1998.
- [57] E. D. Glendening, J. K. Badenhoop, and F. Weinhold. Natural resonance theory: III. chemical applications. *Journal of Computational Chemistry*, 19, 628–646, 1998.
- [58] R. S. Mulliken. Electronic population analysis on LCAO–MO molecular wave functions. I. *The Journal of Chemical Physics*, 23, 1833–1840, 1955.
- [59] P.-O. Löwdin. On the non-orthogonality problem connected with the use of atomic wave functions in the theory of molecules and crystals. *The Journal of Chemical Physics*, 18, 365–375, 1950.
- [60] A. E. Reed, R. B. Weinstock, and F. Weinhold. Natural population analysis. *The Journal of Chemical Physics*, 83, 735–746, 1985.
- [61] C. Fonseca Guerra, J.-W. Handgraaf, E. J. Baerends, and F. M. Bickelhaupt. Voronoi deformation density (VDD) charges: Assessment of the mulliken, bader, hirshfeld, weinhold, and VDD methods for charge analysis. *Journal of Computational Chemistry*, 25, 189–210, 2004.
- [62] A. V. Marenich, S. V. Jerome, C. J. Cramer, and D. G. Truhlar. Charge model 5: An extension of hirshfeld population analysis for the accurate description of molecular interactions in gaseous and condensed phases. *Journal of Chemical Theory and Computation*, 8, 527–541, 2012.
- [63] C. M. Breneman and K. B. Wiberg. Determining atom-centered monopoles from molecular electrostatic potentials. the need for high sampling density in formamide conformational analysis. *Journal of Computational Chemistry*, 11, 361–373, 1990.
- [64] T. A. Manz and D. S. Sholl. Chemically meaningful atomic charges that reproduce the electrostatic potential in periodic and nonperiodic materials. *Journal of Chemical Theory and Computation*, 6, 2455–2468, 2010.
- [65] J. M. Bijvoet, A. F. Peerdeman, and A. J. van Bommel. Determination of the absolute configuration of optically active compounds by means of X-rays. *Nature*, 168, 271–272, 1951.
- [66] H. D. Flack. On enantiomorph-polarity estimation. *Acta Crystallographica Section A*, 39, 876–881, 1983.
- [67] L. K. Templeton, D. H. Templeton, J. C. Phillips, and K. O. Hodgson. Anomalous scattering of X-rays by cesium and cobalt measured with synchrotron radiation. *Acta Crystallographica Section A*, 36, 436–442, 1980.
- [68] D. H. Templeton and L. K. Templeton. X-ray dichroism and polarized anomalous scattering of the uranyl ion. *Acta Crystallographica Section A*, 38, 62–67, 1982.

- [69] D. H. Templeton and L. K. Templeton. X-ray dichroism and anomalous scattering of potassium tetrachloroplatinate(II). *Acta Crystallographica Section A*, 41, 365–371, 1985.
- [70] D. H. Templeton and L. K. Templeton. Polarized dispersion of X-rays in pyrite. *Acta Crystallographica Section A*, 53, 352–355, 1997.
- [71] G. Bunker. *Introduction to XAFS: A Practical Guide to X-ray Absorption Fine Structure Spectroscopy*. Cambridge University Press, Cambridge, 2010.
- [72] J. J. Rehr and R. C. Albers. Theoretical approaches to X-ray absorption fine structure. *Reviews of Modern Physics*, 72, 621–654, 2000.
- [73] Y. Joly. X-ray absorption near-edge structure calculations beyond the muffin-tin approximation. *Physical Review B*, 63, 125120, 2001.

2 Research Objectives

Single-crystal X-ray diffraction is commonly regarded as the definitive method and gold standard for establishing molecular and solid-state structures. Nevertheless, the measured diffraction intensities do not constitute a structure by themselves. Every structural and chemical conclusion depends on the quality of the experiment, the corrections applied to the data, and the electron-density model used during refinement. This distinction has become increasingly important as modern laboratory sources, synchrotrons, and photon-counting detectors have made the collection of large numbers of precise diffraction datasets substantially faster. The principal bottleneck is therefore shifting from data acquisition towards the reliable, reproducible, and chemically meaningful interpretation of the recorded intensities. Achieving this goal requires more accurate crystallographic models and a better understanding of the individual components of the crystallographic workflow.

The objective of this dissertation is to advance and utilise small-molecule single-crystal X-ray diffraction beyond the routine determination of connectivity and geometry. The work pursues two closely connected aims. First, it seeks to identify, quantify, and reduce limitations that compromise the agreement between the measured diffraction data and the crystallographic model (Figure 2.1). Second, it aims to establish how experimentally informed electron-density and wavefunction models can be used to answer chemical questions that are not accessible from an independent atom model alone. The studies therefore span database-scale quality assessment, automated serial refinement, anomalous dispersion, radiation damage, and quantum-crystallographic analyses of bonding in main-group, transition-metal, and actinide compounds.

2.1 Crystallographic models

A first objective is to determine whether the major technological and computational advances in crystallography have translated into a measurable improvement in published crystal structures. For this purpose, quality indicators from approximately 1.4 million entries in the Cambridge Structural Database are analysed as functions of publication year and elemental composition. The temporal analysis is designed to distinguish absolute changes in conventional indicators such as $R1$, $wR2$, and the minimum and maximum residual electron-density peaks from changes caused by the increasing complexity of the structures under investigation. The elemental analysis aims to identify regions of the periodic table in which the independent atom model or the treatment of experimental effects is particularly inadequate. This database-wide perspective provides the statistical context for the more targeted methodological studies in the dissertation.

The rapidly increasing number of diffraction datasets also creates a need for reproducible and efficient model comparison. A further objective is therefore to develop a general procedure for serial crystallographic refinement.

2.2 Anomalous dispersion refinements

Heavy-element structures present a particularly demanding test of crystallographic accuracy because strong absorption, anomalous dispersion, relativistic effects, Fourier trun-

$$f_j = \boxed{f_{j,0}} + \boxed{f'_j + i f''_j}$$

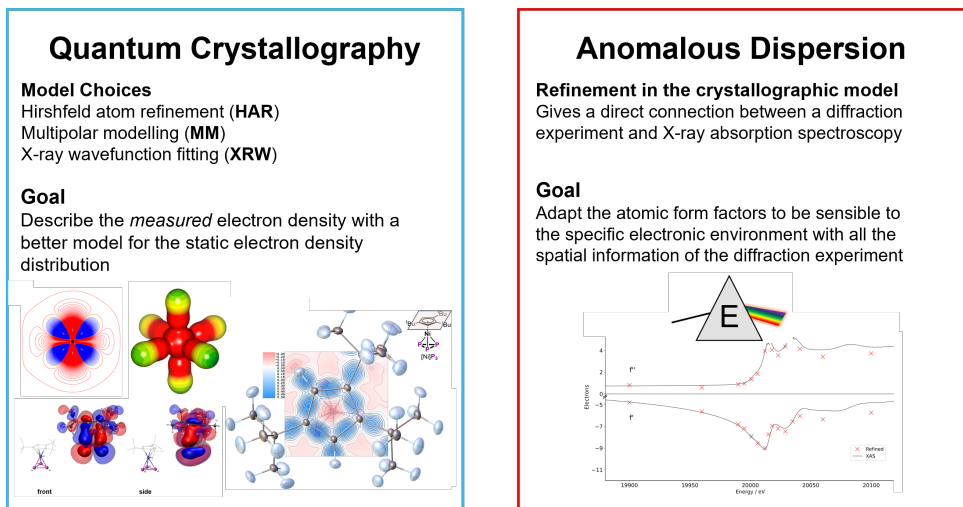


Figure 2.1: Methodological overview of approaches used in this dissertation to improve the crystallographic model and extract chemically meaningful information from it. The atomic form factors can be both improved by quantum crystallography and used as a probe by refining the anomalous dispersion correctional parameters for a specific site in the structure.

cation, and radiation damage can all produce systematic features in the refined model. One objective of this dissertation is to improve the treatment of anomalous dispersion in uranium compounds. The dispersive and absorptive corrections, f' and f'' , are refined directly against single-crystal diffraction data collected around the uranium L absorption edges. Simultaneously recorded X-ray absorption spectra and their Kramers–Kronig transforms serve as independent experimental references. The study is designed to establish whether anomalous dispersion refinement can reproduce element- and site-specific spectral features, whether tabulated values are adequate near an absorption edge, and whether refinement of these parameters can improve structures measured using conventional Mo K α radiation.

A complementary objective is to characterise radiation damage in small-molecule crystallography. Triphenylbismuth (BiPh_3) is investigated through extensive serial diffraction experiments at synchrotron and laboratory sources over a range of energies and temperatures. The purpose is to determine how diffraction intensity, unit-cell dimensions, atomic displacement parameters, bond precision, residual density, and conventional quality indicators evolve with absorbed dose. Measurements around the Bi L_3 edge, together with X-ray absorption spectroscopy and relativistic electronic-structure calculations, are used to distinguish dose-rate effects from changes in the microscopic damage mechanism. Particular attention is given to whether the loss of diffraction arises from specific bond cleavage or from a more general loss of crystalline periodicity.

2.3 Quantum crystallography

The second major part of the dissertation investigates whether diffraction-derived electron-density and wavefunction models can provide robust chemical information. A central methodological principle is the use of complementary descriptions. Multipolar modelling provides a flexible experimental parameterisation of aspherical electron density, Hirshfeld atom refinement combines experimental diffraction data with quantum-chemically derived atomic scattering factors, and X-ray restrained wavefunction fitting introduces the measured structure factors directly into wavefunction optimisation. The convergence of these approaches with conventional quantum-chemical calculations, spectroscopy, and chemically meaningful reference systems serves as the principal criterion for interpretation.

The bonding in $\text{Cp}^{\text{III}}\text{NiP}_3$ is studied to test Hoffmann’s isolobal analogy between the $\text{Cp}^{\text{III}}\text{Ni}$ fragment and a phosphorus atom in white phosphorus. The objective is not only to establish the existence and character of the Ni–P and P–P interactions, but also to determine whether the experimentally informed electronic structure explains the distinct stability and reactivity of $\text{Cp}^{\text{III}}\text{NiP}_3$ and P_4 . Multipolar modelling, Hirshfeld atom refinement, X-ray restrained wavefunction fitting, density-functional calculations, orbital and real-space bonding analyses, and solid-state ^{31}P NMR spectroscopy are combined to relate electron density, bond character, frontier orbitals, and dynamic behaviour. The behavior of anomalous dispersion effects in all three applied quantum crystallographic models is investigated at a borderline case in $\text{Cp}^{\text{III}}\text{NiP}_3$ which contains a highly $\text{CuK}\beta$ absorbing nickel species.

The synthesis and quantum-crystallographic analysis of WYLID address a second class of chemically ambiguous bonding descriptions. The objectives are to identify the red side product formed during the synthesis of the widely used YLID calibration crystal, establish a selective synthetic route, and determine whether its S–C interaction is better described as ylidic or ylenic and whether the adjacent C–O group is better represented as a carbonyl or an enolate. The presence of three C–O groups in different electronic environments, together with comparisons to YLID and indandione, provides an internal reference system for separating local substituent effects from general delocalisation. Multi-wavelength diffraction and complementary charge-density and wavefunction analyses are used to develop a transferable strategy for distinguishing between competing resonance descriptions.

The most stringent test of the quantum-crystallographic approach is the investigation of three-centre thorium–thorium bonding in two trithorium clusters containing either two delocalised electrons or one delocalised electron in the Th_3 core. The objective is to determine whether Hirshfeld atom refinement can be extended to complexes containing three closely spaced $Z = 90$ centres and whether routine-resolution laboratory diffraction data contain sufficient information to visualise the weak actinide–actinide interaction. Agreement between the experimentally based HAR densities and independent relativistic quantum-chemical calculations is assessed using bond critical points, Laplacian distributions, electron-localisability indicators, deformation densities, and residual-density differences. This study is intended both to test the proposed Th_3 bonding models and to establish the practical limits of HAR for heavy-element chemistry.

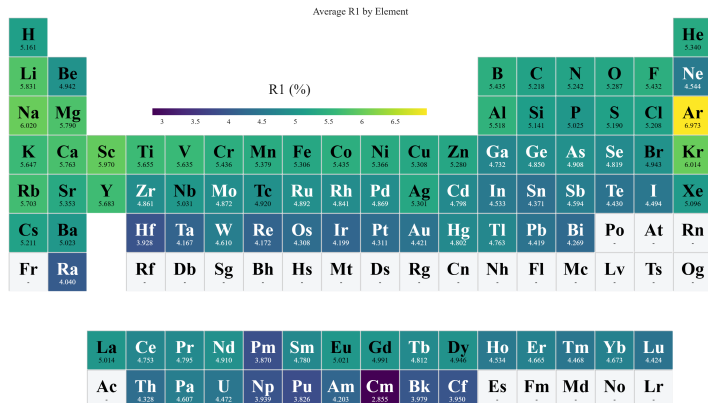
Across all studies, the unifying objective is to establish a workflow in which experimental design, physical corrections, automated model comparison, advanced electron-density modelling, and independent chemical validation are treated as inseparable components. The central premise of this dissertation is that more intense sources and more sophisticated

calculations do not automatically produce more reliable chemical conclusions. Progress instead depends on matching the experiment, correction model, and electron-density description to the scientific question and on demonstrating that the resulting interpretation is stable across complementary methods.

2.4 Software

In order to help systematically evaluate these approaches, effects, and models, the aid of a software package is immensely helpful. For this purpose, a program is developed to automate the refinement of multiple datasets and the comparison of different modelling strategies. The resulting Olex2 module SISYPHOS is designed to refine a common starting model against multiple diffraction datasets or to refine one dataset using multiple modelling strategies, while adapting relevant experimental parameters and extracting the resulting structural and statistical information in a consistent format. The intended applications include crystal screening, multi-temperature experiments, resonant diffraction, radiation-damage series, electron diffraction, mixed-occupancy problems, and the systematic benchmarking of quantum-crystallographic calculations. Automation is not intended to replace crystallographic judgement, but to remove avoidable inconsistencies and make large-scale comparisons traceable and reproducible.

3 A temporal and elemental analysis of the CSD



Preface

The following chapter has been submitted for publication under the title:

“Are crystal structures getting better? A temporal and elemental analysis of the Cambridge Structural Database”

Authors

Florian Meurer

Abstract

In this work, the temporal progression of quality indicators in the Cambridge Structural Database is evaluated statistically. R1, wR2, and the minimum and maximum residual electron density peaks show a trend of stagnation (R1, densities) or regression (wR2) for structural quality over time. In contrast, cell volume-normalised quality indicators show an improvement in recent crystal structures in the CSD. Also, quality indicators are plotted on an elemental basis, and their trends are described.

3.1 Introduction

Single-crystal structure determination by X-ray, neutron, or electron diffraction is the gold standard for qualitative analysis (Bragg & Bragg, 1913; Ewald, 1962; Authier, 2013). With a rich and successful history, structural scientists can look back at over 110 years of development, advances, and applications. As far as data management is concerned, a cornerstone for small-molecule structures was the foundation of the Cambridge Structural Database (CSD) by Olga Kennard in 1965 (Allen, 2002; Groom et al., 2016; Hargittai

& Hargittai, 2023). The CSD quickly became the central home of curated and machine-readable structural data. Today, with about 1.4 million structures, the CSD is one of the largest curated scientific databases in the world (Taylor & Wood, 2019). With a modern software toolkit for structural analysis (Bruno et al., 2002a; Allen & Bruno, 2010), the database is versatile and useful in various fields employing structural science, including small-molecule chemistry, structural chemistry, crystal engineering, pharmaceutical chemistry, computational chemistry, materials science, quantum crystallography, machine-learning and data-driven modelling, and educational applications (Battle et al., 2010; Allen & Bruno, 2010; Pallikara et al., 2024; Stuke et al., 2020). This is especially true in small-molecule crystallography, where CSD-based tools provide duplicate checks for newly determined structures, while the CSD deposition workflow incorporates structural validation through the IUCr checkCIF/PLATON service (Bruno et al., 2002b; Spek, 2009). The database further supports systematic analyses of molecular conformations, intermolecular interactions, crystal packing, crystal engineering, and polymorphism. Single-crystal structure determination has undergone numerous significant improvements, both from a technological and a software perspective. For instance, X-ray radiation sources have experienced a massive improvement: modern rotating-anode sources and metal-jet technology now produce above $10^{11} - 10^{13}$ photons/s (Hemberg et al., 2003; Graw et al., 2023), bringing them to the same level as 3rd-generation synchrotron facilities only a decade ago (Lindley, 1999). On the other hand, 4th-generation modern synchrotron devices can achieve fluxes of up to $10^{13} - 10^{15}$ photons/s (Eriksson et al., 2014; Raimondi et al., 2023; Schroer et al., 2018), making radiation damage an increasingly significant problem in small-molecule crystallography. Photon detection technologies for X-rays have seen stepwise improvement as well, from point-detectors, which were very accurate, but needed a long time and a stable sample for each experiment, to charge-coupled devices (CCD, (Gruner & Ealick, 1995)), which made data acquisition much faster, to "the best of both worlds", modern photon counting devices, detectors that are fast and able to detect "single photons" (Broennimann et al., 2006; Johnson et al., 2014). Software and modelling techniques were similarly improved by incorporating the Debye-Waller factor (Debye, 1913; Waller, 1923) into the crystallographic model, direct methods for structure solution (Karle & Hauptman, 1950), modern integration and processing techniques (Duisenberg et al., 2003), absorption correction (Blessing, 1995; Krause et al., 2015), and charge density/quantum crystallographic models (Coppens & Hermansson, 1998; Grabowsky et al., 2017; Kleemiss et al., 2021). Computer programs for data collection and processing, such as XDS (Kabsch, 2010), EVAL (Duisenberg et al., 2003), CrysAlisPRO (Rigaku Oxford Diffraction Ltd, 2025), and APEX (APEX Software), and modern structure solution and refinement programs, such as the ShelX suite (Sheldrick, 2015b,a), ShelXle (Hübschle et al., 2011), Olex2 (Bourhis et al., 2015; Dolomanov et al., 2009), and JANA (Petříček et al., 2023) have also seen vast improvements in speed and sophistication.

Last year, Tovee et al. (2025) published a survey of crystallographic quality metrics in the CSD. The authors analysed R-factors, max/min residual electron density peaks, goodness-of-fit values, parameter shifts, and resolution, compared the results across several structure classes, and provided a perspective on future adaptations with respect to machine learning and data mining compatibility.

Complementary to the above survey, this work examines the temporal evolution of accessible quality parameters for structures deposited in the CSD through the end of 2025. The chosen parameters were R1, which has the most extensive coverage across the whole CSD data set, and, additionally, wR2 and the minimum and maximum residual electron

density peaks, which have substantial coverage only in this millennium. R1 provides insight into the agreement between the measured and modelled/calculated structure factors, while wR2 describes the weighted agreement between squared measured and modelled/calculated structure factors. Minimum and maximum residual densities complement the two relative agreement factors with a third absolute value, describing the peaks in the difference Fourier map between the observed and calculated electron densities. Cell volume is considered as a relatively coarse measure of structural complexity, and its implications for structural quality are evaluated.

3.2 Data processing and description

For this work, a dataset was generated based on the CSD entries available via the CSD Python API (V3.6.2) as of 14.02.2026. The dataset contained 1,394,755 entries, which were deposited up to the end of 2025. Table 3.1 summarizes the CSD-extracted fields used for the analyses.

Table 3.1: Data fields extracted from the CSD for this work, the number of entries in each field, and statistical descriptors. N gives the number of entries in the dataset. Name refers to the name used within the manuscript. ESD gives the estimated standard deviation.

field	Name	N	average	mean	min	max	ESD
formula	-	1,393,581	NA	NA	NA	NA	NA
publication_year	-	1,394,719	2010.2	2010.2	1923	2025	11.883
cell_volume / Å ³	-	1,394,231	3490.1	3490.1	15.244	11950873	19831
r_factor / %	R1	1,373,754	5.2133	5.2133	0.026	49.24	2.5071
refinement_weighted_r_factor / %	wR2	1,068,869	13.416	13.416	0.19	74.98	7.1756
refinement_residual_electron_density_min / eÅ ⁻³	min	1,063,997	-0.7057	-0.7057	-49.432	-0.001	0.74045
refinement_residual_electron_density_max / eÅ ⁻³	max	1,064,555	0.89118	0.89118	0.001	49.51	0.984

For the residual electron-density fields, values with absolute magnitude above $50\text{e} \cdot \text{\AA}^{-3}$ were excluded before summary statistics were computed. In addition, the minimum residual electron density (min) was restricted to values ≤ 0 , the maximum residual electron density (max) was restricted to values ≥ 0 , and cell volume was restricted to values > 0 . R1 was restricted to values $\leq 50\%$, and wR2 was restricted to values $\leq 75\%$. This removed 524 entries from cell volume, 27 entries from R1, 199 entries from wR2, 576 entries from min, and 532 entries from max.

3.3 Results and discussion

3.3.1 Temporal evolution

As a first approach to answer the title question, it was informative to look at the progression of the structural quality indicators R1, wR2, and $|\min|/\max$ residual electron density peaks over time. Figure 3.1 shows these developments alongside a linear fitting model. For R1, the data is the most complete, and there is a clear break point around 1980. Therefore, separate fits describe the time before, and after the year 1980. Since the data for wR2 show a more consistent trend, the fit covers the entire range of data from 1964 to 2025. Because the average data points for the residual electron density descriptors were highly variable, their fit was restricted to the time span between 2000 and 2025.

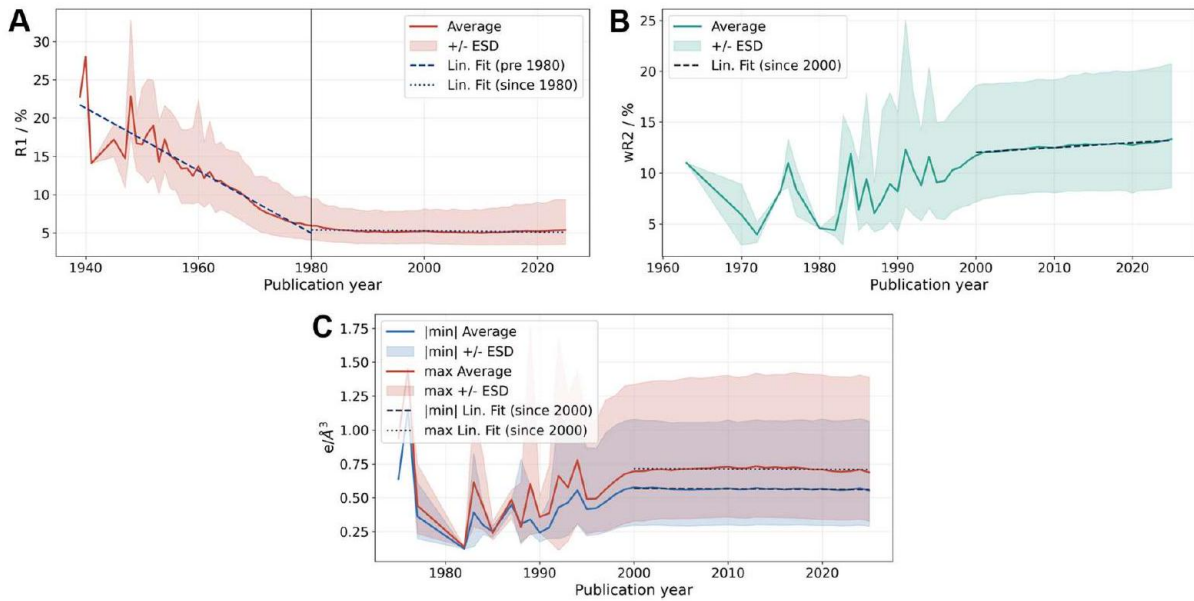


Figure 3.1: Progression of average R1 (A), wR2 (B), and $|\min|/\max$ residual electron density peaks (C) over time, with asymmetric standard deviations around the average value and a linear fit.

The progression of R1 showed a steady decrease with a slope of -0.41% /year until the year 1980, where an average value of 5.92 % was reached. Afterwards, the R1 flattened out with a slope of 0.00% / year . An average R1 value of 5.37% was finally reached for 2025. The progression in R1 indicated a stable plateau after 1980, with an increasing error, and thus more diverging values, but still centred around the post-1980 average of 5.17% (slightly lower than the global average of 5.21%). In contrast, the wR2 showed a steady increase, indicating a worsening of the weighted agreement between measured and calculated squared structure factors. Here, the fit described a 0.05% / year increase, which was low but statistically significant. This trend was also reflected in the $|\min|/\max$ residual electron density peaks, where both again showed a low, but significant increase of $0.007e \cdot \text{\AA}^{-3}$ / year, while their scatter remained essentially unchanged since 2000. The temporal progression shows that the asymmetry, which was also described by Tovee et al. (2025), has been a stable feature in the database since at least the beginning of the millennium, after which this statistic was consistently included in the entries.

Most importantly, these trends describe a generally high quality of crystal structures and immense improvements in the crystal structures' data-model agreement since their beginning. For a timespan of over forty years, the trends describe a combination of improvements in technology and software, and the increased tractability of complicated crystal structures. The most recent trends suggest that the average quality of crystal structures has been decreasing very slowly; this trend is more pronounced in the weighted structure factors than in the measured and calculated intensities themselves. The asymmetry in residual electron density peaks supports the same trend. This asymmetry also shows that, on average, in the entire CSD, there is an excess of positive, or unexplained residual electron density. Alongside systematic or artificial errors, this residual electron density should also capture the shortcomings of the independent atom model, which is unable to describe chemical bonding correct and thus making a strong case for the adoption of non-spherical atomic form factors, which are obtained by quantum crystallographic methods, such as Hirshfeld atom refinement or multipole/database approaches (Jayatilaka & Ditttrich, 2008; Capelli et al., 2014; Hansen & Coppens, 1978; Pichon-Pesme et al., 1995). Non-spherical atomic form factors have especially in the last years become more accessible by recent software developments like NoSpherA2 in Olex2 or DiSCaMB (Kleemiss et al., 2021; Chodkiewicz et al., 2018).

A possible descriptor of increasing complexity in crystal structures is the cell volume, since in general, larger molecules or larger unit cells lead to greater complexity in both the data and the model. For this study, cell volume-normalised quality indicators were calculated and fitted with a linear fit (Figure 3.2).

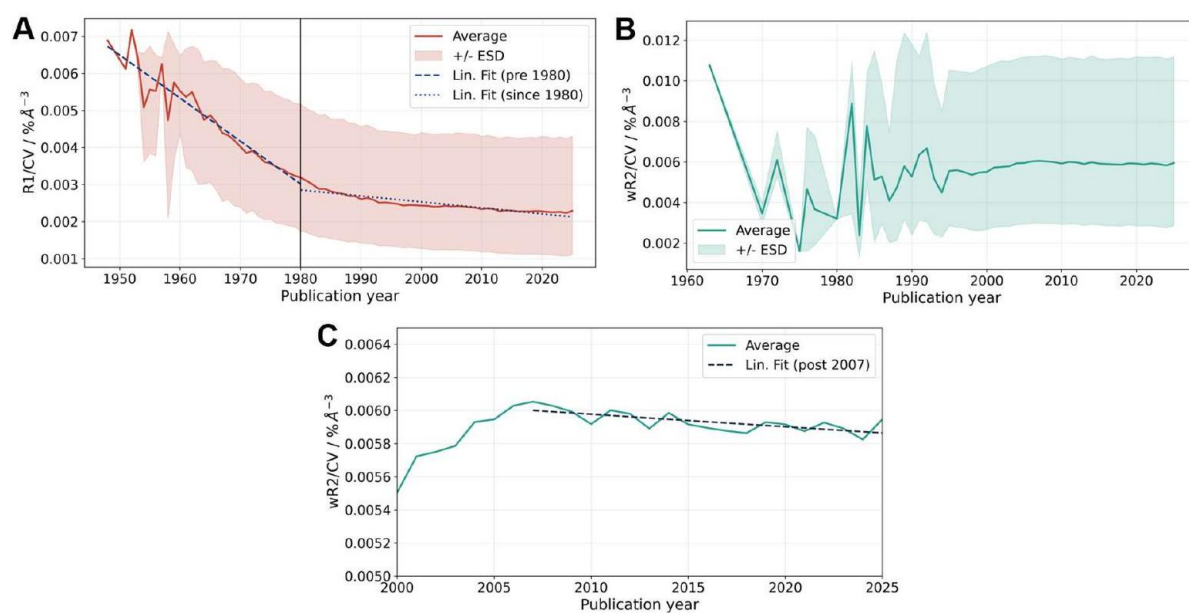


Figure 3.2: Progression of the cell-volume normalised average R1 (A), wR2 (B) over time, with asymmetric standard deviations around the average value, a linear fit and a zoomed region of **B** with a fit from the publication year 2007 (C).

For the cell-volume-normalised R1 metric, the progression pre-1980 also showed a significant decrease with a slope of $-1.16 \times 10^{-4} \% / \text{\AA}^{-3}$ per year. Additionally, the post-1980 progression fit for this metric showed a significant decrease with a slope of $-1.61 \times 10^{-5} \% / \text{\AA}^{-3}$ per year. This showed that the average cell volume per structure, as a proxy for structure

complexity, increased faster than the ratio of measured and calculated reflection intensities. On the other hand, the normalised wR2 remained nearly unchanged, with the linear fit showing a low but significant slope of $-0.80 \times 10^{-5}\%/\text{\AA}^{-3}$ per year, corresponding to recent improvements in wR2 relative to the increase in cell volume.

In summary, the CSD temporal data describe an incongruity between R1 and wR2. While R1 decreased until ca. 1980 and then remained stable to the present day, wR2 rose slowly but significantly every year, indicating a lower agreement between the weighted measured and calculated structure factors on average. When the cell volume as an indicator of structure complexity was taken into account, the trend in normalised wR2 was reversed, as wR2 decreased concomitantly with the normalised R1. This indicated that, on average, the structure quality (after normalizing for cell volume) increased.

3.3.2 Elemental data

Another question that was addressed by the examination of this CSD data set was where in the periodic table problematic regions were located, and which elements had a statistically positive or negative influence on structural quality.

Figure 3.3 shows the average R1 and wR2 values for each element in the Periodic Table (PT). In general, there is a good agreement between the elemental values for R1 and wR2. Carbon-containing structures have R1 and wR2 values of 5.22% and 13.47%, respectively, which are very close to the global averages for R1 and wR2, consistent with most structures in the CSD containing carbon. Notably, the heavier halogens Br and I, which are notorious for absorption issues and artificial residual electron densities, nevertheless show lower-than-average, and thus better, quality indicators.

General trends in these data are that, with increasing atomic number, the quality indicators R1 and wR2 improve, while $|\min|$ and max densities increase. For R1 and wR2, the trend shows that with increasing scattering power, structures are more clearly defined by the heavy atoms, their positions, and ADPs. These two relative quality indicators are less affected by small inaccuracies, e.g., due to disorder or other crystallographic challenges than by the heavy-atom atomic parameters. Also implicated in this trend is that for lighter elements, bonding density, which is uncaptured by the default independent atom model, makes up a higher percentage of the total electron density or scattering power. This effect further worsens the relative quality indicators for lighter atomic structures. To improve quality indicators for lighter-element structures, a non-spherical atomic form factor could provide significant benefits across the CSD and PT.

The $|\min|$ and max residual electron density, however, indicate in absolute terms the features not modelled in the crystal structure. As Z rises, these absolute numbers increase as well and a better treatment of artificial effects, such as absorption correction or anomalous dispersion correction, becomes more and more necessary for heavier element structures.

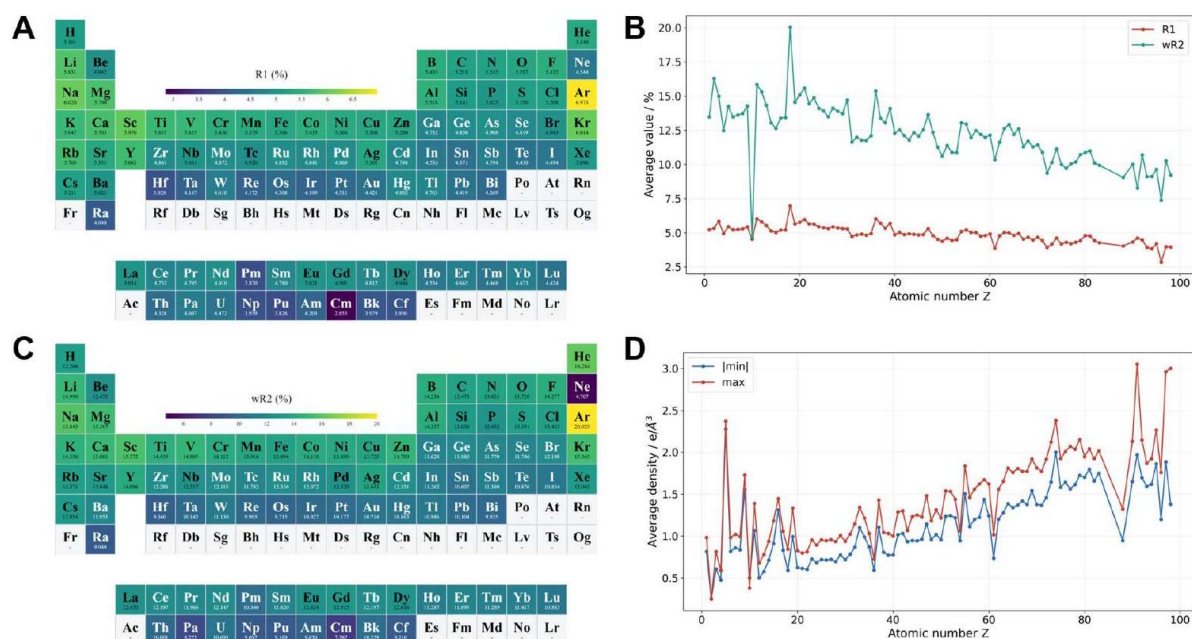


Figure 3.3: Average R1 (A) and wR2 (C) values per element in the periodic table of the elements. Average R1 and wR2 (B) and |min| and max residual electron densities (D) are given as a function of the atomic number Z. Averages are calculated on an occurrence basis, rather than weighted by their molar frequency in a given sum formula. The Ne sample deviates because of only two usable entries.

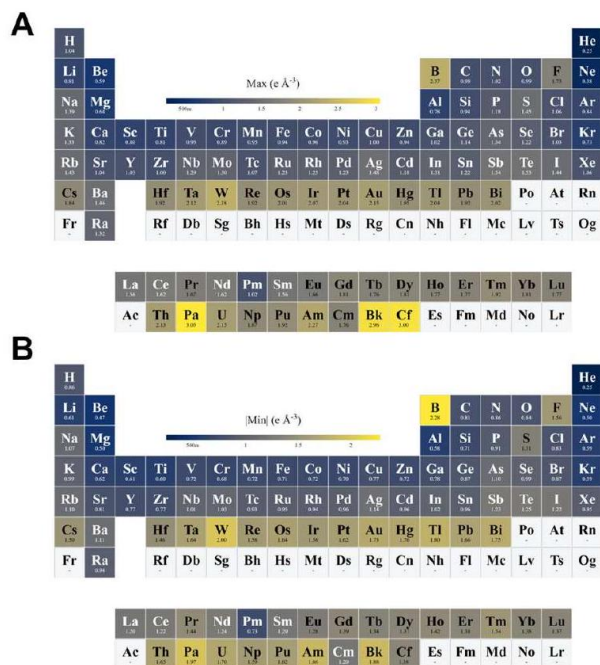


Figure 3.4: Average max(A) and |min|(B) residual electron density values per element in the periodic table of the elements. Averages are calculated on an occurrence basis, rather than weighted by their molar frequency in a given sum formula.

Figure 3.4 shows the PTs color-coded by $|\min|$ and max residual electron density. A surprising outlier is boron, which could indicate high complexity in chemical bonding, which is again not fully captured by the independent atom model, or general crystallographic problems such as low crystal quality in boron-containing structures. A similar pattern is observed to a lesser degree with fluorine, sulfur, and the alkali metals, except for lithium. Tungsten is the subjectively most important element with relatively large residual densities.

3.4 Conclusion

In conclusion, this work presents the temporal evolution of selected quality indicators in the CSD, which comprises almost 1.4 million structures as of the end of 2025. The trends show a significant increase in wR2 and a stable plateau in R1, indicating an influence of either the difference between intensities and structure factors or the employed weighting scheme. When cell volume is taken into account as an index of structural complexity, both normalised wR2 and normalised R1 show improved quality over at least the last 19 years. A comparison of min and max residual electron densities reveals the stable temporal progression of these residuals, possibly attributable to the shortcomings of the independent atom model.

When quality indicators were analysed on an elemental basis, the trends observed were an increase in min and max residual electron density and an improvement in relative quality indicators wR2 and R1 as functions of atomic number. These trends in both the relative and absolute measures were as expected for crystallographic reasons. Part of the trend toward poorer R1 and wR2 values for low-Z structures could also be explained by shortcomings of the independent-atom model, while high min and max densities for heavy elements could be improved by better treatment of their relativistic, absorption, and anomalous dispersion effects.

3.5 References

- Allen, F. H. (2002). *Acta Cryst. B* 58, 380-388.
Allen, F. H. & Bruno, I. J. (2010). *Acta Cryst. B* 66, 380-386.
Authier, A. (2013). *Early Days of X-ray Crystallography*. Oxford: Oxford University Press.
Battle, G. M., Ferrence, G. M. & Allen, F. H. (2010). *J. Appl. Cryst.* 43, 1208-1223.
Blessing, R. H. (1995). *Acta Cryst. A* 51, 33-38.
Bourhis, L. J., Dolomanov, O. V., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2015). *Acta Cryst. A* 71, 59-75.
Bragg, W. H. & Bragg, W. L. (1913). *Proc. R. Soc. London Ser. A* 88, 428-438.
Broennimann, C., Eikenberry, E. F., Henrich, B., Horisberger, R., Huelsen, G., Pohl, E., Schmitt, B., Schulze-Briesse, C., Suzuki, M., Tomizaki, T., Toyokawa, H. & Wagner, A. (2006). *J. Synchrotron Rad.* 13, 120-130.
Bruker (2026). APEX Software, Bruker APEX software page (accessed 22 June 2026).
Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). *Acta Cryst. B* 58, 389-397.
Coppens, P. & Hermansson, K. (1998). *Phys. Today* 51, 66-68.
Debye, P. (1913). *Ann. Phys.* 43, 49-92.

- Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* 42, 339-341.
- Duisenberg, A. J. M., Kroon-Batenburg, L. M. J. & Schreurs, A. M. M. (2003). *J. Appl. Cryst.* 36, 220229.
- Eriksson, M., van der Veen, J. F. & Quitmann, C. (2014). *J. Synchrotron Rad.* 21, 837-842.
- Ewald, P. P. (1962). Editor. *Fifty Years of X-ray Diffraction*. Utrecht: N. V. A. Oosthoek's Uitgeversmaatschappij.
- Grabowsky, S., Genoni, A. & Bürgi, H.-B. (2017). *Chem. Sci.* 8, 4159-4176.
- Graw, N., Ruth, P. N., Ernemann, T., Herbst-Irmer, R. & Stalke, D. (2023). *J. Appl. Cryst.* 56, 13151321.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst. B* 72, 171-179.
- Gruner, S. M. & Ealick, S. E. (1995). *Structure* 3, 13-15.
- Hargittai, M. & Hargittai, I. (2023). *Struct. Chem.* 34, 751-753.
- Hemberg, O., Otendal, M. & Hertz, H. M. (2003). *Appl. Phys. Lett.* 83, 1483-1485.
- Hübschle, C. B., Sheldrick, G. M. & Dittrich, B. (2011). *J. Appl. Cryst.* 44, 1281-1284.
- Johnson, I., Bergamaschi, A., Billich, H., Cartier, S., Dinapoli, R., Greiffenberg, D., Guizar-Sicairos, M., Henrich, B., Jungmann, J., Mezza, D., Mozzanica, A., Schmitt, B., Shi, X. & Tinti, G. (2014). *J. Instrum.* 9, C05032.
- Kabsch, W. (2010). *Acta Cryst. D* 66, 125-132.
- Karle, J. & Hauptman, H. (1950). *Acta Cryst.* 3, 181-187.
- Kleemiss, F., Dolomanov, O. V., Bodensteiner, M., Peyerimhoff, N., Midgley, L., Bourhis, L. J., Genoni, A., Malaspina, L. A., Jayatilaka, D., Spencer, J. L., White, F., Grundkötter-Stock, B., Steinhauer, S., Lentz, D., Puschmann, H. & Grabowsky, S. (2021). *Chem. Sci.* 12, 1675-1692.
- Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* 48, 3-10.
- Lindley, P. F. (1999). *Acta Cryst. D* 55, 1654-1662.
- Pallikara, I., Skelton, J. M., Hatcher, L. E. & Pallipurath, A. R. (2024). *Cryst. Growth Des.* 24, 69116930.
- Petríček, V., Palatinus, L., Plášil, J. & Dušek, M. (2023). *Z. Kristallogr. Cryst. Mater.* 238, 271-282.
- Raimondi, P., Benabderrahmane, C., Berkvens, P., Biasci, J. C., Borowiec, P., Bouteille, J.-F., Brochard, T., Brookes, N. B., Carmignani, N., Carver, L. R., Chaize, J.-M., Chavanne, J., Checchia, S., Chushkin, Y., Cianciosi, F., Di Michiel, M., Dimper, R., D'Elia, A., Einfeld, D., Ewald, F., Farvacque, L., Goirand, L., Hardy, L., Jacob, J., Jolly, L., Krisch, M., Le Bec, G., Leconte, I., Liuzzo, S. M., Maccarrone, C., Marchial, T., Martin, D., Mezouar, M., Nevo, C., Perron, T., Plouviez, E., Reichert, H., Renaud, P., Revol, J.-L., Roche, B., Scheidt, K.-B., Serriere, V., Sette, F., Susini, J., Torino, L., Versteegen, R., White, S. & Zontone, F. (2023). *Commun. Phys.* 6, 82.
- Rigaku Oxford Diffraction (2025). CrysAlisPro software system. Rigaku Corporation, Wrocław, Poland.
- Schroer, C. G., Agapov, I., Brefeld, W., Brinkmann, R., Chae, Y.-C., Chao, H.-C., Eriksson, M., Keil, J., Nuel Gavalda, X., Röhlberger, R., Seeck, O. H., Sprung, M., Tischer, M., Wanzenberg, R. & Weckert, E. (2018). *J. Synchrotron Rad.* 25, 1277-1290.
- Sheldrick, G. M. (2015 a). *Acta Cryst. A* 71, 3-8.
- Sheldrick, G. M. (2015 b). *Acta Cryst. C* 71, 3-8.

- Spek, A. L. (2009). *Acta Cryst. D* 65, 148-155.
- Stuke, A., Kunkel, C., Golze, D., Todorović, M., Margraf, J. T., Reuter, K., Rinke, P. & Oberhofer, H. (2020). *Sci. Data* 7, 58.
- Taylor, R. & Wood, P. A. (2019). *Chem. Rev.* 119, 9427-9477.
- Tovee, C. A., Wiggin, S. B., Johnson, N. T., Andrews, P. I. & Lightfoot, M. P. (2025). *IUCrJ* 12, 647657.
- Waller, I. (1923). *Z. Phys.* 17, 398-408.

3.6 Supporting Information

The supporting information of this work is provided as a single .pdf file with original format and page numbering starting from the next page.

Supporting information

S1. Data collection and processing

S1.1. CSD Python API CSV generation.

The CSV datasets used in this study were generated directly from the CSD Python API. Extraction scripts iterated over `EntryReader('CSD').entries()` and wrote one row per structure to a CSV file. The main export included identifiers, formula, publication metadata, crystal properties, refinement metrics, and experimental information. In particular, the extracted fields included refcode, accession number, formula, cell parameters and volume, calculated density, space group descriptors, R factors, weighted R factors, goodness of fit, residual electron-density extrema, reflection counts, radiation metadata, and publication year.

- The comprehensive CSV export was implemented in scripts such as `enhanced_csd_extraction.py` and `fetch_csd_comprehensive.py`.
- Chunked exports `csd.part*.csv` were used for downstream analyses to keep memory use manageable.
- The filtering utility `analyse_csd.py` wrote `csd_filtered.csv` from the CSD API after applying structure-level criteria.
- The temporal analysis scripts read the part files and derived time-dependent statistics from the exported columns.

S1.2. Derived datasets

The downstream analysis produced yearly trend tables, per-element average datasets, and periodic-table/Z-axis plots. Element-level metrics were computed from parsed molecular formulas and aggregated by element presence. For the Z-axis plots, each element symbol was mapped to its atomic number and plotted in natural periodic order.

S2. Temporal-quality analysis

Table S1 Overview of the linear fit statistics in Figures 1 and 2.

plot	Lin. fit	year_min	year_max	n_years	slope_per_year	r_squared	p_value
R1	≤ 1980	1939	1980	38	-0.409039	0.845496	3.59786×10^{-16}
R1	≥ 1980	1980	2025	46	-0.00678503	0.205408	0.00156144
wR2	≥ 2000	2000	2025	26	0.0465002	0.906753	7.28591×10^{-14}
R1/CV	≤ 1980	1948	1980	31	-0.000116098	0.904031	2.68101×10^{-16}
R1/CV	≥ 1980	1980	2025	46	-1.60555×10^{-5}	0.821375	4.58311×10^{-18}
R2/CV	≥ 2007	2007	2025	19	-7.51897×10^{-6}	0.492812	0.00080676

S3. Elemental-average analysis

Average metrics versus atomic number. Average R1 and wR2 were plotted against atomic number Z, together with average |min| and max residual densities. The R1/wR2 panel includes horizontal reference lines for the global averages, and the wR2 periodic-table plot was also generated without Ne as a sensitivity check.

Table S2 Correlations of elemental averages with the atomic number Z.

metric	n	pearson_r	spearman_rho
R1	93	-0.766414	-0.808361
wR2	93	-0.708099	-0.810973
abs_min_density	93	0.733300	0.771180
max_density	93	0.795960	0.817388

S4. AI statement

For the data analysis and dataset generation, the GitHub Copilot in the Microsoft Visual Studio Code Editor was used.

Role of the AI assistant. An AI coding assistant (GPT-5.4 mini) was used to inspect the existing CSV-generation and analysis scripts, collate the plotting outputs, verify the Ne-specific data source, and draft this Supporting Information document in a concise IUCr-style format. The assistant also generated contents of the supporting information from these outputs.

The author has reviewed all output and code that the AI provided for consistency.

S5. Plotted data

S5.1. Fig 1 A

year	mean	esd_minus	esd_plus	N
1939	22.800	0.000	0.000	1
1940	28.000	0.000	0.000	1
1941	14.100	0.000	0.000	1
1945	17.200	2.267	2.025	4
1947	14.750	3.889	3.889	2
1948	22.822	5.207	10.000	9
1949	16.713	3.613	3.671	15
1950	16.547	4.007	7.435	15
1951	18.016	6.522	7.091	19
1952	19.020	6.495	5.924	21
1953	14.293	4.142	5.277	42
1954	17.228	4.156	4.427	33
1955	15.072	4.275	5.881	29

1956	14.511	3.982	5.411	48
1957	13.403	4.589	5.082	38
1958	13.465	4.614	4.980	57
1959	12.442	3.650	6.381	67
1960	13.723	4.729	8.726	102
1961	12.197	3.861	4.696	133
1962	13.005	4.027	6.639	156
1963	11.770	4.097	4.783	219
1964	11.777	3.750	5.112	243
1965	11.184	3.437	4.722	386
1966	10.806	3.489	4.908	426
1967	10.492	3.610	5.095	569
1968	9.926	3.482	4.335	672
1969	9.256	3.330	4.342	863
1970	8.592	3.052	3.717	941
1971	8.031	2.938	4.385	1200
1972	7.636	2.684	4.646	1678
1973	7.354	2.630	4.308	1721
1974	7.081	2.454	4.480	1871
1975	6.774	2.302	3.971	2029
1976	6.485	2.082	3.819	2494
1977	6.238	1.954	3.444	2768
1978	6.258	1.992	3.459	3050
1979	6.035	1.915	3.778	3428
1980	5.925	1.835	3.525	3764
1981	5.903	1.865	3.609	4350
1982	5.659	1.743	3.130	4820
1983	5.555	1.708	2.989	4911
1984	5.457	1.680	3.098	6106
1985	5.374	1.613	2.826	6424
1986	5.338	1.601	2.858	6516
1987	5.298	1.636	2.888	7144
1988	5.198	1.591	2.864	7420
1989	5.210	1.558	2.733	7648
1990	5.130	1.515	2.670	8721
1991	5.182	1.563	2.847	9744
1992	5.169	1.541	2.841	10527
1993	5.088	1.521	2.646	11825
1994	5.136	1.524	2.663	12059
1995	5.099	1.525	2.702	12797
1996	5.139	1.526	2.656	15387
1997	5.151	1.541	2.774	15760
1998	5.183	1.559	2.735	17195
1999	5.177	1.568	2.757	18593
2000	5.235	1.590	2.934	19839
2001	5.185	1.575	2.836	21648
2002	5.136	1.575	2.971	24104

2003	5.109	1.565	2.962	26287
2004	5.090	1.545	2.838	27853
2005	5.098	1.587	3.048	31523
2006	5.069	1.587	2.982	34739
2007	5.027	1.574	2.942	36419
2008	5.058	1.609	2.937	37107
2009	5.025	1.595	3.075	41193
2010	4.992	1.596	3.031	42306
2011	5.023	1.599	3.124	44865
2012	5.085	1.645	3.174	48022
2013	5.059	1.658	3.188	48888
2014	5.111	1.689	3.287	51827
2015	5.127	1.686	3.226	55074
2016	5.209	1.750	3.526	56741
2017	5.181	1.747	3.480	57573
2018	5.227	1.752	3.521	58096
2019	5.199	1.750	3.560	60847
2020	5.197	1.808	3.829	63447
2021	5.220	1.772	3.664	60269
2022	5.259	1.803	3.792	60456
2023	5.322	1.848	4.001	60434
2024	5.339	1.851	3.996	60176
2025	5.373	1.863	3.972	26951

S5.2. Fig 1 B

year	mean	esd_minus	esd_plus	N
1963	11.000	0.000	0.000	1
1970	5.920	2.998	2.998	2
1972	3.967	0.777	1.222	3
1975	8.230	0.000	0.000	1
1976	10.980	2.376	2.376	2
1977	8.426	2.617	2.190	5
1980	4.580	0.000	0.000	1
1982	4.393	0.600	1.534	7
1983	7.617	4.682	8.109	3
1984	11.900	1.981	1.981	4
1985	6.374	2.042	4.586	7
1986	9.438	4.290	8.427	4
1987	6.067	1.819	2.987	23
1988	7.293	2.819	8.857	15
1989	8.938	3.614	8.971	19
1990	8.192	3.913	7.786	20
1991	12.305	5.568	12.723	23
1992	10.361	4.469	7.495	27
1993	8.816	3.497	5.410	50

1994	11.599	5.042	8.780	121
1995	9.095	3.565	5.836	608
1996	9.235	3.809	5.868	2199
1997	10.299	4.055	5.851	2870
1998	10.587	3.985	6.311	5356
1999	11.239	4.406	6.623	10905
2000	11.733	4.567	6.895	13460
2001	12.049	4.585	6.736	16296
2002	12.075	4.467	6.666	19720
2003	12.142	4.379	6.707	23138
2004	12.259	4.378	6.576	25414
2005	12.341	4.406	6.611	29432
2006	12.359	4.389	6.576	32726
2007	12.479	4.384	6.573	34664
2008	12.577	4.447	6.657	35208
2009	12.526	4.391	6.640	39312
2010	12.471	4.403	6.684	40510
2011	12.560	4.414	6.734	43078
2012	12.754	4.502	6.858	45783
2013	12.738	4.533	6.898	44400
2014	12.843	4.567	7.029	44352
2015	12.786	4.497	6.950	46251
2016	12.834	4.579	7.053	47247
2017	12.825	4.600	7.045	49014
2018	12.921	4.573	7.143	49197
2019	12.848	4.549	7.083	49949
2020	12.737	4.698	7.260	52620
2021	12.891	4.577	7.246	50042
2022	12.977	4.631	7.231	49740
2023	13.014	4.655	7.347	52220
2024	13.172	4.719	7.392	56269
2025	13.329	4.775	7.420	25448

S5.3. Figure 1 C

year	abs_min_mean	max_mean
1975	0.640	0.940
1976	1.150	1.450
1977	0.363	0.443
1982	0.124	0.138
1983	0.391	0.612
1984	0.297	0.434
1985	0.250	0.240
1987	0.451	0.488
1988	0.306	0.284
1989	0.341	0.603

1990	0.244	0.359
1991	0.281	0.386
1992	0.429	0.661
1993	0.465	0.577
1994	0.555	0.777
1995	0.417	0.492
1996	0.423	0.494
1997	0.470	0.563
1998	0.524	0.623
1999	0.561	0.675
2000	0.577	0.696
2001	0.571	0.697
2002	0.576	0.708
2003	0.570	0.711
2004	0.563	0.704
2005	0.561	0.712
2006	0.560	0.713
2007	0.562	0.716
2008	0.563	0.718
2009	0.565	0.724
2010	0.570	0.729
2011	0.562	0.718
2012	0.563	0.718
2013	0.572	0.733
2014	0.565	0.721
2015	0.568	0.726
2016	0.562	0.719
2017	0.568	0.724
2018	0.567	0.718
2019	0.561	0.709
2020	0.568	0.710
2021	0.561	0.697
2022	0.557	0.692
2023	0.561	0.697
2024	0.571	0.709
2025	0.554	0.688

S5.4. Fig 2 A

year	mean	esd_minus	esd_plus	<i>N</i>
1948	0.0069	0.0000	0.0000	1
1951	0.0061	0.0000	0.0000	1
1952	0.0072	0.0000	0.0000	1
1953	0.0064	0.0003	0.0002	3
1954	0.0051	0.0015	0.0015	2
1955	0.0056	0.0017	0.0012	5

1956	0.0055	0.0017	0.0010	4
1957	0.0063	0.0001	0.0002	4
1958	0.0047	0.0026	0.0024	4
1959	0.0058	0.0021	0.0010	13
1960	0.0055	0.0011	0.0010	19
1961	0.0054	0.0019	0.0013	24
1962	0.0055	0.0021	0.0012	40
1963	0.0051	0.0021	0.0015	62
1964	0.0047	0.0017	0.0016	74
1965	0.0049	0.0018	0.0015	132
1966	0.0047	0.0018	0.0016	159
1967	0.0044	0.0019	0.0017	243
1968	0.0043	0.0017	0.0018	347
1969	0.0042	0.0018	0.0019	494
1970	0.0040	0.0016	0.0018	605
1971	0.0038	0.0016	0.0019	842
1972	0.0039	0.0016	0.0018	1214
1973	0.0038	0.0016	0.0019	1257
1974	0.0036	0.0015	0.0019	1454
1975	0.0036	0.0015	0.0020	1579
1976	0.0035	0.0015	0.0019	2087
1977	0.0034	0.0015	0.0019	2363
1978	0.0033	0.0014	0.0020	2595
1979	0.0032	0.0014	0.0020	3004
1980	0.0032	0.0014	0.0020	3297
1981	0.0031	0.0014	0.0019	3887
1982	0.0030	0.0014	0.0020	4369
1983	0.0029	0.0013	0.0020	4492
1984	0.0029	0.0013	0.0020	5675
1985	0.0028	0.0013	0.0020	6014
1986	0.0028	0.0013	0.0020	6083
1987	0.0028	0.0013	0.0020	6713
1988	0.0027	0.0012	0.0020	7015
1989	0.0027	0.0012	0.0020	7254
1990	0.0026	0.0012	0.0020	8286
1991	0.0026	0.0012	0.0020	9282
1992	0.0026	0.0012	0.0019	10057
1993	0.0025	0.0012	0.0019	11327
1994	0.0025	0.0012	0.0019	11543
1995	0.0025	0.0012	0.0019	12291
1996	0.0025	0.0011	0.0019	14761
1997	0.0024	0.0011	0.0020	15198
1998	0.0024	0.0011	0.0019	16547
1999	0.0024	0.0011	0.0019	17812
2000	0.0024	0.0012	0.0020	19021
2001	0.0024	0.0012	0.0020	20804
2002	0.0024	0.0012	0.0020	23081

2003	0.0024	0.0012	0.0020	25265
2004	0.0024	0.0012	0.0019	26775
2005	0.0024	0.0012	0.0020	30250
2006	0.0024	0.0012	0.0020	33315
2007	0.0024	0.0012	0.0020	35067
2008	0.0024	0.0012	0.0020	35682
2009	0.0024	0.0012	0.0020	39631
2010	0.0023	0.0012	0.0020	40771
2011	0.0024	0.0012	0.0020	43296
2012	0.0023	0.0012	0.0020	46363
2013	0.0023	0.0011	0.0020	47223
2014	0.0023	0.0012	0.0020	49963
2015	0.0023	0.0012	0.0020	53101
2016	0.0023	0.0012	0.0020	54598
2017	0.0023	0.0012	0.0020	55464
2018	0.0023	0.0012	0.0020	55854
2019	0.0023	0.0012	0.0020	58608
2020	0.0023	0.0012	0.0020	60686
2021	0.0023	0.0012	0.0020	57933
2022	0.0023	0.0012	0.0020	58216
2023	0.0023	0.0012	0.0020	57895
2024	0.0022	0.0012	0.0020	57706
2025	0.0023	0.0012	0.0020	25808

S5.5. Fig 2 B

year	mean	esd_minus	esd_plus	N
1963	0.0108	0.0000	0.0000	1
1970	0.0035	0.0005	0.0005	2
1972	0.0061	0.0008	0.0014	3
1975	0.0016	0.0000	0.0000	1
1976	0.0046	0.0030	0.0030	2
1977	0.0037	0.0018	0.0036	5
1980	0.0032	0.0000	0.0000	1
1982	0.0089	0.0054	0.0021	7
1983	0.0024	0.0011	0.0019	3
1984	0.0078	0.0028	0.0026	5
1985	0.0051	0.0031	0.0063	7
1986	0.0053	0.0023	0.0045	4
1987	0.0041	0.0020	0.0034	22
1988	0.0047	0.0026	0.0063	15
1989	0.0058	0.0026	0.0066	19
1990	0.0053	0.0029	0.0065	20
1991	0.0064	0.0032	0.0048	24
1992	0.0067	0.0036	0.0057	27
1993	0.0052	0.0027	0.0046	50

1994	0.0045	0.0022	0.0040	123
1995	0.0055	0.0027	0.0050	595
1996	0.0056	0.0028	0.0049	2138
1997	0.0055	0.0028	0.0049	2803
1998	0.0054	0.0027	0.0050	5233
1999	0.0055	0.0029	0.0051	10659
2000	0.0055	0.0028	0.0052	13137
2001	0.0057	0.0029	0.0051	15904
2002	0.0058	0.0029	0.0052	19289
2003	0.0058	0.0029	0.0052	22629
2004	0.0059	0.0030	0.0052	24837
2005	0.0059	0.0030	0.0052	28703
2006	0.0060	0.0030	0.0052	31983
2007	0.0061	0.0031	0.0052	33779
2008	0.0060	0.0031	0.0052	34378
2009	0.0060	0.0030	0.0052	38307
2010	0.0059	0.0030	0.0052	39630
2011	0.0060	0.0031	0.0052	42258
2012	0.0060	0.0030	0.0051	44996
2013	0.0059	0.0030	0.0052	43617
2014	0.0060	0.0031	0.0053	43587
2015	0.0059	0.0030	0.0052	45511
2016	0.0059	0.0030	0.0052	46681
2017	0.0059	0.0030	0.0052	48465
2018	0.0059	0.0030	0.0052	48666
2019	0.0059	0.0030	0.0052	49485
2020	0.0059	0.0031	0.0053	52015
2021	0.0059	0.0030	0.0053	49478
2022	0.0059	0.0031	0.0052	49350
2023	0.0059	0.0031	0.0053	51913
2024	0.0058	0.0031	0.0052	56212
2025	0.0059	0.0031	0.0052	25295

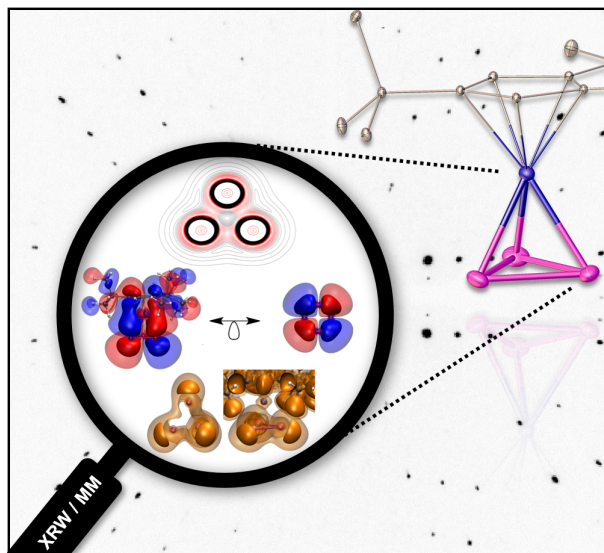
S5.6. Elemental averages

element	Z	R1	wR2	abs_min_density	max_density
H	1	5.219	13.474	0.814	0.982
He	2	5.340	16.284	0.247	0.251
Li	3	5.831	14.990	0.606	0.813
Be	4	4.942	12.473	0.474	0.589
B	5	5.435	14.234	2.277	2.371
C	6	5.218	13.473	0.814	0.982
N	7	5.242	13.623	0.858	1.020
O	8	5.287	13.720	0.835	0.992
F	9	5.432	14.277	1.558	1.729
Ne	10	4.544	4.707	0.501	0.382

Na	11	6.020	15.843	1.066	1.390
Mg	12	5.790	15.307	0.503	0.679
Al	13	5.518	14.337	0.575	0.779
Si	14	5.141	13.036	0.712	0.937
P	15	5.025	12.632	0.910	1.182
S	16	5.190	13.391	1.311	1.447
Cl	17	5.208	13.433	0.830	1.058
Ar	18	6.973	20.029	0.591	0.844
K	19	5.647	14.550	0.992	1.334
Ca	20	5.763	15.081	0.624	0.823
Sc	21	5.970	15.572	0.614	0.798
Ti	22	5.655	14.439	0.602	0.811
V	23	5.635	14.885	0.724	0.952
Cr	24	5.436	14.112	0.683	0.893
Mn	25	5.379	13.916	0.718	0.955
Fe	26	5.306	13.494	0.714	0.944
Co	27	5.435	14.119	0.721	0.956
Ni	28	5.366	13.890	0.697	0.935
Cu	29	5.308	13.725	0.772	1.005
Zn	30	5.280	14.709	0.717	0.937
Ga	31	4.732	11.628	0.780	1.024
Ge	32	4.850	11.980	0.867	1.145
As	33	4.908	11.770	1.100	1.344
Se	34	4.819	11.746	0.989	1.215
Br	35	4.943	12.100	0.870	1.031
Kr	36	6.014	15.365	0.594	0.726
Rb	37	5.703	13.371	1.105	1.431
Sr	38	5.353	13.048	0.808	1.042
Y	39	5.683	14.096	0.771	1.031
Zr	40	4.861	12.288	0.774	1.000
Nb	41	5.031	12.517	1.015	1.287
Mo	42	4.872	12.115	1.032	1.301
Tc	43	4.920	11.782	0.933	1.067
Ru	44	4.892	12.336	0.947	1.232
Rh	45	4.841	12.072	0.943	1.251
Pd	46	4.869	12.529	0.961	1.227
Ag	47	5.301	13.641	1.143	1.481
Cd	48	4.798	12.351	0.958	1.183
In	49	4.533	11.262	1.018	1.312
Sn	50	4.371	10.607	0.957	1.215
Sb	51	4.594	11.380	1.235	1.540
Te	52	4.430	10.876	1.245	1.532
I	53	4.494	10.854	1.217	1.440
Xe	54	5.096	13.041	0.946	1.063
Cs	55	5.211	12.954	1.505	1.836
Ba	56	5.023	11.953	1.112	1.461
La	57	5.014	12.470	1.200	1.562

Ce	58	4.753	12.197	1.224	1.622
Pr	59	4.795	11.966	1.437	1.672
Nd	60	4.910	12.147	1.242	1.623
Pm	61	3.870	10.340	0.735	1.016
Sm	62	4.780	11.620	1.201	1.560
Eu	63	5.021	12.624	1.277	1.656
Gd	64	4.991	12.915	1.387	1.812
Tb	65	4.812	12.197	1.339	1.760
Dy	66	4.946	12.616	1.371	1.807
Ho	67	4.534	11.287	1.419	1.772
Er	68	4.665	11.695	1.379	1.773
Tm	69	4.468	11.289	1.542	1.918
Yb	70	4.673	11.417	1.379	1.813
Lu	71	4.424	10.883	1.366	1.773
Hf	72	3.928	9.360	1.458	1.917
Ta	73	4.167	10.142	1.645	2.123
W	74	4.610	11.130	2.000	2.379
Re	75	4.172	9.993	1.583	1.925
Os	76	4.308	9.715	1.644	2.007
Ir	77	4.199	10.027	1.564	2.072
Pt	78	4.311	10.177	1.616	2.036
Au	79	4.421	10.714	1.726	2.150
Hg	80	4.802	10.863	1.702	1.948
Tl	81	4.763	10.986	1.799	2.042
Pb	82	4.419	10.104	1.658	1.925
Bi	83	4.269	9.935	1.750	2.017
Ra	88	4.040	9.040	0.945	1.321
Th	90	4.328	10.001	1.653	2.131
Pa	91	4.607	8.275	1.968	3.051
U	92	4.472	10.693	1.698	2.146
Np	93	3.939	9.097	1.593	1.867
Pu	94	3.826	9.109	1.618	1.921
Am	95	4.203	9.630	1.861	2.267
Cm	96	2.855	7.387	1.199	1.760
Bk	97	3.979	10.259	1.884	2.959
Cf	98	3.950	9.210	1.380	3.002

4 Isolobal relation between $\text{Cp}^{\text{III}}\text{NiP}_3$ and white phosphorus



Preface

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This chapter is based on the article:

“Probing the Isolobal Relation between $\text{Cp}^{\text{III}}\text{NiP}_3$ and White Phosphorus by Experimental Charge Density Analysis”

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Author Contributions

Florian Meurer – Conceptualisation, crystallographic modelling, data acquisition and analysis, computations, original draft.

Florian Kleemiss – Computations, crystallographic modelling, co-writing final manuscript.

Christoph Riesinger – Chemical synthesis, co-writing final manuscript.

Gábor Balázs – Co-writing final manuscript.

Vedran Vuković – Crystallographic modelling, data acquisition and analysis, co-writing final manuscript.

Ilya G. Shenderovich – Solid-state NMR data acquisition and analysis, co-writing final manuscript.

Christian Jelsch – Crystallographic modelling, co-writing final manuscript.

Michael Bodensteiner – Conceptualisation, co-writing final manuscript.

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Abstract

An in-depth analysis of the description of bonding within $\text{Cp}^{\text{'''}}\text{Ni-cyclo-P}_3$ ($\text{Cp}^{\text{'''}} = 1, 2, 4$ -tri-tert-butylcyclopentadienyl, $[\text{Ni}]\text{P}_3$) employing X-ray diffraction based multipolar modeling, density functional theory (DFT) as well as an "experimental wavefunction" obtained from X-ray restrained wavefunction (XRW) fitting is presented. The results are compared to DFT calculations on white phosphorus - an isolobal analogue to $[\text{Ni}]\text{P}_3$. A complementary bonding analysis shows insights into the reactivity of $[\text{Ni}]\text{P}_3$. The isolobal principle is reflected in every aspect of our analysis and the employed methods seamlessly predict the differences in reactivity of $[\text{Ni}]\text{P}_3$ and P_4 . Crystallographic modeling, solid-state NMR, and DFT calculations describe the dynamic behavior of the cyclo- P_3 unit in the title molecule.

4.1 Introduction

Supporting sophisticated theoretical investigations are now standard in publications in almost every discipline of chemistry. In many cases they are based on previously determined X-ray crystal structures after gas phase geometry optimization. This order shows that there is a tendency to attribute little chemical information content to experimental crystal structure determination. This is astonishing in several respects. On the one hand, it has been shown decades ago that very precise chemical information can be obtained with quantum crystallographic methods. ^[1–3] On the other hand, X-ray sources and detectors have reached a level of development that offers an immense photon flux and simultaneously, the ability to detect single photons. This allows for such precise, fast experiments that crystal structure determinations nowadays are a matter of minutes to hours. ^[4] Finally, it has become feasible to examine two sides of the same medal: both the square of a wavefunction and the Fourier transform of the diffraction pattern provide the electron density distribution. ^[3] However, the most commonly used independent atom model for crystal structure refinements is a very rough description, which assumes that all atoms of an element in a compound are identical and neutral, with spherically distributed electron density. Moving beyond that simplistic model, hand in hand with theoretical

computations of varying degrees of sophistication, allows for obtaining the best of the two worlds: A precise experimental geometry and an appropriately fitted wavefunction.

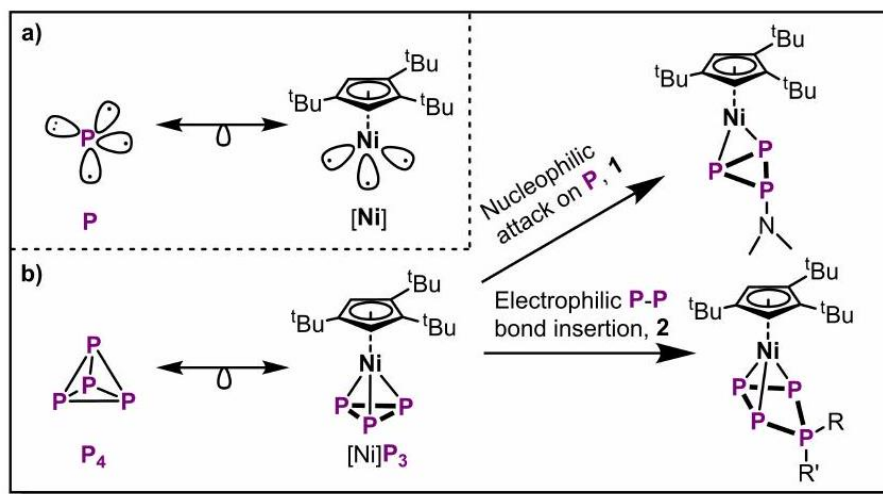


Figure 4.1: Scheme 1. Isolobal relationships between a phosphorus atom of white phosphorus and the [Ni] fragment (a) or [Ni]P₃ (b) with selected reactivities of [Ni]P₃ shown. 1: LiNMe_2 in THF at room temperature; ^[5] 2: selected scope as in reference. ^[6]

In this work, we investigate the P – P and Ni – P bonding in [Ni]P₃ (Scheme 1) with complementary bonding analysis of quantum crystallographic models from multipolar refinement as well as an X-ray restrained wavefunction fitting model. The multipolar model (MM) as a parametrized approach to extend the independent atom model (IAM) by spherical harmonical terms, closely resembling atomic orbitals, has a long history in the description of the electron density within crystals. ^[7,8] However, the modelling of transition metal compounds has proved to be especially challenging. In contrast, X-ray restrained wavefunctions (XRWs) yield an "experimental wavefunction" which can be used to describe a molecule or compound beyond topological analysis. ^[2,3,9]

We compare these findings to theoretical calculations on [Ni]P₃ (see Figure 4.2) and white phosphorus - an isolobal analogue. ^[10] In this context, we describe the electronic structure of the cyclo- P₃ fragment, which can be either seen as a planar ligand coordinating to the transition metal or with separate phosphorus atoms bound individually.

4.2 Results and discussion

4.2.1 Experimental and Methods

A high-resolution ($d_{\min} = 0.54\text{\AA}$) X-ray diffraction data set using Mo K_{α} radiation of a [Ni]P₃ single crystal serves as the basis for the crystallographic studies. Multipolar modeling according to the Hansen & Coppens formalism was performed within the MoPro software with the refinement of multipolar parameters as described in the supporting information. ^[11,12,13] Anisotropic displacement parameters for hydrogen atoms were obtained using the SHADE3 server. ^[14] VMoPro and MoProViewer modules were used to perform the topological analysis. Further information can be found in the supporting information.

A Hirshfeld-Atom Refinement (HAR) yielded the starting geometry for the XRW fitting in the TONTO quantum crystallographic software suite. [15–17] HAR uses the geometry of the (IAM) for a wavefunction calculation and partitions the wavefunction’s corresponding electron density into non-spherical atomic formfactors. These formfactors were then used in the crystallographic refinement of atomic positions and displacement parameters. HAR was performed following this procedure iteratively until a given convergence criterium was met.

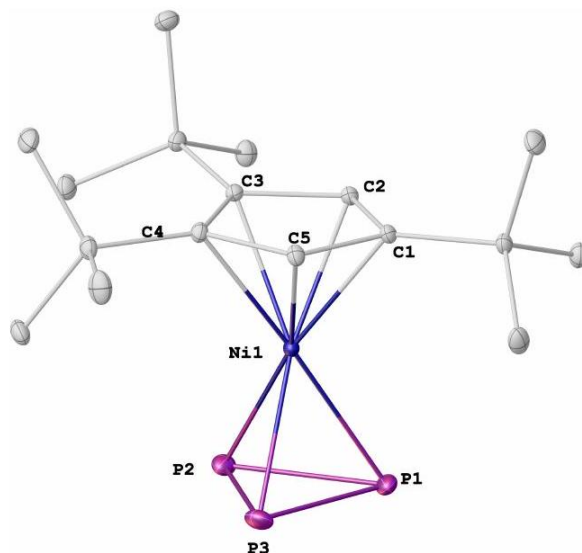


Figure 4.2: Structure and labelling scheme for selected atoms of $[\text{Ni}]\text{P}_3$. Hydrogen atoms are omitted for clarity, ellipsoids are drawn at the 50% probability level (Mo K_α HAR model).

HAR was performed using ORCA5 (M062X/def2-TZVP) and the resulting wavefunction yielded non-spherical atomic form factors for all atoms (including hydrogens) in $[\text{Ni}]\text{P}_3$ using a Hirshfeld partitioning scheme. This calculation was performed by NoSpherA2 in the Olex2 crystallographic suite. [18–22] A procedure of wavefunction generation, partitioning, and refinement was repeated until convergence was achieved. The resulting geometry from HAR was then used as the geometry for the XRW fitting. Contrary to HAR, the XRW fitting is perturbed during the self-consistent-field (SCF) procedure by weighted Lagrange multiplication with the agreement between measured and calculated structure factors defined as follows:

$$J(\Psi) = E(\Psi) + \lambda (\chi^2(\Psi) - \Delta) \quad (1)$$

where the Jayatilaka functional J (Eq. 1) consists of the (singlepoint) energy E of the wavefunction Ψ modified with the λ weighted perturbation term χ^2 and with Δ as the desired agreement for this term. In our specific case, Δ was set to zero in order to extract the maximum possible information from the diffraction data. χ^2 (Eq. 2) represents the weighted differences between the calculated and measured structure factors ($F^{\text{calc/obs}}$) from the Bragg intensities as follows:

$$\chi^2(\Psi) = \frac{1}{N_{\text{refl}} - N_{\text{par}}} \sum_{i=1}^{N_{\text{refl}}} \xi \frac{|F_i^{\text{calc}}(\Psi)|^2 - |F_i^{\text{obs}}|^2}{(\sigma_i^{\text{obs}})^2} \quad (2)$$

where $N_{\text{refl/par}}$ are the number of reflections and parameters (N_{par} is traditionally set to one in XRW determinations, the parameter being λ), ξ is a scaling factor, and σ is the uncertainty of the measured structure factors. This assumes that purely statistical weighting schemes are used throughout the procedure.

During the XRW fitting procedure, the geometry from HAR was used to perform a wavefunction calculation using the (spin-orbital restricted) Hartree-Fock (HF) method using the def2-TZVP basis set. The λ parameter was initially set to zero to yield a pure HF calculation of the solid-state $[\text{Ni}]\text{P}_3$ geometry obtained from HAR. λ was then incrementally increased by steps of 0.01 to increase the influence of the measured structure factors. This procedure was repeated until a maximum perturbation with the corresponding value of λ was achieved while the SCF still converged. This convergence is shown in the supporting information. The resulting wavefunction was then used to generate non-spherical atomic form factors according to Hirshfeld stockholder-partitioning.^[21]

This way, we started with a model based on ab-initio calculated wavefunction and extracted the remaining influences on the electron density, which were not accounted for in HF, such as electron correlation and polarization, from the experimental electron density. A comprehensive overview and discussion on extracting these properties can be found in references [23,24].

X-ray diffraction data were collected using Mo K_α (wavelength = 0.71073 Å) as well as Cu K_β (wavelength = 1.39222 Å) radiation to compare the results obtained using these different data sets for both XRW fitting and multipolar modelling. From the results of this comparison, which can be found in detail in the supporting information, we chose the Mo-XRW model with a λ parameter of 0.42 as the best result to investigate the bonding situation in $[\text{Ni}]\text{P}_3$ without overfitting due to the introduction of experimental noise and errors into the data. MoXRW was then compared to the multipolar model (MM) of Mo K_α data for the topological analysis, while all other bonding indices were extracted from the wavefunction analysis. These characteristics for $[\text{Ni}]\text{P}_3$ were also compared to the DFT optimized geometry of P_4 (M062X/def2-TZVP) or to its normalmode corrected solid-state structure (XRD).^[25]

In this work, we report to the best of our knowledge on the first multipolar model as well as XRW fitting procedure using Cu K_β radiation. The main differences between Mo K_α and Cu K_β radiation lie in the maximum achievable resolution, raw intensity, and peak-splitting. While Mo K_α provides much higher resolution data sets

($d_{\text{min}}(\text{Mo } K_\alpha) = 0.355 \text{ Å}$, $d_{\text{min}}(\text{Cu } K_\beta) = 0.696 \text{ Å}$), Cu K_β gives higher intensity and does not observably exhibit the peak-splitting common to all K_α radiation types. For both charge density modelling approaches we found reasonable results even with the lower resolved Cu K_β data set. In particular, the topological analysis of the multipolar model and wavefunction-based bonding analysis closely resembled the descriptions achieved with Mo K_α radiation, despite the additional challenge associated with using Cu K_β radiation with a nickel compound. Nickel has its K shell absorption edge a slightly lower in energy than Cu K_β radiation, so it has a particularly high elemental absorption for nickel. More comprehensive crystallographic details regarding this effort can be found in the supporting information.

4.2.2 Geometry

White phosphorus exhibits T_d symmetry in the gas phase with six equidistant, chemically equivalent P – P bonds. P_4 is notoriously difficult to crystallize in a manner suitable

for high quality diffraction data, so our results besides the geometry are compared with DFT calculations. The NiP_3 fragment in $[\text{Ni}]\text{P}_3$ shows a tetrahedral geometry, which is distorted by the $[\text{Ni}]$ fragment and shows different interatomic distances and bond angles. The geometry of the molecule in the gas phase differs only slightly from the one in the crystalline phase which can be attributed to the weak intermolecular interactions in the crystalline phase. ^[26]

The $\text{P} - \text{P}$ distances in $[\text{Ni}^3\text{P}_3]$ are significantly shorter than in white phosphorus despite the similar ring strain (see Table 4.1). This might indicate stronger bonds between the phosphorus atoms in $[\text{Ni}]\text{P}_3$ compared to P_4 . In contrast, the $\text{Ni} - \text{P}$ bonds are generally longer than the $\text{P} - \text{P}$ bonds. While the bond angles between the phosphorus atoms are comparable to those in P_4 , the $\text{P} - \text{Ni} - \text{P}$ bond angles differ strongly and are smaller in $[\text{Ni}]\text{P}_3$. Thus, the tetrahedral geometry in P_4 is distorted by the isolobal substitution of a phosphorus atom by the $[\text{Ni}]$ fragment.

4.2.3 Topological Analysis

Table 4.2 shows the selected topological properties of the different models according to Bader's quantum theory of atoms in molecules (QTAIM). This method analyses chemical bonding by following the topology of the total electron density distribution in real space. ^[27,28]

There is generally less electron density at the bond critical points (BCP) between Ni and phosphorus than between two phosphorus atoms (see Table 4.2). The Laplacian values at the bond critical points also indicate a Valence Shell Charge Concentration (VSCC, i.e., negative Laplacian values) at the BCPs between two phosphorus atoms and a Valence Shell Charge Depletion (VSCD, i.e., positive Laplacian values) in all Ni-P bonds. The values of the electron density at the BCP are considerably high in comparison with other literature known transition metal-phosphorus bonds. ^[29,30,31] The positive Laplacians at the BCP indicate intermediate dative bonds.

A closer look at the distribution of the Laplacian of the electron density along the topological bond paths shows symmetrical $\text{P} - \text{P}$ bonds with a negative Laplacian plateau at the BCPs and similar progression between the MM and XRW models. The plateau stays in the negative regime for the XRW and MM model, as expected for covalent non-polarized bonds. ^[32] A value closer to zero is consistent with a systematic comparison of the XRW method with MM by Woinska et al. ^[24]

This study on organic compounds found the Laplacian values overestimated in the MM compared to the XRW method, which itself is consistent with the DFT calculation of P_4 . So far, the differences between XRW and MM in transition-metal complexes have not been systematically studied, but our findings suggest a similar behavior in this case.

The Ni-P bonds exhibit highly asymmetrical Laplacians of the electron density along bonding paths in every model indicative of a dative bonding character. There are pronounced VSCCs between the BCPs and phosphorus atoms, but strong depletions of electron density towards the nickel center. This indicates highly polarized Ni-P bonds which are expected from the differences in electronegativity. Again, a higher Laplacian at the BCP is observed in the MM than in the XRW and DFT calculation of $[\text{Ni}]\text{P}_3$.

The 2D maps of the Laplacian in the cyclo- P_3 (see Figure 4.3) plane indicate a strong smearing of electron density in the $\text{P} - \text{P}$ bonds in the XRW model with a larger overlap of electron density accumulation areas in the vicinity of the bond paths. This smearing was less pronounced in the MM, but generally followed this trend of the 2D Laplacian

Table 4.1: Selected distances and angles in the different models of P_4 and $[\text{Ni}]\text{P}_3$. HAR and XRW geometries are identical.

	P_4		$[\text{Ni}]\text{P}_3$		
	XRD [25]	DFT	DFT	MM (Mo K_α)	HAR (Mo K_α)
P-P distances / $\text{\AA}$	2.201(2)-2.209(1)	2.2031	P1-P2: 2.1549 P1-P3: 2.1550 P2-P3: 2.1558	P1-P2: 2.1481(3) P1-P3: 2.1446(2) P2-P3: 2.1534(3)	P1-P2: 2.1465(1) P1-P3: 2.1432(1) P2-P3: 2.1508(2)
Ni-P distances / $\text{\AA}$	-	-	Ni-P1: 2.2670 Ni-P2: 2.2660 Ni-P3: 2.2970	Ni-P1: 2.2471(2) Ni-P2: 2.2376(2) Ni-P3: 2.2477(2)	Ni-P1: 2.2460(1) Ni-P2: 2.2370(1) Ni-P3: 2.2467(1)
P-P-P angles / $^\circ$	59.74(2)-60.39(2)	60.00	59.98-60.03	59.810(13)-60.217(13)	59.984(4)-60.185(4)

Table 4.2: Values of electron density (ρ) and Laplacian of the electron density ($\nabla^2(\rho)$) at selected bond critical points according to QTAIM for different models of $[\text{Ni}]\text{P}_3$. The DFT model of P_4 is added for comparison.

Atom1	Atom2	DFT		MM (Mo K_α)		XRW (Mo K_α)	
		ρ ($\text{e \AA}^{-3}$)	$\nabla^2(\rho)$ ($\text{e \AA}^{-5}$)	ρ ($\text{e \AA}^{-3}$)	$\nabla^2(\rho)$ ($\text{e \AA}^{-5}$)	ρ ($\text{e \AA}^{-3}$)	$\nabla^2(\rho)$ ($\text{e \AA}^{-5}$)
Ni	P1	0.560	1.844	0.557(6)	3.61(8)	0.596	1.706
Ni	P2	0.562	1.836	0.577(5)	3.72(7)	0.608	1.507
Ni	P3	0.558	1.894	0.536(8)	3.70(9)	0.563	1.804
P1	P2	0.788	-2.418	0.760(5)	-0.3(1)	0.816	-2.514
P1	P3	0.788	-2.430	0.749(5)	-0.22(8)	0.808	-2.690
P2	P3	0.787	-2.411	0.756(6)	-0.20(9)	0.810	-2.595
P(P_4)	P(P_4)	0.202	-1.344	-	-	-	-

map of cyclo- P_3 . The models closely resembled the Laplacian 2D map obtained for the cyclo- P_3 plane in white phosphorus.

The atomic charges (see Table 4.3) were consistent with a positively charged nickel and negatively charged phosphorus atoms. Here, the MM showed a similar positive charge for nickel and a more negative charge on the cyclo- P_3 unit compared to the XRW model.

Generally, the topology of electron density within the $\text{Ni} - \text{P}_2$ rings allowed for a good comparison with the work by Macchi et al. to describe the bonding in terms of the Dewar-ChattDuncanson metal-olefine vs. metallacyclopropane model. [8,33] The topology of this system in Ni_iP_3 (see Figure S8) was similar to the one that has been described for $\text{Ni}(\text{COD})_2$: a σ -donation by the $\text{P}-\text{P}$ bonds to nickel as well as π -back-bonding, indicated by "inwardly curved, but well separated" $\text{Ni}-\text{P}$ bond paths has been also described in this study. This pushes the $\text{Ni} - \text{P}_2$ more to the metallacycle side - despite the positive Laplacian of electron density at the BCP, which is quite small compared to other literature examples. [34] Back-bonding by the metal center was also supported by lower occupancies (see Table S5 in the supporting information) in the $d(xy)$ and $d(yz)$ orbitals - again similar to the case described by Macchi et al. [8] Therefore, the NiP_3 fragment could be described close to a metallatetrahedrane analogue.

4.2.4 Bonding Indices

Table 4.4 shows the bonding indices and parameters of $[\text{Ni}]\text{P}_3$ compared to P_4 . NBO [35] analysis revealed bonding indices near unity for $\text{P}-\text{P}$ bonds with a stronger bond between P 1 and P 3

and slightly weaker bonds of both atoms to P 2. This was consistent with the topological analysis of the XRW model, where less negative charge was assigned to P2. In contrast,

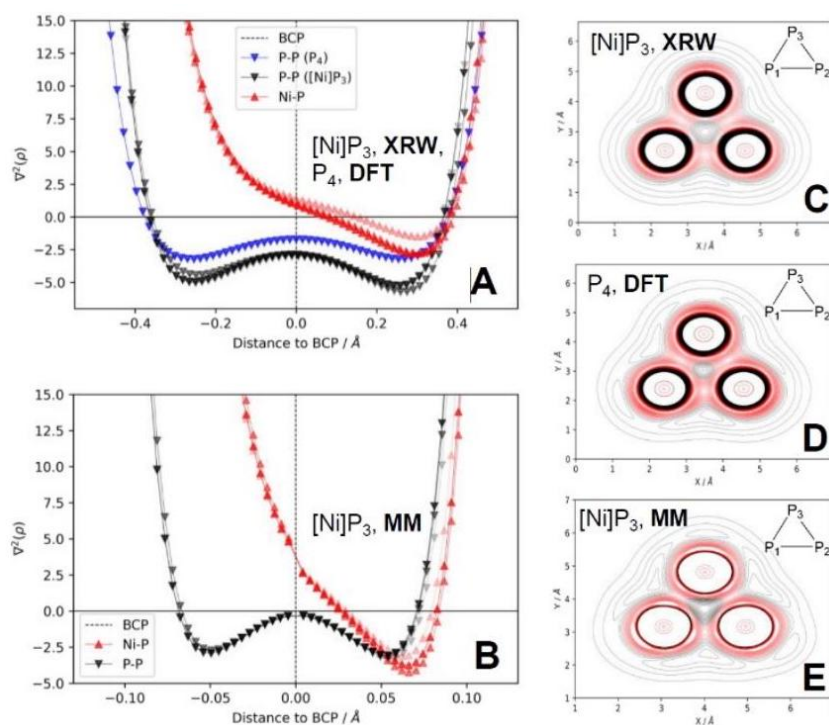


Figure 4.3: Values for the Laplacian of the electron density along bond critical paths between P – P (black:XRD, blue:DFT, upright triangle: P – P bonds, inverted triangles: Ni-P bonds) and Ni-P (red) in the MM and XRW model (A, B) as well as 2D Laplacian maps of the cyclo- P_3 fragment with $0.2\text{e}\text{\AA}^{-5}$ iso-lines for the cyclo- P_3 fragment (C, D, E). In the 2D Laplacian maps, red color indicates a negative, black a positive Laplacian value attributed to valence charge accumulation or depletion, respectively.

all Ni-P bonds had a bond order close to 0.5 . This value for a metal-heteroatom bond is relatively large in comparison to Ni – C bonding orders of 0.02 – 0.01. We observed a high occupancy ($0.64e$) of the Ni – P anti-bonding orbital, which is mainly of Ni – d and P – p orbital character. The second order perturbation theory revealed a strong contribution of the P -lone-pairs (164 and 160 kJ/mol) for the Ni – P anti-bonding combination with no significant Ni-lone-pair contributions. Besides this, a strong contribution of the Cp^{III} ligand's "lonepairs" to the Ni-P anti-bonding was found.

The Wiberg bond index (WBI) following an NPA analysis showed a P – P bond order slightly above unity with about 1.1 electron pairs for each P – P bond. Again, Ni-P bonds possessed about one electron per Ni – P bond. According to the NBO theory, the P – P bonds are expected to be covalent and on average slightly stronger than P – P bonds in white phosphorus. In the natural resonance theory (NRT), the Ni-P bonds

Table 4.3: Bader charges in electrons for selected atoms in each model for $[\text{Ni}]\text{P}_3$ and P_4 .

	DFT	MM	XRW
Ni	0.397	0.46(2)	0.416
P1	-0.077	-0.26(2)	-0.133
P2	-0.078	-0.32(2)	-0.065
P3	-0.077	-0.30(3)	-0.132
P (P_4)	0.000	-	-

Table 4.4: Selected bonding indices for the XRW $[\text{Ni}]\text{P}_3$ model and P_4 . B.O.: bond order, WBI: Wiberg bond index, NLMO: natural localized molecular orbitals, Cov: covalent, D.I.: delocalization index.

Atom1	Atom2	NBO		NLMO*	% Cov	D.I.	Roby-Gould		
		B.O.	WBI				Cov. Ind	Ion. Ind	% Cov
Ni1	P1	0.4779	0.4899	0.5583	69.8	0.79	0.45	0.23	79.53
Ni1	P2	0.5338	0.5338	0.8932	77.9	0.81	0.48	0.21	83.23
Ni1	P3	0.5249	0.5071	0.8633	68.0	0.78	0.45	0.25	76.62
P1	P2	0.9987	1.1192	1.1852	98.3	1.20	1.22	0.00	99.1
P1	P3	1.1626	1.1406	1.2408	99.0	1.23	1.26	0.02	99.98
P2	P3	0.9895	1.1100	1.1713	99.1	1.20	1.22	0.02	99.12
P(P ₄)	P(P ₄)	1.000	1.0149	1.036	100	1.48	1.00	0.00	100

exhibited a covalency of about 70%, i.e., of primarily dative covalent character, despite the large difference in electronegativity. NRT described the bonding of cyclo- P_3 to $[\text{Ni}]$ as a mixture of two covalent interactions on average shared across the three centers. For the Lewis picture of $[\text{Ni}]_3$, the dominant resonance structures (combined 50% weight) exhibited two out of three possible Ni – P bonds (to P 1 and P 3), and three P – P bonds. This was accompanied by four lone pairs of electrons attributed to the nickel atom, as well as 3.5 lone pairs shared over the cyclo P_3 unit. The remaining half lone pair was attributed half to P2, one third to Ni, and the rest shared between the other phosphorus atoms. This suggested that the cyclo- P_3 provided about three electrons for chemical bonding with the $[\text{Ni}]$ fragment. NLMO/NPA bond orders were at 2.31 for Ni excluding Ni-C bonds (3.38 including them), 2.77 for P2 and 3.17 and 3.19 for P 1 and P 3, respectively.

The P – P bonds in the DFT model of P_4 exhibited stronger delocalization than the P – P bonds in $[\text{Ni}]\text{P}_3$ and a very low delocalization index was calculated for Ni – P bonds. This is also borne out by the Roby-Gould bonding indices. Here, the P – P bond in $[\text{Ni}]\text{P}_3$ was even stronger compared to the one in P_4 . A higher covalent character was assumed for the Ni-P bonds according to the Roby-Gould index compared to NBO analysis.

A comparison of the same-spin electron localizability indicator (ELI-D) of P_4 and $[\text{Ni}]\text{P}_3$ in Figure 4.5 showed a strong similarity in what can be attributed to phosphorus lone pairs. Except for the $[\text{Ni}]$ fragment, the cyclo- P_3 fragment matched the shape of the lone pairs in white phosphorus precisely.

A deeper look into the bonding analysis and integration of charges in the Raub-Jansen scheme following the evaluation of the ELI-D distribution was not possible, since the basins were truncated in an unreproducible way, most likely due to extremely subtle details, that could not be resolved with affordable computational effort. We attributed this to the highly delocalized electronic system in both P_4 and $[\text{Ni}]\text{P}_3$.

Figure 4.4 shows the XRW model frontier orbitals of $[\text{Ni}]\text{P}_3$ compared to the frontier orbitals of P_4 . When reduced to the NiP_3 tetrahedron, a similar shape with two nodal planes was observed for the highest occupied molecular orbital. P_4 exhibited lobes of this molecular orbital primarily above and below each phosphorus atom, stretching in the bonding direction. In $[\text{Ni}]\text{P}_3$ a similar behavior was observed for two of the three phosphorus atoms (P1 and P2) with lobes away and towards the $[\text{Ni}]$ fragment but stretched in the direction of P3. A similar shape but with an additional nodal plane was observed for the lowest unoccupied molecular orbital of P_4 . In $[\text{Ni}]\text{P}_3$, a similar pattern was observed around P1 and P2, with a different, less pronounced contribution of the $[\text{Ni}]$ fragment. This suggested that P1 and P2 formed the chemical center for both nucleophilic and elec-

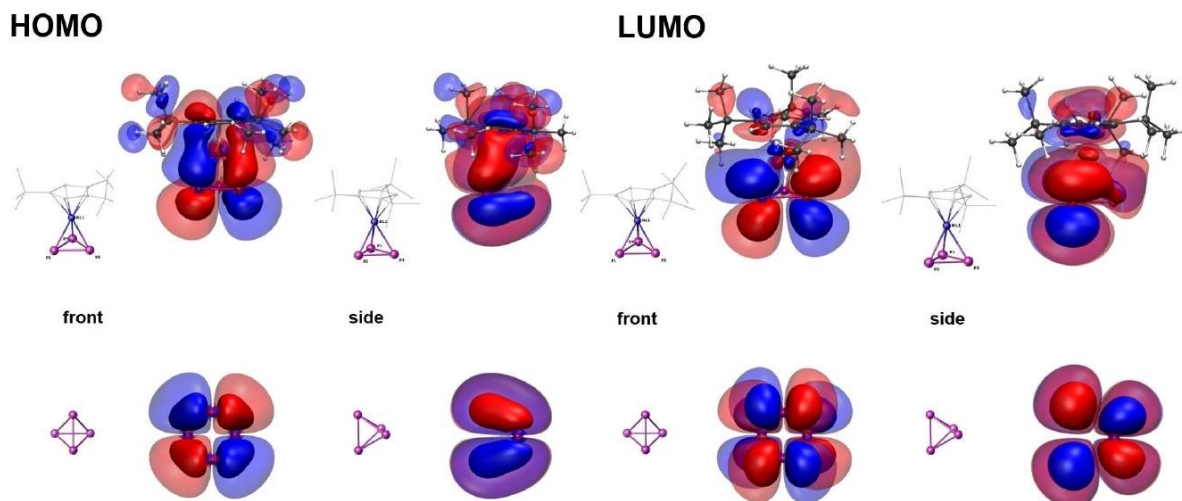


Figure 4.4: Frontier orbitals of the XRW ($\text{Mo } K_{\alpha}$) model of $[\text{Ni}]\text{P}$ (upper half) compared to the DFT calculation of P_4 (lower half).

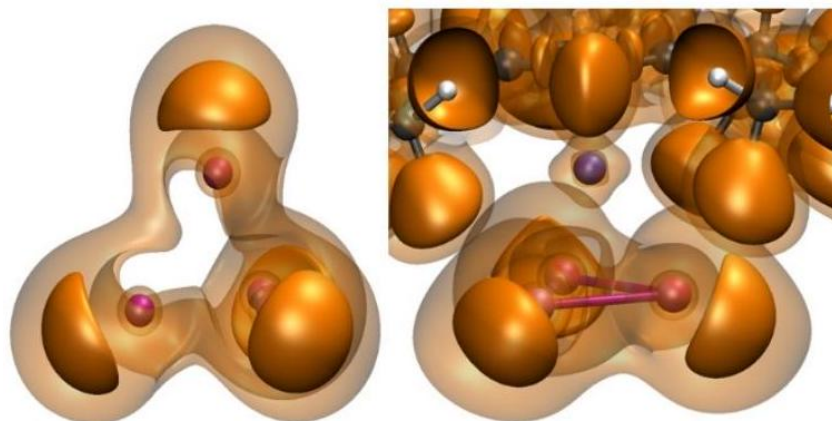


Figure 4.5: Comparison of ELI-D of white phosphorus (left) and $[\text{Ni}]\text{P}_3$ (right) at iso-surfaces of 1.2 (opaque) and $1.7\text{e}/\text{\AA}^3$ (transparent).

trophilic reactions. This did not fully match the description of Mädl et al., who did not find any significant contribution at these two atoms, but rather at their bonds towards the third phosphorus atom. ^[5] The resulting LUMO, however, matched their description and was thus also in accord with their observed reactivity towards main-group nucleophiles. Our updated view of the highest occupied molecular orbital was consistent with successful electrophilic insertion into P-P bonds as reported. ^[6] An overall higher inertness towards air in comparison to white phosphorus could be explained through generally stronger P–P bonds in Ni_3P_3 and by hindrance from the sterically demanding $[\text{Ni}]$ isolobal replacement.

4.2.5 Dynamical Behaviour of the cyclo- P_3 Fragment

The dynamic behavior of the cyclo- P_3 fragment was investigated by solid-state ^{31}P NMR spectroscopy. The experimental static and magic angle spinning spectra of $[\text{Ni}_3]_3$ are shown in Figure S18 in the supporting information. It was difficult to determine from

these spectra the exact values of the principal components of the chemical shift tensors and the corresponding isotropic chemical shifts. The three phosphorus atoms of the cyclo- P_3 fragment were not chemically equivalent, and therefore, their chemical shift tensors were slightly different. The $^1J(^{31}\text{P}^{31}\text{P})$ scalar couplings between them were about 400 Hz, leading to non-first-order NMR spectra. They are also affected by homonuclear $^{31}\text{P} - ^{31}\text{P}$ dipolar interactions. Nevertheless, the experimental values of the principal components δ_{11} , δ_{22} , and δ_{33} of the chemical shift tensors and the isotropic chemical shifts δ_{iso} could be roughly estimated (see Table 4.5). Tables S12 and S13 (SI) report the ^{31}P NMR shielding tensors of $[\text{Ni}]\text{P}_3$ and $^1J(^{31}\text{P}^{31}\text{P})$ couplings calculated using the ω B97XD/def2-QZVP approximation. A reference ^{31}P NMR absolute chemical shielding σ^{ref} is required to convert between the chemical shift scale δ used in experiments and the absolute shielding scale σ used in theoretical calculations. With a high degree of accuracy, $\delta \approx \sigma^{\text{ref}} - \sigma$. The value of σ^{ref} depends on the approximation used for the calculations and is available elsewhere.^[36] For the ω B97XD/def2-QZVP approximation, $\sigma^{\text{ref}} = 300\text{ppm}$. The calculated values of the shieldings σ_{iso} , σ_{11} , σ_{22} , and δ_{33} of the three phosphorus nuclei of the cyclo- P_3 fragment are given in Table S12.

The difference between the experimental and calculated values of δ_{iso} was significant and exceeded the expected margin of error.^[36] This difference was most likely due to the influence of the crystal field, which cannot be accounted for in conventional calculation approaches.^[37] The difference between the experimental and calculated values of the principal components of the tensors was even larger, but it had two characteristic features. First, the experimental tensor was axially symmetric ($\delta_{11}^{\text{exp}} = \delta_{22}^{\text{exp}}$), while the calculated tensors were not. Second, the anisotropy of the experimental tensor was smaller than that of the calculated tensors, $|\delta_{11}^{\text{exp}}| < |\delta_{11}^{\text{calc}}|$ and $|\delta_{33}^{\text{exp}}| < |\delta_{33}^{\text{calc}}|$. Such features are typical of molecular systems undergoing dynamic changes that are fast on the NMR time scale of microseconds.^[38] The δ_{11} and δ_{22} components lay roughly in the plane of the cyclo- P_3 fragment, and the direction of the δ_{33} component roughly coincided with the normal to this plane. An intermittent rotation of this fragment about this normal led to an axially symmetric tensor with $\delta_{11}^{\text{rot}} = \delta_{22}^{\text{rot}} = (\delta_{11}^{\text{calc}} + \delta_{22}^{\text{calc}})/2$. Since the directions of the tensor components did not exactly coincide with the plane of the fragment and the normal, this equality was approximately satisfied, and the rotation also changed the observed value of the δ_{33} component, so that $|\delta_{33}^{\text{rot}}| < |\delta_{33}^{\text{calc}}|$. Figure S19 in the SI shows the resulting relaxed geometry energies for a 120° rotation of the cyclo- P_3 fragment perpendicular to the axis connecting the centers of mass of the two cyclic fragments. The activation barrier was only 8.9 kJ/mol, indicating dynamic exchange of the three phosphorus positions.

Table 4.5: Experimental and calculated values of δ_{iso} , δ_{11} , δ_{22} , and δ_{33} of the cyclo- P_3 fragment.

Nucleus	δ_{iso} / ppm	δ_{11} / ppm	δ_{22} / ppm	δ_{33} / ppm
Experiment	-164	10	10	-520
P1	-190	100	-49	-623
P2	-185	85	-43	-596
P3	-184	128	-49	-632

4.3 Conclusion

In summary, we have extensively characterized $[\text{Ni}]\text{P}_3$ using the most sophisticated methods of experimentally driven charge density analysis. A rare example of a successful X-ray restrained wavefunction fitting of a transition metal complex has provided deep insight into the chemical nature (Scheme 1) of $[\text{Ni}]\text{P}_3$ - an isolobal analogue of white phosphorus with promise as a phosphorus source with rich reactivity.

Our studies showed a reasonable applicability of Hoffman's isolobal principle when $[\text{Ni}]\text{P}_3$ is compared to white phosphorus. We found dative Ni-P bonds in every aspect of our analysis. These bonds were primarily covalent and showed a clear polarization between the more electronegative phosphorus and the electropositive nickel atom, as expected. Hence, we describe $[\text{Ni}]\text{P}_3$ as an metallatetrahedrane analogue. The shorter P - P bonds in $[\text{Ni}]\text{P}_3$ showed comparable or higher bond orders, but slightly less delocalization, than the longer P - P bonds in P_4 . This was consistent with the reported reactivity of the air-stable $[\text{Ni}]\text{P}_3$ - especially when compared to the pyrophoric P_4 .

Finally, this study clearly showed the advantages of a deeper insight into diffraction data supported by theoretical calculations, which can go far beyond a simple determination of the connectivity and geometry of a compound under investigation. It is evident that theoretical studies should much more often be carried out in concert with crystal structure determinations, rather than independently of them.

4.4 References

- [1] A. Genoni, L. Bučinský, N. Claiser, J. Contreras-García, B. Dittrich, P. M. Dominiak, E. Espinosa, C. Gatti, P. Giannozzi, J. Gillet, D. Jayatilaka, P. Macchi, A. Ø. Madsen, L. Massa, C. F. Matta, K. M. Merz, P. N. H. Nakashima, H. Ott, U. Ryde, K. Schwarz, M. Sierka, S. Grabowsky, *Chem. Eur. J.* 2018, 24, 10881-10905.
- [2] H.-B. Bürgi, A. Genoni, *Acta Crystallogr. Sect. B* 2022, 78, 298-304.
- [3] D. Jayatilaka, *Phys. Rev. Lett.* 1998, 80, 798-801.
- [4] E. S. Vosegaard, J. V. Ahlburg, L. Krause, B. B. Iversen, *Acta Crystallogr. Sect. B* 2023, 79, 380-391.
- [5] E. Mädl, G. Balázs, E. V. Peresypkina, M. Scheer, *Angew. Chem.* 2016, 128, 7833-7838.
- [6] C. Riesinger, L. Dütsch, G. Balázs, M. Bodensteiner, M. Scheer, *Chem. Eur. J.* 2020, 26, 17165-17170.
- [7] R. Bianchi, G. Gervasio, D. Marabello, *C. R. Chim.* 2005, 8, 1392-1399.
- [8] P. Macchi, D. M. Proserpio, A. Sironi, *J. Am. Chem. Soc.* 1998, 120, 13429-13435.
- [9] A. Genoni, B. Meyer, *Adv. Quantum Chem.* 2016, 73, 333-362.
- [10] M. Elia, M. M. L. Chen, D. M. P. Mingos, R. Hoffmann, *Inorg. Chem.* 1976, 15, 1148-1155.
- [11] C. Jelsch, B. Guillot, A. Lagoutte, C. Lecomte, *J. Appl. Crystallogr.* 2005, 38, 38-54; N. K. Hansen, P. Coppens, *Acta Crystallogr. Sect. A* 1978, 34, 909-921.
- [12] B. Guillot, L. Viry, R. Guillot, C. Lecomte, C. Jelsch, *J. Appl. Crystallogr.* 2001, 34, 214-223.
- [13] N. K. Hansen, P. Coppens, *Acta Crystallogr. Sect. A* 1978, 34, 909-921.
- [14] A. Ø. Madsen, *J. Appl. Crystallogr.* 2006, 39, 757-758.
- [15] D. Jayatilaka, D. J. Grimwood, in *Computational Science - ICCS 2003*, Springer

Berlin Heidelberg, Berlin, Heidelberg, 2003, 142-151.

- [16] S. C. Capelli, H.-B. Bürgi, B. Dittrich, S. Grabowsky, D. Jayatilaka, *IUCrJ* 2014, 1, 361-379.
- [17] D. Jayatilaka, B. Dittrich, *Acta Crystallogr. Sect. A* 2008, 64, 383-393.
- [18] F. Neese, F. Wennmohs, U. Becker, C. Riplinger, *J. Chem. Phys.* 2020, 152, 224108.
- [19] F. Kleemiss, O. V. Dolomanov, M. Bodensteiner, N. Peyerimhoff, L. Midgley, L. J. Bourhis, A. Genoni, L. A. Malaspina, D. Jayatilaka, J. L. Spencer, F. White, B. Grundkötter-Stock, S. Steinhauer, D. Lentz, H. Puschmann, S. Grabowsky, *Chem. Sci.* 2021, 12, 1675-1692.
- [20] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* 2009, 42, 339-341.
- [21] F. L. Hirshfeld, *Theor. Chim. Acta* 1977, 44, 129-138.
- [22] F. D. Proft, R. Vivas-Reyes, A. Peeters, C. Van Alsenoy, P. Geerlings, *J. Comput. Chem.* 2003, 24, 463-470.
- [23] E. Hupf, F. Kleemiss, T. Borrmann, R. Pal, J. M. Krzeszczakowska, M. Wońska, D. Jayatilaka, A. Genoni, S. Grabowsky, *J. Chem. Phys.* 2023, 158, 124103.
- [24] M. Wońska, D. Jayatilaka, B. Dittrich, R. Flaig, P. Luger, K. Woźniak, P. M. Dominiak, S. Grabowsky, *ChemPhysChem* 2017, 18, 3334-3351.
- [25] A. Simon, H. Borrmann, J. Horakh, *Chem. Ber.* 1997, 130, 1235-1240.
- [26] V. Vukovic, PhD thesis, Université de Lorraine (France).
- [27] R. F. W. Bader, *Atoms in Molecules: A Quantum Theory*, Clarendon Press; Oxford University Press, Oxford [England]: New York, 1994.
- [28] R. F. W. Bader, *Chem. Rev.* 1991, 91, 893-928.
- [29] M. Haimerl, M. Piesch, G. Balázs, P. Mastrorilli, W. Kremer, M. Scheer, *Inorg. Chem.* 2021, 60, 5840-5850.
- [30] A. T. Normand, E. D. S. Carrizo, C. Manoux, E. Lobato, H. Cattey, P. Richard, S. Brandès, C. H. Devillers, A. Romieu, P. Le Gendre, P. FleuratLessard, *Chem. Sci.* 2021, 12, 253-269.
- [31] F. Spitzer, M. Sierka, M. Latronico, P. Mastrorilli, A. V. Virovets, M. Scheer, *Angew. Chem. Int. Ed.* 2015, 54, 4392-4396.
- [32] M. Fugel, J. Beckmann, D. Jayatilaka, G. V. Gibbs, S. Grabowsky, *Chem. Eur. J.* 2018, 24, 6248-6261.
- [33] a) J. S. Dewar, *Bull. Soc. Chim. Fr.* 1951, 18, C71; b) J. Chatt, L. A. Duncanson, *J. Chem. Soc.* 1953, 2939-2947.
- [34] R. Bianchi, C. Gatti, V. Adovasio, M. Nardelli, *Acta Crystallogr. Sect. B* 1996, 52, 471-478; G. T. Smith, P. R. Mallinson, C. S. Frampton, L. J. Farrugia, R. D. Peacock, J. A. K. Howard, *J. Am. Chem. Soc.* 1997, 119, 5028-5034.
- [35] E. D. Glendening, C. R. Landis, F. Weinhold, *J. Comput. Chem.* 2019, 40, 2234-2241.
- [36] I. G. Shenderovich, *Chem. Methods* 2021, 1, 61-70.
- [37] I. G. Shenderovich, *J. Chem. Phys.* 2020, 153, 184501.
- [38] I. G. Shenderovich, *Langmuir* 2020, 36, 11383-11392.
- [39] CrysAlisPro (V.42) Rigaku Oxford Diffraction Ltd, 2019.
- [40] G. M. Sheldrick, *Acta Crystallogr. Sect. A* 2015, 71, 3-8.
- [41] L. J. Bourhis, O. V. Dolomanov, R. J. Gildea, J. A. K. Howard, H. Puschmann, *Acta Crystallogr. Sect. A* 2015, 71, 59-75.
- [42] K. Meindl, J. Henn, *Acta Crystallogr. Sect. A* 2008, 64, 404-418.
- [43] B. Guillot, *Acta Crystallogr. Sect. A* 2012, 68, 204.

- [44] J. C. Slater, *Phys. Rev.* 1951, 81, 385-390.
- [45] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* 1988, 37, 785-789.
- [46] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* 2005, 7, 3297.
- [47] Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* 2008, 120, 215-241.
- [48] V. Bezugly, P. Wielgus, M. Kohout, F. R. Wagner, *J. Comput. Chem.* 2009, 31, 1504-1519.
- [49] K. Alhameedi, G. S. Chandler, D. Jayatilaka, *Results in Chemistry* 2020, 2, 100053.
- [50] T. Lu, F. Chen, *J. Comput. Chem.* 2012, 33, 580-592.
- [51] F. Meurer, O. V. Dolomanov, C. Hennig, N. Peyerimhoff, F. Kleemiss, H. Puschmann, M. Bodensteiner, *IUCrJ* 2022, 9, 604-609.
- [52] W. F. Kuhs, *Aust. J. Phys.* 1988, 41, 369-382.
- [53] H. B. Bürgi, S. C. Capelli, H. Birkedal, *Acta Crystallogr. Sect. A* 2000, 56, 425-435.
- [54] J. Schefer, D. Schwarzenbach, P. Fischer, Th. Koetzle, F. K. Larsen, S. Haussühl, M. Rüdlinger, G. McIntyre, H. Birkedal, H.-B. Bürgi, *Acta Crystallogr. Sect. B* 1998, 54, 121-128.
- [55] Gaussian, M. J. Frisch, G. W. Trucks, G. E. Schlegel, G. E. Scuseris, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, 2013.
- [56] B. Zarychta, J. Zaleski, J. Kyziol, Z. Daszkiewicz, C. Jelsch, *Acta Crystallogr. Sect. B* 2011, 67, 250-262.

4.5 Supporting information

The supporting information of this work is provided as a single .pdf file with original format and page numbering starting from the next page.

Chemistry–A European Journal

Supporting Information

Probing the Isolobal Relation between $\text{Cp}''' \text{NiP}_3$ and White Phosphorus by Experimental Charge Density Analysis

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Experimental Procedures

Data collection and modeling of X-ray diffraction data

Data were collected from orange crystals suitable for X-ray diffraction experiments crystallized from *n*-hexane (dry, SPS) and synthesized following the literature procedure.^[1] Diffraction experiments were performed on a Rigaku Oxford Diffraction SuperNova diffractometer equipped with an Atlas S2 CCD detector on two different specimens using Mo K α radiation ($\lambda = 0.71073$ Å) and Cu K β radiation ($\lambda = 1.39222$ Å), respectively. The recorded diffraction patterns were integrated and processed with *CrysAlisPro*, the initial structure solution was found using *SHELXT*. The initial refinement of the independent-atom-model of [Ni]P₃ was performed using *olex2.refine* within the *Olex2* crystallographic software suite and the reflections used for the advanced models were merged used *Olex2*.^[2–5]

The details of the quality indicators and refinement parameters for the six distinct crystallographic models are shown in Table S1.

The Hansen-Coppens multipolar formalism for individual atoms was used to describe the experimental charge density within in the program *MoPro*.^[6,7] Multipolar coefficients were refined at a dipolar level for hydrogen, at an octopolar level for carbon, and at hexadecapolar level for nickel and phosphorous. Scaling factor coefficients, positional and anisotropic displacement parameters (anharmonic displacement parameters of 3rd degree for all P atoms), valence populations, and anomalous dispersion parameters for nickel (only in Cu K β model) were refined and tested against values obtained from the *olex2.refine* routine in *Olex2*.^[4] Anharmonic displacement parameters were validated using a multitemperature approach (100 K, 150 K, 200 K, and 250 K). For each temperature the probability distribution function as well as displacement parameters were analyzed. κ coefficients were refined to model expansion/contraction of multipoles. Constrained anisotropic parameters for hydrogen atoms were obtained using the *SHADE3* server and tested against anisotropic displacement parameters from a HAR model, where the ones from *SHADE3* were subsequently chosen for the models.^[8] Additionally, the weighting of restraints was optimized by R_{free} refinements. For the Cu K β multipolar model, an extinction correction was also applied, and the modelling parameter refined. An R_{free} refinement according to the published method^[9] helped to optimize weights for the applied restraints while avoiding overfitting.

In the global R_{free} refinement, twenty different R_{free} refinements are performed where one reflection out of twenty is omitted. The twenty different tests sets have no common reflections and globally constitute the whole diffraction data. The global R_{free} is then computed on the complete set of reflections. $R_{\text{free_global}} = \sum_{\text{hkl}} [W_{\text{hkl}} (I_{\text{o}} - I_{\text{c_free}})]^2 / \sum_{\text{hkl}} [W_{\text{hkl}} \cdot I_{\text{o}}]^2$

The quality of both models is evaluated using a DR plot (Fig. S1) and resolution plot (Fig. S3) from *XDRKplots*, fractal dimension plot (Fig. S2) from *jnk2RDA*^[10], and residual density plots (Fig. S4) from *VMoPro*.

VMoPro calculated the topological properties of the complex for both models, while the three-dimensional representations were visualized within *MoProViewer*.^[11]

CCDC numbers for MM-Mo K α (2305140), HAR-Mo K α (2305141), MM-Cu K β (2305139) and HAR-Cu K β (2305142) contain additional information as well as the collected intensities.

(Semi-) Theoretical procedures and analyses

X-ray restrained wavefunction fitting (XRW) was achieved using the same data set of reflections used for multipolar modelling. XRW was performed within the *TONTO*^[12] (V. e277d81c) software package. Calculations were performed at a Hartree-Fock^[13] (HF) level of theory with increased perturbation from the experimental X-ray data. The pure HF ansatz as well as the XRW calculation were compared with the highest experimental perturbation, which converged in the SCF iterative procedure. The weighting parameter λ was increased in 0.01 increments and a final λ value of 0.42 was found for the Mo K α XRW model. For the Cu K β XRW model, the highest converging perturbation step ($\lambda = 0.98$) disagreed strongly with the Mo K α model and theoretical calculations in the topological analysis. We determined the final λ step with an agreement in the topological analysis at $\lambda = 0.55$. Atomic form factors were calculated according to a Hirshfeld partitioning scheme.^[14] Additionally, a theoretical density-functional-theory gas phase optimized structure (B3LYP / def2-TZVP)^[15,16], as well as wavefunction calculation (M062x / def2-TZVP)^[17] were performed using *ORCA5*.^[18]

The topological analysis according to the "Quantum theory of atoms in molecules" was performed using the software suite *AIMALL* (V. 19.10.12).^[19,20] Natural bonding order analysis was performed within *NBO7*^[21] and calculations of the electron localizability index (ELI-D) were performed in *dgrid*.^[22] *TONTO* also performed the Roby-Gould analysis of the resulting experimental and theoretical wavefunctions.^[23] *Multiwfn* calculated Laplacian values along the interatomic distances as well as 2D Laplacian grids.^[24]

Crystallographic information table

Table S1: Crystallographic information of the various crystallographic models used. Additional information is provided in the crystallographic information files.

Radiation (λ / Å)	Mo K α (0.71073)			Cu K β (1.39222)		
Formula	C ₁₇ H ₂₉ P ₃ Ni			C ₁₇ H ₂₉ P ₃ Ni		
Mass / g mol ⁻¹	385.034			385.034		
Crystal size / mm ³	0.29 x 0.27 x 0.23			0.15 x 0.20 x 0.27		
Space group	<i>P</i> 2 ₁ / <i>c</i>			<i>P</i> 2 ₁ / <i>c</i>		
<i>a</i> / Å	9.26444(5)			9.2696(2)		
<i>b</i> / Å	14.5889(1)			14.5952(2)		
<i>c</i> / Å	14.5261(1)			14.5316(1)		
β / °	105.9347(6)			105.978(1)		
<i>V</i> / Å ³	1887.87(2)			1889.59(5)		
<i>D</i> / g cm ⁻³	1.355			1.353		
μ / mm ⁻¹	1.270			7.848		
θ range / °	2.68 – 41.15			3.96 – 74.77		
<i>T</i> / K	100.0(1)			100.15(2)		
<i>hkl</i> range	17	≥ <i>h</i> ≥	-17	12	≥ <i>h</i> ≥	-12
	26	≥ <i>k</i> ≥	-26	20	≥ <i>k</i> ≥	-20
	26	≥ <i>l</i> ≥	-26	20	≥ <i>l</i> ≥	-20
Resolution / Å	0.54			0.72		
<i>I</i> / σ (<i>I</i>)	112.5			81.0		
<i>R</i> _{int} / %	2.93			4.43		
Tot. reflections	283834			97248		
Ind. reflections, <i>I</i> > 2 σ	11126			5123		
Completeness / %	99.9			99.8		
Multipole model indicators						
Nr. refined parameters	837			838*		
Goodness-of-fit	1.062			0.949		
Final <i>R</i> indices, <i>I</i> > 2 σ / %	1.26			1.36		
<i>R</i> indices (all data) / %	1.49			2.01		
<i>wR</i> 2 indices / %	1.90			2.53		
Largest diff. peak and hole / e Å ⁻³	0.203, -0.230			0.175, -0.225		
HAR model indicators						
Nr. refined parameters	525			528*		
Goodness-of-fit	1.062			1.071		
Final <i>R</i> indices, <i>I</i> > 2 σ / %	1.24			1.31		
<i>R</i> indices (all data) / %	1.46			1.34		
<i>wR</i> 2 indices / %	2.29			3.21		
Largest diff. peak and hole / e Å ⁻³	0.286, -0.269			0.171, -0.298		
XRW model indicators						
Goodness-of-fit (1/ σ weighting)	1.886			2.248		
Final <i>R</i> indices, <i>I</i> > 2 σ / %	1.01			0.97		
<i>R</i> indices (all data) / %	1.11			1.53		
<i>wR</i> 2 indices / %	1.56			2.02		
Largest diff. peak and hole / e Å ⁻³	0.165, -0.201			0.126, -0.337		

* Extinction correction was applied and anomalous dispersion parameters *f'*, *f''* for Ni refined in HAR and used in HAR, MM and XRW-Cu models [25]

Analysis of the multipolar models

Normal probability plots

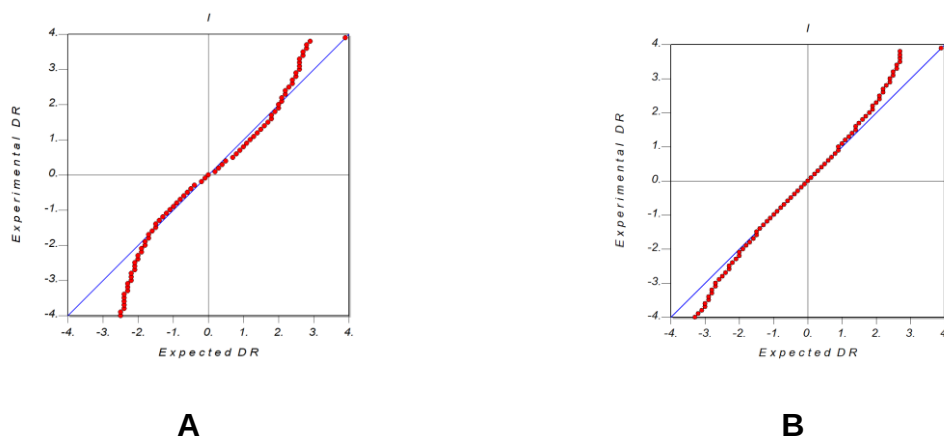


Figure S1: Quantile-quantile plots of the Mo K α (A) and the Cu K β (B) data set.

The quantile-quantile plots a linear distribution in the center of the data. Both tails deviate from the normal, and this behavior is more pronounced in the Mo K α data set due to the lower quality of very high-resolution data.

Fractal dimension plots

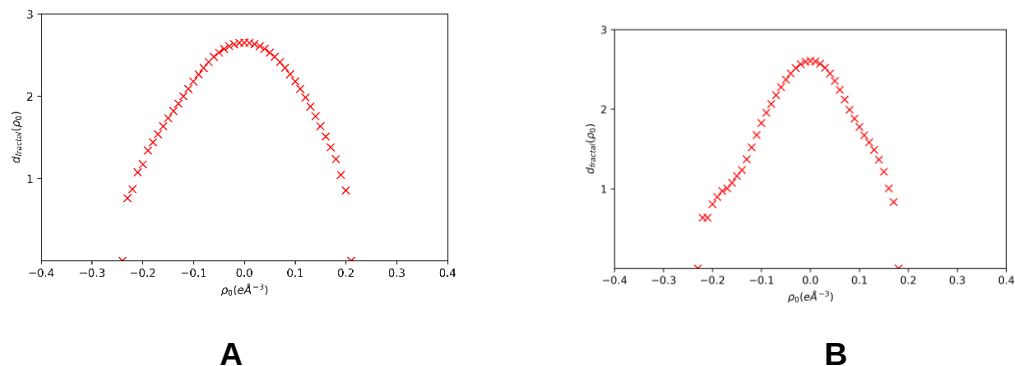


Figure S2: Fractal dimension plots according to Henn & Meindl^[10] of the Mo K α (A) and the Cu K β (B) data set.

The distribution of residual electron density reveals a small shoulder in the Cu K β XRW model. This can be attributed to the close environment around the metal atom (see figure S11 D and H).

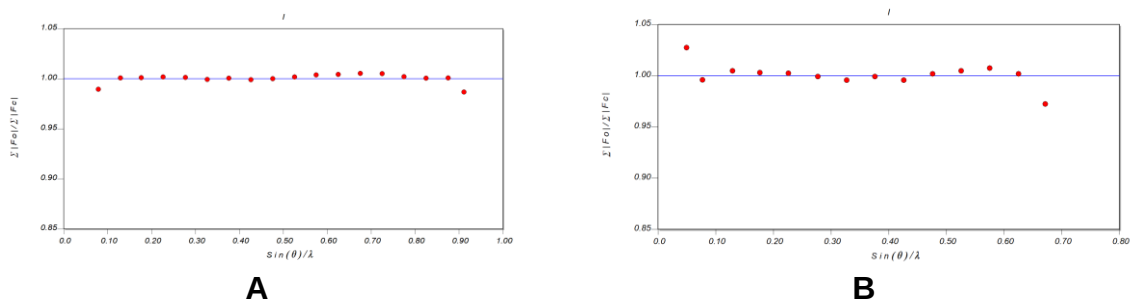
The ratio of $F_{\text{obs}} / F_{\text{calc}}$ over resolution

Figure S3: Ratio of $F_{\text{obs}} / F_{\text{calc}}$ over the full resolution range of the Mo K α (A) and the Cu K β (B) data set.

With the exception of extremely low and high resolution, the modelled and observed structure factors match well.

Residual electron density plots

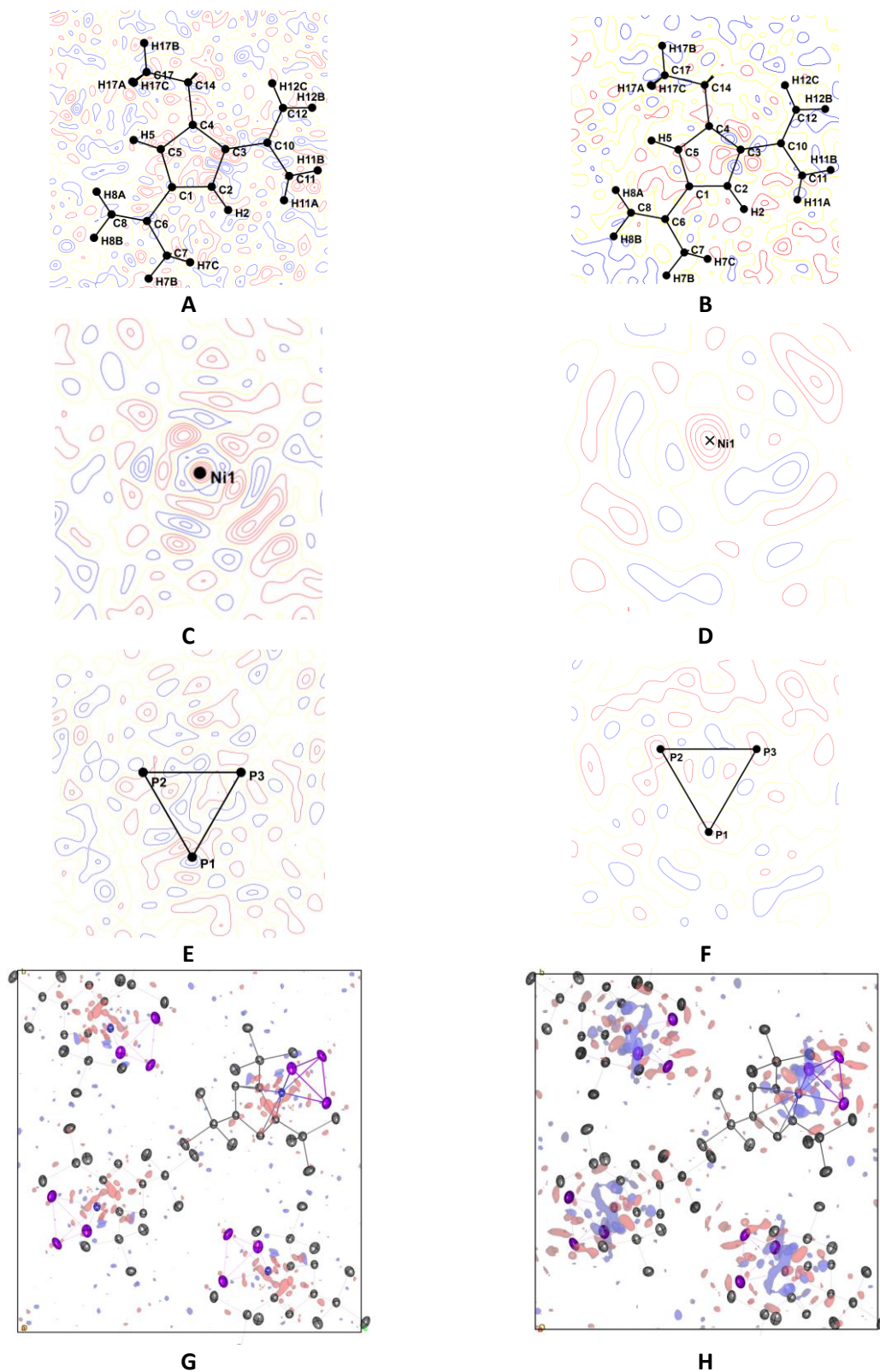


Figure S4: 2D Residual density maps of the Cp''' ligand, the metal centre perpendicular to the Cp-plane, and the cyclo-P3 ligand of 1 of the Mo K α (A,C,E) and the Cu K β (B,D,F) data set. Lines are drawn at 0.05 e difference. Blue: positive, red: negative, yellow: zero contour. 3D residual plots for [Ni]P₃ of the Mo K α (G) and Cu K β (H) model with an iso-surface of 0.15 e /Å³ (Mo K α , G) and 0.10 e /Å³ (Cu K β , H). Blue/red: positive/negative residual electron density.

Topological analysis

Table S2: Atomic charges according to Bader.[19]

Name	Mo K α		Cu K β	
	N / e	Charge /e	N / e	Charge /e
Ni	27.539	0.461	26.720	1.280
P1	15.232	-0.232	15.437	-0.437
P2	15.295	-0.295	15.407	-0.407
P3	15.296	-0.297	15.386	-0.386
C1	6.088	-0.088	6.016	-0.016
C2	6.143	-0.143	6.050	-0.050
H2	0.995	0.005	0.941	0.059
C3	6.098	-0.098	5.919	0.081
C4	6.094	-0.094	6.210	-0.210
C5	6.161	-0.161	6.083	-0.083
H5	1.021	-0.021	0.954	0.046
C6	5.917	0.083	5.975	0.025
C7	5.968	0.032	6.159	-0.159
H7A	1.001	-0.001	0.963	0.037
H7B	0.983	0.017	0.946	0.054
H7C	0.968	0.032	0.938	0.062
C8	6.004	-0.004	6.169	-0.169
H8A	0.962	0.038	0.938	0.062
H8B	0.990	0.010	0.943	0.057
H8C	0.976	0.024	0.963	0.037
C9	5.969	0.031	6.148	-0.148
H9A	0.977	0.021	0.945	0.055
H9B	0.985	0.015	0.948	0.052
H9C	0.985	0.015	0.946	0.054
C10	5.867	0.133	5.977	0.023
C11	5.937	0.063	6.118	-0.118
H11A	1.005	-0.005	0.947	0.053
H11B	0.990	0.010	0.945	0.055
H11C	1.007	-0.007	0.955	0.045
C12	5.948	0.052	6.117	-0.117
H12A	0.997	0.003	0.958	0.042
H12B	0.981	0.019	0.946	0.054
H12C	0.997	0.003	0.949	0.051
C13	5.990	0.010	6.142	-0.142
H13A	0.978	0.022	0.939	0.061
H13B	0.975	0.025	0.947	0.053
H13C	0.973	0.027	0.944	0.056
C14	5.912	0.088	5.942	0.058
C15	5.978	0.022	6.151	-0.151

H15A	0.998	0.002	0.959	0.041
H15B	0.971	0.029	0.948	0.052
H15C	0.982	0.018	0.969	0.031
C16	5.980	0.020	6.158	-0.158
H16A	0.980	0.020	0.945	0.055
H16B	0.974	0.026	0.942	0.058
H16C	0.979	0.021	0.939	0.061
C17	5.995	0.005	6.175	-0.175
H17A	0.982	0.018	0.945	0.055
H17B	0.976	0.024	0.937	0.063
H17C	0.978	0.022	0.940	0.060

Critical points

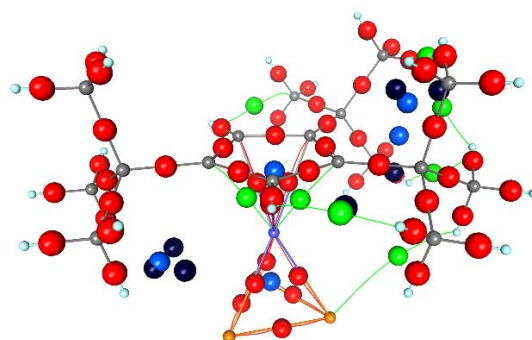


Figure S5: Bond (red), cage (light blue), ring (dark blue) and non-covalent interaction (green) critical points in the [Ni]P₃ models.

Table S3: Bond critical points (3,-1) for the **Mo Ka** multipolar model

Atom1	Atom2	Distance	DCP1	DCP2	ρ / eA^{-3}	$\nabla^2(\rho) / \text{eA}^{-5}$
Ni1	P1	2.2609	1.1832	1.0777	0.557(6)	3.61(8)
Ni1	P2	2.2486	1.1777	1.0709	0.577(5)	3.72(7)
Ni1	P3	2.2571	1.1741	1.083	0.536(8)	3.70(9)
Ni1	C2	2.1187	1.0624	1.0563	0.53502	6.323
Ni1	C4	2.1097	1.0608	1.0489	0.54124	6.424
Ni1	C5	2.076	1.0303	1.0458	0.54701	6.671
P1	P2	2.1563	1.0828	1.0735	0.760(5)	-0.3(1)
P1	P3	2.1504	1.0843	1.0662	0.749(5)	-0.22(8)
P1	H7A	7.3846	1.1815	6.2031	0.04746	0.501
P2	P3	7.2913	1.0907	6.2006	0.756(6)	-0.20(9)
P2	H12A	7.4582	1.2498	6.2084	0.03454	0.390
C1	C2	1.4281	0.7144	0.7137	1.99015	-14.307
C1	C5	1.4286	0.7109	0.7177	1.95979	-13.336
C1	C6	1.5179	0.7357	0.7821	1.71043	-11.894
C2	H2	1.0264	0.3621	0.6643	1.95404	-18.945
C2	C3	1.4451	0.6778	0.7673	1.82143	-10.144
C3	C4	1.4775	0.7393	0.7382	1.80100	-10.314
C3	C10	1.5372	0.7515	0.7856	1.58237	-8.9360
C4	C5	1.4472	0.7412	0.706	1.89657	-11.920

C4	C14	1.5406	0.7466	0.7941	1.6286	-10.106
C5	H5	1.0337	0.3716	0.6621	1.95927	-18.142
C6	C7	1.5338	0.7605	0.7733	1.59684	-9.343
C6	C8	1.5306	0.7661	0.7646	1.5995	-9.566
C6	C9	1.5407	0.7635	0.7772	1.55893	-8.572
C7	H7A	1.0343	0.3714	0.6629	1.8339	-14.965
C7	H7B	1.0568	0.3799	0.6769	1.76141	-13.052
C7	H7C	1.0474	0.3698	0.6776	1.77678	-13.793
C8	H8A	1.0530	0.3696	0.6834	1.78566	-13.745
C8	H8B	1.0535	0.3770	0.6765	1.80876	-13.81
C8	H8C	1.0479	0.3695	0.6784	1.78534	-13.915
C9	H9A	1.0497	0.3777	0.672	1.75039	-12.863
C9	H9B	1.0558	0.3795	0.6763	1.75493	-12.513
C9	H9C	1.0467	0.3765	0.6702	1.77868	-13.212
C10	C11	1.5432	0.7726	0.7706	1.5439	-8.293
C10	C12	1.5340	0.7727	0.7613	1.58791	-9.347
C10	C13	1.5443	0.7754	0.7689	1.56357	-8.924
C11	H11A	1.0421	0.3778	0.6642	1.82197	-13.935
C11	H11B	1.0454	0.3797	0.6656	1.79757	-13.678
C11	H11C	1.0476	0.3775	0.6701	1.80378	-13.734
C12	H12A	1.0467	0.3756	0.6711	1.82675	-14.671
C12	H12B	1.0582	0.3804	0.6779	1.7724	-13.403
C12	H12C	1.0455	0.3760	0.6694	1.83732	-14.662
C13	H13A	1.0499	0.3717	0.6782	1.80364	-14.095
C13	H13B	1.0551	0.3738	0.6812	1.79322	-14.088
C13	H13C	1.0490	0.3719	0.6771	1.80233	-14.238
C14	C15	1.5421	0.7705	0.7716	1.55421	-8.691
C14	C16	1.5422	0.7690	0.7731	1.56038	-8.528
C14	C17	1.5410	0.7729	0.7681	1.5646	-8.653
C15	H15A	1.0328	0.3730	0.6598	1.82313	-14.797
C15	H15B	1.0405	0.3706	0.6699	1.79954	-14.165
C15	H15C	1.0434	0.3700	0.6734	1.79186	-14.060
C16	H16A	1.0460	0.3724	0.6737	1.79538	-13.603
C16	H16B	1.0523	0.3753	0.677	1.76921	-13.257
C16	H16C	1.0408	0.3728	0.6681	1.79685	-13.884
C17	H17A	1.0489	0.3717	0.6772	1.79569	-13.903
C17	H17B	1.0544	0.3769	0.6775	1.78349	-13.308
C17	H17C	1.0479	0.3723	0.6756	1.80661	-13.798
Ni1	C1	2.1129	1.0586	1.0542	0.53974	6.460
H2	H11A	2.5367	1.3355	1.2011	0.10636	1.406
H12C	H15A	2.2309	0.9823	1.2485	0.09243	1.232
H12C	H16C	2.0692	1.0425	1.0267	0.07061	1.048
H13A	H16C	2.2479	1.1425	1.1054	0.05233	0.775

Table S4: Bond critical points (3,-1) for the **Cu K β** multipolar model.

Atom1	Atom2	Distance	DCP1	DCP2	$\rho / \text{e}\text{\AA}^{-3}$	$\nabla^2(\rho) / \text{e}\text{\AA}^{-5}$
Ni1	P1	2.2763	1.194	1.0823	0.52797	3.653
Ni1	P2	2.2795	1.1892	1.0903	0.52951	3.498
Ni1	P3	2.2514	1.0679	1.2204	0.50578	3.434
Ni1	C1	2.1051	1.0766	1.0286	0.5214	6.323
Ni1	C4	2.0954	1.0570	1.0384	0.49581	6.553
Ni1	C5	2.0807	1.0514	1.0294	0.51141	6.583
Ni1	C3	2.1262	1.0892	1.037	0.51357	5.870
P1	P2	2.1715	1.0733	1.0982	0.76416	-1.287
P1	P3	2.162	1.0700	1.0920	0.75973	-1.266
P1	H7A	7.3407	1.1555	6.1852	0.05637	0.532
P2	P3	7.2678	1.0826	6.1852	0.76638	-1.423
C1	C2	1.4292	0.7348	0.6944	1.91741	-13.472
C1	C5	1.4298	0.7304	0.6994	1.88154	-12.489
C1	C6	1.5193	0.7568	0.7624	1.69005	-11.066
C2	H2	1.0623	0.3748	0.6875	1.84029	-18.244
C2	C3	1.4432	0.6601	0.7831	1.62245	-5.673
H2	C11	2.9386	1.7306	1.208	0.10679	1.381
C3	C4	1.4700	0.8005	0.6695	1.64133	-5.799
C3	C10	1.5382	0.8154	0.7228	1.40969	-4.281
C4	C5	1.4483	0.7398	0.7085	1.8494	-12.34
C4	C14	1.5439	0.7574	0.7865	1.61896	-9.916
C5	H5	1.0611	0.3774	0.6837	1.8382	-18.026
C6	C7	1.5332	0.7732	0.76	1.59164	-9.113
C6	C8	1.5306	0.7697	0.7609	1.60244	-9.357
C6	C9	1.5408	0.7767	0.7641	1.5615	-8.759
C7	H7A	1.0794	0.382	0.6974	1.76738	-14.569
C7	H7B	1.0844	0.3854	0.6989	1.74976	-14.295
C7	H7C	1.0796	0.3814	0.6982	1.75919	-14.587
C8	H8A	1.0936	0.3859	0.7076	1.72252	-13.625
C8	H8B	1.094	0.3871	0.7069	1.73287	-13.664
C8	H8C	1.0918	0.387	0.7048	1.72836	-13.51
C9	H9A	1.0859	0.386	0.700	1.7361	-13.967
C9	H9B	1.0859	0.3862	0.6997	1.75099	-14.085
C9	H9C	1.0874	0.3851	0.7022	1.74512	-14.112
C10	C11	1.5436	0.7728	0.7708	1.57152	-8.793
C10	C12	1.533	0.7648	0.7681	1.60498	-9.613
C10	C13	1.5438	0.7729	0.7708	1.57356	-8.845
C11	H11A	1.0741	0.3821	0.692	1.78957	-15.108
C11	H11B	1.0848	0.3852	0.6996	1.74879	-14.127
C11	H11C	1.0797	0.3841	0.6955	1.76519	-14.668
C12	H12A	1.0893	0.386	0.7033	1.74492	-14.167
C12	H12B	1.0983	0.3905	0.7078	1.71097	-13.289
C12	H12C	1.0871	0.3851	0.7019	1.7457	-14.136
C13	H13A	1.0811	0.3826	0.6985	1.76608	-14.526
C13	H13B	1.0924	0.387	0.7054	1.73715	-13.829

C13	H13C	1.0864	0.3849	0.7015	1.74771	-14.007
C14	C15	1.5409	0.776	0.7649	1.57022	-8.844
C14	C16	1.5416	0.777	0.7646	1.57225	-8.912
C14	C17	1.5397	0.7761	0.7636	1.57935	-8.973
C15	H15A	1.0683	0.3808	0.6875	1.7861	-15.215
C15	H15B	1.0873	0.3863	0.701	1.73987	-13.988
C15	H15C	1.0896	0.3865	0.703	1.73566	-13.983
C16	H16A	1.0884	0.3855	0.7029	1.74258	-13.871
C16	H16B	1.0913	0.3855	0.7058	1.73648	-13.821
C16	H16C	1.0829	0.3836	0.6994	1.74751	-14.203
C17	H17A	1.0953	0.3863	0.709	1.72587	-13.593
C17	H17B	1.1064	0.3909	0.7155	1.68877	-12.807
C17	H17C	1.0946	0.3865	0.7081	1.72261	-13.452
H12C	H15A	2.2356	0.9673	1.2684	0.09906	1.255
H12C	H16C	2.0561	1.0411	1.0151	0.07536	1.067
H13A	H16C	2.261	1.1517	1.1094	0.05381	0.776

Laplacian of the electron density plots along Ni-P and P-P bonds

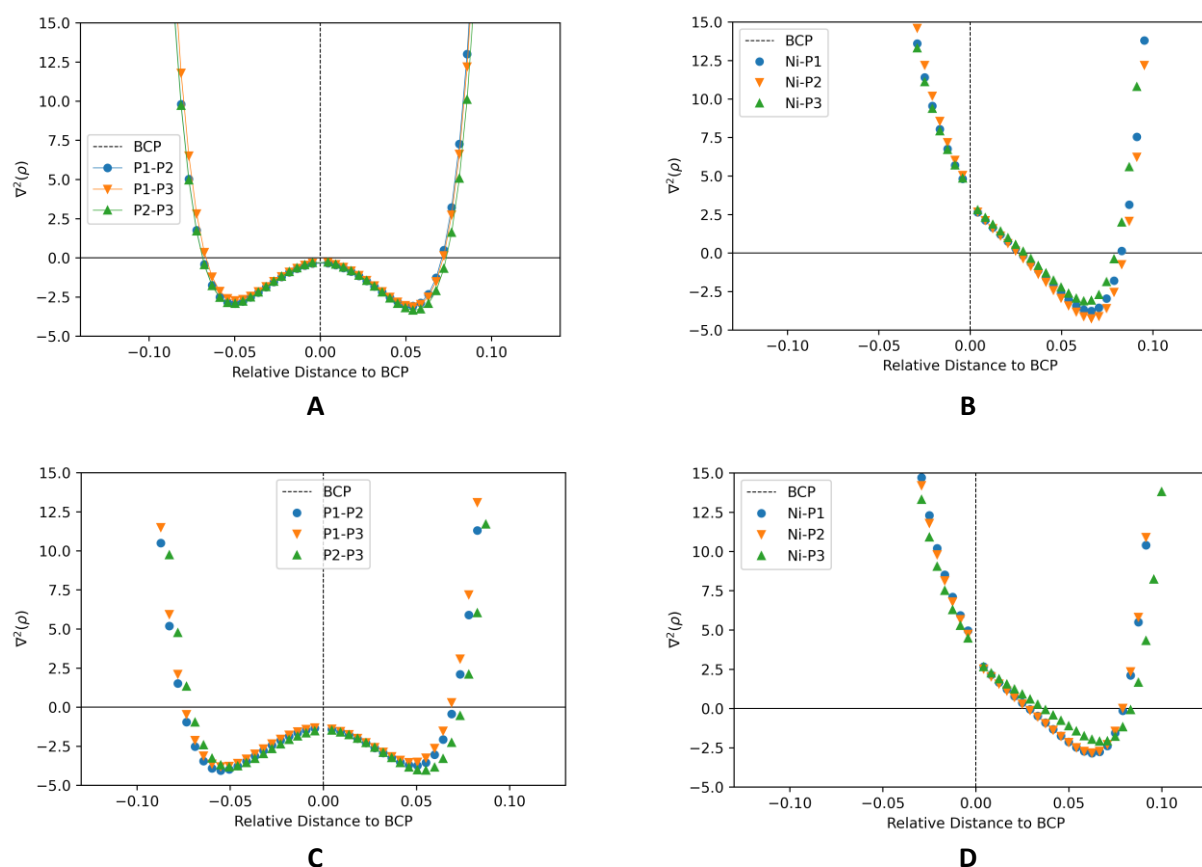


Figure S6: Values of the Laplacian ($\text{e}/\text{\AA}^5$) of the electron density ($\text{e}/\text{\AA}^3$) along the bonding path with relative distances ($\text{\AA}$) to the bond critical point for the Mo K α (A and B) and the Cu K β (C and D) multipolar model. Left: P-P bonds, right: Ni-P bonds.

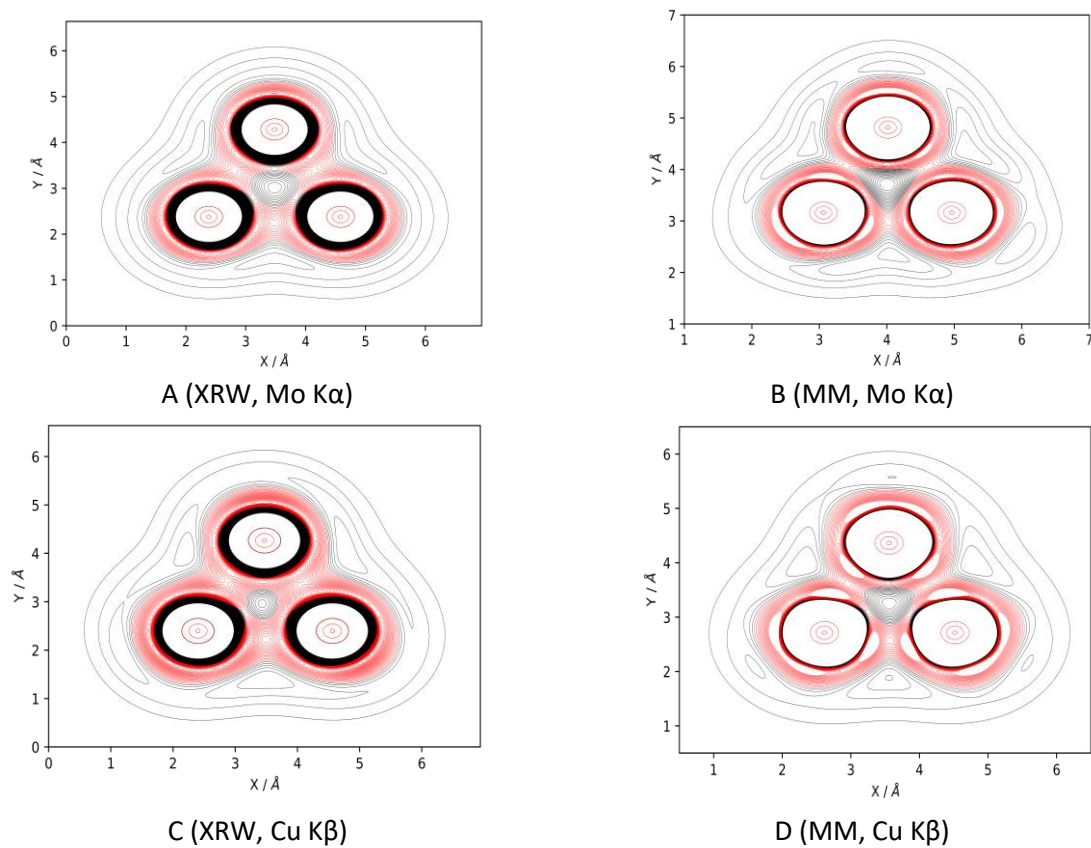
2D Laplacian of the electron density contour maps of *cyclo*-P₃

Figure S7: 2D Laplacian maps with $0.1 \text{ e}\text{\AA}^{-5}$ iso-lines for the *cyclo*-P₃ fragment compared for Mo K α XRW (A), Mo K α MM (B), Cu K β XRW (C) and Cu K β MM (D).

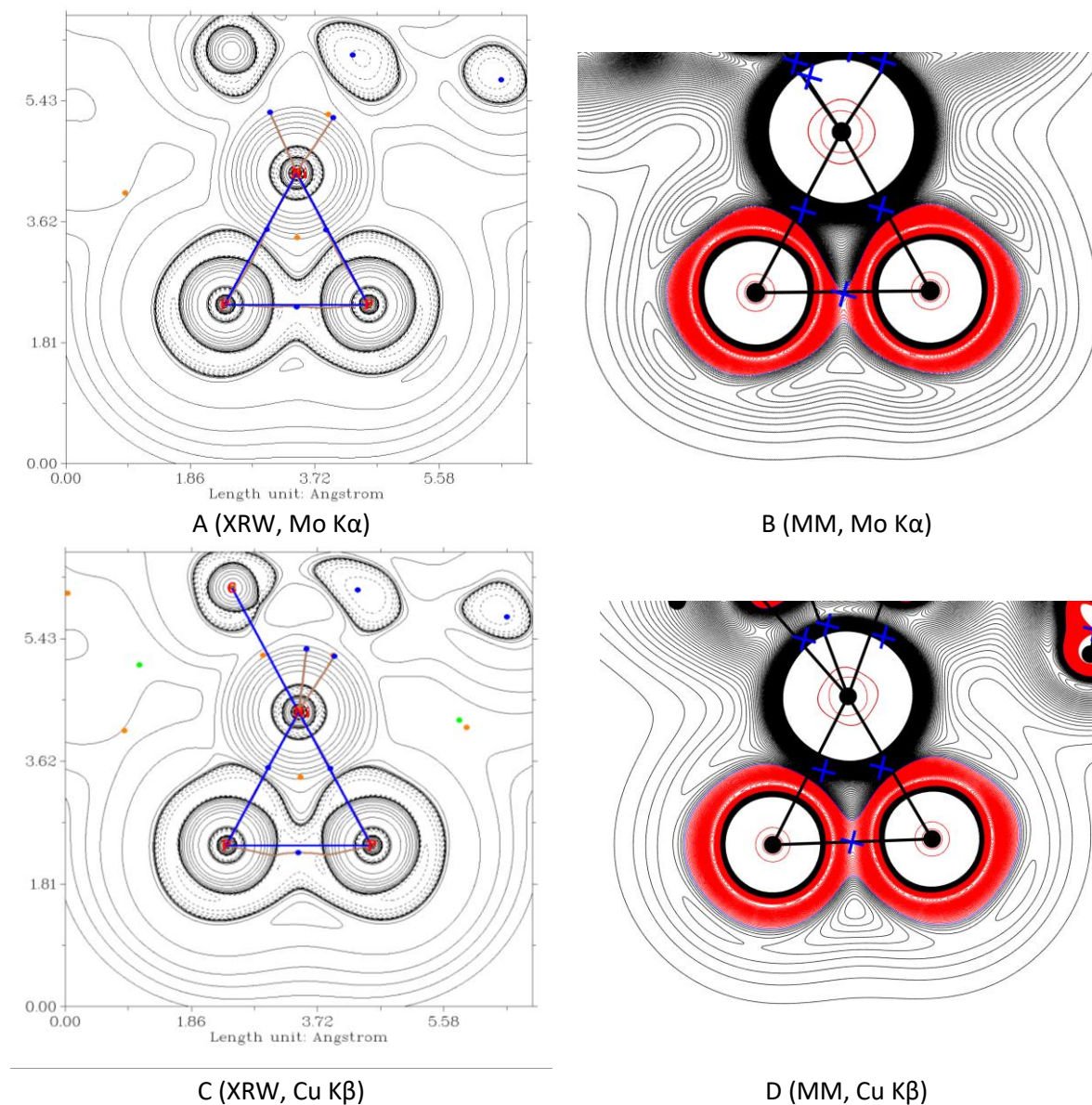
2D Laplacian of the electron density contour maps of the Ni-P₂ ring

Figure S8: 2D Laplacian maps with $0.1 \text{ e}\text{\AA}^{-5}$ iso-lines for the NiP₂-ring fragment compared for Mo K α XRW (A), Mo K α MM (B), Cu K β XRW (C) and Cu K β MM (D). Left side: pictures from multiwfn^[24], black lines: positive Laplacian values, dotted lines: negative Laplacian values, blue dots: BCPs, blue lines: interatomic path, orange line: bond path. Right side: pictures from MoProViewer^[11], red: negative Laplacian values, black: positive Laplacian values, blue cross: BCPs, black lines: interatomic path.

Electrostatic potential maps

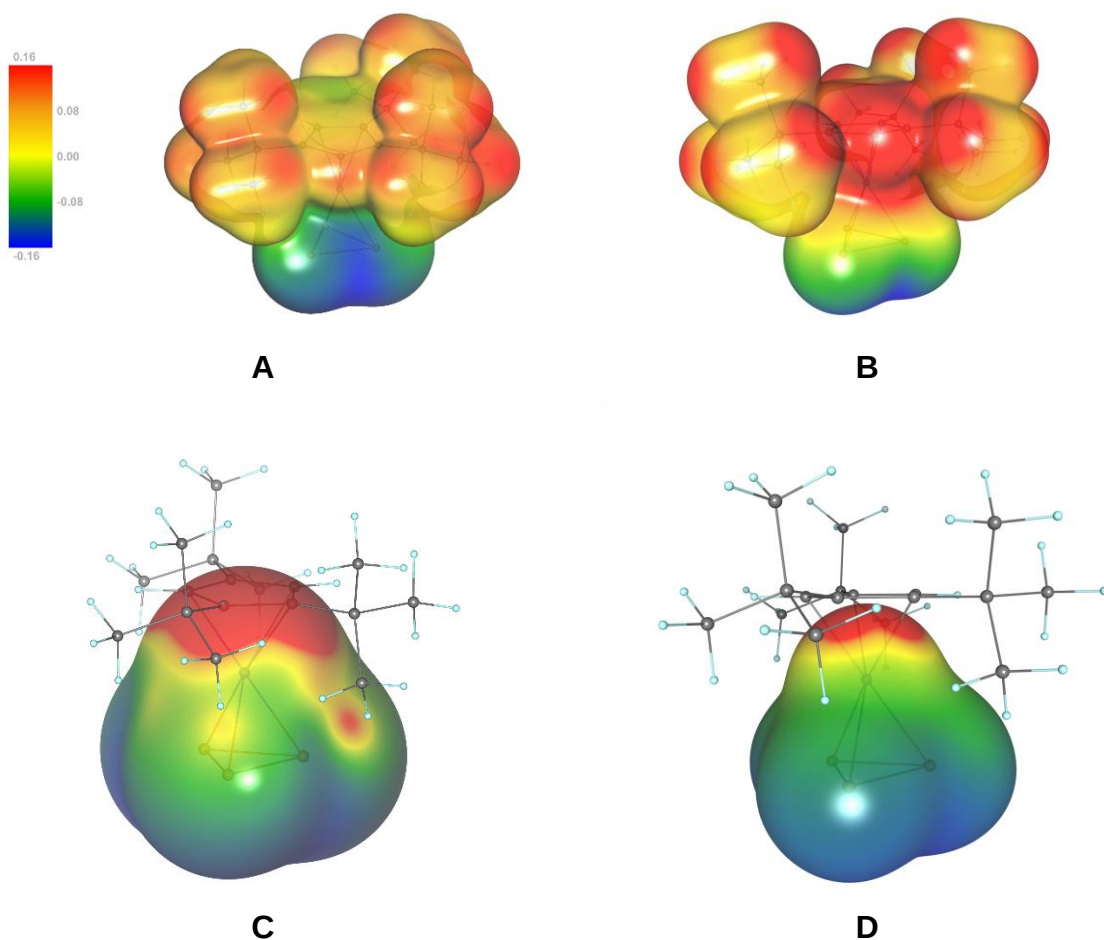


Figure S9: Values of the electrostatic potential at the $0.05 \text{ e}/\text{\AA}^3$ iso-surface for $[\text{Ni}]\text{P}_3$ (A and B) as well as the NiP_3 fragment for Mo $K\alpha$ (A and C) and Cu $K\beta$ (B and D) multipolar model.

d-Orbital populations

Table S5: Valence populations of the multipolar models, ESD were calculated according to ref. [26].

	Mo $K\alpha$ MM	Cu $K\beta$ MM
$d(z^2) / e$	1.63(3)	2.0(2)
$d(xz) / e$	1.30(5)	1.4(8)
$d(yz) / e$	1.13(5)	1.0(8)
$d(x^2-y^2) / e$	1.98(5)	1.7(3)
$d(xy) / e$	2.00(7)	1.2(2)
Total / e	8.04(1)	7.29(2)

The d-orbital populations show a much larger deviation for the Cu $K\beta$ model than for the Mo $K\alpha$ model. Whether this large deviation is due to the lower observed resolution (especially for $d(xy)$ and $d(yz)$ values ranged from 0.2 to 2.1 electrons) or due to the wavelength of Cu $K\beta$ being close to the Ni K absorption edge needs further investigation. The total population however, although different by about 0.7 electrons, is consistently preserved in both models.

Deformation electron density maps

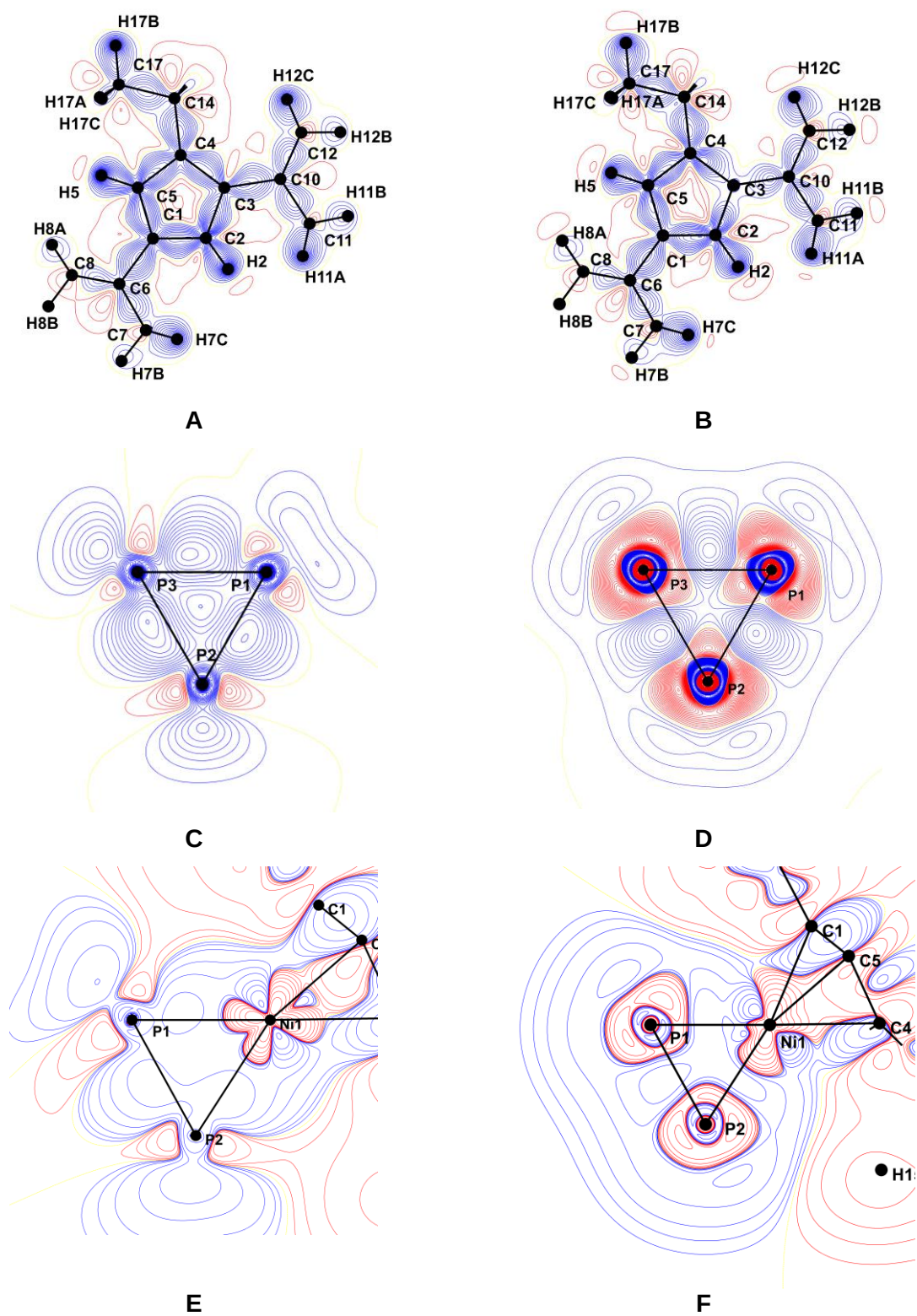


Figure S10: 2D deformation density maps of the Cp* ligand (0.05 e iso-levels), cyclo-P₃ fragment (0.01 e iso-levels), and the Ni-P1-P2 plane (logarithmic) for Mo K α (left) and the Cu K β (right) multipolar model.

Evaluation of the X-ray restrained wavefunction fitting

Geometry of the Mo K α XRW model

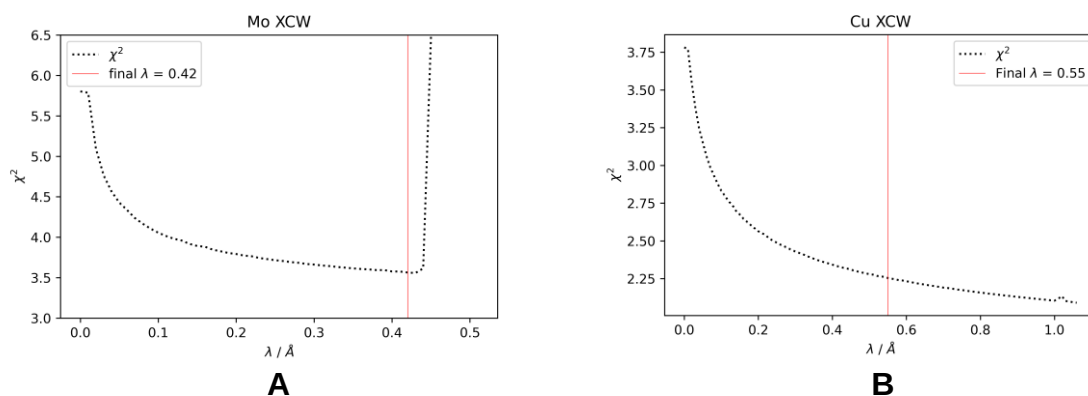
Nr	Name	Z	x	y	z
1	Ni1	28	0.481867(4)	0.660115(3)	0.769839(2)
2	P2	15	0.500981(10)	0.762970(7)	0.886798(6)
3	P1	15	0.281214(10)	0.727736(7)	0.799140(6)
4	P3	15	0.406288(11)	0.630914(7)	0.901222(6)
5	C4	6	0.66377(3)	0.584782(19)	0.751865(19)
6	C2	6	0.51164(3)	0.678121(19)	0.634728(19)
7	C5	6	0.52343(3)	0.539208(19)	0.707630(19)
8	C3	6	0.65644(3)	0.673684(18)	0.704149(18)
9	C1	6	0.42900(3)	0.596024(19)	0.636091(18)
10	C6	6	0.27545(3)	0.57195(2)	0.571025(19)
11	C10	6	0.77024(3)	0.75059(2)	0.70552(2)
12	C11	6	0.68710(4)	0.84101(2)	0.67025(2)
13	C14	6	0.78647(3)	0.53738(2)	0.83085(2)
14	C7	6	0.18546(3)	0.65852(2)	0.53194(2)
15	C15	6	0.82148(4)	0.58770(2)	0.92779(2)
16	C9	6	0.29755(4)	0.51561(3)	0.48625(2)
17	C12	6	0.87985(3)	0.77135(2)	0.80336(2)
18	C13	6	0.85944(4)	0.72422(2)	0.63386(2)
19	C8	6	0.18723(4)	0.51455(3)	0.62528(2)
20	C16	6	0.93013(4)	0.52526(3)	0.79819(2)
21	C17	6	0.73457(4)	0.44066(3)	0.84987(3)
22	H2	1	0.4706(6)	0.7353(4)	0.5886(4)
23	H5	1	0.4941(6)	0.4733(4)	0.7278(4)
24	H11a	1	0.6228(7)	0.8374(4)	0.5962(4)
25	H11b	1	0.6111(7)	0.8589(4)	0.7133(4)
26	H11c	1	0.7672(7)	0.8963(4)	0.6770(5)
27	H7a	1	0.1712(7)	0.7010(4)	0.5895(4)
28	H7b	1	0.2404(7)	0.6990(4)	0.4886(5)
29	H7c	1	0.0744(6)	0.6394(4)	0.4864(4)
30	H15a	1	0.8515(8)	0.6594(4)	0.9243(4)
31	H15b	1	0.7248(7)	0.5852(5)	0.9568(4)
32	H15c	1	0.9129(7)	0.5543(5)	0.9787(4)
33	H9a	1	0.3569(7)	0.5556(5)	0.4441(4)
34	H9b	1	0.3601(7)	0.4535(4)	0.5109(5)
35	H9c	1	0.1887(7)	0.4966(5)	0.4384(4)
36	H12a	1	0.8207(7)	0.7891(4)	0.8561(4)
37	H12b	1	0.9538(6)	0.7152(4)	0.8320(4)
38	H12c	1	0.9496(7)	0.8296(4)	0.7956(5)
39	H13a	1	0.9245(7)	0.6620(4)	0.6546(5)
40	H13b	1	0.7841(7)	0.7131(5)	0.5632(4)
41	H13c	1	0.9370(7)	0.7789(4)	0.6289(5)
42	H8a	1	0.2450(7)	0.4512(4)	0.6499(5)

43	H8b	1	0.1722(7)	0.5511(5)	0.6877(4)
44	H8c	1	0.0776(6)	0.4969(5)	0.5784(4)
45	H16a	1	0.9044(7)	0.4882(5)	0.7314(4)
46	H16b	1	0.9826(7)	0.5891(5)	0.7884(5)
47	H16c	1	1.0122(7)	0.4863(5)	0.8514(5)
48	H17a	1	0.6349(7)	0.4428(5)	0.8767(5)
49	H17b	1	0.7129(8)	0.3986(4)	0.7858(5)
50	H17c	1	0.8235(8)	0.4081(4)	0.9043(5)

Geometry of the Cu K β XRW model

Nr	Name	Z	x	y	z
1	Ni1	28	0.481943(9)	0.660059(6)	0.769814(6)
2	P2	15	0.50092(5)	0.76284(3)	0.88678(3)
3	P1	15	0.28134(5)	0.72771(3)	0.79919(3)
4	P3	15	0.40604(5)	0.63087(3)	0.90110(3)
5	C4	6	0.52342(6)	0.53915(4)	0.70755(4)
6	C2	6	0.4956(11)	0.4721(6)	0.7274(7)
7	C5	6	0.66366(6)	0.58476(4)	0.75181(4)
8	C3	6	0.51169(6)	0.67812(4)	0.63485(4)
9	C1	6	0.4718(11)	0.7360(6)	0.5886(7)
10	C6	6	0.65639(6)	0.67363(4)	0.70417(4)
11	C10	6	0.27547(6)	0.57201(4)	0.57101(4)
12	C11	6	0.77023(6)	0.75043(4)	0.70552(4)
13	C14	6	0.42907(6)	0.59605(4)	0.63614(4)
14	C7	6	0.78638(7)	0.53730(4)	0.83078(4)
15	C15	6	0.87978(7)	0.77122(5)	0.80332(5)
16	C9	6	0.8202(12)	0.7893(7)	0.8554(7)
17	C12	6	0.9539(12)	0.7142(7)	0.8324(7)
18	C13	6	0.9490(13)	0.8298(7)	0.7961(8)
19	C8	6	0.85934(8)	0.72411(5)	0.63394(5)
20	C16	6	0.9244(13)	0.6625(7)	0.6547(8)
21	C17	6	0.7851(13)	0.7142(8)	0.5625(8)
22	H2	1	0.9385(13)	0.7786(8)	0.6292(8)
23	H5	1	0.68723(8)	0.84089(4)	0.67039(5)
24	H11a	1	0.6255(13)	0.8391(6)	0.5972(8)
25	H11b	1	0.6109(12)	0.8600(7)	0.7128(8)
26	H11c	1	0.7680(13)	0.8964(7)	0.6778(9)
27	H7a	1	0.92986(8)	0.52511(5)	0.79815(5)
28	H7b	1	0.9042(13)	0.4868(8)	0.7311(8)
29	H7c	1	0.9821(13)	0.5898(8)	0.7888(9)
30	H15a	1	1.0123(12)	0.4850(9)	0.8505(8)
31	H15b	1	0.18558(7)	0.65852(4)	0.53203(5)
32	H15c	1	0.1713(13)	0.7008(7)	0.5905(8)
33	H9a	1	0.2395(13)	0.6986(9)	0.4889(8)
34	H9b	1	0.0751(12)	0.6398(8)	0.4876(8)
35	H9c	1	0.82144(8)	0.58757(5)	0.92768(4)
36	H12a	1	0.8504(16)	0.6586(7)	0.9241(9)

37	H12b	1	0.7241(13)	0.5837(9)	0.9559(8)
38	H12c	1	0.9142(13)	0.5534(9)	0.9791(8)
39	H13a	1	0.18741(7)	0.51459(5)	0.62522(5)
40	H13b	1	0.2448(14)	0.4494(8)	0.6501(9)
41	H13c	1	0.1726(14)	0.5523(8)	0.6869(8)
42	H8a	1	0.0779(12)	0.4981(8)	0.5793(9)
43	H8b	1	0.29766(8)	0.51571(5)	0.48634(5)
44	H8c	1	0.3587(13)	0.5558(9)	0.4447(8)
45	H16a	1	0.3620(13)	0.4535(7)	0.5115(8)
46	H16b	1	0.1908(12)	0.4960(8)	0.4394(8)
47	H16c	1	0.73443(9)	0.44064(5)	0.84980(6)
48	H17a	1	0.6340(13)	0.4428(8)	0.8770(8)
49	H17b	1	0.7129(14)	0.3982(7)	0.7858(8)
50	H17c	1	0.8239(13)	0.4088(8)	0.9059(9)

 χ^2 vs λ plots**Figure S11:** χ^2 vs λ for the Mo K α XRW (A) and the Cu K β XRW (B) model.

Normal probability plots

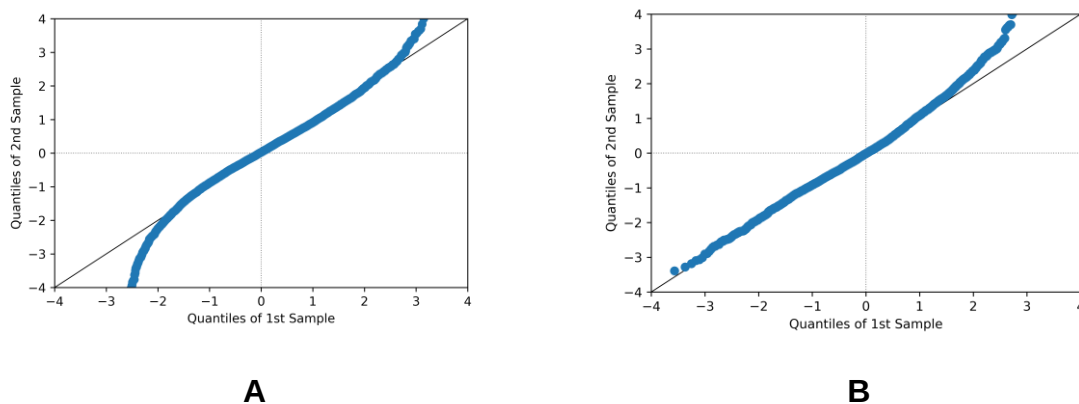


Figure S12: Quantile-quantile plots of the Mo K α (A) and the Cu K β (B) data set.

The quantile-quantile plots a linear distribution in the center of the data. Both tails deviate from the normal, and this behavior is more pronounced in the Mo K α data set due to the lower quality of very high-resolution data. The progression is similar to the ones obtained after multipolar modelling.

Fractal dimension plots

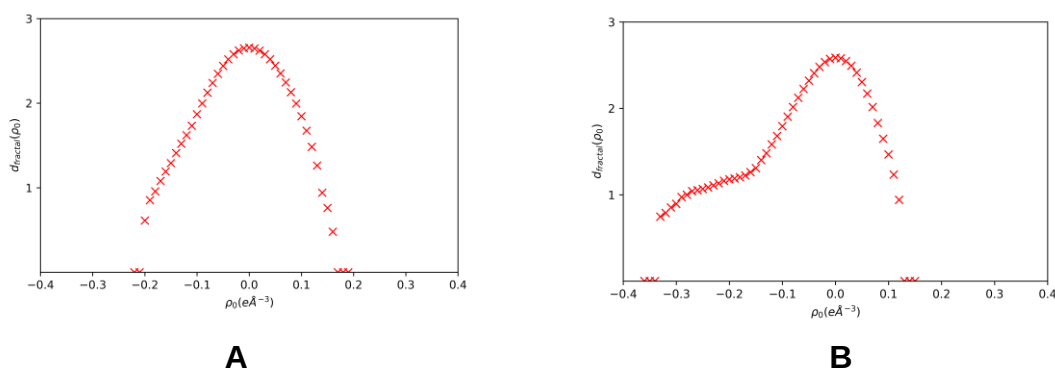


Figure S13: Fractal dimension plots according to Henn & Meindl^[110] of the Mo K α (A) and the Cu K β (B) data set.

The distribution of residual electron density reveals a significant shoulder in the Cu K β XRW model. This can be attributed to the close environment around the metal atom (see figure S11 D and H).

Residual electron density maps of the XRW models

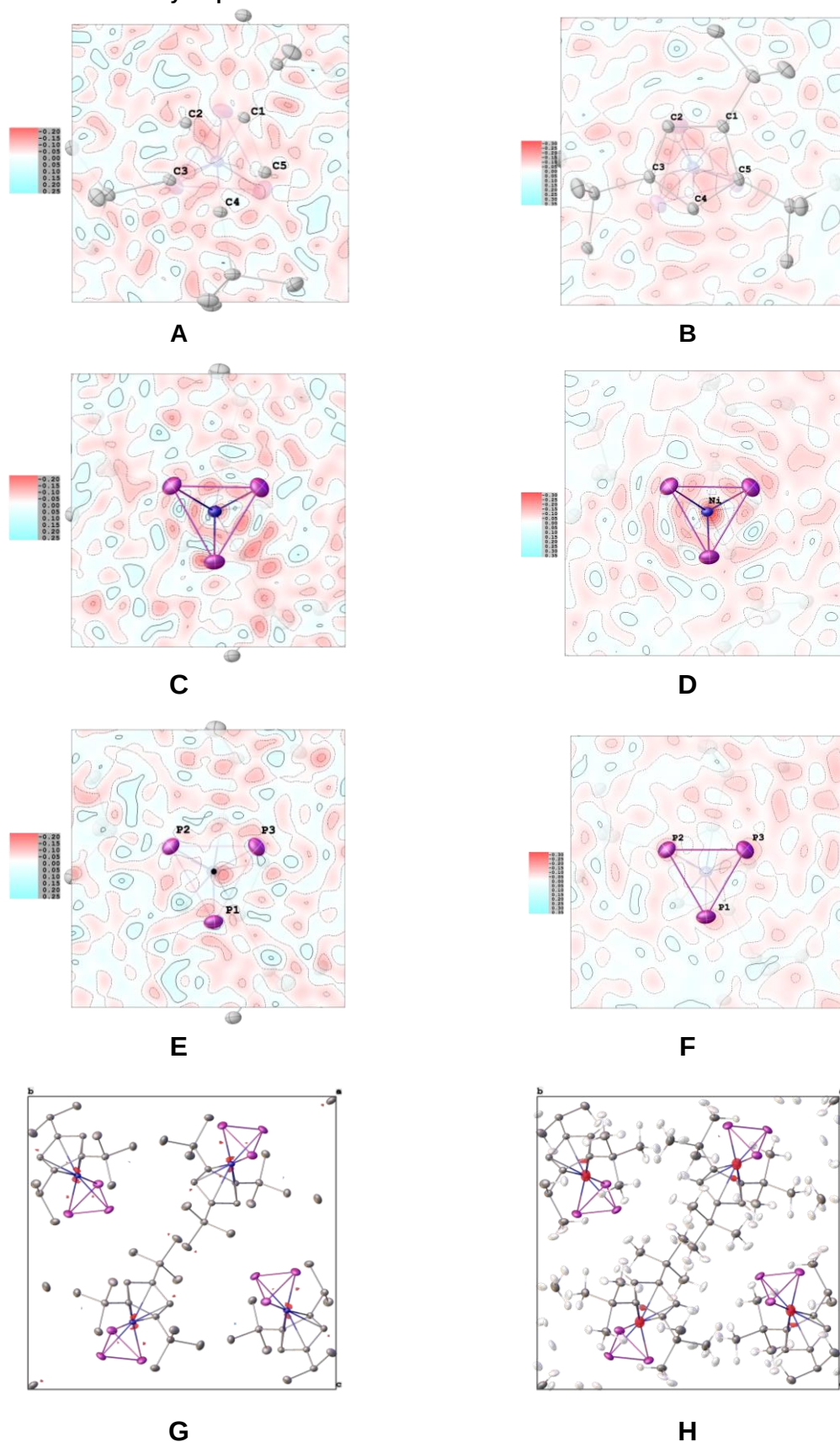


Figure S14: 2D Residual density maps of the Cp''' ligand, the metal centre perpendicular to the Cp-plane, and the cyclo-P3 ligand of 1 of the Mo K α (A,C,E) and the Cu K β (B,D,F) data set. Lines are drawn at 0.05 e difference. Blue: positive, red: negative, yellow: zero contour. 3D residual plots for [Ni]P₃ of the Mo K α (G) and Cu K β (H) model with an iso-surface of 0.15 e/Å³ (Mo K α , G). Blue/red: positive/negative residual electron density.

3D deformation density of the XRW models

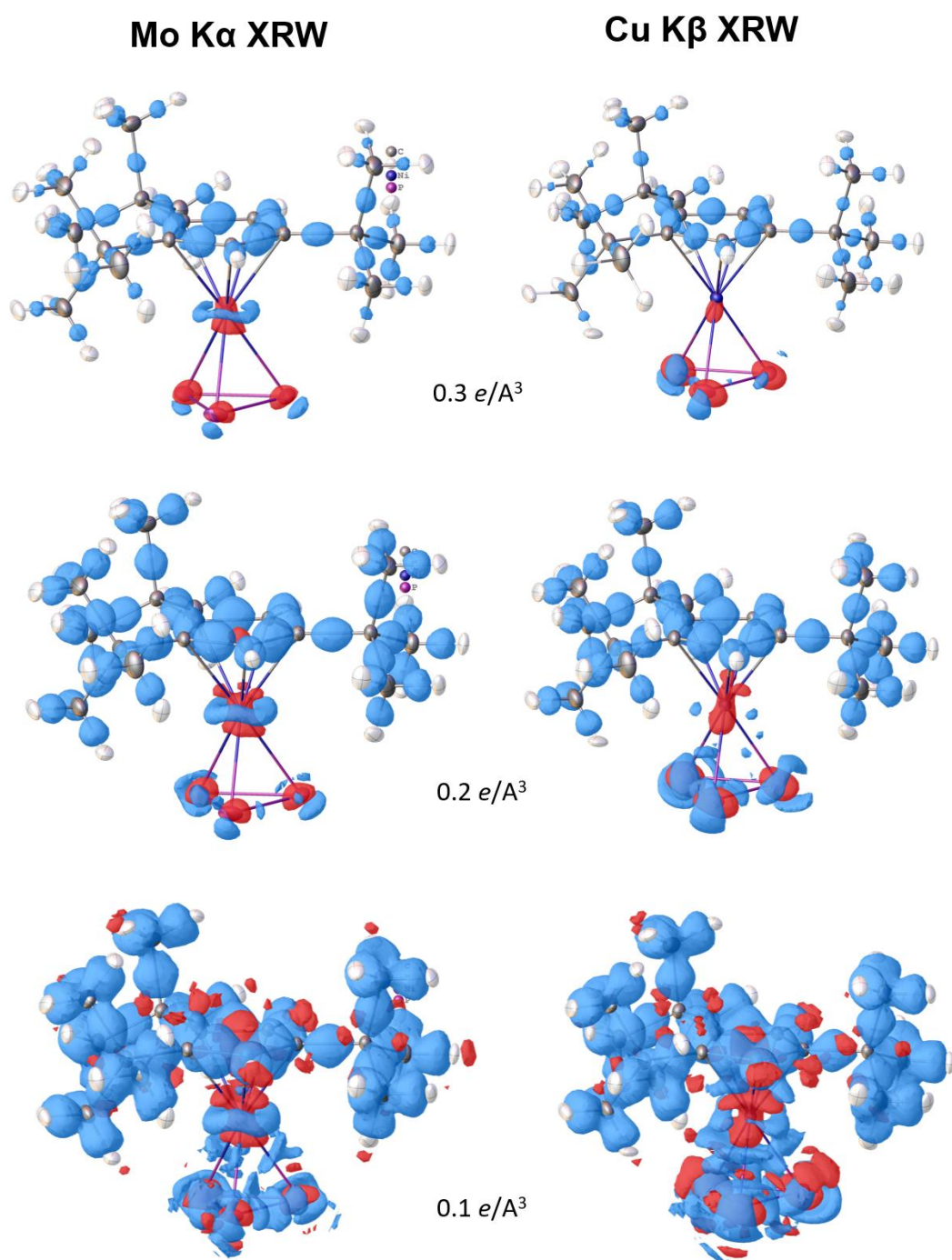


Figure S15: 3D deformation density maps of [Ni]P₃ of the Mo K α (left) and the Cu K β (right) data set at iso-surfaces of 0.3, 0.2 and 0.1 $e/\text{\AA}^3$

Comparison of the Cu K β and Mo K α XRW bonding analysis**Table S6:** Values of electron density (ρ) and Laplacian of the electron density ($\nabla^2(\rho)$) at selected bond critical points according to the QTAIM for the different models of [Ni]P₃. The P₄ DFT model is added for comparison below.

Atom1	Atom2	DFT		XRW Cu K β		XRW Mo K α	
		$\rho / e \cdot \text{\AA}^3$	$\nabla^2(\rho) / e \cdot \text{\AA}^5$	$\rho / e \cdot \text{\AA}^3$	$\nabla^2(\rho) / e \cdot \text{\AA}^5$	$\rho / e \cdot \text{\AA}^3$	$\nabla^2(\rho) / e \cdot \text{\AA}^5$
Ni	P1	0.5604	1.8443	0.6602	0.0718	0.5960	1.7060
Ni	P2	0.5616	1.8364	0.6573	0.8131	0.6082	1.5074
Ni	P3	0.5576	1.8944	0.6286	1.0757	0.5625	1.8044
P1	P2	0.7879	-2.4184	0.7880	-2.7214	0.8163	-2.5142
P1	P3	0.7881	-2.4298	0.8293	-3.7036	0.8081	-2.6899
P2	P3	0.7869	-2.4105	0.8535	-3.9254	0.8095	-2.5954
P(P ₄)	P(P ₄)	0.2023	-1.3443	-	-	-	-

Table S7: Selected bonding indices for the XRW-Cu [Ni]P₃ model and P₄. B. O.: bonding order, WBI: Wiberg bond index, NLMO: natural localized molecular orbitals, Cov: covalent, D.I.: delocalization index.

NBO						D.I.	Roby-Gould		
Atom1	Atom2	B.O.	WBI	NLMO	% Cov		Cov. Ind	Ion. Ind	% Cov
Ni1	P1	0.6424	0.5576	0.8596	62.0%	0.82	0.50	0.2	86.23
Ni1	P2	0.4899	0.572	0.5858	85.2%	0.84	0.51	0.14	93.29
Ni1	P3	0.604	0.6132	0.9706	89.0%	0.83	0.43	0.21	81.11
P1	P2	1.093	1.1338	1.1984	98.6%	1.24	1.24	0.02	99.98
P1	P3	1.0464	1.0863	1.1356	96.9%	1.18	1.21	0.01	100
P2	P3	1.0387	1.0803	1.1134	98.7%	1.20	1.20	0.02	99.96
P(P ₄)	P(P ₄)	1.000	1.0149	1.036	100	1.48	1.00	0.00	100

Table S8: Selected bonding indices for the XRW-Mo [Ni]P₃ model and P₄ for comparison to the above XRW Cu model. B. O.: bonding order, WBI: Wiberg bond index, NLMO: natural localized molecular orbitals, Cov: covalent, D.I.: delocalization index.

NBO						D.I.	Roby-Gould		
Atom1	Atom2	B.O.	WBI	NLMO	% Cov		Cov. Ind	Ion. Ind	% Cov
Ni1	P1	0.4779	0.4899	0.5583	69.8	0.79	0.45	0.23	79.53
Ni1	P2	0.5338	0.5338	0.8932	77.9	0.81	0.48	0.21	83.23
Ni1	P3	0.5249	0.5071	0.8633	68.0	0.78	0.45	0.25	76.62
P1	P2	0.9987	1.1192	1.1852	98.3	1.20	1.22	0.00	99.1
P1	P3	1.1626	1.1406	1.2408	99.0	1.23	1.26	0.02	99.98
P2	P3	0.9895	1.1100	1.1713	99.1	1.20	1.22	0.02	99.12
P(P ₄)	P(P ₄)	1.000	1.0149	1.036	100	1.48	1.00	0.00	100

Multi-temperature experiments to validate anharmonic displacement parameters

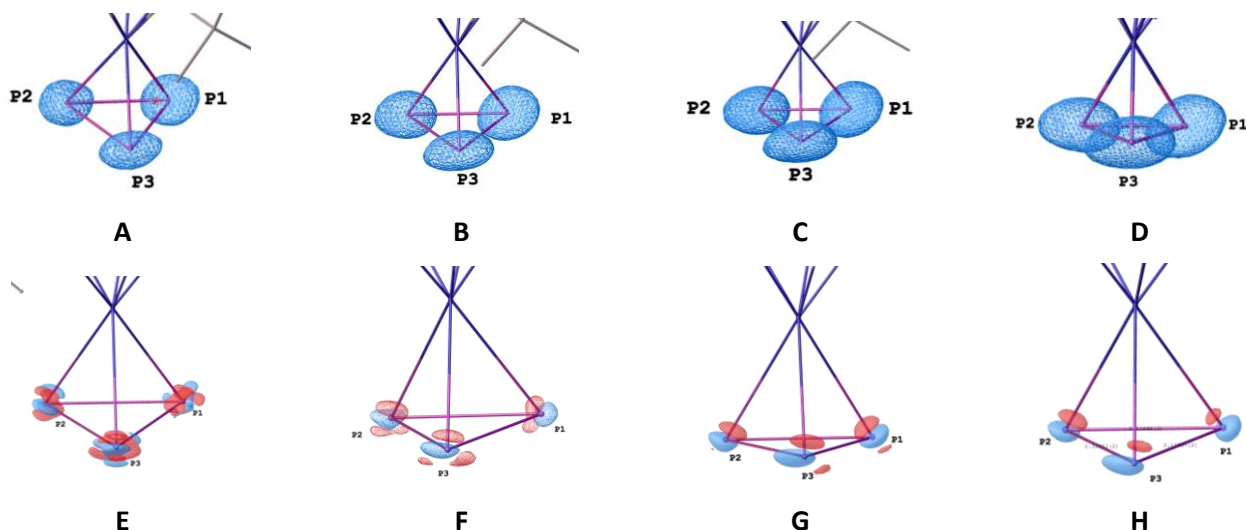


Figure S16: Three-dimensional probability-distribution function (blue: positive, red: negative) at the 0.05 level of each phosphorus atom after anharmonic displacement parameters were refined (upper row) and only the contribution of 3rd and 4th order Gram-Charlier coefficients (lower row) against data of [Ni]P₃ at 100 K (A, E), 150 K (B, F), 200 K (C, G), and 250 K (D, H).

A different single crystal of [Ni]P₃ was measured at 100 K, 150 K, 200 K, and 250 K (CCDC 2305143, 2300961, 2300962, 2300963). Figure S12 shows the probability distribution function of the phosphorus atoms at four different temperatures. A trend in increased anharmonic motion is observable with rising temperature. Only at the lowest temperature, 100 K, “Kuhns’ rule”^[26], which recommends a required resolution to distinguish anharmonic behavior is not fulfilled and a small segment of negative probability in the 3D-PDF can be found. The multi-temperature approach confirms our approach to refine P-atoms anharmonically (4th order in HAR & XRW, 3rd order in MM). This agrees with our struggle to find a valid MM without considering anharmonic motion.

In the Mo K α XRW model, the consideration of anharmonic motion did not drastically change the resulting model. This suggests that the wavefunction fitting approach is capable of modelling residual density from anharmonic motion into the “experimental wavefunction” and thus atomic formfactors. Contrary, the multipolar model improved drastically in crystallographic quality parameters and agreements in the topological analysis with XRW and theoretical approaches when atomic displacement was modelled anharmonically.

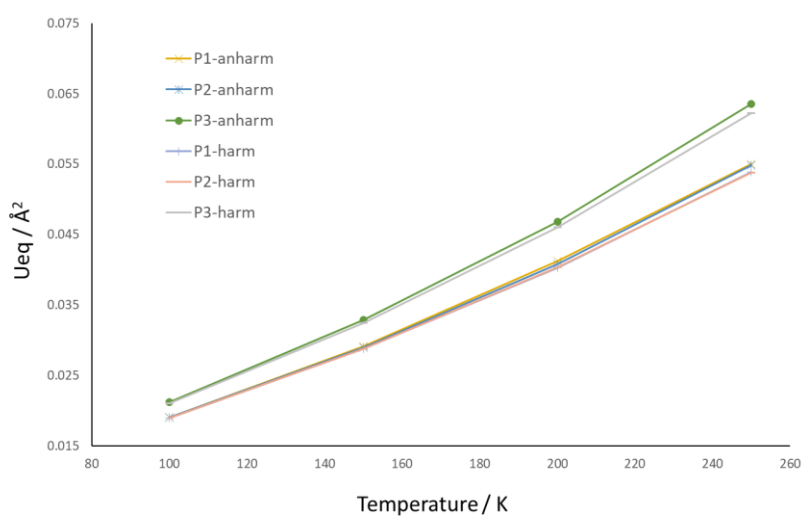
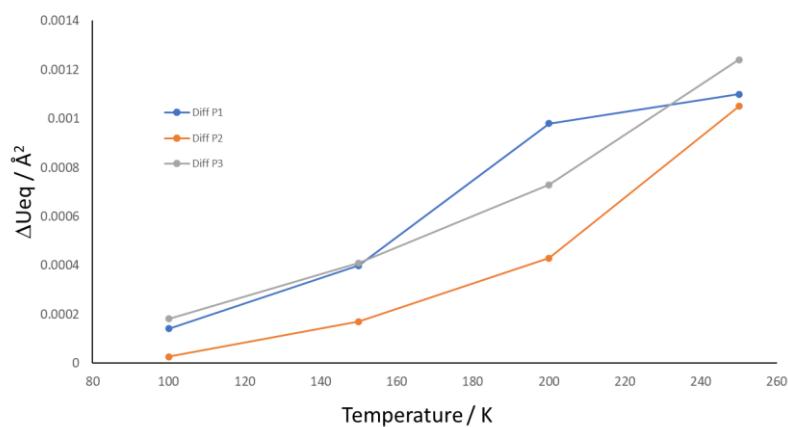
**A****B**

Figure S17: Temperature dependence of the U_{eq} values for each phosphorus atom in the cyclo-P3 fragment (A) and the differences in U_{eq} s between an anharmonic and a harmonic model ($\Delta U_{eq} = U_{eq}(\text{anharm.}) - U_{eq}(\text{harm.})$).

The general trend of the U_{eq} s of each phosphorus atom in the harmonic and anharmonic model increases with increasing temperature. The differences between the U_{eq} s in the anharmonic and harmonic models show a non-linear behavior which is typical for anharmonic systems.^[27,28]

Comparison of bonding indices between DFT, HF, and XRW-Mo model

To gain insight into which information was extracted by including the measured diffraction data in the SCF procedure, we compare the results to the gas-phase optimized density functional theory and pure Hartree-Fock model (at $\lambda = 0.00$ XRW step). The geometry optimization for $[\text{Ni}]P_3$ was obtained at wB97X-V/def2-TZVP level of theory and the concluding single-point calculation as a basis for the analysis was obtained at M062X/def2-TZVP level of theory.

Optimized geometry of gas phase $[\text{Ni}]P_3$

Nr	Name	Z	x	y	z
1	Ni1	28	1.388573	9.663626	10.77278
2	P2	15	1.187964	10.99782	12.53959
3	P1	15	-0.39868	10.93621	11.1269
4	P3	15	-0.05896	9.280884	12.41403
5	C4	6	3.136666	8.545674	10.50902
6	C2	6	2.190689	9.902669	8.886725
7	C5	6	2.009647	7.888500	9.911753
8	C3	6	3.251756	9.842796	9.851101
9	C1	6	1.416459	8.711732	8.918531
10	C6	6	0.272187	8.327107	8.000398
11	C10	6	4.29124	10.97221	9.882998
12	C11	6	3.644841	12.29656	9.431645
13	C14	6	3.99438	7.825909	11.56232
14	C7	6	-0.29638	9.558356	7.287386
15	C15	6	3.925423	8.488556	12.94847
16	C9	6	0.825091	7.347977	6.949018
17	C12	6	4.919785	11.25771	11.25115
18	C13	6	5.397192	10.62154	8.867835
19	C8	6	-0.85115	7.640134	8.787934
20	C16	6	5.449883	7.707574	11.07797
21	C17	6	3.487815	6.385078	11.75723
22	H2	1	1.99409	10.74146	8.237471
23	H5	1	1.650918	6.908628	10.18638
24	H11a	1	3.334797	12.27524	8.384144
25	H11b	1	2.774413	12.54225	10.0484
26	H11c	1	4.375351	13.10470	9.533174
27	H7a	1	-0.65911	10.29922	8.006718
28	H7b	1	0.454385	10.03429	6.648489
29	H7c	1	-1.13474	9.263189	6.648635
30	H15a	1	4.200785	9.540486	12.93613
31	H15b	1	2.908459	8.415965	13.34653
32	H15c	1	4.597694	7.967228	13.63932
33	H9a	1	1.639313	7.807093	6.379138
34	H9b	1	1.212956	6.441479	7.424416
35	H9c	1	0.03623	7.056420	6.247561
36	H12a	1	4.153748	11.52784	11.98405
37	H12b	1	5.497483	10.42281	11.64305
38	H12c	1	5.604503	12.10644	11.15371
39	H13a	1	5.921514	9.701941	9.136773
40	H13b	1	4.970437	10.48439	7.869134

41	H13c	1	6.132061	11.43230	8.817423
42	H8a	1	-0.48853	6.754989	9.319265
43	H8b	1	-1.28602	8.323281	9.523909
44	H8c	1	-1.64415	7.317718	8.105022
45	H16a	1	5.487873	7.230844	10.09269
46	H16b	1	5.953337	8.670550	11.00467
47	H16c	1	6.021518	7.087885	11.77671
48	H17a	1	2.457744	6.365088	12.1259
49	H17b	1	3.544021	5.804189	10.8313
50	H17c	1	4.114361	5.887509	12.50347

Topological analysis and comparison

Table S9: Values of electron density (ρ) and Laplacian of the electron density ($\nabla^2(\rho)$) at selected bond critical points according to the QTAIM for the different calculations of [Ni]P₃ compared to DFT P₄.

Atom1	Atom2	DFT (gas-phase)		HF		XRW (Mo K α)	
		$\rho / e \cdot \text{\AA}^{-3}$	$\nabla^2(\rho) / e \cdot \text{\AA}^{-5}$	$\rho / e \cdot \text{\AA}^{-3}$	$\nabla^2(\rho) / e \cdot \text{\AA}^{-5}$	$\rho / e \cdot \text{\AA}^{-3}$	$\nabla^2(\rho) / e \cdot \text{\AA}^{-5}$
Ni	P1	0.6064	1.8341	0.5911	1.2013	0.5960	1.7060
Ni	P2	0.6053	1.8913	0.6135	1.0423	0.6082	1.5074
Ni	P3	0.6074	1.8392	0.6074	1.0224	0.5625	1.8044
P1	P2	0.6074	-2.6607	0.8299	-3.4113	0.8163	-2.5142
P1	P3	0.8247	-2.6755	0.8353	-3.5037	0.8081	-2.6899
P2	P3	0.8232	-2.6603	0.8266	-3.4610	0.8095	-2.5954
P(P ₄)	P(P ₄)	0.2023	-1.3443	-	-	-	-

Bonding analysis

Table S10: Selected bonding indices for the **DFT** (gas-phase) [Ni]P₃ model and P₄ for comparison. B. O.: bonding order, WBI: Wiberg bond index, NLMO: natural localized molecular orbitals, Cov: covalent, D.I.: delocalization index.

NBO							Roby-Gould		
Atom1	Atom2	B.O.	WBI	NLMO	% Cov	D.I.	Cov. Ind	Ion. Ind	% Cov
Ni1	P1	0.4951	0.4805	0.9231	50.0	0.80	0.44	0.29	69.29
Ni1	P2	0.3815	0.4739	0.4995	38.0	0.79	0.43	0.30	68.06
Ni1	P3	0.4038	0.4857	0.9314	54.8	0.80	0.44	0.30	68.00
P1	P2	1.1464	1.1658	1.2527	99.3	1.23	1.23	0.00	100
P1	P3	1.2111	1.1737	1.3015	99.8	1.24	1.23	0.01	100
P2	P3	1.1205	1.1648	1.2231	99.6	1.23	1.25	0.00	100
P(P ₄)	P(P ₄)	1.000	1.0149	1.036	100	1.48	1.00	0.00	100

Table S11: Selected bonding indices for the **HF** [Ni]P₃ model.

NBO							Roby-Gould		
Atom1	Atom2	B.O.	WBI	NLMO	% Cov	D.I.	Cov. Ind	Ion. Ind	% Cov
Ni1	P1	0.5597	0.4915	0.6147	54.2	0.77	0.47	0.28	73.10
Ni1	P2	0.5323	0.5436	0.8453	75.7	0.81	0.47	0.24	79.80
Ni1	P3	0.5774	0.5584	0.9449	78.1	0.81	0.47	0.23	79.93
P1	P2	1.1038	1.1510	1.2061	97.8	1.24	1.29	0.01	99.99
P1	P3	1.1148	1.1453	1.1862	97.9	1.24	1.21	0.00	100.00
P2	P3	1.0078	1.0892	1.1367	99.8	1.19	1.29	-0.02	99.99

Table 4 (main text): Selected bonding indices for the **XRW-Mo** [Ni]P₃ model for comparison to the above tables.

NBO							Roby-Gould		
Atom1	Atom2	B.O.	WBI	NLMO	% Cov	D.I.	Cov. Ind	Ion. Ind	% Cov
Ni1	P1	0.4779	0.4899	0.5583	69.8	0.79	0.45	0.23	79.53
Ni1	P2	0.5338	0.5338	0.8932	77.9	0.81	0.48	0.21	83.23
Ni1	P3	0.5249	0.5071	0.8633	68.0	0.78	0.45	0.25	76.62
P1	P2	0.9987	1.1192	1.1852	98.3	1.20	1.22	0.00	99.1
P1	P3	1.1626	1.1406	1.2408	99.0	1.23	1.26	0.02	99.98
P2	P3	0.9895	1.1100	1.1713	99.1	1.20	1.22	0.02	99.12

Inputs for TONTO

```
Mo Kα
{
  keyword_echo_on
  name= NiP3_Mo

  charge= 0
  multiplicity= 1

  ! Process the CIF
  cif= {
    file_name= ./NiP3_small.cif
  }
  process_cif

  name= NiP3_Mo

  basis_directory= /home/xrz/tonto/basis_sets/
  basis_name= def2-TZVP

  dispersion_coefficients= {
    C 0.0033 0.0016
    H 0.0000 0.0000
    P 0.1023 0.0942
    Ni 0.3301 1.2739
  }

  crystal= {
    xray_data= {
      thermal_smearing_model= hirshfeld
      partition_model= mulliken
      optimise_extinction= false
      correct_dispersion= TRUE
      optimise_scale_factor= true
      wavelength= 0.71073 angstrom

      REDIRECT ./NiP3.hkl

      f_sigma_cutoff= 4.0
    }
  }

  ! Geometry
  put

  ! Tight grid
  becke_grid = {
    set_defaults
    accuracy= normal
    pruning_scheme= jayatilaka2
  }

  ! More accuracy
  output_style_options= {
    real_precision= 8
    real_width= 20
```

```
}

! Normal SCF
scfdata= {
  initial_density= promolecule
  kind=          rhf
  use_SC_cluster_charges= FALSE
  convergence= 0.001
  linear_dependence_tol= 0.001
  diis= {          ! This is the extrapolation procedure
    save_iteration= 1
    start_iteration= 3
    keep=          10
    convergence_tolerance= 0.09
  }
  max_iterations= 200    ! The maximum number of SCF iteration

  use_damping= YES      ! These are used to damp the SCF iteration process
  damp_factor= 0.80     ! by including 60% of the previous result
  damp_finish= 7
  use_level_shift= NO
}
scf

scfdata= {
  initial_density= restricted
  kind=          xray_rhf
  direct=        yes
  convergence= 0.00001
  linear_dependence_tol= 0.001
  use_SC_cluster_charges= FALSE
  diis= {          ! This is the extrapolation procedure
    save_iteration= 1
    start_iteration= 3
    keep=          10
    convergence_tolerance= 0.09
  }
  max_iterations= 200    ! The maximum number of SCF iteration
  do_outputs= TRUE

  use_damping= YES      ! These are used to damp the SCF iteration process
  damp_factor= 0.80     ! by including 60% of the previous result
  damp_finish= 7
  use_level_shift= YES
  initial_lambda= 0.000 ! These specify the "lambda value"
  lambda_step= 0.010    ! used to mix the energy with the chi^2
  lambda_max= 2.000
}
scf
}
```

Cu K β

```
{

name= NiP3_Cu

charge= 0
multiplicity= 1

! Process the CIF
cif= {
  file_name= ./NiP3_cub_small.cif
}
process_cif

name= NiP3_Cu

basis_directory= /home/xrz/tonto/basis_sets/
basis_name= def2-TZVP

dispersion_coefficients= {
  C 0.0147 0.0073
  H 0.00000 0.00000
  Ni -1.743 3.628
  P 0.2653 0.3578
}

crystal= {
  xray_data= {
    thermal_smearing_model= hirshfeld
    partition_model= mulliken
    optimise_extinction= false
    correct_dispersion= TRUE
    optimise_scale_factor= true
    wavelength= 1.39222 angstrom

    REDIRECT ./NiP3_cub_merged.hkl

    f_sigma_cutoff= 4.0
  }
}

! Geometry
put

! Tight grid
becke_grid = {
  set_defaults
  accuracy= normal
  pruning_scheme= jayatilaka2
}

! More accuracy
output_style_options= {
  real_precision= 8
  real_width= 20
}

! Normal SCF
```

```
scfdata= {
  initial_density= promolecule
  kind=          rhf
  use_SC_cluster_charges= FALSE
  convergence= 0.001
  linear_dependence_tol= 0.001
  diis= {          ! This is the extrapolation procedure
    save_iteration= 1
    start_iteration= 3
    keep=          10
    convergence_tolerance= 0.09
  }
  max_iterations= 200    ! The maximum number of SCF iteration

  use_damping=  YES      ! These are used to damp the SCF iteration process
  damp_factor=  0.80     ! by including 60% of the previous result
  damp_finish=  7
  use_level_shift= NO
}
scf

scfdata= {
  initial_density= restricted
  kind=          xray_rhf
  direct=        yes
  convergence=   0.00001
  linear_dependence_tol= 0.001
  use_SC_cluster_charges= FALSE
  diis= {          ! This is the extrapolation procedure
    save_iteration= 1
    start_iteration= 3
    keep=          10
    convergence_tolerance= 0.09
  }
  max_iterations= 200    ! The maximum number of SCF iteration
  do_outputs= TRUE

  use_damping=  YES      ! These are used to damp the SCF iteration process
  damp_factor=  0.80     ! by including 60% of the previous result
  damp_finish=  7
  use_level_shift= YES
  initial_lambda= 0.000  ! These specify the "lambda value"
  lambda_step=   0.010   ! used to mix the energy with the chi^2
  lambda_max=    2.000
}
scf
}
```

Solid state NMR spectroscopy of $[\text{Ni}]\text{P}_3$

Solid-state ^{31}P NMR measurements were performed on an Infinityplus spectrometer system (Agilent) operated at 7 T, equipped with a Chemagnetics Varian 6 mm pencil cross polarization (CP) magic angle spinning (MAS) probe. $^{31}\text{P}\{^1\text{H}\}$ CP NMR spectra were recorded using a cross-polarization contact time of 3 ms, a 90° pulse length of $5.0\ \mu\text{s}$, and a delay of 5 s. The spectra were indirectly referenced to $[\text{NH}_4][\text{H}_2\text{PO}_4]$ (0.81 ppm with respect to 85% H_3PO_4 in H_2O).

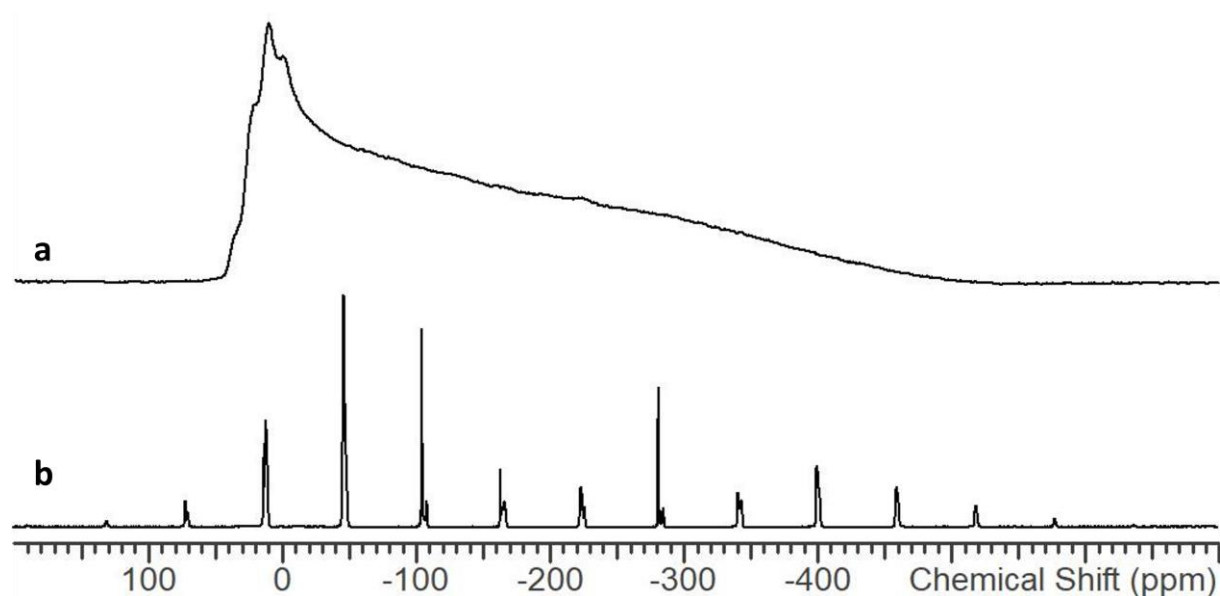


Figure S18: $^{31}\text{P}\{^1\text{H}\}$ CP NMR spectra of $[\text{Ni}]\text{P}_3$. (a) Static spectrum. (b) MAS spectrum at 7170 Hz.

^{31}P NMR absolute shielding tensors were calculated using the Gaussian 09.D.01 program package^[29] in the $\omega\text{B97XD/Def2QZVP}$ approximation. $^1J(^{31}\text{P}^{31}\text{P})$ scalar coupling constants were calculated in the $\omega\text{B97XD/Def2TZVP}$ approximation. The chemical shift, δ , is a relative value. It is calculated based on the absolute shielding of the nucleus in the molecule of interest, σ , and in a reference compound, σ^{ref} . With a high level of accuracy, $\delta \approx \sigma^{\text{ref}} - \sigma$.^[30] The value of σ^{ref} depends on the approximation in use. For the $\omega\text{B97XD/Def2QZVP}$ and $\omega\text{B97XD/Def2TZVP}$ approximations σ^{ref} is 300 ppm and 292 ppm, respectively.^[31]

Table S12: ^{31}P NMR shielding tensors of $[\text{Ni}]\text{P}_3$ calculated using the wB97XD/def2qzvp, GIAO, SCRF=(Solvent=water) approximation.

Nucleus	$\sigma_{\text{iso}}^{\text{a}}$ /ppm	σ_{11}^{b} /ppm	σ_{22}^{b} /ppm	σ_{33}^{b} /ppm
P1	490.4638	199.9614	348.8710	922.5590
P2	484.8062	215.4488	343.2082	895.7616
P3	484.4211	171.6951	349.0931	932.4751

^aAverage absolute shielding. ^bTensor components.**Table S13:** $^1\text{J}(^{31}\text{P}^{31}\text{P})$ scalar coupling constants in $[\text{Ni}]\text{P}_3$ calculated using the wB97XD/def2tzvp, GIAO, SCRF=(Solvent=water) approximation.

Nuclei	$^1\text{J}(^{31}\text{P}^{31}\text{P})$ /Hz
P1-P2	414
P1_P3	423
P2_P3	420

Table S14: The molecular structure of $[\text{Ni}]\text{P}_3$ in Å.

Ni	1.3940	9.6304	10.7530	H	4.4077	13.076	9.4563
P	1.1047	11.1309	12.3867	H	-0.7649	10.2268	8.2341
P	-0.5818	10.6169	11.1623	H	0.2786	10.1976	6.8247
P	0.1699	9.2043	12.5882	H	-1.2505	9.3281	6.794
C	3.1509	8.5313	10.502	H	4.2024	9.6199	12.9105
C	2.2087	9.893	8.8658	H	2.899	8.5374	13.3645
C	2.0272	7.8665	9.8841	H	4.5543	8.0866	13.6704
C	3.2733	9.8283	9.8355	H	1.5354	8.1056	6.2032
C	1.4376	8.6953	8.8849	H	1.2986	6.6161	7.1362
C	0.2746	8.3441	7.976 0	H	-0.0002	7.2448	6.1235
C	4.3221	10.9503	9.8546	H	4.1891	11.5121	11.9579
C	3.6926	12.2694	9.3620	H	5.5183	10.434	11.6213
C	3.9727	7.8398	11.6052	H	5.6245	12.103	11.1129
C	-0.4033	9.6071	7.4301	H	5.9543	9.6579	9.1434
C	3.9104	8.5739	12.9593	H	5.0181	10.4033	7.8667
C	0.8174	7.5222	6.7919	H	6.1726	11.3633	8.7844
C	4.9474	11.2531	11.2213	H	-0.3221	6.5825	9.0777
C	5.4343	10.5656	8.8537	H	-1.1473	8.0399	9.6057
C	-0.7591	7.5067	8.7339	H	-1.5878	7.2492	8.079
C	5.4338	7.663	11.1491	H	5.4618	7.1223	10.2161
C	3.416	6.4287	11.8709	H	5.959	8.5943	11.0123
H	2.0124	10.7272	8.2215	H	5.982	7.0946	11.8923
H	1.675	6.9049	10.1658	H	2.3856	6.46	12.2457
H	3.3922	12.2167	8.3277	H	3.4707	5.8151	10.976
H	2.8168	12.5304	9.9633	H	4.0228	5.9537	12.6312

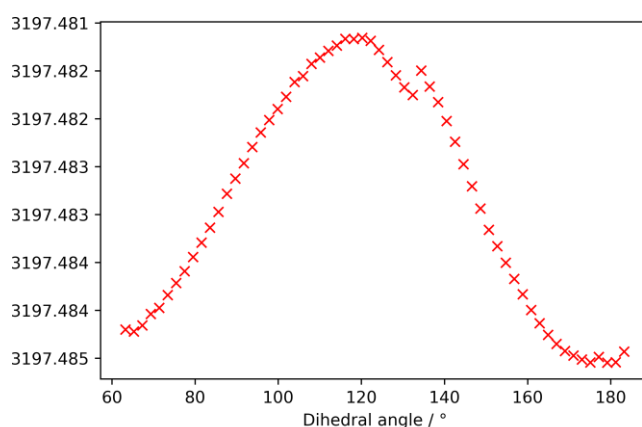
(Relaxed) Potential energy surface scan for the *cyclo*-P₃ fragment

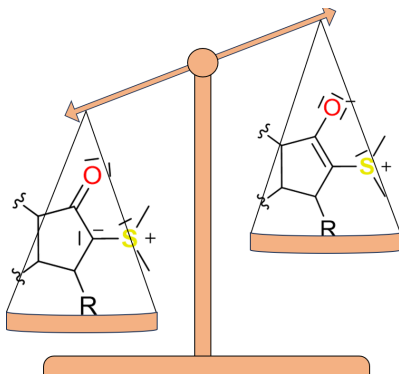
Figure S19: Energies of the relaxed potential energy surface scan of a 120° rotation of the *cyclo*-P₃ fragment around the axis connecting center-of-geometry of the *cyclo*-P₃ ligand and the Ni metal center. Calculations were performed in ORCA, using B3LYP / def2-TZVP level of theory.^[15,16,18]

References

- [1] E. Mädl, G. Balázs, E. V. Peresypkina, M. Scheer, *Angew. Chem.* **2016**, *128*, 7833–7838.
- [2] Rigaku Oxford Diffraction Ltd, **2019**.
- [3] G. M. Sheldrick, *Acta Crystallogr A Found Adv* **2015**, *71*, 3–8.
- [4] L. J. Bourhis, O. V. Dolomanov, R. J. Gildea, J. A. K. Howard, H. Puschmann, *Acta Crystallogr A Found Adv* **2015**, *71*, 59–75.
- [5] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J Appl Crystallogr* **2009**, *42*, 339–341.
- [6] N. K. Hansen, P. Coppens, *Acta Cryst A* **1978**, *34*, 909–921.
- [7] C. Jelsch, B. Guillot, A. Lagoutte, C. Lecomte, *J Appl Crystallogr* **2005**, *38*, 38–54.
- [8] A. Ø. Madsen, *J Appl Crystallogr* **2006**, *39*, 757–758.
- [9] B. Zarychta, J. Zaleski, J. Kyzioł, Z. Daszkiewicz, C. Jelsch, *Acta Crystallogr. B* **2011**, *67*, 250–262.
- [10] K. Meindl, J. Henn, *Acta Crystallogr A Found Crystallogr* **2008**, *64*, 404–418.
- [11] B. Guillot, *Acta Crystallogr A Found Crystallogr* **2012**, *68*, s204–s204.
- [12] D. Jayatilaka, D. J. Grimwood, in *Computational Science — ICCS 2003* (Eds.: P.M.A. Sloot, D. Abramson, A.V. Bogdanov, Y.E. Gorbachev, J.J. Dongarra, A.Y. Zomaya), Springer Berlin Heidelberg, Berlin, Heidelberg, **2003**, pp. 142–151.
- [13] J. C. Slater, *Phys. Rev.* **1951**, *81*, 385–390.
- [14] F. L. Hirshfeld, *Theoret. Chim. Acta* **1977**, *44*, 129–138.
- [15] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789.
- [16] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.
- [17] Y. Zhao, D. G. Truhlar, *Theor Chem Account* **2008**, *120*, 215–241.
- [18] F. Neese, F. Wennmohs, U. Becker, C. Riplinger, *J. Chem. Phys.* **2020**, *152*, 224108.
- [19] R. F. W. Bader, *Chem. Rev.* **1991**, *91*, 893–928.
- [20] R. F. W. Bader, *Atoms in Molecules: A Quantum Theory*, Clarendon Press ; Oxford University Press, Oxford [England] : New York, **1994**.
- [21] E. D. Glendening, C. R. Landis, F. Weinhold, *J Comput Chem* **2019**, jcc.25873.
- [22] V. Bezugly, P. Wielgus, M. Kohout, F. R. Wagner, *J. Comput. Chem.* **2009**, n/a–n/a.
- [23] K. Alhameedi, G. S. Chandler, D. Jayatilaka, *Results in Chemistry* **2020**, *2*, 100053.
- [24] T. Lu, F. Chen, *J. Comput. Chem.* **2012**, *33*, 580–592.

- [25] F. Meurer, O. V. Dolomanov, C. Hennig, N. Peyerimhoff, F. Kleemiss, H. Puschmann, M. Bodensteiner, *IUCrJ* **2022**, 9, 604–609.
- [26] W. F. Kuhs, *Aust. J. Phys.* **1988**, 41, 369–382.
- [27] H. B. Bürgi, S. C. Capelli, H. Birkedal, *Acta Crystallogr A Found Crystallogr* **2000**, 56, 425–435.
- [28] J. Schefer, D. Schwarzenbach, P. Fischer, Th. Koetzle, F. K. Larsen, S. Haussühl, M. Rüdinger, G. McIntyre, H. Birkedal, H.-B. Bürgi, *Acta Crystallogr B Struct Sci* **1998**, 54, 121–128.
- [29] M. J. Frisch, G. W. Trucks, G. E. Schlegel, G. E. Scuseris, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, **2013**.
- [30] I. G. Shenderovich, H.-H. Limbach, *Solids* **2021**, 2, 139–154.
- [31] I. G. Shenderovich, *Chem. Methods* **2021**, 1, 61–70.

5 Synthesis and quantum crystallographic evaluation of WYLID



Preface

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This chapter is based on the article:

"Synthesis and quantum crystallographic evaluation of WYLID: YLID's red rival"

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Florian Meurer – Conceptualisation, original synthesis, crystallographic modelling, data acquisition and analysis, computations, original draft.

Maximilian Schimpf – Synthesis optimisation, crystallisation, co-writing draft.

Birgit Hischa – Crystallographic data acquisition, co-writing final draft.

Christoph Hennig – Acquisition of synchrotron data, co-writing final draft.

Julia Rehbein – Co-writing final draft.

Florian Kleemiss – Computations, crystallographic modelling, co-writing final draft.

Michael Bodensteiner – Conceptualisation, funding acquisition, co-writing final manuscript.

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Abstract

The synthesis and characterization of WYLID [2-(dimethyl- λ^4 -sulfaneylidene)-[1,2'-bi-indenylidene] – 1',3,3'(2*H*)-trione], a side product that appears during the synthesis of YLID, is presented in this study. Quantum crystallographic insights into the bonding situation in WYLID are provided on the basis of Hirshfeld atom refinement (HAR), multipolar modelling and X-ray restrained wavefunction fitting. We compare these results with theoretical calculations on a gas-phase optimized density functional theory and a Hartree-Fock calculation based on the geometry obtained by HAR. The S-C bond in WYLID is best described as an ylid-type bond and the SMe_2 fragment does not affect the nearest C – O carbonyl/enolate equilibrium. This work may contribute to an ongoing debate in the quantum crystallography community about the bonding situation in YLID and provides a routine for distinguishing between carbonyls and enolates.

5.1 Introduction

Since its inception in the year 1912 (Friedrich et al., 1912), X-ray crystallography has become the primary method for definitive structural elucidation. The continuous advancement in X-ray sources, goniometers and detectors has facilitated tremendous growth of X-ray crystallography over the past century, leading to its current position as a dominant technique. We recently demonstrated what extensive chemical information can be obtained nowadays using diffraction data from a state-of-the-art in-house diffractometer on the example of $\text{Cp}^{\text{'''}}\text{NiP}_3$ ($\text{Cp}^{\text{'''}} = 1,2,4\text{-tri-tert-butylcyclopentadienyl}$) and P_4 in the context of Hoffmann's isolobal principle (Meurer et al., 2024).

Today, most institutions engaged in structural science, chemistry, physics, biology or geology have access to such inhouse X-ray diffractometers or synchrotron facilities and rely on accurate crystal structures. One of the most important prerequisites for successful and accurate structure elucidation is the calibration of the instrument in question, for which a suitable calibration crystal is required. 2-Dimethylsulfuran-ylidene-1,3-indanedione, better known as YLID (see Figure 5.1), has been established as a reliable, stable and well crystallizing reference. The orthorhombic form of the structure was initially used as a calibration crystal by the company Syntex in 1969 with the market release of their P-1 diffractometer. YLID's structure was then published in 1971 by Christensen & Thom (1971). Following this, it was adopted as a calibrant by numerous different diffractometer manufacturers and has

undoubtedly been the most widely measured crystal structure on single-crystal X-ray devices (Guzei et al., 2008; Balmohammadi et al., 2025a; Balmohammadi et al., 2025b).

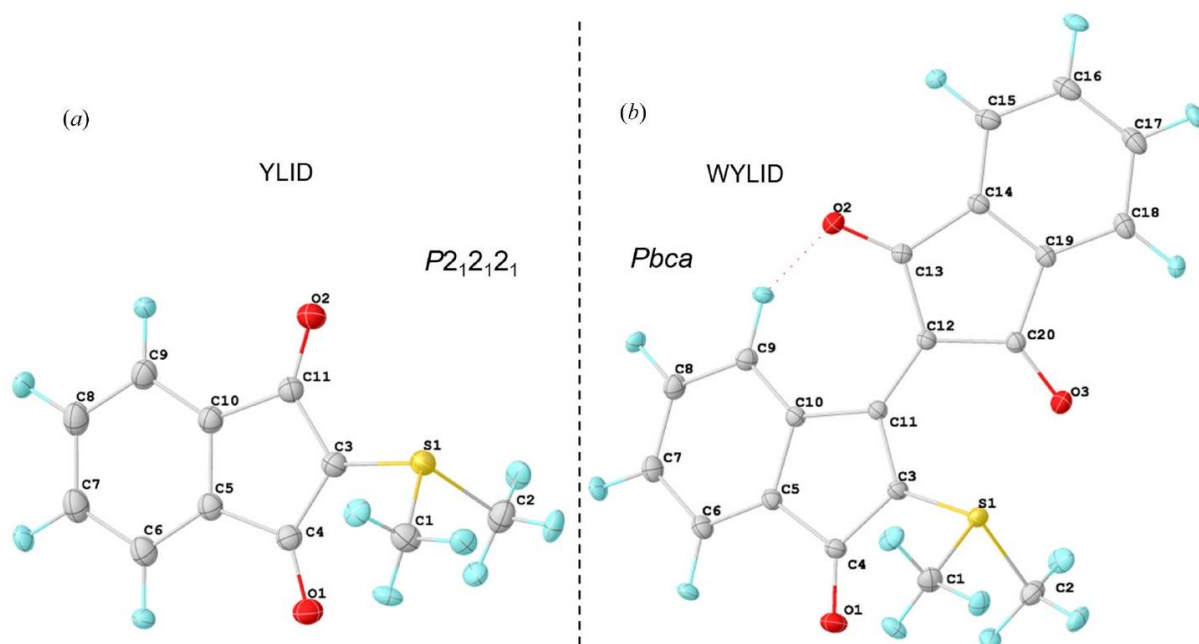


Figure 5.1: Comparison of YLID (Graw et al., 2023) (110 K) and WYLID (100 K) after Hirshfeld atom refinement, with their space groups and labelling schemes. Displacement ellipsoids are drawn at the 50% probability level.

YLID possesses the advantageous properties of orthonormal cell parameters, short and long unit-cell dimensions, and a non-centrosymmetric space group ($P2_12_12_1$). It is stable enough to be ground into crystals of spherical shape, which are well suited for a default multi-scan spherical absorption correction (Blessing, 1995; Krause et al., 2015) and can be conveniently used to align the microscope of the goniometer.

Speculations of a phase transition to a second, monoclinic, modification of YLID at low temperature were disproven by Guzei et al. (2008), who demonstrated that both the monoclinic and orthorhombic forms are indefinitely stable between 100 and 298 K. However, the orthorhombic form was shown to be slightly favoured, as it crystallizes first and has a higher density.

Even though the original purpose of YLID was the investigation of unusual bonding situations involving sulfur, the first quantum crystallographic study of YLID was only recently published by Graw et al. (2023). This work described YLID's favoured resonance structure according to the quantum theory of atoms in molecules (QTAIM) (Bader, 1991) based on a multipolar modelling approach. Their YLID data were also the first instance of a successful charge-density study using In $K\alpha$ radiation. Graw et al. (2023) concluded that the enolate resonance form is the most accurate picture of the chemical bonding in YLID (C in Figure 5.2).

Balmohammadi et al. (2025a,b) were kind enough to share their insights into the quantum crystallography of YLID with us before publication so that we could compare our results here. They investigated several structures of YLID at low and room temperature, at ambient and high pressure, and using X-rays of four distinct wavelengths (Cu $K\alpha$, Mo $K\alpha$ and Ag $K\alpha$, and 0.2483Å at the SPring-8 synchrotron facility). Their study also performed a topological analysis of the total electron density according to QTAIM.

In the work by Guzei et al. (2008) a maroon-coloured reaction mixture is first mentioned,

despite the two obtained YLID polymorphs being of yellow and orange colour, respectively. The maroon impurity could not be further identified. Upon attempting to synthesize YLID, we also observed a deep-red-coloured reaction mixture. However, the formation of red crystals alongside the yellow YLID crystals was an unexpected outcome, given that the synthesis described by Lácová & Sisková (1983) was maintained to obtain the orthorhombic and monoclinic (Guzei et al., 2008) polymorphs of YLID. Single-crystal X-ray diffraction revealed the structure of these red crystals to be a condensation product between YLID and a second molecule of indandione (see Figure 5.1), termed WYLID. Both WYLID and YLID exhibit a large conjugated π system and thus many possible resonance structures. For the ylid/ylene case, the relevant structures are shown in Figure 5.2. There is an ongoing debate in the quantum crystallography community about which resonance form best describes the bonding situation in YLID. While motif A has been ruled out

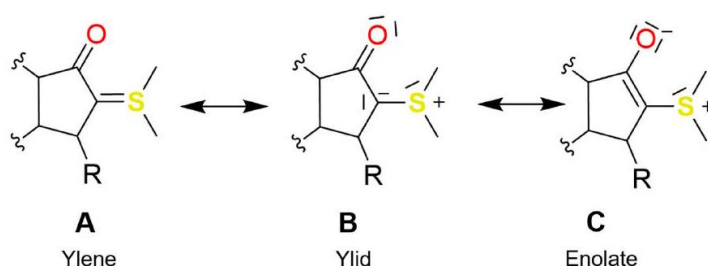


Figure 5.2: Relevant mesomeric structures of the ylid system of this study.

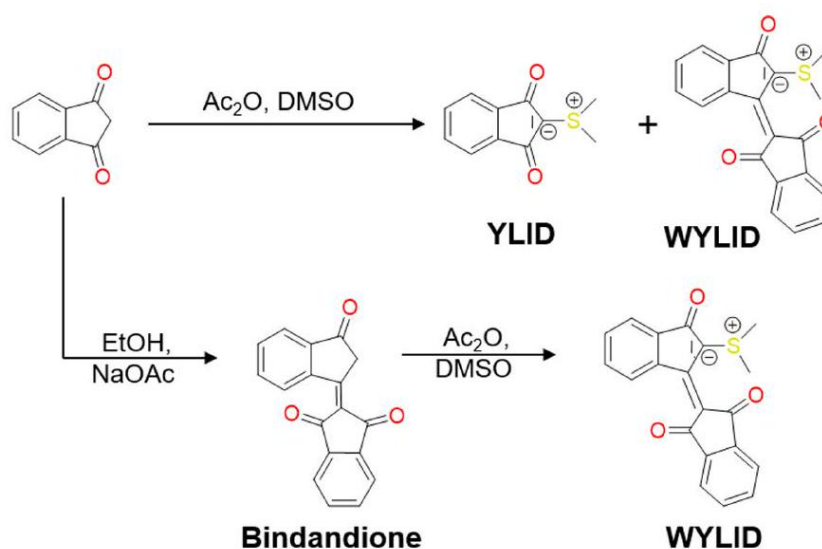


Figure 5.3: Synthesis pathways according to Lácová & Sisková (1983) and the synthesis route adapted from Bürckstümmer et al. (2011) for the selective synthesis of WYLID presented in this work. The reactants are acetic anhydride (Ac_2O), dimethylsulfoxide (DMSO) and ethanol (EtOH).

by several observations before (Cook & Moffatt, 1968; Guzei et al., 2008; Graw et al., 2023), B and C are still controversial. By presenting a quantum crystallographic analysis

of WYLID with a structure that exhibits one C–O functionality similar to YLID, but also two C–O bonds distant to the SMe₂ functionality, we anticipated gaining a clearer insight into distinguishing between the carbonyl and enolate structures. For additional comparison, we also crystallized and investigated the intermediate Bindandione (see Figure 5.3), which gives an insight into the C–O bonding situation without the SMe₂ group.

In this work, we describe the modified synthesis of WYLID, its characterization and its quantum crystallographic description compared with YLID. To explain and compare the C–S bonding situation in this YLID derivative, we performed a complementary bonding analysis from both experimentally driven (multipolar modelling, MM) and wavefunction-based [Hirshfeld atom refinement (HAR) and X-ray restrained wavefunction fitting (XRW)] charge-density approaches. We compare our results with those of Balmohammadi et al. (2025*a, b*) on YLID from their high-quality data set and with the data published by Graw et al. (2023). The suitability of WYLID as a calibration crystal for these quantum crystallographic descriptions has been tested using different wavelengths (CuK α , CuK β and Mo K α radiation, and synchrotron radiation at 22.000keV, $\lambda = 0.56356\text{\AA}$).

Experiments and methods

5.1.1 Synthesis and characterization

The first synthetic strategy applied to reproduce WYLID was to vary the reaction conditions reported for YLID (Cook & Moffatt, 1968). This approach was based on changes in reaction time, temperature, stoichiometry (e.g. excess of indandione) and the order of reactants. Additionally, different methods for isolating the desired compound were tested. Despite the strong red coloration of the reaction mixture, neither of the two YLID polymorphs was selectively formed or could be isolated by the modification of this route. To obtain WYLID exclusively, 1,3-indandione is replaced by its condensed dimer, Bindandione ([1,2']biindenylidene-3,1,3'-trione). The synthesis of Bindandione was carried out following the literature procedure according to B rckst mmer et al. (2011) (see Section S1.2 in the supporting information). Bindandione was subsequently reacted with DMSO in acetic anhydride under conditions similar to the classic synthesis of YLID. After the reaction, the dark-red compound was recrystallized to obtain the desired WYLID selectively in moderate yields of 33%. All WYLID crystals that were used in this study were obtained via this route.

The spectral properties of WYLID in the UV-Vis region were investigated and showed a maximum absorption at $\lambda_{\text{max}} = 508\text{ nm}$ with additional absorption peaks at $\lambda = 362\text{ nm}$ and $\lambda = 301\text{ nm}$ (Fig. S3 in the supporting information). This is consistent with the strong red colour of the crystals and solutions of WYLID. All details of the synthesis and the full characterization of WYLID can be found in the supporting information.

5.1.2 XRD measurements, data processing and modelling

The crystallographic results within this work originate from various setups using different wavelengths, different crystals, and different settings concerning the goniometer and detector used for data acquisition. Except for the CuK β data set, which was recorded on an Atlas S2 CCD detector, all data sets were recorded on photon counting devices,

namely a HyPix-Arc 150°(Mo $K\alpha$ and Cu $K\alpha$) at our home laboratory XtaLAB Synergy-DW diffractometer or a Pilatus3 X 2 M at the European Synchrotron on beamline BM20 (Scheinost et al., 2021). The same crystal was used for the Mo $K\alpha$ and Cu $K\alpha$ data collections, but different crystals were used for the corresponding Cu $K\beta$ and synchrotron experiments.

An earlier data set of a different WYLID crystal recorded at 20 keV at the ESRF is also compared. Due to the high flux, this measurement showed an oversaturation of the detector and therefore some strong reflections were measured with nonlinear intensity. An empirical extinction correction similar to the model presented by Ahmed et al. (1970) was applied to 'correct' this effect. Despite this misuse of extinction correction, this data set achieved a reasonable agreement between the calculated and recorded structure factors. However, we base our bond analysis on other, more reliable, data sets (Table 5.1) without oversaturation. Nevertheless, we consider it worth reporting on the influence of detector saturation on the results of an electron-density refinement and comparing them with the benchmark data set recorded at 22 keV without detector saturation.

An initial structure solution was obtained using SHELXT (Sheldrick, 2015) and the independent atom model (IAM) was refined using olex2.refine (Bourhis et al., 2015) within Olex2 (Dolomanov et al., 2009).

Table 5.1: Comparison of the different data sets recorded at 100 K and the crystallographic models used in this study.

	Cu $K\alpha$	Cu $K\beta$	Mo $K\alpha$	Synchrotron
Crystal No.	1	2	1	3
Wavelength ($\pm$)	1.54187	1.39222	0.71073	0.56356
Total reflections	204454	83609	527077	508696
Unique reflections $< 2\sigma(I)$	3187	4385	8605	8745
R_{int} (%)	2.69	7.67	2.71	4.88
Multiplicity	64.15	19.07	57.3	54.7
$I/\sigma(I)$	208.1	49.3	138.0	95.3
Resolution ($\text{\AA}$)	0.80	0.72	0.55	0.55
IAM				
R_1 (%)	2.82	5.12	2.86	2.63
wR^2 (%)	7.36	13.24	8.91	8.49
Goodness of fit	1.066	1.042	1.022	1.020
Max, min peak ($\text{e \AA}^{-3}$)	0.320, -0.370	0.626, -0.502	0.598, -0.233	0.574, -0.380
HAR				
R_1 (%)	0.88	3.89	1.10	1.00
wR^2 (%)	1.94	10.0	1.43	1.83
Goodness of fit	1.118	1.068	1.103	1.070
Max, min peak ($\text{e \AA}^{-3}$)	-0.100, 0.065	-0.330, 0.360	0.131, -0.121	0.106, -0.117
MM				
R_1 (%)			1.27	1.32
wR^2 (%)			1.34	1.99
Goodness of fit			1.06	1.02
Max, min peak ($\text{e \AA}^{-3}$)			0.182, -0.171	0.143, -0.169
XRW				
R_1 (%)			0.85	
wR^2 (%)			0.76	
Goodness of fit			1.43	
Max, min peak ($\text{e \AA}^{-3}$)			0.132, -0.114	

Multipolar modelling according to the Hansen-Koppens formalism (Hansen & Coppens, 1978) was performed on the symmetry-merged data sets using the MoPro (Guillot et

al., 2001) software and evaluated using VMoPro and MoProViwer (Jelsch et al., 2005). Anisotropic hydrogen-atom displacement parameters were adopted from a HAR (Capelli et al., 2014; Hirshfeld, 1977) procedure employing NoSpherA2 (Kleemiss et al., 2021), which itself invoked the software Orca5 (Neese et al., 2020) to determine single-point molecular wavefunctions at the r2SCAN/def2-TZVP (Weigend & Ahlrichs, 2005; Furness et al., 2020) level of theory. The Mo $K\alpha$ HAROptimized X-ray geometry was used for the TONTO (Jayatilaka & Grimwood, 2003) software to perform an XRW fitting procedure (Jayatilaka, 1998). This XRW fitting procedure was carried out by including the weighted perturbation of the energy in the self-consistent-field (SCF) method of a HartreeFock calculation (Hartree, 1928; Fock, 1930; Jayatilaka, 1998). The weight was increased until no convergence could be reached anymore in the SCF procedure and the last converging step ($\lambda = 0.07$) was used as the final XRW model. The quality of each model is assessed using residual electron density, normal probability (Abrahams & Keve, 1971), DRK (Stash, 2007) and fractal dimension plots (Meindl & Henn, 2008) in the supporting information. Table 5.1 shows the recorded WYLID data sets, modelling strategies and quality indicators. For further crystallographic

Table 5.2: Selected interatomic distances ($\text{\AA}$) in WYLID at 100 K (HAR Mo $K\alpha$) compared with the data set presented by Graw et al. (2023) at 110 K and the synchrotron data set at 100 K presented by Balmohammadi et al. (2025a).

Bond	WYLID, 100 K	YLID, 110 K (Graw et al.)	YLID, 100 K (Balmohammadi et al.)
S1-C3	1.7340 (1)	1.7107 (3)	1.7098 (2)
C3 - C4†	1.4534 (2)	1.4363 (4), 1.4426 (3)	1.4351 (2), 1.4416 (2)
C4 - O1†	1.2270 (2)	1.2349 (2), 1.2304 (3)	1.2348 (2), 1.2303 (2)
S1 - C1	1.7956 (2)	1.7885 (4)	1.7889 (2)
S1 - C2	1.7972 (2)	1.7975 (3)	1.7964 (2)
C11 - C12	1.4014 (2)		
C13 - O2	1.2261 (2)		
C20-O3	1.2316 (2)		

† For YLID, both comparable distances are given. Distances originate from the re-refinement at the same level of theory as employed in this study.

information, the raw data and the structure data, we refer the reader to Table S1 in the supporting information.

Except for the model based on $\text{Cu}K\beta$ radiation, all nonspherical models agreed well between the observed and calculated structure factors. As shown in the supporting information, we attribute this difference to the low raw intensity of our $\text{Cu}K\beta$ micro-focus CCD detector setup compared with that of the rotating anode/synchrotron dual photon counting detectors used in the others. We relied on the three data sets with significantly lower R factors for our quantum crystallographic analysis.

5.2 Results and discussion

5.2.1 Crystal structure of WYLID

The general geometric description and Hirshfeld surface analysis using CrystalExplorer (Furness et al., 2020) were conducted using the HAR model of the Mo $K\alpha$ data set.

WYLID crystallized in the centrosymmetric orthorhombic space group $Pbca$, different from the non-centrosymmetric $P2_12_12_1$ space group of YLID. Table 5.2 shows interatomic

distances in WYLID at 100 K compared with the 110 K data set for YLID obtained by Graw et al. (2023) and the synchrotron measurement of YLID by Balmohammadi et al. (2025a).

The S1-C3 bond in WYLID is slightly shorter than the other S-methyl bonds (C2 and C3), indicating a stronger S-C interaction. Compared with the YLID model of Graw and coworkers, the S1-C3 bond is slightly longer. All three carbonyl C – O bonds in WYLID are of comparable length, with a slight exception for the C20 – O3 bond which points to the C2 methyl group and exhibits a C – O $\cdots$ H2C interaction with a distance of 2.625 (2) Å.

A search and comparison in the Cambridge Structural Database (CSD) using the MOGUL tool (Bruno et al., 2004) revealed that the C–O bonds in WYLID are within the estimated ranges for similar structures (Fig. S18 in the supporting information). In contrast, the S1 – C3 bond in WYLID is situated between two bond distances that are more prevalent, with the shorter ones associated with YLID entries in the database (CCDC reference code MSULIN; Christensen & Thom, 1971) and the longer ones belonging to organometallic coordination complexes (e.g. CCDC refcode LUNHOU; Thorarinsdottir et al., 2019). The most comparable C-S distance of 1.734 Å is found in a diester structure (CCDC refcode WOBTUE; Giovannitti et al., 2014).

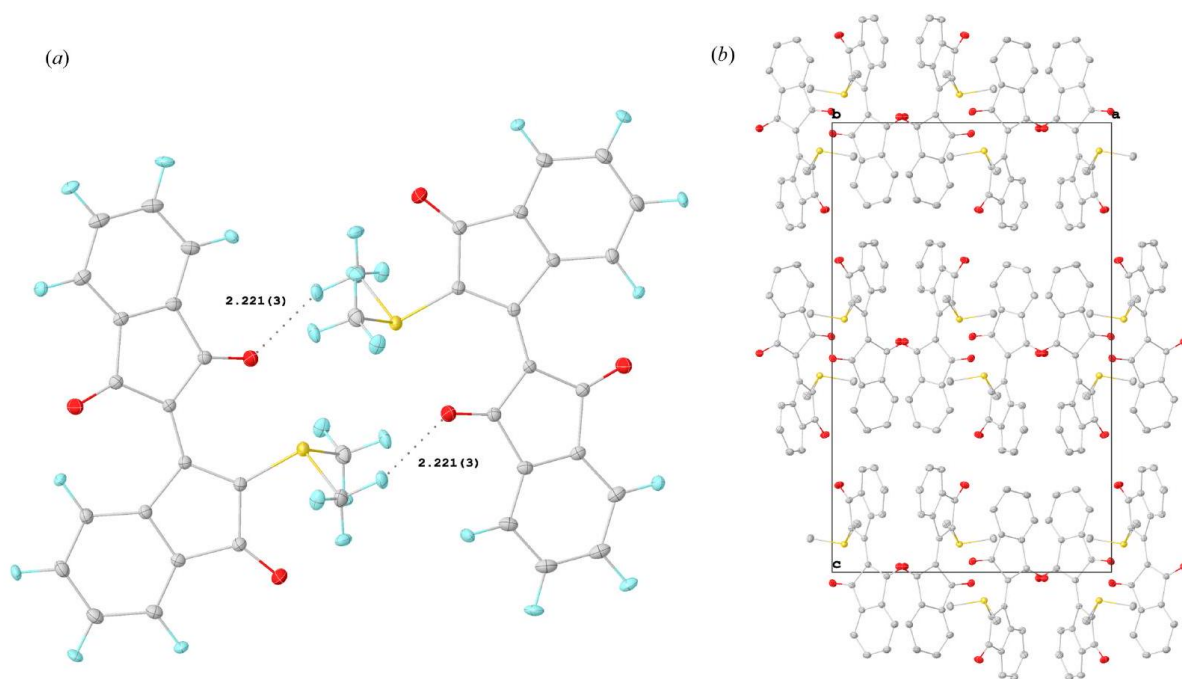


Figure 5.4: (a) Closest O $\cdots$ H contacts between two molecules of WYLID. (b) Crystal packing of the pairs in the *b* direction (H atoms omitted for clarity). Displacement ellipsoids are shown at the 50% probability level.

In the solid state, WYLID forms closely interacting pairs in Figure 5.4 dominated by O $\cdots$ H contacts between O 3 and the two methyl groups. The two moieties of WYLID are positioned around a crystallographic centre of inversion, thus preventing a similar form of helical chirality as observed in YLID. These WYLID pairs align along the crystallographic *b* axis in a zigzag fashion, exhibiting weak interactions and adopting a sheet-like configuration in the crystallographic *a* direction.

Structurally, YLID and WYLID are very similar. The main difference is that one of the carbonyl oxygen atoms in YLID is replaced by another indandione moiety. This expands the aromatic system in WYLID, resulting in the colour change from yellow (YLID) to deep red (WYLID).

The sulfur atom in WYLID is slightly tilted out of the five-membered ring plane involving atoms C3, C4, C5, C10 and C11 by an angle of $8.26(1)^\circ$, which is more than the 7° distortion in the orthorhombic YLID reported by Balmohammadi et al. (2025a). The non-chiral monoclinic polymorph of YLID shows no distortion of the SMe_2 fragment. This can be attributed to the steric and carbonyl electronic influence of the second indandione fragment.

Balmohammadi et al. (2025a) further refined the anomalous dispersion parameters of the sulfur atoms in the $\text{CuK}\alpha$ data sets and found small deviations from the tabulated values. We also performed an anomalous dispersion refinement (Meurer et al., 2022; Balmohammadi et al., 2025a) on our $\text{CuK}\alpha$ WYLID data set and found small deviations from the standard tables in the same range. Details are given in the supporting information.

5.2.2 Quantum crystallographic analyses

5.2.2.1 Charge density analysis

Figure 5.5 shows the atomic Bader charges according to the QTAIM (Bader, 1991) analysis of various combinations. Further atomic charges can be found in the supporting information.

In all models of WYLID, there is a significant charge separation between the sulfur atom and the attached atom C3 and between the carbonyl oxygen and their connected carbon atoms. A significant negative charge on the ylid carbon is found in the HAR and the two 'experimental wavefunction/ electron density' approaches of XRW and MM. This is also reflected in a pure density functional theory (DFT) calculation after geometry optimization of WYLID (Section S2.4). While the multipolar model approach gives a more significant charge separation for the S1 – C3 bond than the wavefunction-based methods, the opposite is true for all three carbonyl C – O pairs. The S1-C3 charge separation in the XRW model is close to that obtained by HAR (both have a difference of 0.70 e). For the C – O charges, the XRW model yields the highest charge separation of the three models (2.30 and 2.31 e). The multipolar model yields the highest S1-C3 charge separation with 1.12 e but has a lower charge separation on the carbonyls (1.79, 1.88 and 1.93 e).

The comparison data sets between WYLID and Bindandione were recorded using different wavelengths (Mo $K\alpha$ and Cu $K\alpha$). Despite their different maximum resolutions (0.55 and 0.80 Å, respectively), the Bader charges from each HAR model are almost identical. This indicates a similar bonding pattern, particularly for the carbonyl/enolate groups, and suggests that the presence of the SMe_2 group does not additionally favour the enolate form (labelled C in Figure 5.6). In contrast, the most significant difference between the WYLID and Bindandione charges lies in the ylid C3 atom, which is significantly negatively charged after the introduction of the SMe_2 group.

In general, the charges we have obtained for WYLID using wavefunction-based methods agree with the charges that Balmohammadi et al. (2025a) found in their analysis of YLID.

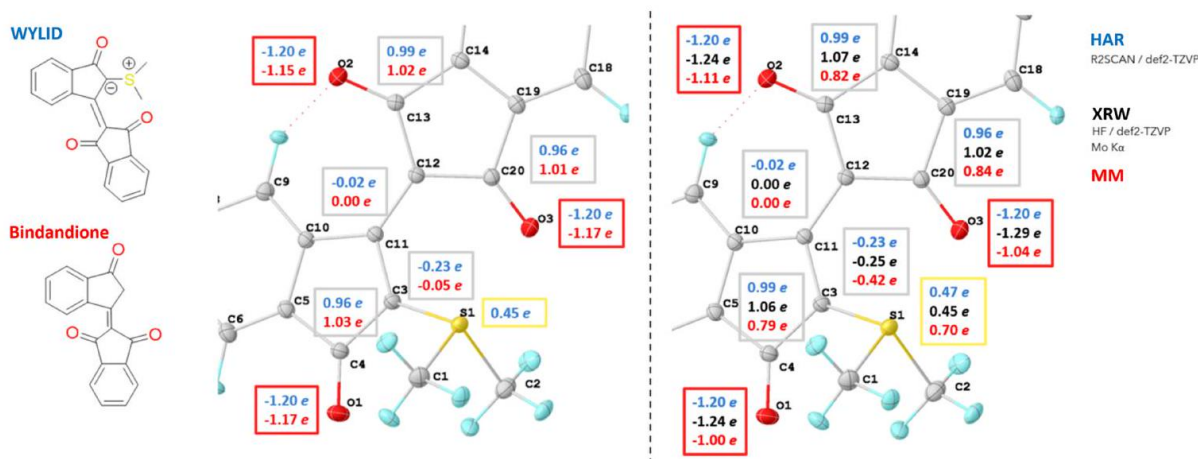


Figure 5.5: (Left) A comparison of Bader charges in WYLID (blue) and the respective charges in Bindandione (red), based on the HAR model (Mo K α for WYLID, Cu K α for Bindandione, r2SCAN/def2-TZVP). (Right) The Bader charges of WYLID from the different Mo K α models, namely HAR (r2SCAN/def2-TZVP), XRW (X-ray-HF/def2-TZVP) and MM.

5.2.2.2 Bonding analysis

The Laplacians of the total electron density in Figure 5.6 (labelled A-F) reveal a close similarity for the three carbonyl groups in WYLID. The negative Laplacian around the carbonyl O atom shows distinct lone pairs in each case, which are in plane with the C – O bond. This indicates a preference for the carbonyl bonding scheme and an absence of the enolate form. Figure 5.6 panel G shows signs of the lone pair at S1 in pseudo-tetrahedral geometry and the three S – C bonds. Table 5.3 shows selected bonding indices for the relevant atomic pairs in WYLID based on the Mo K α models. The electrostatic potential (ESP) mapped onto the static total electron density in Figure 5.6 panel H shows the lowest negative ESP at the O2 carbonyl group and a higher, very similar, ESP at the O1 and O3 carbonyl groups. The highest positive ESP is found at the methyl units of the SMe₂ group.

There is more electron density and valence-shell charge concentration at the bond critical points between the sulfur atom and the ylid carbon atom than between sulfur and the two methyl groups. This is consistent with a stronger bond between the sulfur and the ylid carbon. All bonding indices suggest a predominantly covalent single bond with a larger ionic contribution than the methyl S – C bonds exhibit. For all selected topological and bonding indicators, there is no systematic difference between the three C – O bonds in WYLID. The Wiberg bond index (WBI) suggests a bond order between 1.65 and 1.70 for each carbonyl, close to a double bond. The natural bonding orbital (NBO) analysis, however, shows that the C – O bonds have a strong ionic contribution, which is common for carbonyl systems and more so in enolate systems. The delocalization index suggests lower delocalization in the carbonyl bonds than in the S – C bonds.

The Laplacian of the total electron density along the C – O bond path for the three carbonyls in Figure 5.7 is similar for all three carbonyl bonds. Interestingly, the largest difference was found for the O3 carbonyl bond, which interacts noncovalently with the S1 – C1 anti-bond, resulting in a slightly longer S1 – C1 than S1 – C2 bond. This

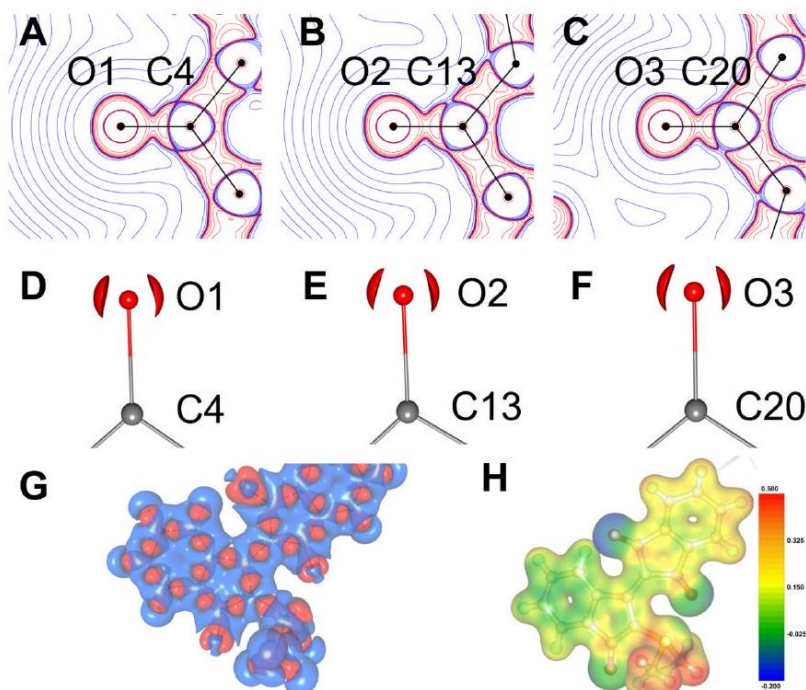


Figure 5.6: Two-dimensional Laplacians (panels A-C, -50 to $50 \text{ e } \text{\AA}^{-5}$, logarithmic iso-levels), 3D carbonyl Laplacians (panels D-F, at the $-100 \text{ e } \text{\AA}^{-5}$ iso-level) and 3D Laplacians (panel G, at the $0.2 \text{ e } \text{\AA}^{-5}$ isosurface) of the total electron density in the MM Mo $K\alpha$ model of the carbonyl groups in WYLID. Blue lines show negative Laplacian values and indicate valence-shell charge concentration. Red lines show positive Laplacian values and indicate valence-shell charge depletion. Panel H shows the electrostatic potential in $\text{e } \text{\AA}^{-1}$ mapped onto the static total electron density at the $0.2 \text{ e } \text{\AA}^{-5}$ iso-surface.

intramolecular interaction has a larger influence on the C–O bond than the proximity to the ylid bond. Compared with the reference systems of 4-heptanone and 4-hept-3-enolate, all three systems in WYLID are more similar to the Laplacian in the carbonyl than to the enolate resonance form.

In summary, the bond analysis strongly supports the ylidtype S-C bond and does not show a significant contribution from the ylene form. While the ylid bond has no significant influence on the bonding of O1 and C4, the large amount of ionic bonding together with a $\text{WBI}(\text{C} - \text{O})$ between 1.5 and 2 suggests that the carbonyl form has the largest contribution. A comparison of the Laplacian of the total electron density along the bond path compared with a reference carbonyl and enolate fully supports the carbonyl form. This finding is also consistent with the other bond indices, which point more towards the carbonyl structure.

5.2.2.3 Natural resonance theory

The resonance structures in WYLID were investigated employing natural resonance theory (NRT) in NBO 7 (Frisch et al., 2013; Glendening et al., 2019) using the XRW Mo $K\alpha$ model. Due to the highly delocalized π system in WYLID, a total of 175 resonance structures were found, covering 97.3% of the compound's resonance weight, with the leading

Table 5.3: Selected bonding indices of WYLID from the 'experimental charge density' (MM) and the 'experimental wavefunction' (XRW).

Topological features of the bond critical points according to QTAIM, the ellipticity, the Wiberg bond index (WBI), the delocalization index (DI) and the natural bonding orbital (NBO) bond orders are shown.

Atom pair	MM Mo K α			XRW Mo K α				
	ρ_{BCP} ($\text{e} \text{ \AA}^{-3}$)	$\nabla(\rho_{\text{BCP}})$ ($\text{e} \text{ \AA}^{-5}$)	Ellipticity	WBI	DI	NBO total	NBO covalent	NBO ionic
S1-C3	1.42	-6.81	0.087	1.018	0.575	1.0798	0.9636	0.1162
S1-C2	1.28	-4.95	0.060	0.977	0.560	0.9209	0.8884	0.0325
S1-C1	1.26	-4.36	0.015	0.978	0.555	0.9147	0.8879	0.0268
O1-C4	2.79	-28.25	0.085	1.682	0.362	1.7568	1.1207	0.6361
O2-C13	2.78	-27.96	0.085	1.702	0.365	1.8104	1.1503	0.6601
O3-C20	2.79	-25.55	0.082	1.653	0.358	1.7787	1.1106	0.6681
C11-C12	2.11	-18.26	0.212	1.375	0.297	1.441	1.2970	0.1440

structure contributing only 2.54%. This emphasizes the difficulty of finding meaningful Lewis structures for these highly delocalized systems. Nevertheless, the summed resonance weights provide valuable information about the tendency of a Lewis structure of WYLID.

The resonance weights were analysed for atoms S1, C3, C4, O1, O2 and O3. The NRT analysis suggests a high dominance of the ylid S1-C3 bond over an ylene-type bonding. Here, the S1-C3 double bond is present in 12.0% of all resonance structures, while the ylid carbon atom C3 exhibits a lone pair in 11.1% of cases. At first glance, this seems to indicate equal ylid/yene bonding. However, the lone pair and negative

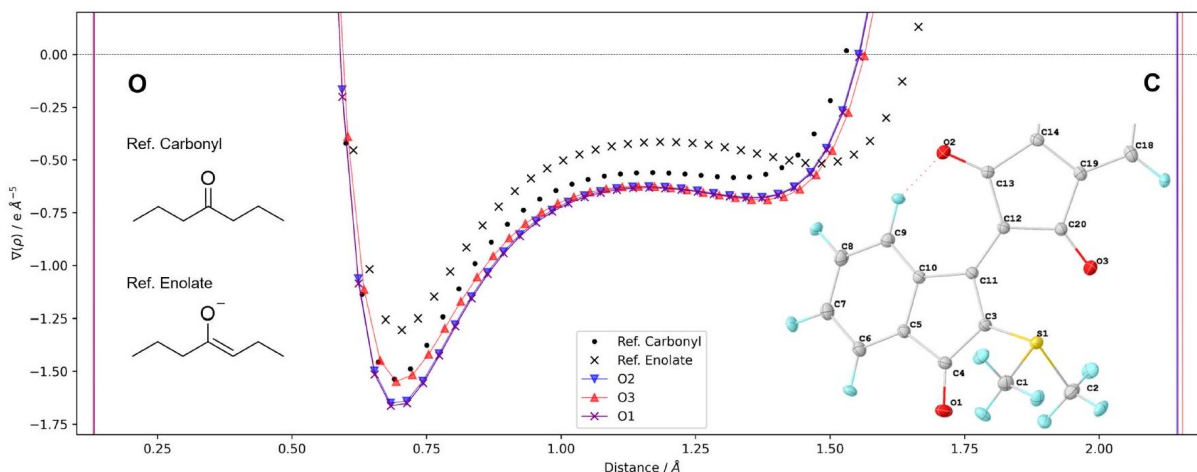


Figure 5.7: Comparison of the Laplacians of the total electron density along the topological bond path of the XRW Mo K α model in the three carbonyl groups in WYLID compared with the reference ketone 4-heptanone and its enolate form. More details can be found in Section S2.4 in the supporting information.

charge on C3 are most likely strongly delocalized via the π system in WYLID. In every case where the S1-C3 double bond was present, at least one other S-C bond, if not both, was cleaved.

For the carbonyl groups, the largest proportion of resonance structures prefer the carbonyl bonding scheme, being a little lower at 60.4% for O1 than for O2 and O3 (67.0% and 64.8%,

respectively). This suggests that in the NRT the presence of the SMe_2 group has a small effect on the bonding situation for O1 – C4, but the difference is in the same range as between the other two carbonyl groups in WYLID. The remainder of the probabilities are mainly the enolate form but also include a third resonant structure, where only one lone pair is located at the oxygen atoms. The NBO charges and the 'lone pairs' as diagonals in the NBO matrix support these findings.

5.2.2.4 Comparison with YLID

To compare our results with the classic YLID, we conducted a comparison HAR of the high-resolution data set generated by the In $K\alpha$ metal jet - one of the brightest X-ray sources apart from storage-ring facilities - and compared these results with our findings on WYLID. Specifically, we evaluated it against our best high-resolution model of WYLID coming from the BM20-CRG beamline at the ESRF. This is because the wavelength used in the synchrotron experiment ($\lambda = 0.5634 \text{ \AA}$, 22.0 keV) is closer to the wavelength of 0.5134 $\text{\AA}$ for the In $K\alpha$ radiation used by Graw et al. (2023) and has an even better agreement between the measured and calculated structure factors than the Mo $K\alpha$ HAR model.

The Bader charges in Figure 5.8 for WYLID and YLID (Graw et al., 2023) on the same level of theory and for similar wavelength reveal a similar bonding situation in YLID. The negative charge at the ylid carbon atom is even more pronounced in YLID than in WYLID, while the carbonyl system is almost identical. This suggests a similar ylid S – C bond as well as a similar carbonyl C – O bond in YLID.

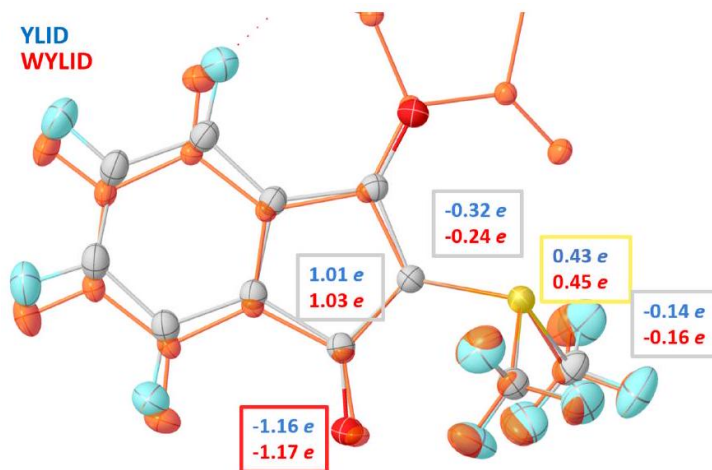


Figure 5.8: Comparison of Bader charges in electrons for YLID obtained by Graw et al. (2023) with a HAR using the same settings as for WYLID (transparent orange overlay).

5.2.2.5 Comparison between XRW, HAR, HF, DFT and MM

Table 5.4 compares the details of the charges for the Mo $K\alpha$ based models. Generally, there was a close agreement between the wavefunction-based models. With respect to the multipolar model, the general trend is also preserved. However, the absolute charges are larger for the ylid sulfur and carbon atoms and lower in the carbonyl groups.

Table 5.4: Bader charges of selected atoms in WYLID from the Mo $K\alpha$ data-based models. Charges given in e per atomic basin.

Atom	XRW	HAR	DFT	MM
S1	0.453	0.470	0.400	0.708
C3	-0.247	-0.238	-0.244	-0.407
C1	-0.220	-0.159	-0.178	-0.118
C2	-0.217	-0.142	-0.264	-0.138
C4	1.062	0.992	0.982	0.839
C13	1.065	0.990	1.000	0.823
C20	1.021	0.960	0.920	0.786
O1	-1.240	-1.198	-1.142	-1.002
O2	-1.237	-1.197	-1.175	-1.110
O3	-1.285	-1.185	-1.120	-1.040

Table 5.5: Results of the NBO/NRT analysis of the Mo $K\alpha$ based HAR, HF and XRW models.

		WBI			NBO					
		HAR	HF	XRW	HAR total	HAR covalent	HF total	HF covalent	XRW total	XRW covalent
S1	C3	1.035	1.020	1.018	1.112	1.001	1.067	0.940	1.080	0.964
S1	C2	0.961	0.977	0.977	0.899	0.882	0.940	0.930	0.921	0.888
S1	C1	0.970	0.979	0.978	0.904	0.892	0.927	0.906	0.915	0.888
C4	O1	1.652	1.641	1.682	1.750	1.138	1.793	1.080	1.757	1.121
C13	O2	1.689	1.666	1.702	1.886	1.197	1.786	1.081	1.810	1.150
C20	O3	1.633	1.611	1.653	1.875	1.162	1.813	1.074	1.779	1.111

The NBO/NRT results are compared between the HAR, pure Hartree-Fock (HF) and XRW models concerning their natural charges, WBI and NBO. Table 5.5 shows the bonding parameters. In general, all parameters are in good agreement with each other and there are only small differences.

For all bonds with the exception of C13 – O2, the XRW approach shows bond orders in between the pure HF approach and the HAR model. This demonstrates the general capability of XRW to include effects which are neglected in HF, such as electron correlation and polarization, and to bring additional effects into the model to the right extent. For the WBI, the XRW results in slightly weaker S-C but slightly stronger C – O bonds.

A comparison of the synchrotron data sets with the detector-saturated data set, as well as a HAR comparison using the hybrid functional ω B97X (Chai & Head-Gordon, 2008), can be found in the supporting information.

5.3 Conclusion

The synthesis and comprehensive characterization of WYLID, a byproduct of the literature synthesis of YLID, which is

potentially the most extensively measured calibration material, have been presented. The combination of data from the 'experimental charge density' derived from multipolar modelling and the 'experimental wavefunction' obtained from X-ray restrained wavefunction fitting offer a profound understanding of the diverse bonding schemes observed in the WYLID compound.

A multi-wavelength complementary quantum crystallographic analysis has been employed to gain insight into the C – S and C – O bonding situation of the ylide/ylenes and carbonyl/enolate systems. In the principal aspects of our analysis, the ylide structure is

preferred over the ylene and the carbonyl structure is preferred over the enolate resonance form. This preference has been established by a comparison of the bonding indices for the C–S and the three C–O systems present in WYLID. In this approach, the C–O system adjacent to the ylid bond exhibits no notable distinction from the other two C–O bonds.

The analysis of WYLID was also compared with a HAR model of Bindandione, i.e. WYLID without the SMe₂ group. This comparison demonstrates that the C–O bond in question exhibits no notable difference upon the introduction of the SMe₂ group.

It can be concluded that quantum crystallography is an effective approach for elucidating the bonding situation in chemically relevant moieties, such as ylide/ylene or, arguably more importantly, carbonyl/enolate.

5.4 References

- Abrahams, S. C. & Keve, E. T. (1971). *Acta Cryst.* A27, 157-165.
- Ahmed, F. R., Hall, S. R. & Huber, C. P. (1970). Crystallographic computing: proceedings of an International Summer School organized by The Commission on Crystallographic Computing of the International Union of Crystallography and held in Ottawa, 4-11 August 1969. Copenhagen: Munksgaard.
- Bader, R. F. W. (1991). *Chem. Rev.* 91, 893-928.
- Balmohammadi, Y., Malaspina, L. A., Nakamura, Y., Cametti, G., Andrzejewski, M., Siczek, M. & Grabowsky, S. (2025a). *Sci. Rep.* 15. In the press.
- Balmohammadi, Y., Malaspina, L. A., Nakamura, Y., Cametti, G., Siczek, M. & Grabowsky, S. (2025b). *Sci. Rep.* 15. Submitted.
- Blessing, R. H. (1995). *Acta Cryst.* A51, 33-38.
- Bourhis, L. J., Dolomanov, O. V., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2015). *Acta Cryst.* A71, 59-75.
- Brennan, S. & Cowan, P. L. (1992). *Rev. Sci. Instrum.* 63, 850-853.
- Bruno, I. J., Cole, J. C., Kessler, M., Luo, J., Motherwell, W. D. S., Purkis, L. H., Smith, B. R., Taylor, R., Cooper, R. I., Harris, S. E. & Orpen, A. G. (2004). *J. Chem. Inf. Comput. Sci.* 44, 2133-2144.
- Bürkstümmer, H., Tulyakova, E. V., Deppisch, M., Lenze, M. R., Kronenberg, N. M., Gsänger, M., Stolte, M., Meerholz, K. & Würthner, F. (2011). *Angew. Chem. Int. Ed.* 50, 11628-11632.
- Capelli, S. C., Bürgi, H.-B., Dittrich, B., Grabowsky, S. & Jayatilaka, D. (2014). *IUCrJ*, 1, 361-379.
- Chai, J.-D. & Head-Gordon, M. (2008). *J. Chem. Phys.* 128, 084106.
- Christensen, A. T. & Thom, E. (1971). *Acta Cryst.* B27, 581-586.
- Cook, A. F. & Moffatt, J. G. (1968). *J. Am. Chem. Soc.* 90, 740-746.
- Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* 42, 339-341.
- Fock, V. (1930). *Z. Phys.* 61, 126-148.
- Friedrich, W., Knipping, P. & Laue, M. (1912). *Sitzungsberichte*, 2, 303-322.
- Frisch, M. J., Trucks, G. W., Schlegel, G. E., Scuseris, G. E., Robb, M. A., Cheeseman, J. R., Scalmani, G., Barone, V., Mennucci, B., Petersson, G. A., Nakatsuji, H., Caricato, M., Li, X., Hratchian, H. P., Izmaylov, A. F., Bloino, J., Zheng, G., Sonnenberg, J. L., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Montgomery, J. A., Peralta, J. E., Ogliaro, F., Bearpark, M., Heyd, J. J., Brothers, E., Kudin, K. N., Staroverov, V. N., Keith, T., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A., Burant, J. C., Iyengar, S. S., Tomasi, J., Cossi, M., Rega, N., Millam, J. M., Klene, M., Knox, J. E., Cross, J. B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R. E., Yazyev, O., Austin, A. J., Cammi, R., Pomelli, C., Ochterski, W., Martin, R. L., Morokuma, K., Zakrzewski, V. G., Voth, G. A., Salvador, P., Dannenberg, J. J., Dapprich, S., Daniels, A. D., Farkas, O., Foresman, J. B., Ortiz, J. V., Cioslowski, J. & Fox, D. J. (2013). *GAUSSIAN 09. Revision D.01*. Gaussian Inc., Wallingford, Connecticut, USA.
- Furness, J. W., Kaplan, A. D., Ning, J., Perdew, J. P. & Sun, J. (2020). *J. Phys. Chem. Lett.* 11, 9248.
- Gasevic, T., Stückerath, J. B., Grimme, S. & Bursch, M. (2022). *J. Phys. Chem. A*, 126, 3826-3838.

- Giovannitti, A., Seifermann, S. M., Bihlmeier, A., Muller, T., Topic, F., Rissanen, K., Nieger, M., Kloppe, W. & Bräse, S. (2014). Personal communication (refcode 949722). CCDC, Union Road, Cambridge, England.
- Glendening, E. D., Landis, C. R. & Weinhold, F. (2019). *J. Comput. Chem.* 40, 2234-2241.
- Graw, N., Ruth, P. N., Ernemann, T., Herbst-Irmer, R. & Stalke, D. (2023). *J. Appl. Cryst.* 56, 1315-1321.
- Guillot, B. (2012). *Acta Cryst.* A68, s204.
- Guillot, B., Viry, L., Guillot, R., Lecomte, C. & Jelsch, C. (2001). *J. Appl. Cryst.* 34, 214-223.
- Guzei, I. A., Bikzhanova, G. A., Spencer, L. C., Timofeeva, T. V., Kinnibrugh, T. L. & Campana, C. F. (2008). *Cryst. Growth Des.* 8, 2411-2418.
- Hansen, N. K. & Coppens, P. (1978). *Acta Cryst.* A34, 909-921.
- Hartree, D. R. (1928). *Math. Proc. Camb. Philos. Soc.* 24, 89-110.
- Henke, B. L., Gullikson, E. M. & Davis, J. C. (1993). *At. Data Nucl. Data Tables*, 54, 181-342.
- Hirshfeld, F. L. (1977). *Theor. Chim. Acta*, 44, 129-138.
- Jayatilaka, D. (1998). *Phys. Rev. Lett.* 80, 798-801.
- Jayatilaka, D. & Grimwood, D. J. (2003). *Computational science ICCS 2003*, edited by P. M. A. Sloot, D. Abramson, A. V. Bogdanov, Y. E. Gorbachev, J. J. Dongarra & A. Y. Zomaya, pp. 142-151. Berlin, Heidelberg: Springer.
- Jelsch, C., Guillot, B., Lagoutte, A. & Lecomte, C. (2005). *J. Appl. Cryst.* 38, 38-54.
- Kleemiss, F., Dolomanov, O. V., Bodensteiner, M., Peyerimhoff, N., Midgley, L., Bourhis, L. J., Genoni, A., Malaspina, L. A., Jayatilaka, D., Spencer, J. L., White, F., Grundkötter-Stock, B., Steinhauer, S., Lentz, D., Puschmann, H. & Grabowsky, S. (2021). *Chem. Sci.* 12, 1675-1692.
- Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* 48, 3-10.
- Lácová, M. & Sisková, N. (1983). *Chem. Zvesti*, 38, 687-692.
- Lu, T. & Chen, F. (2012). *J. Comput. Chem.* 33, 580-592.
- Meindl, K. & Henn, J. (2008). *Acta Cryst.* A64, 404-418.
- Meurer, F., Dolomanov, O. V., Hennig, C., Peyerimhoff, N., Kleemiss, F., Puschmann, H. & Bodensteiner, M. (2022). *IUCrJ*, 9, 604-609.
- Meurer, F., Kleemiss, F., Riesinger, C., Balázs, G., Vuković, V., Shenderovich, I. G., Jelsch, C. & Bodensteiner, M. (2024). *Chem. Eur. J.* 30, e202303762.
- Neese, F., Wennmohs, F., Becker, U. & Riplinger, C. (2020). *J. Chem. Phys.* 152, 224108.
- Rigaku Oxford Diffraction (2024). CrysAlisPro software system. Rigaku Oxford Diffraction, Wroclaw, Poland.
- Sasaki, S. (1989). KEK Report 88-14, pp. 1-136. National Laboratory for High Energy Physics, Ibaraki-keri, Japan.
- Scheinost, A. C., Claussner, J., Exner, J., Feig, M., Findeisen, S., Hennig, C., Kvashnina, K. O., Naudet, D., Prieur, D., Rossberg, A., Schmidt, M., Qiu, C., Colomp, P., Cohen, C., Dettona, E., Dyadkin, V. & Stumpf, T. (2021). *J. Synchrotron Rad.* 28, 333-349.
- Sheldrick, G. M. (2015). *Acta Cryst.* A71, 3-8.
- Stash, A. (2007). DRK-Plot. Moscow, Russian Federation.
- Thorarinsdottir, A. E., Bjornsson, R. & Harris, T. D. (2019). Personal communication (refcode 1926462). CCDC, Union Road, Cambridge, England.
- Weigend, F. & Ahlrichs, R. (2005). *Phys. Chem. Chem. Phys.* 7, 3297.

5.5 Supporting Information

The supporting information of this work is provided as a single .pdf file with original format and page numbering starting from the next page.



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Supporting information for article:

**Synthesis and quantum crystallographic evaluation of WYLID:
YLID's red rival**

**Florian Meurer, Maximilian Schimpf, Birgit Hischa, Christoph Hennig, Julia
Rehbein, Florian Kleemiss and Michael Bodensteiner**

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S1. Synthesis

S1.1. General Information

All reactions were performed under a dry nitrogen atmosphere by using standard Schlenk techniques. DMSO and ethanol were dried over 4 Å and 3 Å molar sieves respectively. Other solvents were used without further purification or drying. Commercially available chemicals were purchased in high quality and used without further purification. For moisture-sensitive reactions, oven-dried glassware was used. NMR spectra were recorded at room temperature using a Bruker Avance 300 NMR spectrometer (300.13 MHz for ^1H , 75.47 MHz for ^{13}C). Mass spectra were recorded on an Agilent Q-TOF 6540 UHD instrument. Elemental analysis was performed using a Vario microcube. All UV-Vis spectra were measured using a SPECORD® 50 PLUS spectrometer from Analytik Jena with an optical path length of 10 mm. IR spectra were recorded on a Cory 630 FTIR from Agilent Technologies.

S1.2. Synthetic Procedure

([1,2']biindenylidene-3,1',3'-trione), Bindandione

A solution of dry ethanol (24 ml) and 1,3-indandione (2.04 g, 14.0 mmol, 1 equiv.) was prepared in an oven-dried Schlenk tube and stirred for 5 min. Sodium acetate (1.53 g, 18.6 mmol, 1.3 equiv.) was added and the mixture was stirred for 1 h at room temperature. The solution was then diluted with water (50 ml) and acidified with HCl to a pH of about 1. The precipitate was filtered off and dried under vacuum to give a green powder (1.67 mg, 43 %).

^1H NMR (300.13 MHz, CDCl_3): δ 9.67 (m, 1H), 8.04-7.99 (m, 1H), 7.99-7.92 (m, 2H), 7.89-7.84 (m, 1H), 7.84-7.79 (m, 2H), 7.78-7.70 (m, 1H), 4.16 (s, 2H); ^{13}C NMR (75.47 MHz, CDCl_3): δ 201.0, 191.1, 189.4, 155.4, 145.9, 141.7, 141.3, 140.4, 135.4, 134.2, 131.7, 125.9, 123.5, 123.4, 123.1, 43.5

Crystals suitable for X-ray diffraction experiments were grown by applying the vapour diffusion method. For this purpose, a concentrated solution of Bindandione in benzene was filled into a Schlenk tube, which was connected via joints to a small flask containing diethyl ether. The setup was then placed in a refrigerator at 6°C and left until crystals formed.

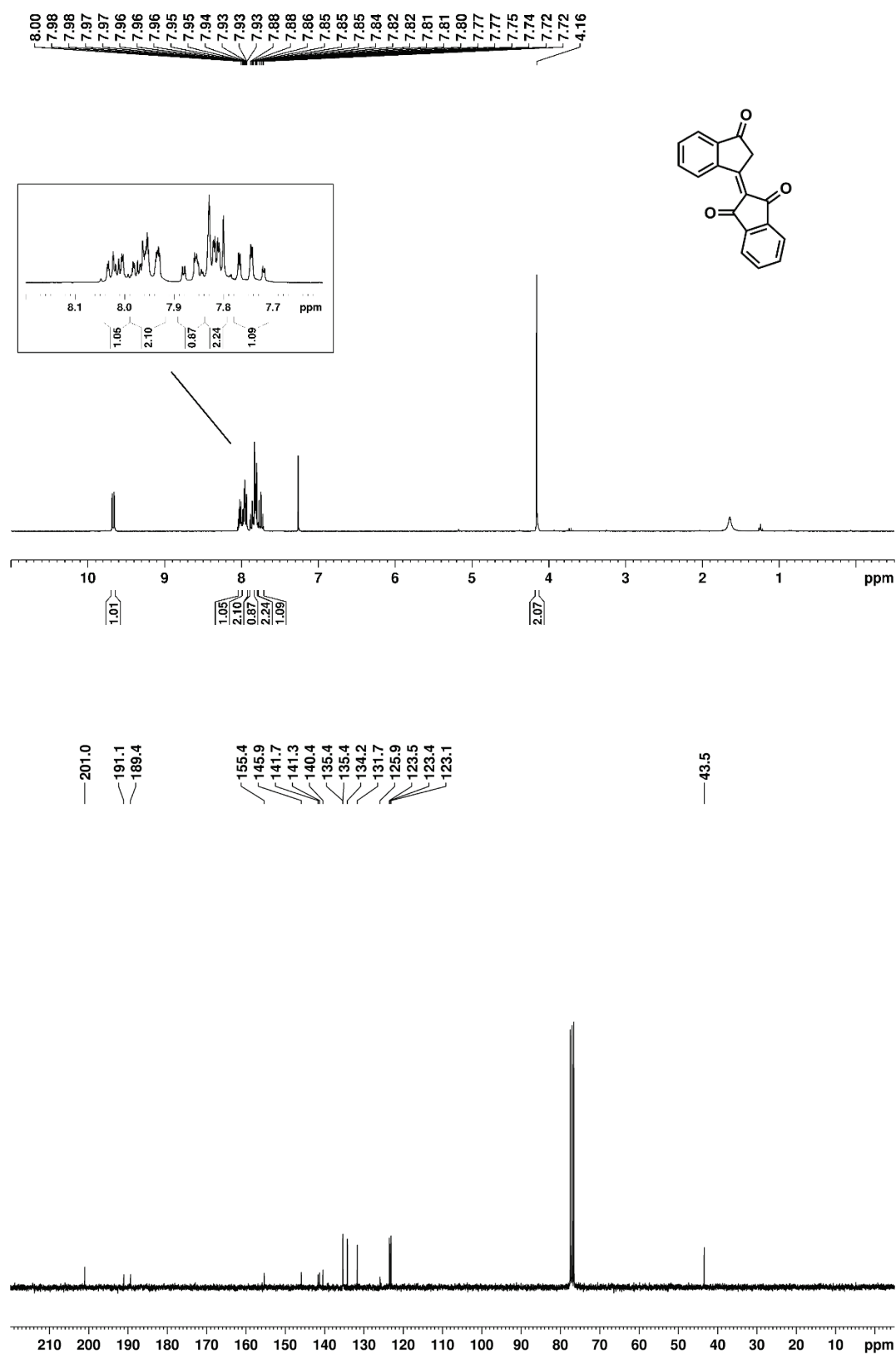


Figure S1: ¹H-NMR (top) and ¹³C-NMR (bottom) spectra of Bindandione.

2-(dimethyl- λ 4-sulfaneylidene)-[1,2'-biindenylidene]-1',3,3'(2H)-trione, WYLID

Bindandione (200 mg, 0.73 mmol, 1 equiv.) was suspended in acetic anhydride (2 ml) in an oven-dried Schlenk tube under a dry N₂ atmosphere. DMSO (71 μ L, 1.4 equiv.) was added and the reaction mixture was stirred at 85°C for 4 h. At the end of the reaction time, the solution was allowed to cool to room temperature and then quenched with potassium carbonate. DCM and water were added in equal parts (20 ml) and transferred to a separating funnel. The aqueous phase was then extracted with DCM (3x 20 ml) and the collected organic phases were dried over MgSO₄. The drying agent was filtered off and the solution was then dried under vacuum to give a dark red solid. Recrystallization from ethyl acetate/petroleum ether afforded WYLID as a bright red crystalline powder (80.4 mg, 33%).

¹H NMR (300.13 MHz, CDCl₃): δ 8.42 (m, 1H), 7.80 (m, 1H), 7.69 (m, 1H), 7.61 (m, 2H), 7.53 (m, 1H), 7.47 (m, 1H), 7.34 (m, 1H), 3.25 (s, 6H); ¹³C NMR (75.47 MHz, CDCl₃): δ 190.3, 163.3, 140.6, 134.9, 132.9, 131.1, 128.4, 121.6, 120.8, 109.1, 86.7, 27.9.

HR-ESI-MS: (C₂₀H₁₃O₃S+H)⁺ : m/z_{calc} = 335.0736, m/z_{found} = 335.074

EA: Anal. Calcd. (%) for C₂₀H₁₃O₃S: C 71.84, H 4.22, S 9.59; found: C 71.66, 4.33, S 8.59

IR: IR (solid-state): ν / cm⁻¹ = 3012, 1655, 1625, 1580, 1510, 992, 738.

Crystals suitable for X-ray diffraction experiments were grown by the vapour diffusion method.

Therefore, a concentrated solution of WYLID in benzene was added in a Schlenk tube, which was connected to a small flask containing diethyl ether. The setup was then placed in a refrigerator at 6°C and left until crystals suitable for the diffraction experiments were formed.

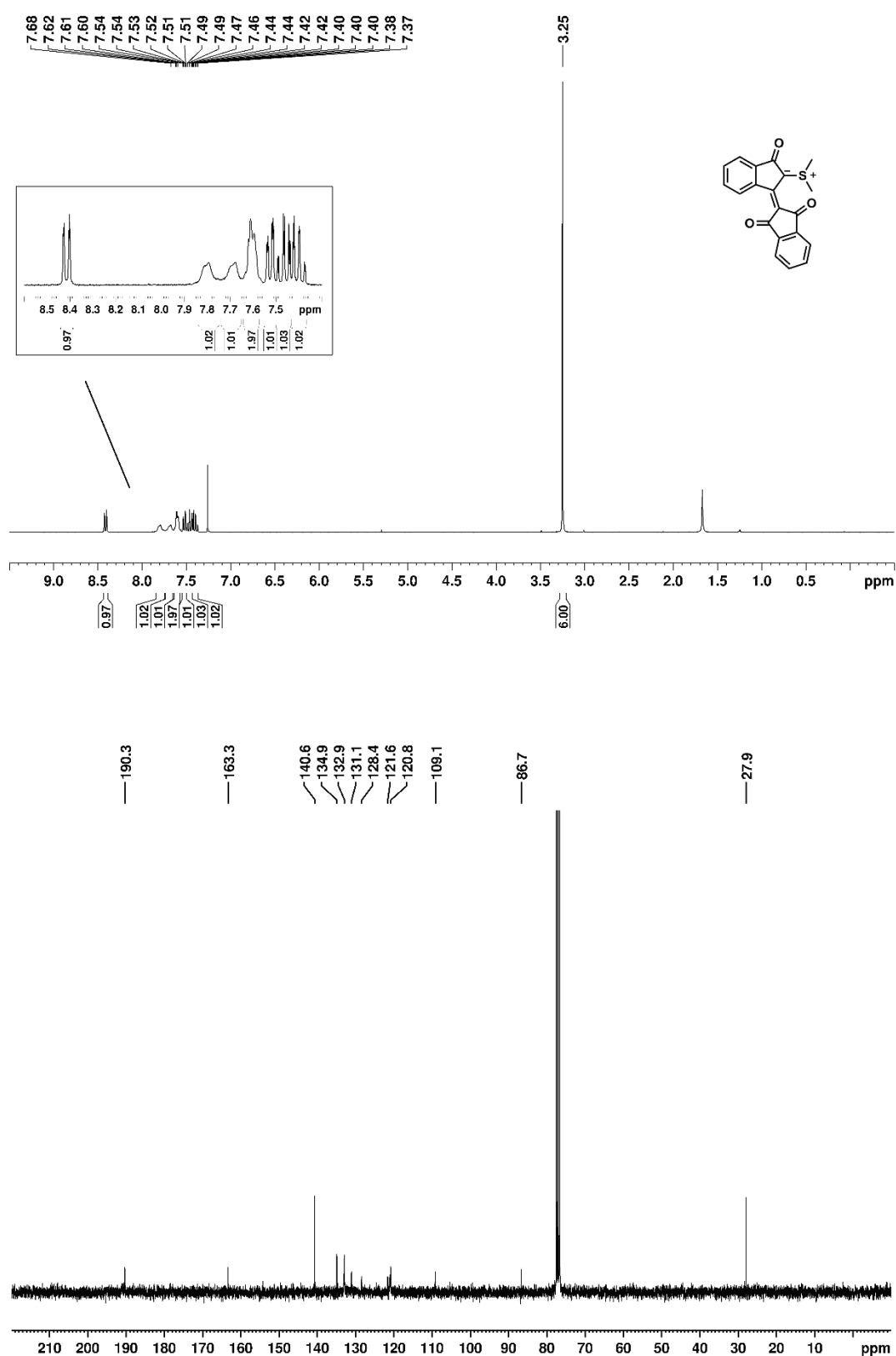


Figure S2: ^1H -NMR (top) and ^{13}C -NMR (bottom) spectra of WYLID.

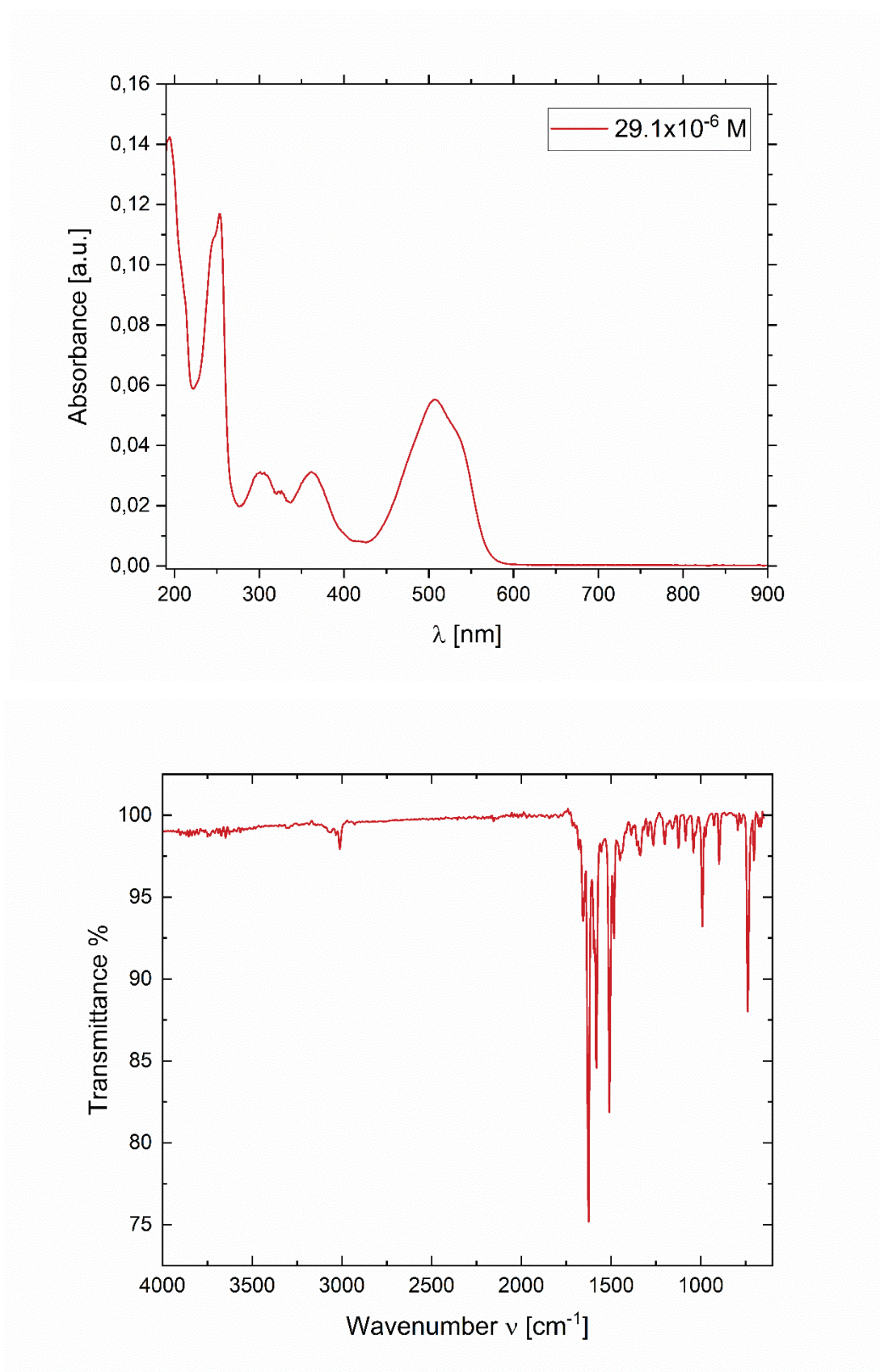


Figure S3: UV/VIS (top) and IR (bottom) spectra of WYLID.

S2. Crystallographic Analysis

All data sets were processed and integrated using *CrysAlisPro* V.43 (Rigaku Oxford Diffraction Ltd, 2019). The initial structure solution for each model was obtained using *ShelXT* (Sheldrick, 2015). Structural refinement for all models except for the multipolar models was performed using *Olex2* software (Dolomanov *et al.*, 2009) with *olex2.refine* (Bourhis *et al.*, 2015) as the refinement engine. All HAR models were obtained by using *NoSpherA2* (Kleemiss *et al.*, 2021) with the quantum chemical software *ORCA5* (Neese *et al.*, 2020). All calculations were performed using the r2SCAN/def2-TZVP (Weigend & Ahlrichs, 2005; Furness *et al.*, 2020) method/basis set combination unless otherwise noted (see below for the comparison with the hybrid functional, ω B97X). The parameters set in *NoSpherA2* / *ORCA* for the calculations were a normal integration accuracy, the *NoSpherA2* custom SCF threshold, a normal convergence strategy in the SCF procedure and a toluene or DMSO solvation model. In this work, neither the choice of a solvation model nor the inclusion of the nearest neighbour molecules to include interatomic interactions significantly changed the results of the HAR procedure. In all models, we used the r2SCAN method and employed a toluene solvation model. The HAR procedure (Capelli *et al.*, 2014) was performed iteratively, switching between the single-point wavefunction calculation in *ORCA*, adjusting the new atomic form factors using *NoSpherA2* and the Hirshfeld stockholder partitioning scheme (Hirshfeld, 1977), and then iteratively updating the atomic coordinates and anisotropic displacement parameters until convergence was reached.

The multipolar models and visualization of their topological analysis were performed using the *MoPro*, *VMoPro* (Jelsch *et al.*, 2005) and the *MoProViewer* (Guillot, 2012) software packages. Refinement was conducted against the squared structure factors F^2 . We employed positional and ADPs restraints on all H-atoms according to the freely refined parameters from the HAR procedure on the same data set.

The X-ray restrained wavefunction fitting was performed using the *TONTO* software (Jayatilaka & Grimwood, 2003). The input file for the calculation in *TONTO* is given in S2.1. The XRW procedure was run starting with the HAR geometry and increasing the perturbation by the agreement of measured and calculated intensities by a weight step size of 0.01 (“ λ -step”). The procedure was terminated already after the 8th step ($\lambda = 0.07$).

Throughout the analysis, the first step of the XRW, without any X-ray diffraction contribution is referred to as the “HF model”. This is different from the “DFT model”, which is based on a gas-phase optimized (r2SCAN-3//r2SCAN/def2-TZVP (Gasevic *et al.*, 2022)) DFT calculation. All wavefunction-based models were investigated using the *multiwfn* software. (Lu & Chen, 2012) The data sets using Cu K α and Mo K α radiation were collected with a Rigaku Oxford Diffraction Synergy-DW rotating anode diffractometer with HyPix Arc 150° photon counting detector.

The data set using Cu K β radiation was recorded on a Rigaku Oxford Diffraction SuperNova system using an Oxford Instruments microfocus tube and specially optimized Axo Dresden Cu K β multilayer optic as well as an Atlas S2 CCD detector.

Table S1 shows the crystallographic information for each of the quantum crystallographic models of the different wavelength structures.

Table S1: Crystallographic information of data sets and quality parameters of the models. Structures used within this work were deposited in the CCDC with merged measured structure factors. The raw data and structures can be obtained from zenodo.org using the DOI provided. The models can be found in the respective "struct" directories, starting with the model name "IAM", "HAR", "MM" or "XRW".

Radiation (λ / $\text{\AA}$)	Cu K α (1.54187)	Cu K α (1.39222)	Mo K α (0.71073)	Synchrotron (0.56356)
Data DOI	10.5281/zenodo.14699349	10.5281/zenodo.14699464	10.5281/zenodo.14699544	10.5281/zenodo.14723884
Formula	$\text{C}_{20}\text{H}_{14}\text{O}_3\text{S}$			
Mass / g mol^{-1}	334.40			
Crystal size / mm^3	0.079 x 0.083 x 0.160	0.113 x 0.184 x 0.238	0.079 x 0.083 x 0.160	0.10 x 0.10 x 0.10
Space group	<i>Pbca</i>			
<i>a</i> / $\text{\AA}$	14.47962(7)	14.4765(2)	14.49062(7)	14.54072(7)
<i>b</i> / $\text{\AA}$	9.15557(4)	9.1539(1)	9.1569(4)	9.17361(2)
<i>c</i> / $\text{\AA}$	23.2502(19)	23.3338(4)	23.3290(1)	23.40310(7)
<i>V</i> / $\text{\AA}^3$	3093.50(3)	3092.11(6)	3095.51(2)	3121.7(2)
<i>D</i> / g cm^{-3}	1.436	1.437	1.435	1.423
μ / mm^{-1}	1.989	1.447	0.224	0.122
θ range / $^\circ$	3.79-67.68	4.39-76.18	2.22-40.48	2.24-40.40
<i>T</i> / K	100	100	100	100
Resolution / $\text{\AA}$	0.80	0.72	0.55	0.55
<i>I</i> / σ (<i>I</i>)	208.1	49.3	138.0	95.3
<i>R</i> _{int} / %	2.69	7.67	2.71	4.88
Total reflections	187273	78182	527077	508696
Unique reflections > 4 σ	3130	4227	8605	8745
Completeness / %	100.0	100.0	99.9	100.0
HAR				
CCDC Nr.	2392768	2392769	2392771	2392770
Data set	"data_Ylidanhydrate-CuKaDW"	"data_WYlid_Large6_Cub_100K_fm2"	"data_Ylidanhydrate_MoKaDW_cut"	"data_WYlid_4_22000_abs"
Nr. refined parameters	343	343	418	444
Goodness-of-fit	1.118	1.068	1.011	1.070
<i>R</i> indices, <i>I</i> > 2 σ / %	0.88	3.89	1.10	1.00
<i>R</i> indices (all data) / %	0.92	4.09	1.61	1.39
<i>wR</i> ₂ indices / %	1.94	10.00	1.43	1.83
Diff. peak, hole / $\text{e \AA}^{-3}$	0.065, -0.100	0.362, -0.332	0.131, -0.121	0.106, -0.117
MM				
CCDC Nr.	-	-	2393562	2393564
Data set	-	-	"data_Ylidanhydrat-MoKADW2_MM"	"data_WYlid_22keV_MM"
Nr. refined parameters	-	-	756	756
Goodness-of-fit	-	-	1.06	1.02
<i>R</i> indices, <i>I</i> > 2 σ / %	-	-	1.27	1.32
<i>R</i> indices (all data) / %	-	-	1.59	1.36
<i>wR</i> ₂ indices / %	-	-	1.34	1.02
Diff. peak, hole / $\text{e \AA}^{-3}$	-	-	0.182, -0.171	0.143, -0.169
XRW				
Data set	-	-	"data_Ylidanhydrate_MoKaDW_XRW"	-
Goodness-of-fit	-	-	1.43	-
<i>R</i> indices, <i>I</i> > 2 σ / %	-	-	0.85	-
<i>wR</i> ₂ indices / %	-	-	0.76	-
Diff. peak, hole / $\text{e \AA}^{-3}$	-	-	0.132, -0.114	-

S2.1. Input for the X-ray restrained wavefunction fitting

```
{

charge= 0
multiplicity= 1

! Process the CIF
cif= {
  file_name= ./WYLID_MoKa_small.cif
}
process_cif

name= Ylideanhydrate-MoKa-XRW

basis_directory= /home/xrz/tonto/basis_sets/
basis_name= def2-TZVP

dispersion_coefficients= {
  C 0.0035 0.00160
  H 0.00000 0.00000
  O 0.0116 0.0061
  S 0.1242 0.1244
}

crystal= {
  xray_data= {
    thermal_smearing_model= hirshfeld
    partition_model= mulliken
    optimise_extinction= false
    correct_dispersion= TRUE
    optimise_scale_factor= true
    wavelength= 0.6198 angstrom

    REDIRECT ./WYLID_MoKa_merged.hkl

    f_sigma_cutoff= 4.0
  }
}

! Geometry
put

! Tight grid
becke_grid= {
  set_defaults
  accuracy= normal
  pruning_scheme= jayatilaka2
}

! More accuracy
output_style_options= {
  real_precision= 8
  real_width= 20
}

! Normal SCF
scfdata= {
  initial_density= promolecule
  kind= rhf
  use_SC_cluster_charges= FALSE
  convergence= 0.001
  linear_dependence_tol= 0.001
  diis= { ! This is the extrapolation procedure
    save_iteration= 1
    start_iteration= 3
    keep= 10
    convergence_tolerance= 0.09
  }
  max_iterations= 200 ! The maximum number of SCF iteration

  use_damping= YES ! These are used to damp the SCF iteration process
  damp_factor= 0.80 ! by including 60% of the previous result
  damp_finish= 7
  use_level_shift= NO
}
scf

scfdata= {
  initial_density= restricted
  kind= xray_rhf
  direct= yes
  convergence= 0.00001
  linear_dependence_tol= 0.001
  use_SC_cluster_charges= FALSE
}
```

```
diis= {
    ! This is the extrapolation procedure
    save_iteration= 1
    start_iteration= 3
    keep= 10
    convergence_tolerance= 0.09
}
max_iterations= 200    ! The maximum number of SCF iteration
do_outputs= TRUE

use_damping= YES      ! These are used to damp the SCF iteration process
damp_factor= 0.80     ! by including 60% of the previous result
damp_finish= 7
use_level_shift= YES
initial_lambda= 0.000 ! These specify the "lambda value"
lambda_step= 0.010   ! used to mix the energy with the chi^2
lambda_max= 2.000
}
scf
}
```

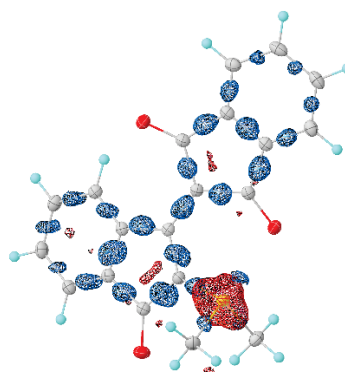
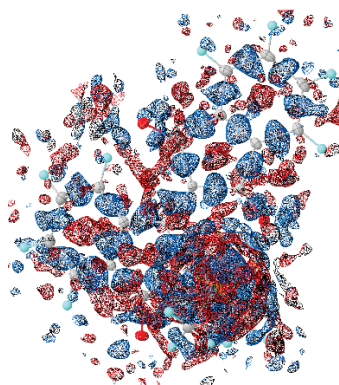
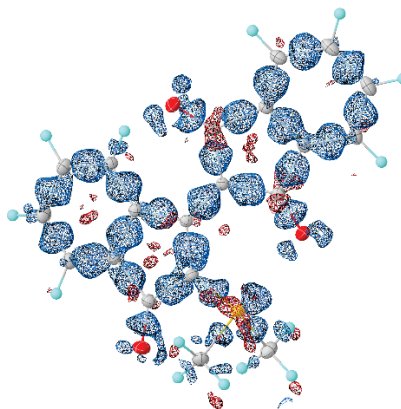
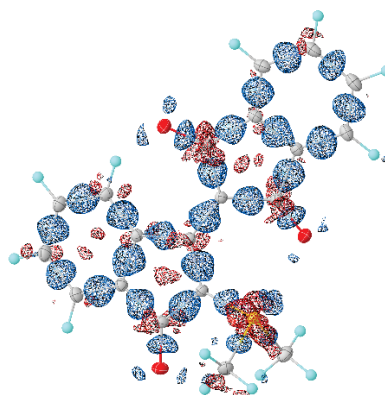

S2.2. Model quality evaluation**Cu K α** **Cu K β** **Mo K α** **Synchrotron**

Figure S4a: Residual electron density of the independent atom models for each data set at the 0.15 e/Å³ iso level projected onto the asymmetric unit. Blue indicates positive, red negative residual electron density. Non-hydrogen atoms are shown with a 50% probability.

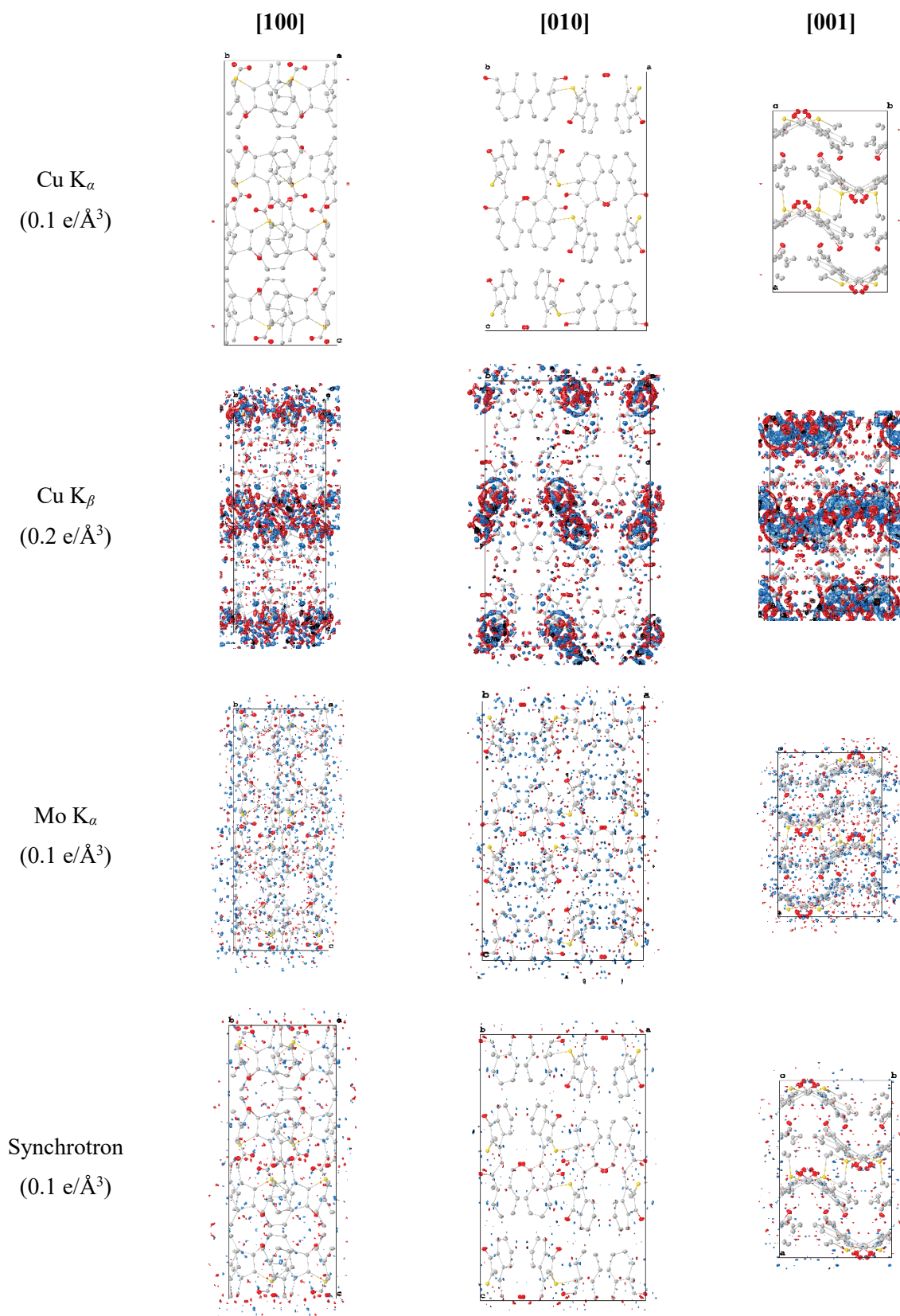


Figure S4b: Residual electron densities of the HAR models along each crystallographic axis with the iso level indicated below each wavelength. Blue indicates positive, red negative residual electron density. All atoms are shown with 50% probability. Hydrogen atoms have been omitted for clarity.

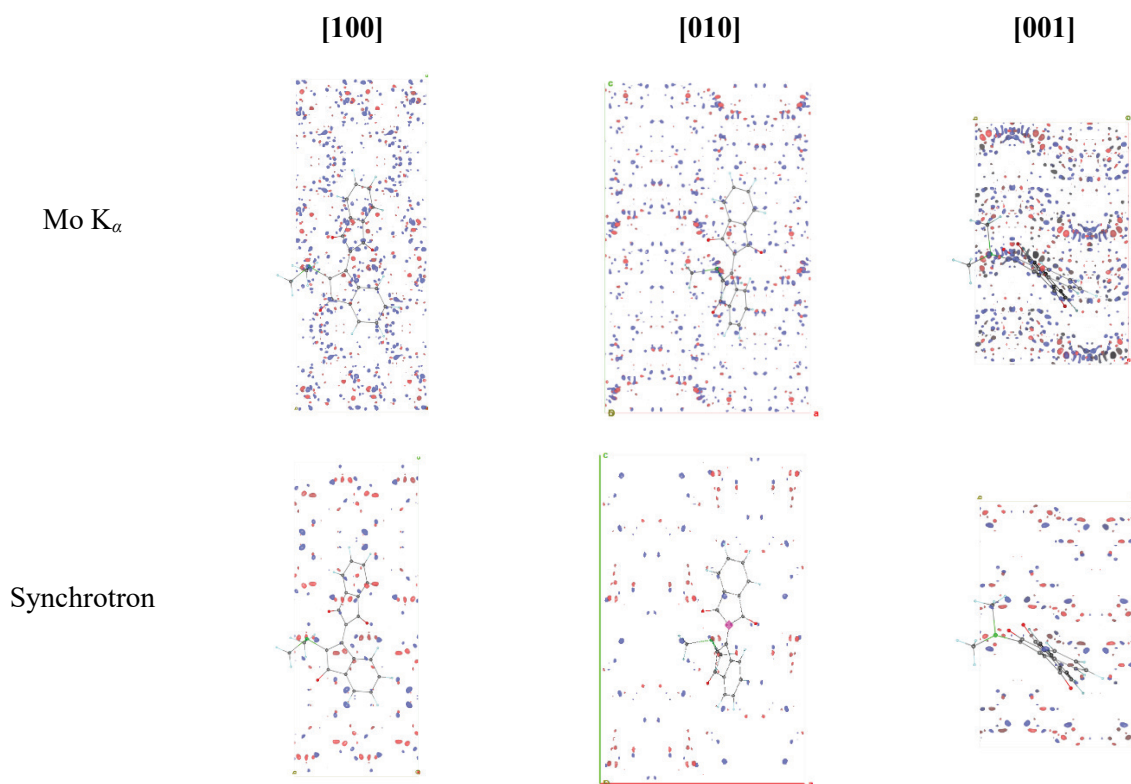


Figure S5: Residual electron densities of the multipole models along each crystallographic axis at a $0.1 \text{ e}/\text{\AA}^3$ iso level. Blue indicates positive, red negative residual electron density. All atoms are shown with 50% probability. Hydrogen atoms have been omitted for clarity.

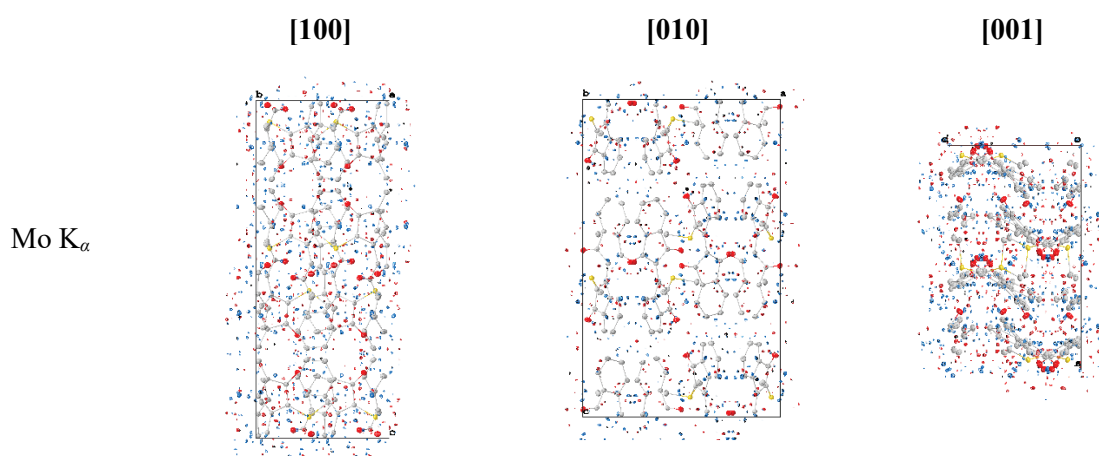


Figure S6: Residual electron densities of the XRW model along each crystallographic axis at an $0.1 \text{ e}/\text{\AA}^3$ iso level. Blue indicates positive, red negative residual electron density. All atoms are shown with 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity.

The residual electron density in Figures S4-S6 is generally low for all models, except the $\text{Cu K}\beta$ based models. We attribute this to the much weaker $\text{Cu K}\beta$ raw intensity compared to the $\text{Cu K}\alpha$ / $\text{Mo K}\alpha$

rotating anode and synchrotron radiation. The residual density in the Cu K_β models is mostly concentrated near the sulfur atom, which is the heaviest atom in the structure.

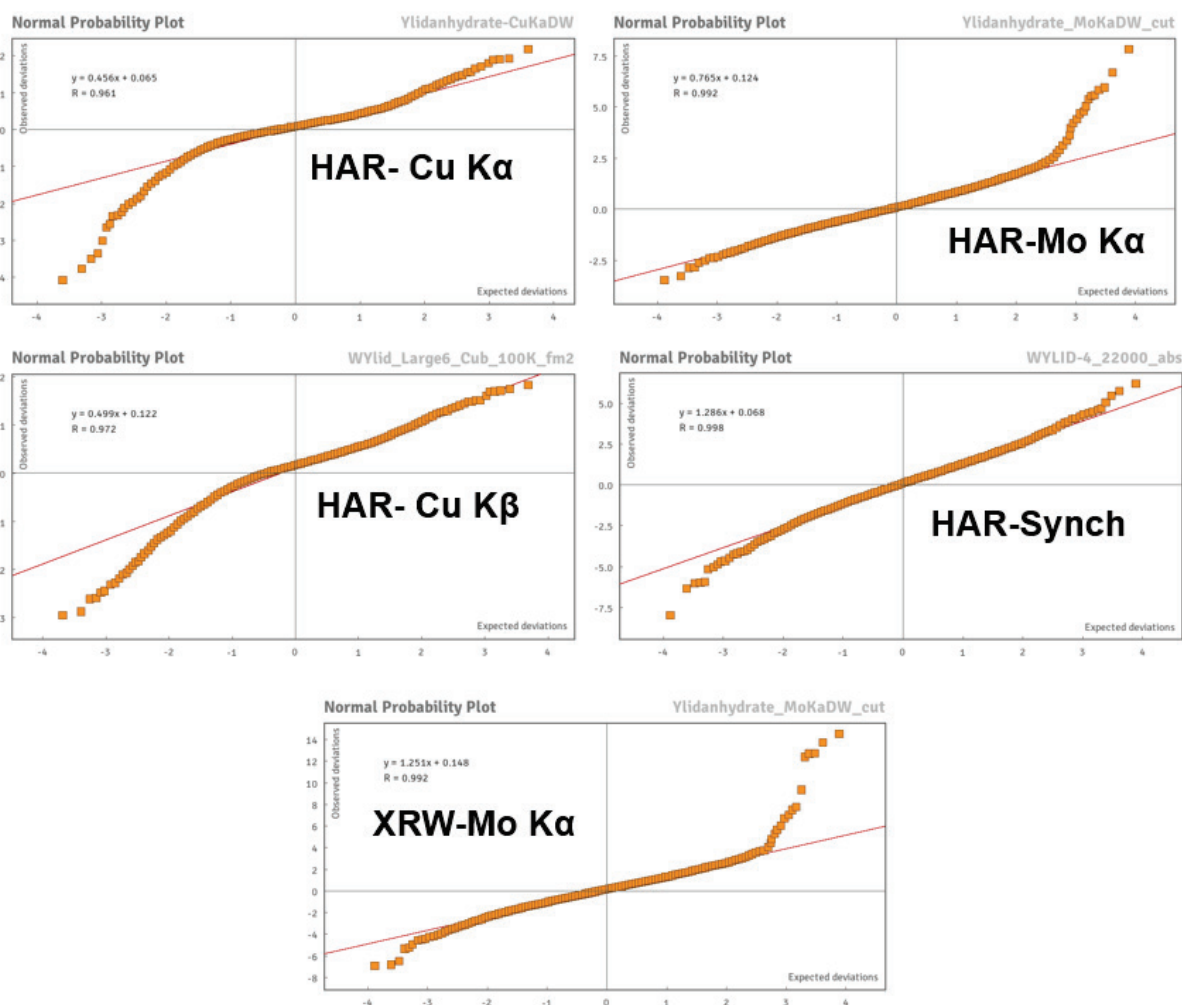


Figure S7: Normal probability plots of the wavefunction based quantum crystallographic models of WYLID.

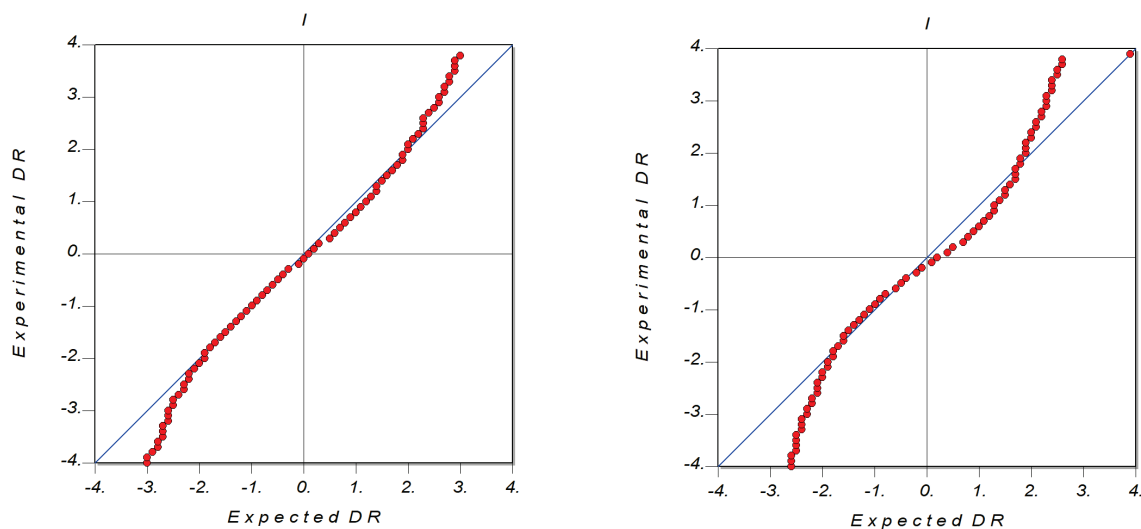


Figure S8: Normal probability plots of the multipolar models of Mo K α (left) and synchrotron (right).

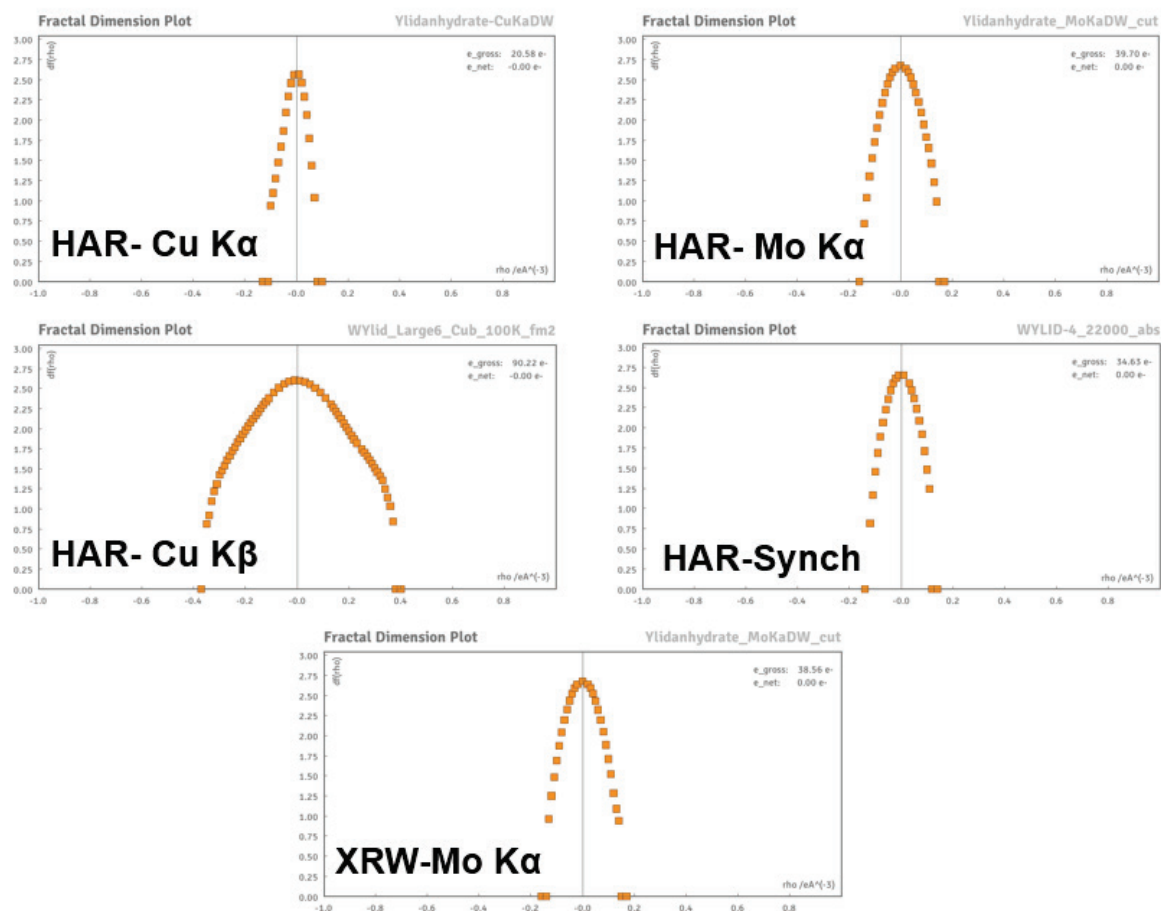


Figure S9: Fractal dimension plots according to Meindl & Henn (2008) of the wavefunction based models of WYLID.

S2.3. Quantum Crystallographic Analysis

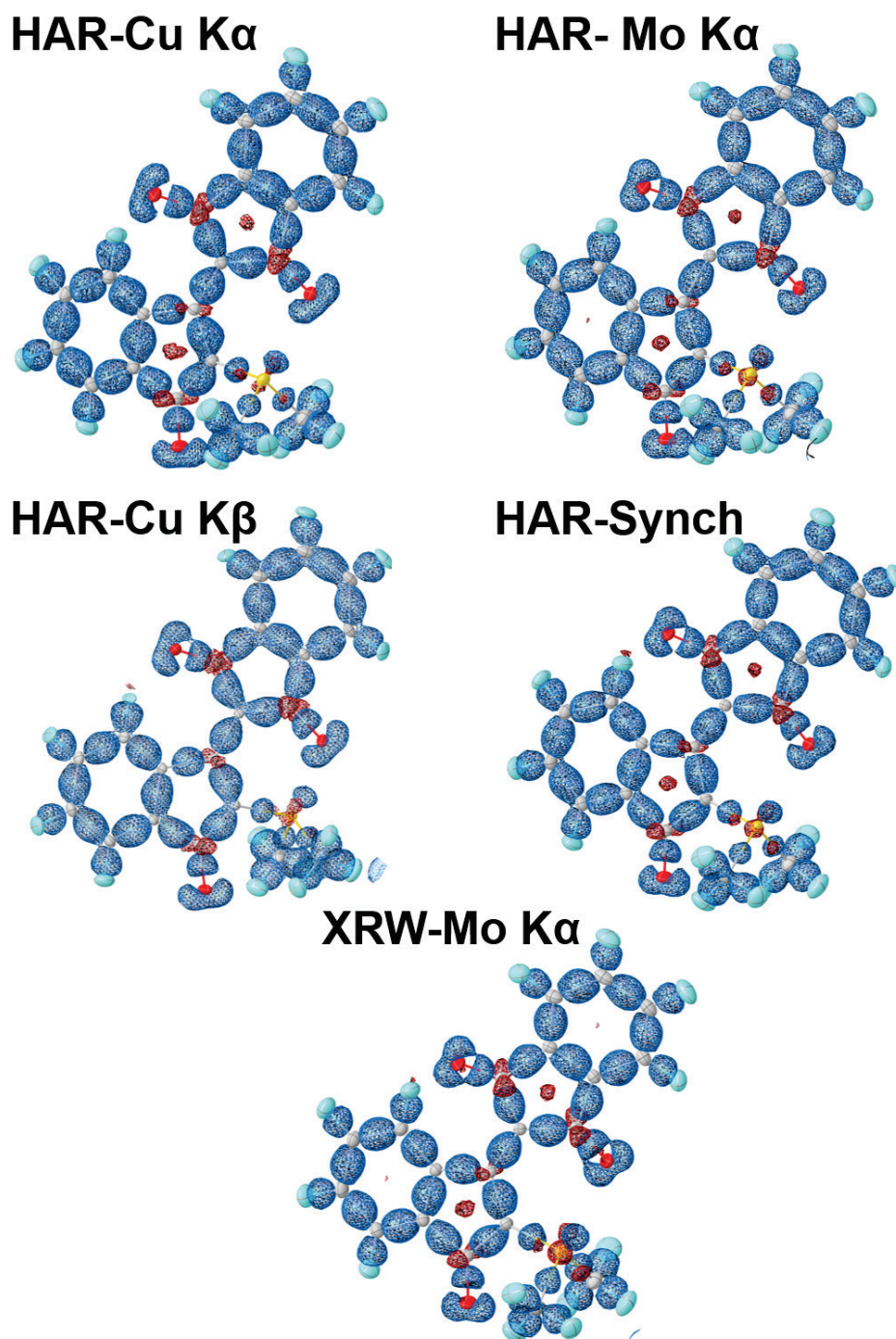
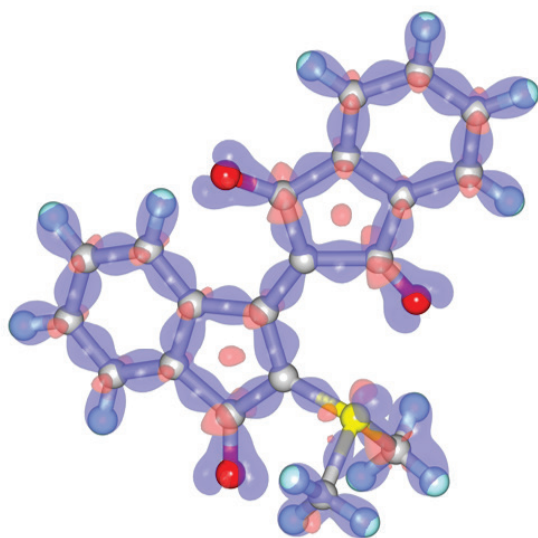


Figure S10: Deformation densities of the wavefunction based models of WYLID at the 0.15 e/Å³ iso surface. Blue indicates positive, red negative residual electron density. Atoms are drawn at a 50% probability.

The deformation density maps (Fig. S10) reveal the valence interaction in WYLID, that the independent atom model could not describe. In particular, the oxygen lone-pairs and the delocalized π -system, π -holes, along the p-holes on the carbonyl carbons are well visible. Despite the lower quality of the data used in the Cu K β model, the deformation density is very similar to the models based on the best possible data sets. This underscores the fact that HAR does not necessitate the use of

high-resolution perfect-quality data, which is typically required for multipolar modelling in order to obtain accurate quantum chemical insights.

MM-Mo K α



MM-Synchrotron

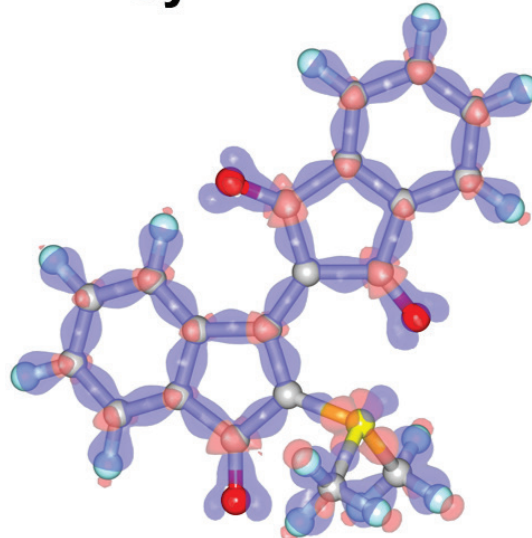


Figure S11: Deformation densities of the MM models of WYLID at the 0.15 e/Å³ iso surface. Blue indicates positive, red negative residual electron density. Atoms are drawn at a 50% probability.

S2.3.1. Laplacians of several bonds from XRW and MM

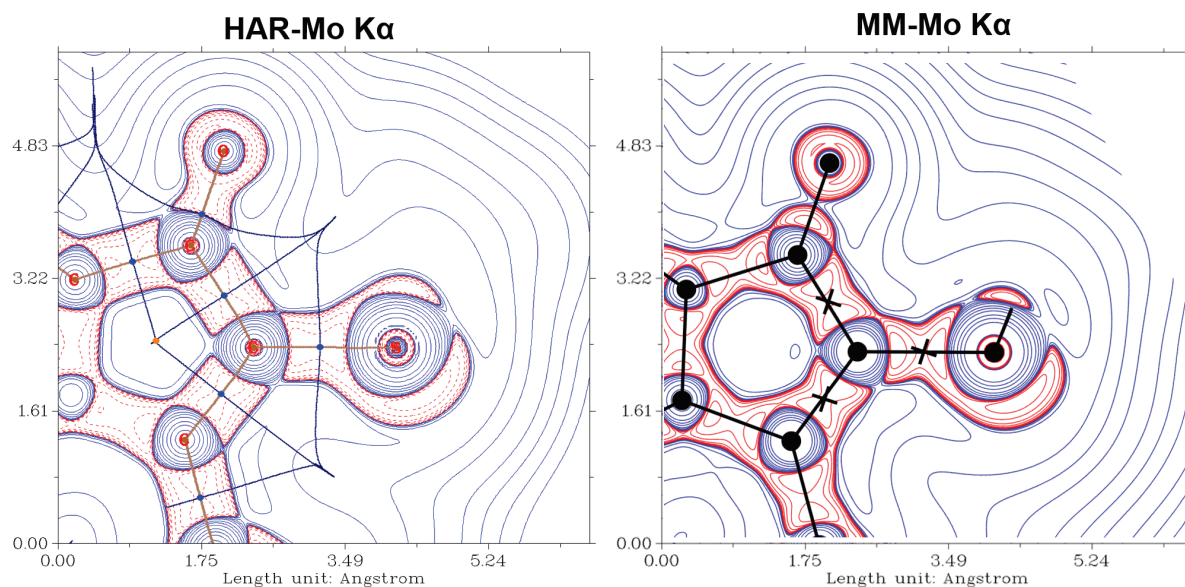


Figure S12: Laplacian (e·Å⁻⁵) of the total electron density around the S1-C3 and C4-O1 bonds from the XRW model (left) and MM model (right) of the Mo K α data set. Contour lines are shown at a logarithmic iso-level to a total of 62 iso-levels. Red indicates a positive and therefore VSCD, blue a negative value of the Laplacian and therefore VSCC. In the left image, BCPs are shown in blue and RCPs in orange, while on the right only the three BCPs from C3 are shown.

Overall, the Laplacian of the total electron density is of similar shape for the MM and XRW models of the Mo K α data set. The main difference is found in the C4-O1 bond, where in the MM model, the Laplacian shows a different structure, reaching positive values after the BCP, while in the XRW model, the Laplacian stays in the negative from C to O.

S2.3.2. Laplacians along the C-O Bonds from MM

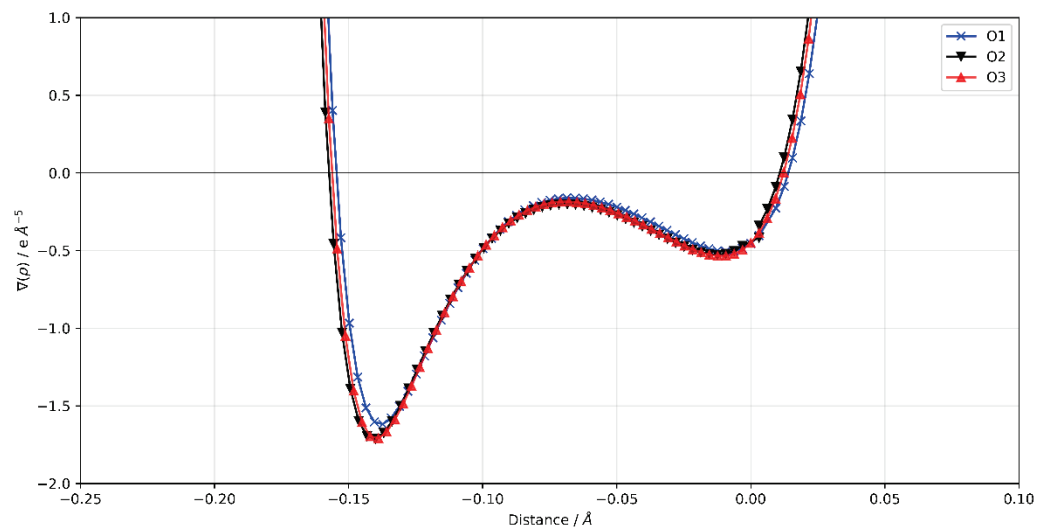


Figure S13: Laplacian ($e\cdot\text{\AA}^{-5}$) of the total electron density along the carbonyl bonds from the MM-Mo K_α model.

S2.3.3. Topological Data at the BCPs from the XRW model

Table S2: Information the BCPs compared between the MM and XRW model analogous to Table 3 in the main text.

Atom pair	MM-Mo K_α		XRW-Mo K_α	
	$\rho_{\text{BCP}} / e\text{\AA}^{-3}$	$\nabla(\rho_{\text{BCP}}) / e\text{\AA}^{-5}$	$\rho_{\text{BCP}} / e\text{\AA}^{-3}$	$\nabla(\rho_{\text{BCP}}) / e\text{\AA}^{-5}$
S1-C3	1.42	-6.81	1.50	-12.6
S1-C2	1.28	-4.95	1.37	-10.7
S1-C1	1.26	-4.36	1.35	-9.69
O1-C4	2.79	-28.25	2.71	-0.55
O2-C13	2.78	-27.96	2.71	-0.51
O3-C20	2.79	-25.55	2.70	-0.51
C11-C12	2.11	-18.26	2.14	-0.24

Table S3: Bader charges in electrons for the HAR models based on the different wavelength data sets. Charges calculated by the *multiwfn* software. (Lu & Chen, 2012)

	Cu Kα	Cu Kβ	Mo Kα	Synchrotron
S1	0.469147	0.455535	0.470229	0.463612
O3	-1.17921	-1.18082	-1.18519	-1.17387
O2	-1.17239	-1.17688	-1.19703	-1.18106
O1	-1.18601	-1.18962	-1.19767	-1.16967
C20	0.962802	0.965077	0.960325	0.958144
C11	0.023775	0.024566	0.021741	0.024433
C12	-0.08348	-0.08699	-0.05147	-0.08457
C19	-0.04938	-0.05175	-0.08643	-0.05093
C3	-0.24157	-0.24082	-0.05039	-0.23717
C5	-0.0466	-0.04725	-0.02898	-0.04737
C9	-0.02307	-0.01702	-0.03355	-0.02929
C10	-0.02812	-0.02938	-0.23764	-0.02789
C13	0.988571	0.99575	0.989896	0.987584
C14	-0.04896	-0.05175	-0.05591	-0.04997
C4	0.989865	0.993727	0.992493	0.984101
C6	-0.02864	-0.01989	-0.03294	-0.03023
C15	-0.02400	-0.02077	-0.02932	-0.02538
C18	-0.02683	-0.02242	-0.03317	-0.03124
C7	-0.03416	-0.03024	-0.0326	-0.03514
C1	-0.15599	-0.11184	-0.15888	-0.16027
C8	-0.04022	-0.02973	-0.04618	-0.04432
C17	-0.03407	-0.03021	-0.03318	-0.03449
C2	-0.14106	-0.10830	-0.14198	-0.14135
C16	-0.03499	-0.01958	-0.03774	-0.04009
H6	0.0734	0.06554	0.077099	0.076201
H7	0.056294	0.050864	0.06448	0.058718
H8	0.057318	0.049159	0.06638	0.060472
H9	0.116442	0.111938	0.110215	0.121045
H18	0.072257	0.068839	0.080857	0.076932
H17	0.058891	0.055767	0.071176	0.060623
H16	0.059023	0.046792	0.071019	0.062094
H15	0.076402	0.071487	0.080271	0.079147
H1a	0.088273	0.111245	0.093833	0.088287
H1b	0.12381	0.07522	0.094955	0.123913
H1c	0.071662	0.06189	0.11969	0.076475
H2a	0.104727	0.107231	0.104487	0.106174
H2b	0.110381	0.097935	0.094412	0.109947
H2c	0.07569	0.056702	0.106688	0.076399

All HAR based models have comparable Bader charges on the atoms in WYLID. Surprisingly, this is also true for the Cu K β data-based model, despite its higher R values, lower multiplicity, lower intensity and larger residuals.

Table S4: Bader charges in electrons for the Mo K α XRW model based on the different wavelength data sets.Charges are calculated by the *multiwfn* software. (Lu & Chen, 2012)

S1	0.453336	C14	-0.05318	H18	0.106701
O3	-1.28532	C20	1.020904	H15	0.103442
O2	-1.23662	C8	-0.11282	H2a	0.134519
O1	-1.24039	C17	-0.03634	H8	0.095375
C6	-0.05575	C11	0.002501	H1a	0.124056
C4	1.062076	C12	-0.04598	H6	0.108222
C15	-0.03131	C13	1.064963	H2b	0.109136
C5	-0.06658	C1	-0.21979	H1b	0.109289
C7	-0.06788	C2	-0.21738	H17	0.114349
C19	-0.03570	C9	-0.05143	H7	0.098269
C3	-0.24682	C10	-0.02910	H1c	0.155698
C18	-0.09335	H9	0.144558	H2c	0.143070
C16	-0.10524	H16	0.080518		

Table S5: Bader charges in electrons for the MM models based on the different wavelength data sets. Chargesare calculated by the *MoPro* software.

	Mo K α	Synchrotron
S1	0.708	0.644
O3	-1.04	-0.829
O2	-1.11	-0.852
O1	-1.002	-0.802
C20	0.786	0.782
C11	0.078	0.029
C12	-0.136	-0.168
C19	-0.08	-0.13
C3	-0.07	-0.123
C5	-0.073	-0.035
C9	-0.407	-0.239
C10	-0.146	-0.099
C13	-0.069	-0.041
C14	-0.051	-0.055
C4	0.839	0.769
C6	-0.051	-0.118
C15	-0.101	-0.003
C18	0.001	-0.001
C7	-0.1	-0.093
C1	0.823	0.77
C8	-0.118	-0.3
C17	-0.138	-0.315
C2	-0.05	-0.009
C16	-0.062	-0.077
H6	0.115	0.059
H7	0.068	0.081
H8	0.073	0.073
H9	0.108	0.1

H18	0.093	0.064
H17	0.05	0.038
H16	0.127	0.071
H15	0.097	0.059
H1a	0.129	0.092
H1b	0.086	0.138
H1c	0.141	0.092
H2a	0.139	0.098
H2b	0.079	0.16
H2c	0.124	0.089

S2.4. Laplacians along the C-O bonds compared to 4-heptone

Figure S12 shows the Laplacians of the total electron density from the XRW-Mo K_α models compared to a geometry optimized DFT calculation (r2SCAN-3c//r2SCAN/def2-TZVP) of the carbonyl reference structure 4-heptanone and its carbonylate form (r2SCAN/def2-TZVPD//r2SCAN/def2-TZVPD). The difference in basis set was chosen to accommodate for the diffuse character in the anionic enolate/carbonylate.

The carbonyl bonds including O1, close to the SMe_2 group, and O2, the most distant carbonyl to the SMe_2 group, are slightly different from the O3 carbonyl group, which shows slightly less valence shell charge concentration at the oxygen atom and slightly more at the carbon atom.

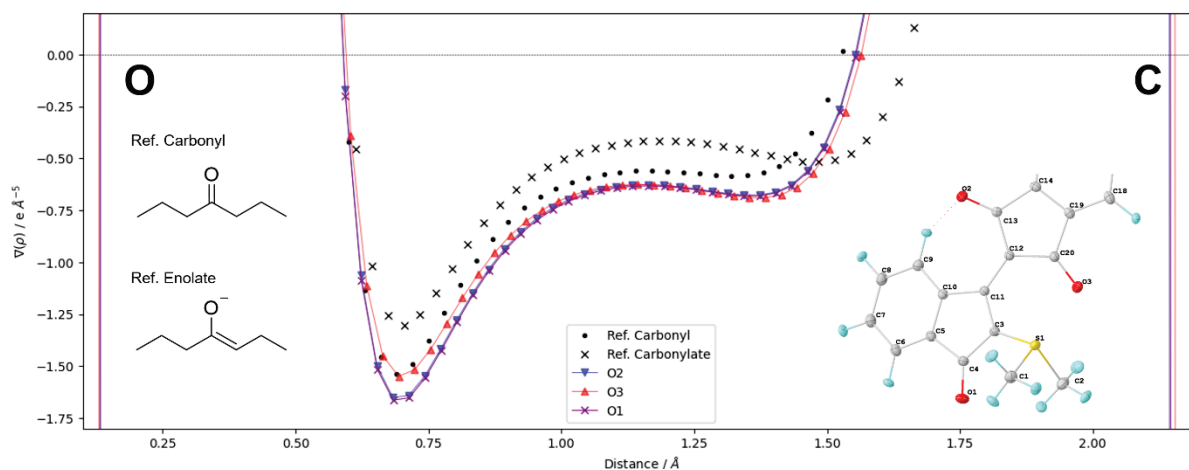


Figure S14: Comparison of the Laplacians of the total electron density along the topological bond path in the three carbonyl groups in WYLID compared to the reference ketone 4-heptanone.

S2.5. Density Functional Theory Calculations of WYLID

Table S6: Geometry after optimization (R2SCAN-3c//R2SCAN/def2-TZVP) for single-point calculation

C	-6.57807	0.930103	-0.42939
C	-6.24253	-0.40103	-0.12085
C	-4.89200	-0.75159	-0.07059
C	-3.91284	0.225512	-0.35214
C	-4.23791	1.535989	-0.67273
C	-5.59709	1.889988	-0.70081
H	-5.89088	2.91713	-0.93956
H	-7.63428	1.216781	-0.45592
H	-3.44834	2.259984	-0.89876
H	-7.02212	-1.13078	0.099336
C	-2.55922	-0.39636	-0.26799
C	-2.81687	-1.79278	0.066871
C	-4.20548	-2.06299	0.152149
C	-4.80538	-3.32877	0.266169
C	-6.15466	-3.67067	0.752079
C	-6.32151	-5.14587	0.534857
C	-5.16612	-5.66145	-0.06501
C	-4.17364	-4.55831	-0.23594
C	-7.40923	-5.96165	0.830095
C	-7.31187	-7.32273	0.499348
C	-6.15380	-7.83909	-0.10522
H	-8.30777	-5.54605	1.29727
H	-8.14993	-7.99417	0.71269
C	-5.06050	-7.00887	-0.39858
H	-6.10604	-8.90540	-0.34879
H	-4.15227	-7.40042	-0.86757
O	-7.00209	-2.95932	1.282293
O	-3.07213	-4.69517	-0.77255
O	-1.48000	0.171573	-0.44005
S	-1.56320	-2.89840	0.549637
C	-0.52291	-1.88726	1.657175
H	0.35112	-2.50275	1.922197
H	-1.12576	-1.68673	2.555835
H	-0.22972	-0.95217	1.160463
C	-0.46891	-3.00148	-0.90026
H	-1.03729	-3.55420	-1.66040
H	0.431913	-3.56069	-0.60309
H	-0.22352	-1.98082	-1.22854

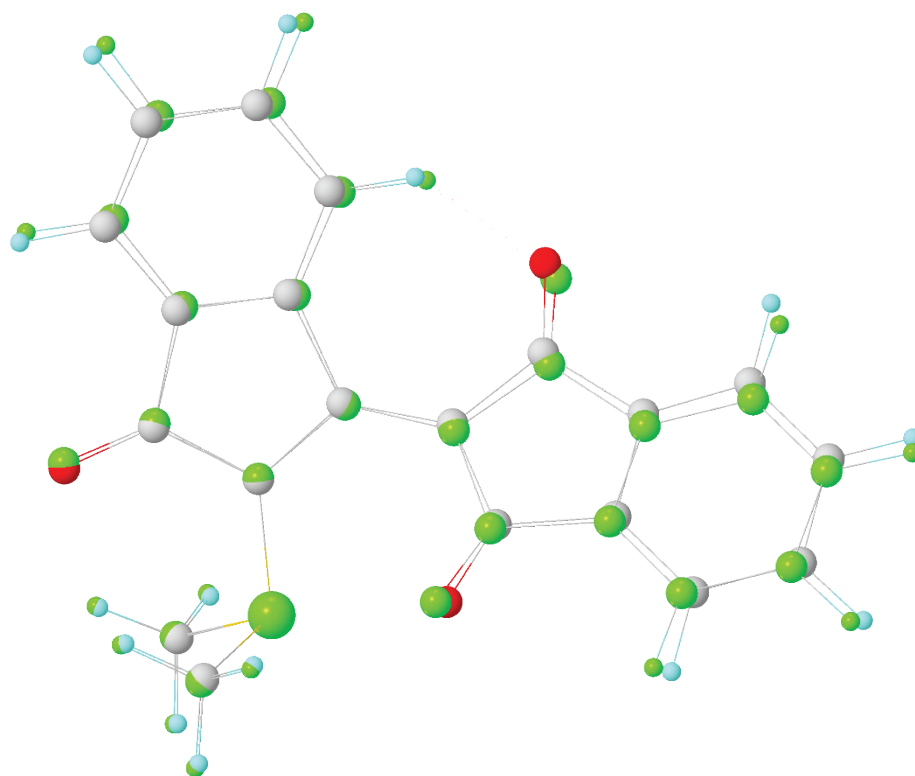


Figure S15: Overlay of the optimized geometry (green) of WYLID and the one obtained in the HAR-Mo K_{α} model.

The comparison of the optimized geometry (r2SCAN-3c) of WYLID and the HAR-Mo K_{α} model from single crystal X-ray diffraction in Fig. S15 shows a close similarity between both geometries. This is consistent with similar charges in the quantum crystallographic evaluation.

Table S7: Bader charges of the DFT calculation of WYLID.

C8	-0.0962
C9	-0.02955
C10	-0.02184
C5	-0.07083
C6	-0.09984
C7	-0.10109
H8	0.125476
H7	0.11177
H6	0.147795
H9	0.117614
C4	0.982127
C3	-0.24394
C11	0.028121
C12	-0.09113
C13	1.000304
C14	-0.05188
C19	-0.06447
C20	0.920088
C15	-0.03008
C16	-0.04121
C17	-0.06941
H15	0.082195
H16	0.064142
C18	-0.08857
H17	0.094581
H18	0.142043
O2	-1.1751
O3	-1.12001
O1	-1.14241
S1	0.40022
C1	-0.17759
H1A	0.08441
H1B	0.093117
H1C	0.125157
C2	-0.26356
H2A	0.182628
H2B	0.098057
H2C	0.17886

S2.6. Comparison of saturated and unsaturated detector synchrotron data sets

The saturation of a modern dual-pixel photon-counting detector, such as the PILATUS3 X 2M, occurs when the number of photons incident upon the detector exceeds the capacity of the electronic readout for each pixel to process. Accordingly, the observed intensity is less than what would be anticipated. This indicates that particularly high-intensity reflections in a diffraction experiment may be influenced by oversaturation, whereas low-intensity reflections are still measured to their full extent.

The data set for the detector saturation can be found in the CSD (2401360 and as “data_Ylideanhydrate-20000eV” data set in this publication) and the raw data with additional models are available at via zenodo.org (DOI: **10.5281/zenodo.14725036**).

Figure S16 shows the measured structure factors F_{obs} versus the calculated structure factors F_{calc} . The result for oversaturation in this plot looks similar to strong multiple scattering events, such as extinction, and can be corrected to some extent by an extinction correction (Sheldrick, 2015). The main difference is that reflections suffering from oversaturation are strongly dispersed compared to classical extinction, where reflections should all fall on the $F_{\text{obs}} / F_{\text{calc}}$ diagonal.

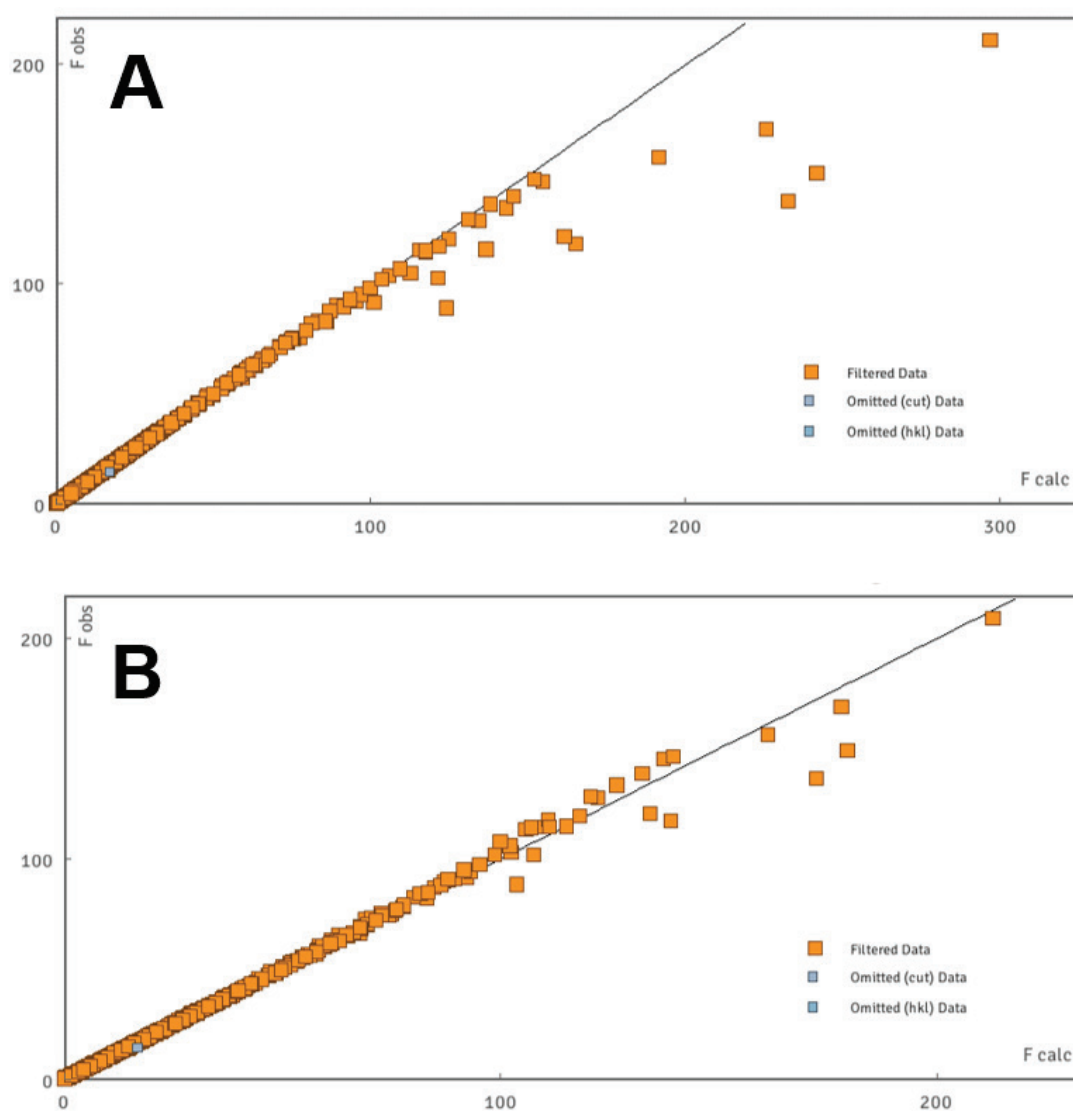


Figure S16: Comparison of the $F_{\text{obs}} / F_{\text{calc}}$ plot exhibiting detector saturation for the strong reflection before (A) and after (B) extinction correction.

Table S8: Bader charges with of the reference model at 22 keV compared to the model of the data set at 20 keV exhibiting detector oversaturation with (“EXTI”) and without (“NoExti”) applied extinction correction as well as their differences to the reference model.

	22keV	NoExti	20 keV- NoExti	EXTI	20 keV- EXTI
S1	0.464	0.469	-0.005	0.469	-0.006
O3	-1.174	-1.178	0.004	-1.178	0.004
O1	-1.181	-1.186	0.005	-1.186	0.005
O2	-1.170	-1.176	0.006	-1.175	0.006
C13	0.988	0.993	-0.006	0.994	-0.006
C10	-0.028	-0.038	0.010	-0.029	0.001
C4	0.984	0.025	0.959	0.990	-0.006
C9	-0.029	-0.034	0.005	-0.024	-0.005
C14	-0.050	-0.029	-0.021	-0.048	-0.002
C11	0.024	-0.026	0.050	0.024	0.001
C19	-0.051	-0.026	-0.025	-0.052	0.001
C5	-0.047	-0.084	0.037	-0.047	-0.001
C3	-0.237	-0.241	0.004	-0.241	0.004
C15	-0.025	-0.046	0.021	-0.028	0.002
C18	-0.031	-0.038	0.007	-0.026	-0.005
C12	-0.085	-0.049	-0.036	-0.085	0.000
C1	-0.160	-0.150	-0.010	-0.150	-0.010
C6	-0.030	0.962	-0.993	-0.026	-0.004
C8	-0.044	-0.024	-0.020	-0.039	-0.005
C2	-0.141	-0.140	-0.001	-0.140	-0.002
C7	-0.035	-0.052	0.016	-0.029	-0.006
C17	-0.034	-0.028	-0.006	-0.033	-0.002
C16	-0.040	-0.025	-0.016	-0.035	-0.005
C20	0.958	0.989	-0.031	0.962	-0.004
H6	0.076	0.070	0.006	0.071	0.005
H7	0.059	0.055	0.004	0.052	0.006
H8	0.060	0.052	0.008	0.056	0.005
H9	0.121	0.118	0.003	0.117	0.004
H18	0.077	0.079	-0.002	0.071	0.006
H17	0.061	0.061	0.000	0.059	0.002
H16	0.062	0.060	0.002	0.060	0.003
H15	0.079	0.071	0.008	0.078	0.001
H1a	0.088	0.087	0.002	0.086	0.002
H1b	0.124	0.123	0.000	0.123	0.001
H1c	0.076	0.069	0.008	0.068	0.008
H2a	0.106	0.103	0.003	0.104	0.002
H2b	0.110	0.111	-0.001	0.110	0.000
H2c	0.076	0.075	0.002	0.075	0.001
SUM	-2E-06	-3E-05	3.1E-05	0.000	1.8E-16

In general, the errors introduced into the HAR model of the synchrotron data by the detector saturation are small. When an extinction correction is applied, the difference is almost imperceptible.

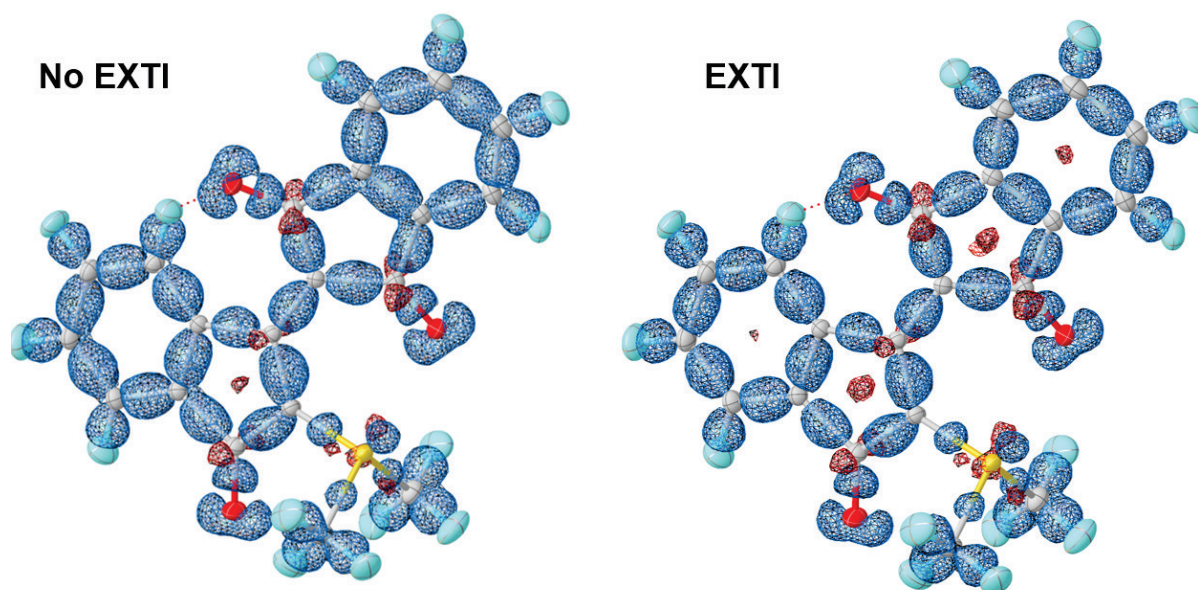


Figure S17: Deformation density at the $0.15 \text{ e}/\text{\AA}^3$ iso level of WYLID using the detector saturating data set of WYLID. Blue indicates positive, red negative deformation density.

While the deformation density is similar in both cases, fine features such as the π -holes of the aromatic ring systems are absent or less pronounced without extinction correction. This suggests that extinction correction improves the quantum crystallographic models when the detector is oversaturated and could generally be applied *a posteriori*. However, saturation of the detector should be avoided by attenuating the beam as much as possible.

S2.7. Comparison of HAR results between r2SCAN and α B97X**Table S9:** Comparison of Bader charges between the HAR-synchrotron models using either the meta GGA functional r2SCAN or the hybrid function ω B97X. In both cases, the def2-TZVP basis sets were used.

Level of DFT	r2SCAN	α B97X
Formula	C ₂₀ H ₁₄ O ₃ S	
Mass / g mol ⁻¹	334.40	
Crystal size / mm ³	0.1 x 0.1 x 0.1	
Space group	<i>Pbca</i>	
<i>a</i> / Å	14.54072(7)	
<i>b</i> / Å	9.17361(2)	
<i>c</i> / Å	23.40310(7)	
<i>V</i> / Å ³	3121.7(2)	
<i>D</i> / g cm ⁻³	1.423	
μ / mm ⁻¹	0.122	
θ range / °	2.24–40.40	
<i>T</i> / K	100	
Resolution / Å	0.55	
<i>I</i> / σ (<i>I</i>)	95.3	
<i>R</i> _{int} / %	4.88	
Total reflections	508696	
Unique reflections > 4 σ	8745	
Completeness / %	100.0	
Model Indicators		
Nr. refined parameters	444	444
Goodness-of-fit	1.070	1.051
<i>R</i> indices, <i>I</i> > 2 σ / %	1.00	1.01
<i>R</i> indices (all data) / %	1.39	1.42
<i>wR</i> ₂ indices / %	1.83	1.95
Diff. peak, hole / e Å ⁻³	0.106, -0.117	0.105, -0.202

The resulting structures from HAR on r2SCAN and ω B97X were identical to the degree that we could not spot any parts of the structure that were not completely overlaid.

Table S10: Comparison of Bader charges between the HAR-synchrotron models using either the meta GGA functional r2SCAN or the hybrid function ω B97X. In both cases, the def2-TZVP basis sets were used.

	r2SCAN	ω B97X	r2SCAN - ω B97X
S1	0.464	0.438	0.026
O3	-1.174	-1.206	0.033
O1	-1.181	-1.207	0.026
O2	-1.170	-1.198	0.028
C13	0.988	1.012	-0.024
C10	-0.028	-0.028	0.000
C4	0.984	1.012	-0.028
C9	-0.029	-0.022	-0.007
C14	-0.050	-0.053	0.003
C11	0.024	0.034	-0.009
C19	-0.051	-0.054	0.003
C5	-0.047	-0.049	0.002
C3	-0.237	-0.238	0.001
C15	-0.025	-0.019	-0.006
C18	-0.031	-0.026	-0.005
C12	-0.085	-0.099	0.014
C1	-0.160	-0.125	-0.035
C6	-0.030	-0.022	-0.008
C8	-0.044	-0.038	-0.006
C2	-0.141	-0.109	-0.032
C7	-0.035	-0.031	-0.005
C17	-0.034	-0.028	-0.006
C16	-0.040	-0.036	-0.005
C20	0.958	0.980	-0.022
H6	0.076	0.073	0.003
H7	0.059	0.056	0.003
H8	0.060	0.057	0.003
H9	0.121	0.119	0.002
H18	0.077	0.074	0.002
H17	0.061	0.054	0.006
H16	0.062	0.056	0.006
H15	0.079	0.076	0.004
H1a	0.088	0.082	0.006
H1b	0.124	0.119	0.005
H1c	0.076	0.071	0.006
H2a	0.106	0.100	0.006
H2b	0.110	0.105	0.005
H2c	0.076	0.070	0.006

To estimate the influence of the choice of the functional used in the HAR procedure a second HAR was performed using the synchrotron data set at 22 keV. We chose to compare the meta-GGA functional r2SCAN with the hybrid functional ω B97X, which includes part of a Hartree-Fock calculation. The incorporation of Hartree-Fock into the HAR procedure resulted in a greater overall charge on the S and O atoms, as well as on the carbonyl C atoms.

S2.8. CSD search using MOGUL

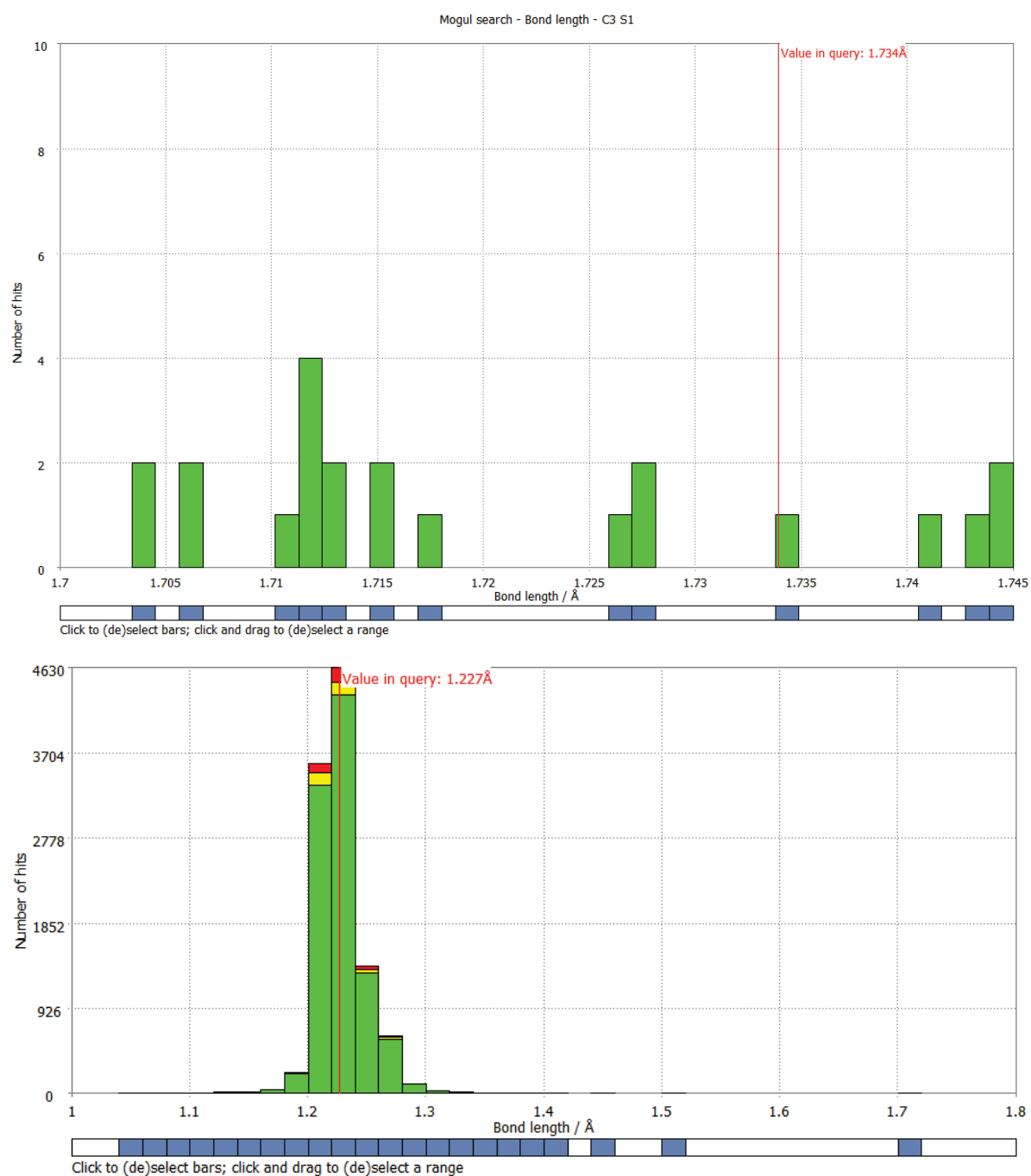


Figure S18: Results of the MOGUL search for the S1-C3 (top, 23 hits) and O1-C4 (bottom, 10670 hits) bond lengths of the HAR-Mo K_α structure compared to similar structures.

s2.9. Hirshfeld Surface Analysis of WYLID

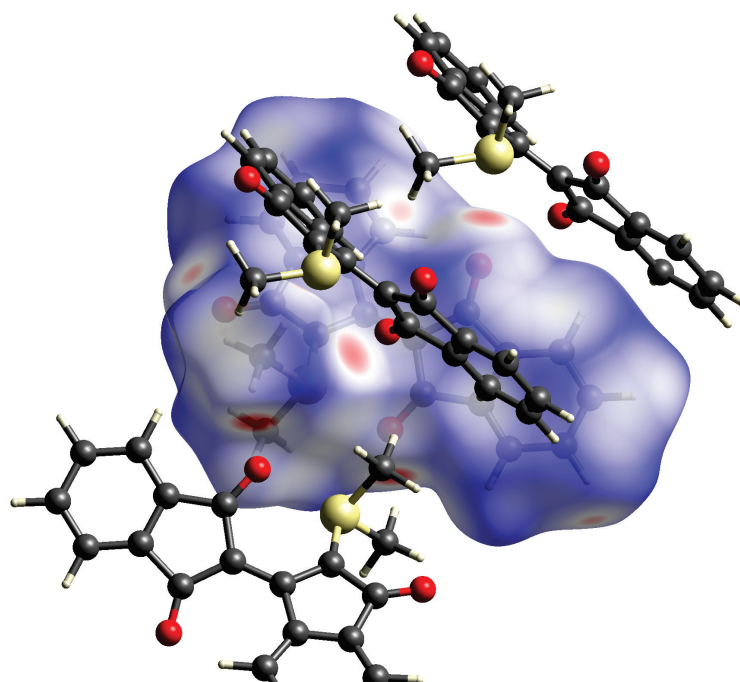


Figure S19: Hirshfeld surface at an iso level of 0.5 of WYLID with closest contacts imprinted on its surface and the closest interacting symmetry equivalents.

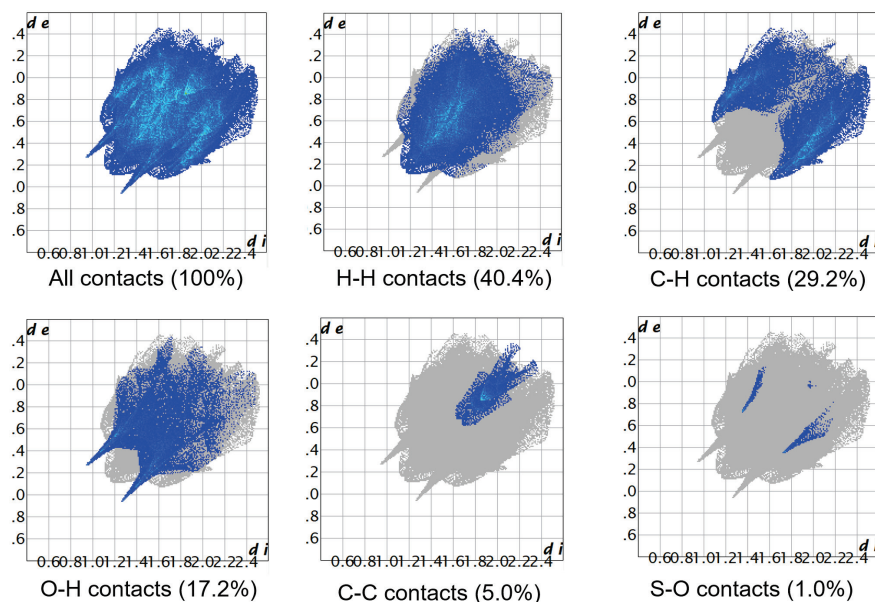


Figure S20: Fingerprint plots of the closest contacts of WYLID on the Hirshfeld surface.

The Hirshfeld surface mapped with d_{norm} (Fig. S19) shows the closest intermolecular contacts in the crystal packing of WYLID. The interactions are predominantly of the O...H and O...S type. While the latter is one of the closest contacts, its total contribution to all interactions is quite small, accounting for only 1% of the contacts (Fig. S20). The main interactions are of the H...H and C...H type.

S2.10. Anomalous Dispersion Refinement

Table S11: Anomalous dispersion parameters from different sources for S at Cu K α excitation wavelength compared to experimental values obtained by ADR in Olex2. (Meurer *et al.*, 2022)

	f' / e	f'' / e
WYLID HAR-Cu K α	0.36(1)	0.69(2)
YLID Balmohammadi <i>et al.</i> (2025), Avg.	0.27(5)	0.58(4)
Henke <i>et al.</i> (1982)	0.3354	0.5514
Sasaki (1989)	0.328	0.590
Brennan & Cowan (1992)	0.3338	0.5584

Table S11 shows the values obtained by ADR compared to those of Balmohammadi *et al.* (2025) over nine different data sets and temperatures. Interestingly, while f'' is closer to the tabulated values and f' differs more in the Balmohammadi et al. data sets, the opposite is true for our measurement on WYLID.

S2.11. Crystallographic Details of Bindandione

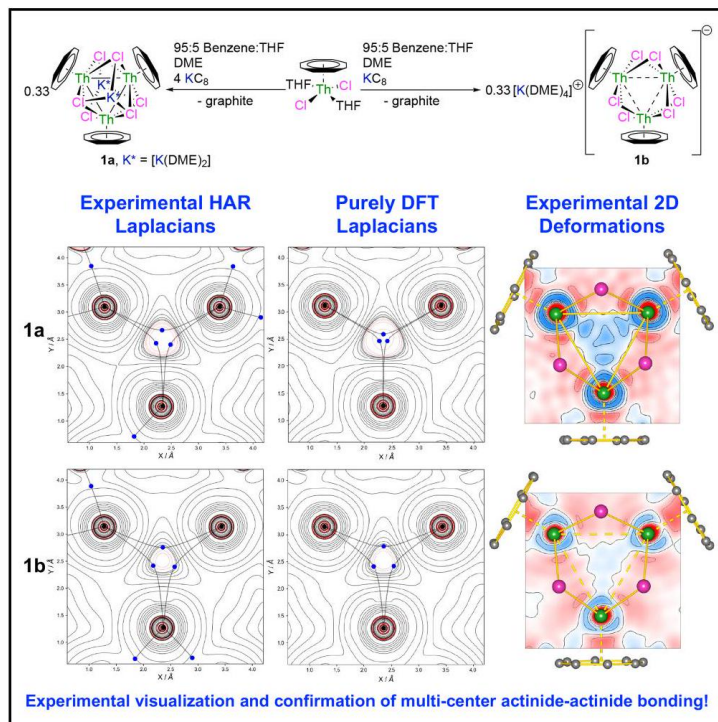
Table S12: Crystallographic data of the Bindandione data set as well as the quality indicators of its HAR model.

Formula	C ₃₆ H ₂₀ O ₆
Mass / g mol ⁻¹	548.556
Crystal size / mm ³	0.1 x 0.1 x 0.1
Space group	<i>Fdd2</i>
a / Å	18.0174(1)
b / Å	20.922(2)
c / Å	26.0847(2)
V / Å ³ /	9832.94(13)
D / g cm ⁻³	1.482
μ / mm ⁻¹	0.827
θ range / °	3.65 – 75.32
T / K	100.0(1)
Resolution / Å	0.80
I/σ(I)	85.2
Rint / %	4.52
Total reflections	102230
Unique reflections > 4σ	5027
Completeness / %	100.0
Quality Indicators	
Nr. refined parameters	559
Goodness-of-fit	1.079
R indices, I > 2σ / %	1.60
R indices (all data) / %	1.63
wR2 indices / %	3.67
Diff. peak, hole / e Å ⁻³	0.096, -0.090
Hooft	0.00(3)

S3. References

- Balmohammadi, Y., Malaspina, L. A., Nakamura, Y., Cametti, G., Andrzejewski, M., Siczek, M. & Grabowsky, S. (2025). *Sci. Rep.* In the press.
- Bourhis, L. J., Dolomanov, O. V., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2015). *Acta Cryst. A* **71**, 59–75.
- Brennan, S. & Cowan, P. L. (1992). *Rev. Sci. Instrum.* **63**, 850–853.
- Capelli, S. C., Bürgi, H.-B., Dittrich, B., Grabowsky, S. & Jayatilaka, D. (2014). *IUCrJ* **1**, 361–379.
- Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
- Furness, J. W., Kaplan, A. D., Ning, J., Perdew, J. P. & Sun, J. (2020). *J. Phys. Chem. Lett.* **11**, 8208–8215.
- Gasevic, T., Stückrath, J. B., Grimme, S. & Bursch, M. (2022). *J. Phys. Chem. A* **126**, 3826–3838.
- Guillot, B. (2012). *Acta Cryst. A* **68**, 204–204.
- Henke, B. L., Gullikson, E. M. & Davis, J. C. (1993). *At. Data Nucl. Data Tables* **54**, 181–342.
- Hirshfeld, F. L. (1977). *Theoret. Chim. Acta* **44**, 129–138.
- Jayatilaka, D. & Grimwood, D. J. (2003). Vol. 2660, *Computational Science — ICCS 2003*, edited by P. M. A. Sloot, D. Abramson, A. V. Bogdanov, Y. E. Gorbachev, J. J. Dongarra & A. Y. Zomaya. pp. 142–151. Berlin, Heidelberg: Springer Berlin Heidelberg.
- Jelsch, C., Guillot, B., Lagoutte, A. & Lecomte, C. (2005). *J. Appl. Cryst.* **38**, 38–54.
- Kleemiss, F., Dolomanov, O. V., Bodensteiner, M., Peyerimhoff, N., Midgley, L., Bourhis, L. J., Genoni, A., Malaspina, L. A., Jayatilaka, D., Spencer, J. L., White, F., Grundkötter-Stock, B., Steinhauer, S., Lentz, D., Puschmann, H. & Grabowsky, S. (2021). *Chem. Sci.* **12**, 1675–1692.
- Lu, T. & Chen, F. (2012). *J. Comput. Chem.* **33**, 580–592.
- Meindl, K. & Henn, J. (2008). *Acta Cryst. A* **64**, 404–418.
- Meurer, F., Dolomanov, O. V., Hennig, C., Peyerimhoff, N., Kleemiss, F., Puschmann, H. & Bodensteiner, M. (2022). *IUCrJ* **9**, 604–609.
- Neese, F., Wennmohs, F., Becker, U. & Riplinger, C. (2020). *J. Chem. Phys.* **152**, 224108.
- Rigaku Oxford Diffraction (2024). *CrysAlisPro Software System*, Wroclaw, Poland
- Sasaki, S. (1989). KEK Report 88–14, pp. 1–136. Ibaraki-keri, Japan: National Laboratory for High Energy Physics.
- Sheldrick, G. M. (2015). *Acta Cryst. A* **71**, 3–8.
- Weigend, F. & Ahlrichs, R. (2005). *Phys. Chem. Chem. Phys.* **7**, 3297.

6 Actinide-actinide bonding visualized by Hirshfeld atom refinement



Preface

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Abstract

The concept of covalency in chemical bonding has been established since 1939. However, the essential details are often difficult to determine and agree on because few spectroscopic and structural methods experimentally measure covalency, and each method has advantages and disadvantages, so none is a panacea. Quantum crystallography X-ray charge density determination could be the most powerful structural determination method, but its stringent requirements have prevented routine implementation, especially in heavy f-element complexes. Hirshfeld atom refinement (HAR) has begun to emerge as an alternative, potentially more accessible, quantum crystallography approach for experimentally visualizing covalency, but it has remained limited and technically impracticable regarding heavy element complexes, such as actinides, due to the challenges of partitioning and modeling core and valence electron densities in relativistic regimes. Here, we apply HAR to two extreme test cases of clusters containing three proximate heavy actinides exhibiting multi-center thorium-thorium bonding. We demonstrate exceptional agreement between experimental HAR and purely density functional theory analyses, thus visualizing and hence confirming the presence of the thorium-thorium bonding and resolving a longstanding challenge. By visualizing covalency in two challenging test cases, this study paves the way to making experimental HAR visualization of chemical bonding as routine

as regular crystal structure refinements and applicable across the chemical and materials sciences.

6.1 Introduction

The concept of covalency in chemical bonding has been established since 1939.¹ However, the essential details are often difficult to determine and agree on because few spectroscopic and structural methods experimentally measure covalency, and each method has advantages and disadvantages, so none is a panacea.^{2–4}

Since X-rays are scattered by electron density, X-ray diffraction patterns contain valuable information on the total electron density within a crystal.^{5,6} A powerful method to experimentally access the electron density is through quantumcrystallography,^{7,8} which seeks to model the electron density directly from the X-ray scattering data of a crystal.⁹ Traditionally, this has been accomplished through charge density multipolar modeling, in which the spherical atomic electron density is expanded in a series of atom-centered spherical harmonics, enabling direct modeling of bonding features. However, this requires that many additional parameters be refined, so obtaining high-resolution data is essential in order to maintain a statistically robust data-to-parameter ratio.⁷ This in turn necessitates exceptionally stringent requirements on crystal and data quality and data collection, including little or no disorder, preferably no lattice solvent, diffraction to very wide angles, collection at nonroutine low temperatures, minimal absorption and extinction effects, very low R values, and preferably synchrotron radiation rather than normal laboratory sealed-sources. Additionally, the multipole refinement must also be able to discern core and valence electron densities with great accuracy. These conditions accumulate to be so stringent that they are rarely met by crystalline molecular species, especially those with large, sensitive, or heavy-element-containing molecules such as the f-elements.^{10–17}

An emerging, potentially more accessible quantum crystallography alternative to multipolar modeling is Hirshfeld atom refinement (HAR).^{18–21} HAR combines aspherical atomic scattering factors derived from computed wavefunctions with experimental diffraction data, enabling refinement of geometries and even hydrogen atom positions with accuracy similar to that of neutron diffraction.²² Critically, HAR is less demanding in terms of crystal and data requirements.²³ Since chemistry occurs at the valence shell level, and low-angle diffraction data is the most significant source of this information, it can be obtained from standard resolution measurements using conventional sealed-tube X-ray sources at temperatures of 100 K – 150 K.²⁴ HAR has been applied to the study of aurophilic interactions,²⁵ but it has remained unclear whether it could be extended as far as actinide bonding rather than focusing on associated ligands in actinide complexes.²⁶ Generally, it has remained limited^{26–29} and technically impracticable with heavy elements such as actinides due to the challenges of partitioning and modeling core and valence electron densities in relativistic regimes. However, as valence information, electron correlation and scalar relativistic effects are significantly important in low-order reflections, but negligible in the high-order region.²⁷

Here, we apply HAR to two extreme test cases of clusters containing three proximate heavy actinides exhibiting multi-center thorium-thorium (Th-Th) bonding.^{30–32} We demonstrate exceptional agreement between experimental HAR and purely density functional theory analyses,^{33,34} thus visualizing the Th-Th bonding and resolving a longstanding challenge. By visualizing covalency in two challenging test cases, this advance paves the

way for making experimental HAR visualization of chemical bonding as routine as regular crystal structure refinements and applicable across the chemical and materials sciences.

6.2 Results and discussion

Recently, a class of trithorium clusters, $[\{(\eta^8 - \text{C}_8\text{H}_8) \text{ThCl}_2\}_3]^{2-}$ ($[\mathbf{1}]^{2-}$) and $[\{(\eta^8 - \text{C}_8\text{H}_8) \text{ThCl}_2\}_3]^{1-}$ ($[\mathbf{1}]^{1-}$), which exhibit three-center two- and one-electron Th-Th bonding, respectively, have emerged.^{30–32} While experimental UV-vis-NIR and EPR spectroscopies and magnetic susceptibility data on these clusters have provided insights into the consequential effects of their Th-Th bonding, these techniques do not enable direct visualization of the Th-Th bonds. Instead, visualization has relied on purely quantum-mechanical (QM) calculations,^{30–34} which, when describing elements in an appreciable relativistic regime, can be open to theoretical debate and dramatically differing interpretations.^{30–42} As a physical observable, the total electron density, which corresponds to the square of the many-electron wavefunction, offers a direct and unambiguous connection between experiment and quantum theory, providing a foundation for analyzing chemical bonding. Since $[\mathbf{1}]^{2-}$ and $[\mathbf{1}]^{1-}$ each contain three $Z = 90$ elements in close proximity, but the multicenter trithorium bonding involves only one or two delocalized electrons, extending HAR analysis to such complexes would establish the potential of this method in exceedingly challenging scenarios, and hence demonstrate and encourage its applicability to any molecular species.

The complexes $[\{\text{Th}(\eta^8 - \text{C}_8\text{H}_8)(\mu_3 - \text{Cl})_2\}_3\{\text{K}(\text{DME})_2\}_2]$ (**1a**) and $[\text{K}(\text{DME})_4][\{\text{Th}(\eta^8 - \text{C}_8\text{H}_8)(\mu_3 - \text{Cl})_2\}_3]$ (**1b**)-containing $[\mathbf{1}]^{2-}$ and $[\mathbf{1}]^{1-}$, respectively-were prepared by reactions between $[(\eta^8 - \text{C}_8\text{H}_8) \text{Th}(\text{Cl})_2(\text{THF})_2]$ and KC_8 in 1:4 and 1:1 ratios, respectively, in 95:5 benzene:THF solvent mixtures, Figure 6.1A.³² After workup and exposure to DME, these clusters are reproducibly isolated as dark blue microcrystalline powders. The characterization data (Figures S1-S60; Tables S1-S27) unequivocally support the proposed formulations. The magnetism of **1a** and **1b** are discussed in detail elsewhere,³² but in particular, for **1a** and **1b**, characteristic inelastic scattering bands corresponding to Th-Th vibrations are found in their Raman spectra at 73, 87, and 135 and 67, 92, and 137 cm^{-1} ,^{30–32} and Robin-Day class III intervalence charge transfer bands are evidenced at 16,252 and 16,181 cm^{-1} ($\Gamma_{\text{av}} = 0.63$ for both) in their UV-vis-NIR spectra, respectively.^{31,32} EPR spectroscopy on **1b** finds g values that are characteristic of low-valent Th-Th bonding ($g_x = g_y \approx 1.98$; $g_z \approx 1.94$),^{31,32} and little variation of g values over 5 K – 270 K confirms retention of $S = 1/2$ character over all experimentally relevant temperatures.

Dark blue crystals of **1a** and **1b** were grown by diffusion of pentane into DME solutions at -30°C . We collected Mo and Cu K α X-ray data sets for **1a** and **1b**-to rule out absorption and anomalous dispersion effects-in routine temperature ranges (100 K – 155 K), then centered HAR analysis on the Mo K α data sets (**1aMo** and **1bMo**); details of the Cu K α HAR data sets (**1aCu** and **1bCu**) and regular independent atom model (IAM) data sets (**1a** and **1b**) can be found in the supplemental information. A key advantage of the HAR procedure is its experimentally based geometry. QM calculations are generally based on optimized geometries, which depend on the theoretical method employed. In contrast, HAR is based on an experimental geometry using spherical atomic form factors-the IAM^{8,20} which the procedure then improves by using calculated, nonspherical atomic form factors.^{18,43} Specifically, an IAM geometry is used in a QM single point energy

calculation, and the resulting wavefunction is partitioned into non-spherical atom form factors that feed into the next crystallographic refinement. This procedure is iterated to convergence, generating a wavefunction and thus an electron density description from the QM calculation at the final HAR geometry. The dynamic deformation density of the HAR is the combination of crystallographic anisotropic displacement parameters and the static QM deformation, which identifies the difference from purely spherical electron density distributions. Therefore, the geometry resulting from the HAR procedure is based on a combination of experiment and theory, and we found that employing an experimental geometry was the dominant and essential property for arriving at an accurate theoretical description.

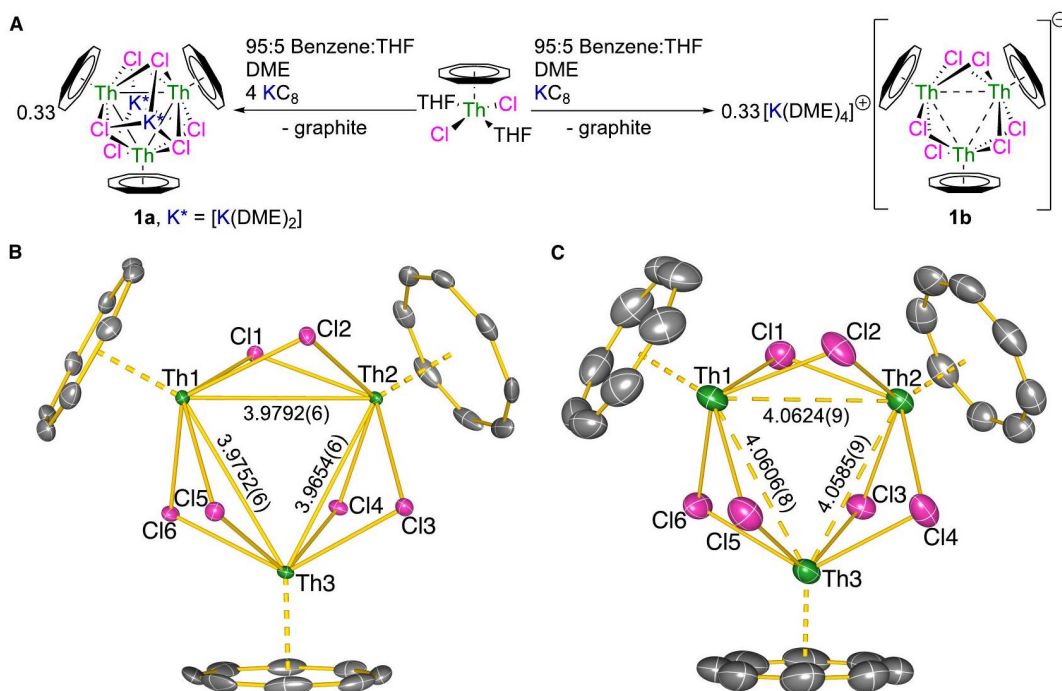


Figure 6.1: Synthesis and structures of **1a** and **1b**

(A) Synthesis of **1a** and **1b**.

(B) Trithorium core ($[1]^{2-}$) of **1a** (HAR models, **1aMo**) with key metrical data (Å) obtained at 100 K and displacement ellipsoids at 50%.

(C) Trithorium core ($[1]^{1-}$, HAR models, **1bMo**) of **1b** with key metrical data (Å) obtained at 100 K and displacement ellipsoids at 50%.

Hydrogen atoms and $\{K(DME)_n\}^{1+}$ ($n = 2(\mathbf{1a}), 4(\mathbf{1b})$) are omitted for clarity. Solid Th-Th bonds indicate three-center two-electron bonding; dashed Th-Th bonds indicate three-center one-electron bonding.

The cluster cores of **1a** ($[1]^{2-}$) and **1b** ($[1]^{1-}$) are shown in Figures 6.1B and 6.1C, and they exhibit Th-Th distances that are respectively similar to the analogous distances found in $[\{Th(\eta^8-C_8H_8)(\mu_3-Cl)_2\}_3\{K(THF)_2\}_2]_\infty^{30}$ and $[K(2.2.2-cryptand)][\{Th(\eta^8-C_8H_8)(\mu_3-Cl)_2\}_3]^{31}$. The Th-Th distances in $[1]^{1-}$ are $\sim 0.08\text{\AA}$ longer than the Th-Th distances in $[1]^{2-}$, consistent with their core one- and two-electron natures.

Laplacian plots of the HAR- and purely QM-derived electron densities of the Th_3 -planes in the cores of $[1]^{2-}$ and $[1]^{1-}$ are shown in Figures 6.2A, 6.2B, 6.2D, and 6.2E. The HAR

and purely QM- derived QTAIM data are generally in good agreement across the whole molecule, noting that small variations are to be expected for the slightly different experimental and computational geometries that modulate the electron densities and hence bond critical point (BCP) properties. For $[1]^{2-}$ and $[1]^{1-}$, these topological analyses reveal three Th-Th BCPs, with associated bond paths (BPs) and central ring critical points (RCPs), experimentally confirming the presence of Th-Th BCPs that had been computationally predicted,³⁰ subsequently questioned,³⁷ then reaffirmed when an extended computational BCP search routine was employed.³³ For each HAR-/QM-derived pair of plots, the agreement is remarkably good and, reflecting their analogous three-center Th-Th bonding, the topology of the electron density for both species is quite similar. Reassuringly, the HAR-derived data confirm the previous finding from purely QM studies that the BPs are more curved and centralized for the two-electron species than for the one-electron species.^{30–33} For $[1]^{1-}$, the area of significant valence shell charge accumulation in the Th₃ center is marginally smaller than for $[1]^{2-}$, consistent with their respective three-center one-electron and three-center two-electron bonding motifs. Specifically, toward the BCPs and, more generally, in the central regions of the trithorium rings, the Laplacians of the total electron density become negative for $[1]^{2-}$ and $[1]^{1-}$. For $[1]^{2-}$, this reaches up to $-0.06e/\text{Bohr}^5$, compared with $-0.03e/\text{Bohr}^5$ for $[1]^{1-}$, indicating stronger Th-Th bonding in the former than the latter.

The Th-Th BCPs in $[1]^{2-}$ show stronger bonding features ($\rho(r) = 2.06 \times 10^{-2}e/\text{Bohr}^3$, $\nabla^2\rho(r) = -5.43 \times 10^{-3}e/\text{Bohr}^5$) than in $[1]^{1-}$ ($\rho(r) = 1.33 \times 10^{-2}e/\text{Bohr}^3$, $\nabla^2\rho(r) = -0.35 \times 10^{-3}e/\text{Bohr}^5$), but both indicate relatively weak covalent bonding. This is also reflected by the values at the central RCP for $[1]^{2-}$ ($\rho(r) = 2.11 \times 10^{-2}e/\text{Bohr}^3$, $\nabla^2\rho(r) = -6.12 \times 10^{-3}e/\text{Bohr}^5$) and $[1]^{1-}$ ($\rho(r) = 1.35 \times 10^{-2}e/\text{Bohr}^3$, $\nabla^2\rho(r) = -0.30 \times 10^{-3}e/\text{Bohr}^5$). Importantly, the experimentally derived Th-Th bond topology data are in good agreement with prior purely QM-derived metrics,^{30–33} whereas in contrast, previously computed and charge density multipole derived BCP agreements were poor, which was attributed to deficiencies in the experimental diffraction data.¹³ Integrating the total electron density in a 1.0 Bohr sphere ($0.5292\text{\AA}$) positioned at the geometric center of the Th₃ rings of $[1]^{2-}$ and $[1]^{1-}$ reveals electron densities of 0.087 and 0.055 e, respectively, which is a 1.6 : 1 ratio that, factoring in experimental uncertainties, is approaching the 2:1 ratio expected for $[1]^{2-}$ and $[1]^{1-}$, respectively.

The topologies of the HAR-derived Th₃-plane electron densities of $[1]^{2-}$ and $[1]^{1-}$ are also fully consistent with their respective electron localizability index density (ELI-D) plots (Figures 6.2C and 6.2F). Specifically, a significant concentration of relative electron density is found in the middle of the Th₃-planes, again with a weaker density in $[1]^{1-}$ compared with $[1]^{2-}$. The ELI-D plots also reveal a lobe-like shape contribution from each thorium atom pointing toward the central interaction density, with less accumulation between the central region and these lobes. This highlights the overlap of the unique thorium constructive contributions to the three-center bonding in each case.

The two- and three-dimensional dynamic electron deformation density of the HAR models of $[1]^{2-}$ and $[1]^{1-}$ are shown in Figure 6.3. For both compounds, significant and systematic positive deformation electron density is found in the center of each Th₃-core, along with clear contributions from all three thorium atoms. Qualitatively, the deformation densities for $[1]^{2-}$ and $[1]^{1-}$ do not differ in their general shapes, but variation in the amount of electron density between the rings is self-evident; one-electron $[1]^{1-}$ exhibits less deformation density in the center of the Th₃-core than two-electron $[1]^{2-}$. This suggests different electron occupation numbers but otherwise similar electronic orbital structures, providing

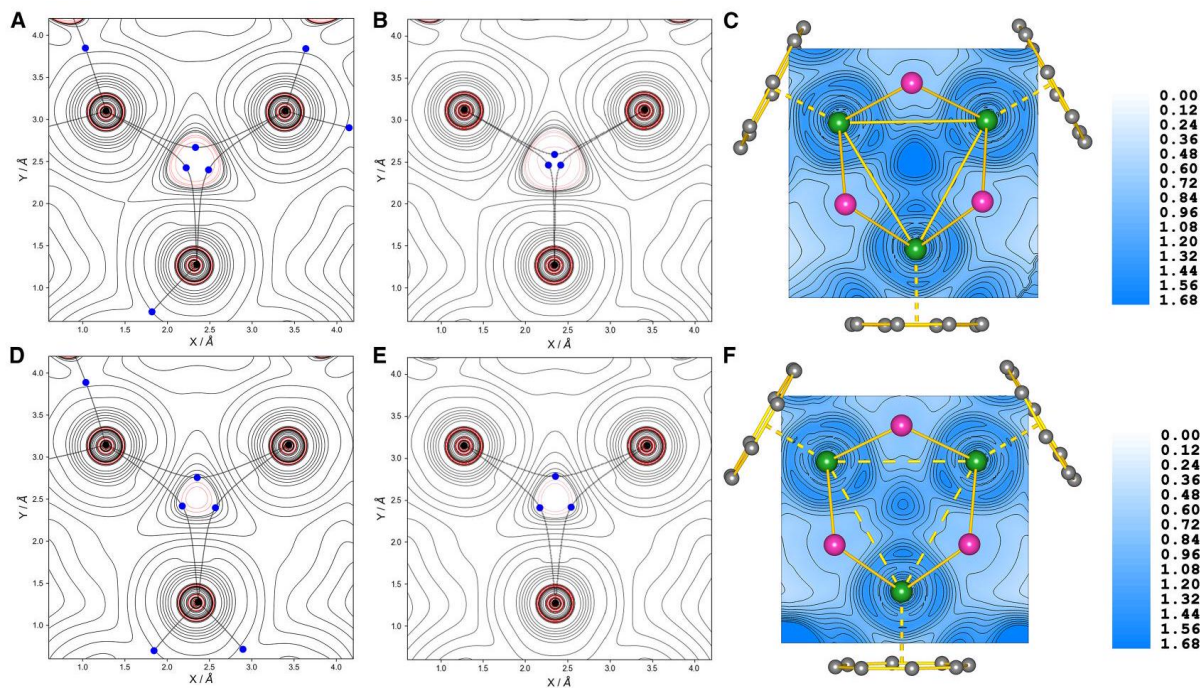


Figure 6.2: Two-dimensional Laplacian ($\nabla^2\rho(r)$) and electron localizability index density (ELI-D, in a.u.) plots in the planes defined by the trithorium cores of $[1]^{2-}$ and $[1]^{1-}$. (A) Experimental HAR Laplacian plot for $[1]^{2-}$. (B) Computed QM Laplacian plot for $[1]^{2-}$. (C) Computed ELI-D plot for $[1]^{2-}$. (D) Experimental HAR Laplacian plot for $[1]^{1-}$. (E) Computed QM Laplacian plot for $[1]^{1-}$. (F) Computed ELI-D plot for $[1]^{1-}$.

Each Laplacian contour represents an increment of 0.12 a.u., and hydrogen atoms are omitted for clarity. Blue dots are covalent bond critical points. Black and red contours represent valence shell depletion (positive Laplacian) and concentration (negative Laplacian), respectively. Bond paths are depicted with black lines. Atom color key: thorium, green; chloride, purple; and carbon, gray.

experimental confirmation of previous purely QM electronic structure descriptions of both systems.^{30–33,42} Integrating the three-dimensional deformation density in a sphere at the center of the Th_3 -core with a radius of 1.0 Bohr gave average positive deformation densities for $[1]^{2-}$ and $[1]^{1-}$ of 4.720×10^{-2} and $0.701 \times 10^{-2} \text{ e/Bohr}^3$, respectively, reflecting the more spatially delocalized nature of the single electron in $[1]^{1-}$ compared with the pair in $[1]^{2-}$ as demonstrated by the Laplacian plots and less curved BPs of the former compared with the latter.

The experimental deformation densities of $[1]^{2-}$ and $[1]^{1-}$ are both in good agreement with the presence of cooperative $\text{Th}_3\sigma$ -bonding, in which the positive deformation densities in the Th_3 -cores reflect the constructive overlap of three $6d_{z^2}$ -type orbitals that combine to give superatomic $1S^2$ and $1S^1$ magic numbers.^{30–42,44}

An important measure of the effectiveness of the HAR refinements of $[1]^{2-}$ and $[1]^{1-}$ is the resulting difference in residual electron density maps,⁴⁵ Figure 6.4. If any contributions in the Th_3 -cores are overestimated in the respective deformation densities, and there-

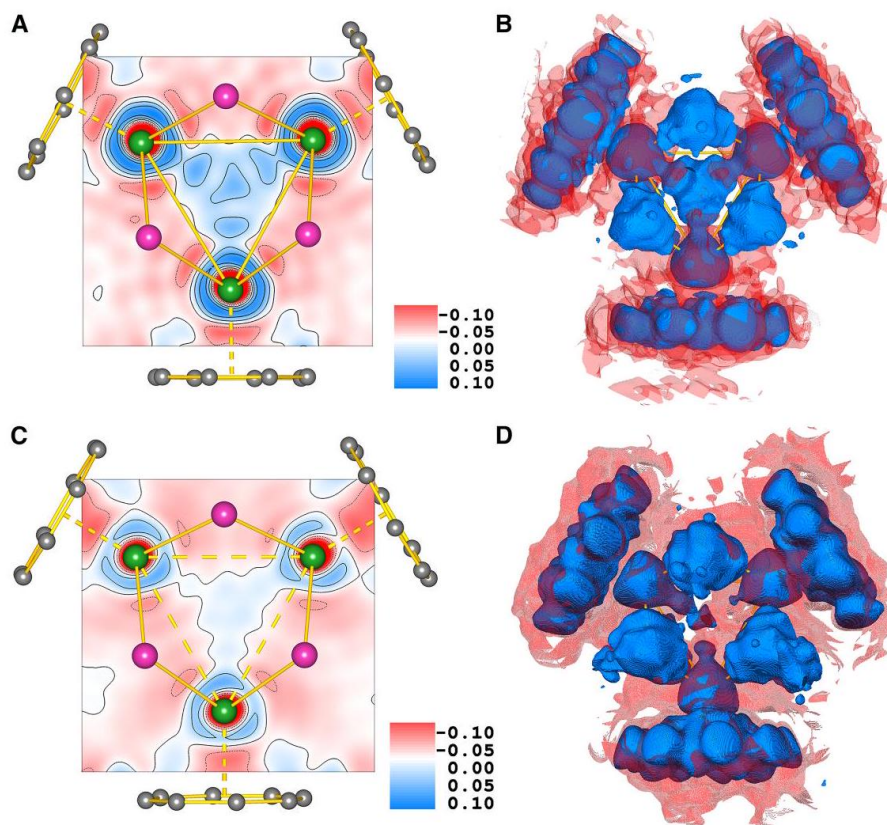


Figure 6.3: Dynamic deformation densities (eA^{-3}) for $[\mathbf{1}]^{2-}$ and $[\mathbf{1}]^{1-}$

(A) Two-dimensional deformation density plot of $[\mathbf{1}]^{2-}$.

(B) Three-dimensional deformation density plot of $[\mathbf{1}]^{2-}$.

(C) Two-dimensional deformation density plot of $[\mathbf{1}]^{1-}$.

(D) Three-dimensional deformation density plot of $[\mathbf{1}]^{1-}$.

Plots are rendered at the 0.05 e iso-level, and hydrogen atoms are omitted for clarity. Blue and red colors indicate positive and negative deformation densities, respectively, relative to the spherical model. Atom color key: thorium, green; chloride, purple; and carbon, gray.

fore the HAR refinement models, significant negative residual densities would be found, which would correspond to too much electron density being attributed to the region in question. However, the residuals show mostly randomly distributed electron densities, and not predominantly negative but rather still positive residual electron densities. This effect is more pronounced for $[\mathbf{1}]^{2-}$ than for $[\mathbf{1}]^{1-}$, reflecting the greater contrast for two versus one-electron. There are no insignificant, systematic residuals near the thorium atoms; however, this is to be expected for heavy atom structural refinements, even after absorption corrections and HAR.²³

Inspection of residual density maps usually gives a clear understanding of the shortcomings in the IAM approach regarding bonding electron density and electron lone-pairs, and in structures containing only light elements, this assumption has been shown to hold quite closely.^{9,46,47} However, since the diffraction data of heavy elements are often contaminated with artifacts, e.g., absorption, anomalous dispersion, Fourier ripples, radiation damage, and the Th-Th interaction density is small in comparison to the three $Z = 90$

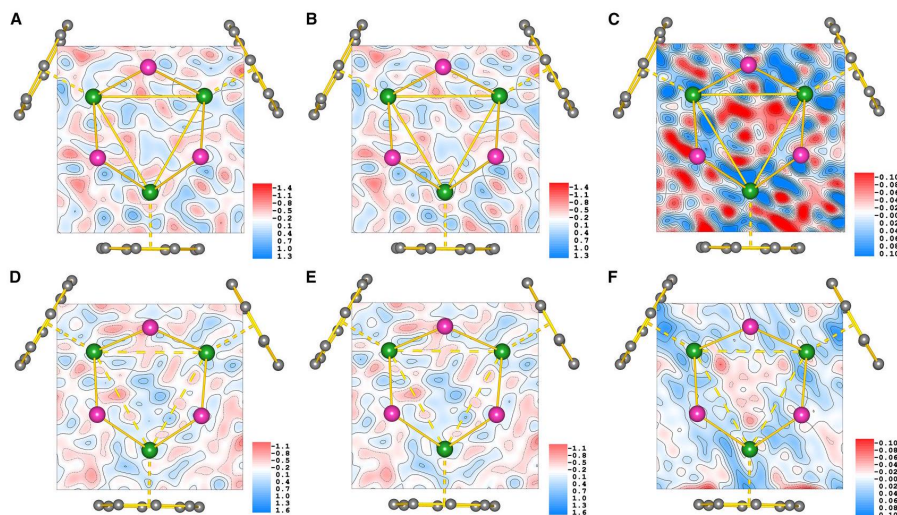


Figure 6.4: Difference residual electron density maps ($e\text{\AA}^{-3}$) for $[\mathbf{1}]^{2-}$ and $[\mathbf{1}]^{1-}$

(A) IAM residual for $[\mathbf{1}]^{2-}$.

(B) HAR residual for $[\mathbf{1}]^{2-}$.

(C) $|F_{\text{residual}}(\text{HAR})| - |F_{\text{residual}}(\text{IAM})|$ difference residual for $[\mathbf{1}]^{2-}$.

(D) IAM residual for $[\mathbf{1}]^{1-}$.

(E) HAR residual for $[\mathbf{1}]^{1-}$.

(F) $|F_{\text{residual}}(\text{HAR})| - |F_{\text{residual}}(\text{IAM})|$ difference residual for $[\mathbf{1}]^{1-}$.

Hydrogen atoms are omitted for clarity. Blue and red colors indicate positive and negative electron densities, respectively. Atom color key: thorium, green; chloride, purple; and carbon, gray.

cores surrounding it, they show the expected effect only slightly. To provide a reliable measure of agreement between the measured and modeled electron density after HAR, we analyzed the difference between the residual electron density maps for the IAM and HAR models (Figures 6.4C and 6.4F). The central region for two-electron $[\mathbf{1}]^{2-}$ clearly shows a significant negative difference in residual density, indicating a modeling of electron density, which was not captured in the IAM. While its shape is not identical to the deformation density, the general shape of the Th_3 interaction is clear. For one-electron $[\mathbf{1}]^{1-}$, despite the difference in residual density map being an order of magnitude lower than for $[\mathbf{1}]^{2-}$, we still observe a close match between the residual-density difference map and the deformation density.

6.3 Conclusion

In summary, we have demonstrated that HAR can be applied to investigate even the metal-metal bonding of heavy actinides, extending the reach of experimentally analyzing electron density of aurophilic interactions ($Z = 79$) to thorium ($Z = 90$). Furthermore, by investigating $[\mathbf{1}]^{2-}$ and $[\mathbf{1}]^{1-}$ with HAR, we have shown that it is possible to unravel the electronic structure of polymetallic complexes that are, by definition, exceedingly challenging to refine due to the close, and highly asymmetrically disposed, proximity of so many core and valence electrons. Through an interleaved combination of Laplacian electron density, ELI-D, two- and three-dimensional deformations, and residual density

maps, this work has provided an internally consistent set of topologies of electron densities, experimentally confirming and visualizing the Th-Th bonding in $[\mathbf{1}]^{2-}$ and $[\mathbf{1}]^{1-}$. The HAR analysis of $[\mathbf{1}]^{2-}$ and $[\mathbf{1}]^{1-}$ validates prior descriptions of their bonding by purely quantum-chemical calculations, mutually confirming and benchmarking the effectiveness of QM and HAR approaches. HAR analysis can be applied to routine X-ray diffraction data sets rather than requiring specialist high-quality data that need frequently inaccessible high crystal quality or access to synchrotron facilities, which can be difficult to secure with air-sensitive and radioactive compounds. Thus, we anticipate that by demonstrating visualization and quantification of the chemical bonding in two extreme heavy-atom test cases, this advance will encourage the use of HAR to become as powerful and routine as regular X-ray crystal structure determinations, benefiting the chemical and materials sciences.

6.4 References

1. Pauling, L. (1989). The Nature of the Chemical Bond and the Structure of Molecules and Crystals: an Introduction to Modern Structural Chemistry (Cornell University Press).
2. Kaltsoyannis, N., and Kerridge, A. (2024). Understanding covalency in molecular *f*-block compounds from the synergy of spectroscopy and quantum chemistry. *Nat. Rev. Chem.* 8, 701-712. <https://doi.org/10.1038/s41570-024-00641-y>.
3. Mathe, Z., Maganas, D., Neese, F., and DeBeer, S. (2025). Coupling experiment and theory to push the state-of-the-art in X-ray spectroscopy. *Nat. Rev. Chem.* 9, 436-453. <https://doi.org/10.1038/s41570-025-00718-2>.
4. Hayton, T.W., and Autschbach, J. (2025). Using NMR Spectroscopy to Evaluate Metal-Ligand Bond Covalency for the f-Elements. *Acc. Chem. Res.* 58, 488-498. <https://doi.org/10.1021/acs.accounts.4c00727>.
5. Compton, A.H. (1915). The Distribution of the Electrons in Atoms. *Nature* 95, 343-344. <https://doi.org/10.1038/095343b0>.
6. Waller, I., and Hartree, D.R. (1929). On the Intensity of Total Scattering of X-Rays. *Proc. R. Soc. Lond. A* 124, 119-142. <https://doi.org/10.1098/rspa.1929.0101>.
7. Hansen, N.K., and Coppens, P. (1978). Testing aspherical atom refinements on small-molecule data sets. *Acta Cryst. A* 34, 909-921. <https://doi.org/10.1107/S0567739478001886>.
8. Genoni, A., Bučinský, L., Claiser, N., Contreras-García, J., Dittrich, B., Dominiak, P.M., Espinosa, E., Gatti, C., Giannozzi, P., Gillet, J.M., et al. (2018). Quantum Crystallography: Current Developments and Future Perspectives. *Chemistry A European J.* 24, 10881-10905. <https://doi.org/10.1002/chem.201705952>.
9. Grabowsky, S., Genoni, A., and Bürgi, H.-B. (2017). Quantum crystallography. *Chem. Sci.* 8, 4159-4176. <https://doi.org/10.1039/C6SC05504D>.
10. Iversen, B.B., Larsen, F.K., Pinkerton, A.A., Martin, A., Darovsky, A., and Reynolds, P.A. (1998). Characterization of Actinide Bonding in Th(S₂PMe₂)₄ by Synchrotron X-ray Diffraction. *Inorg. Chem.* 37, 4559-4566. <https://doi.org/10.1021/ic9715613>.
11. Zhurov, V.V., Zhurova, E.A., and Pinkerton, A.A. (2011). Chemical Bonding in Cesium Uranyl Chloride Based on the Experimental Electron Density Distribution. *Inorg. Chem.* 50, 6330-6333. <https://doi.org/10.1021/ic200759u>.
12. Zhurov, V.V., Zhurova, E.A., Stash, A.I., and Pinkerton, A.A. (2011). Characterization of Bonding in Cesium Uranyl Chloride: Topological Analysis of the Experimental Charge Density. *J. Phys. Chem. A* 115, 13016-13023. <https://doi.org/10.1021/jp204965b>.

13. Wellington, J.P.W., Kerridge, A., and Kaltsoyannis, N. (2016). Should environmental effects be included when performing QTAIM calculations on actinide systems? A comparison of QTAIM metrics for $\text{Cs}_2\text{UO}_2\text{Cl}_4$, $\text{U}(\text{Se}_2\text{PPh}_2)_4$ and $\text{Np}(\text{Se}_2\text{PPh}_2)_4$ in gas phase, COSMO and PEECM. *Polyhedron* 116, 57-63. <https://doi.org/10.1016/j.poly.2016.02.048>.
14. Gianopoulos, C.G., Zhurov, V.V., Minasian, S.G., Batista, E.R., Jelsch, C., and Pinkerton, A.A. (2017). Bonding in Uranium(V) Hexafluoride Based on the Experimental Electron Density Distribution Measured at 20 K. *Inorg. Chem.* 56, 1775-1778. <https://doi.org/10.1021/acs.inorgchem.6b02971>.
15. Gianopoulos, C.G., Zhurov, V.V., and Pinkerton, A.A. (2019). Charge densities in actinide compounds: strategies for data reduction and model building. *IUCrJ* 6, 895-908. <https://doi.org/10.1107/S2052252519010248>.
16. Gao, C., Genoni, A., Gao, S., Jiang, S., Soncini, A., and Overgaard, J. (2020). Observation of the asphericity of 4f-electron density and its relation to the magnetic anisotropy axis in single-molecule magnets. *Nat. Chem.* 12, 213-219. <https://doi.org/10.1038/s41557-019-0387-6>.
17. Cossard, A., Gianopoulos, C.G., Desmarais, J.K., Casassa, S., Gatti, C., Erba, A., and Pinkerton, A.A. (2025). The electron-density distribution of UCl_4 and its topology from X-ray diffraction. *Angew. Chem. Int. Ed.* 64, e202413883. <https://doi.org/10.1002/anie.202413883>.
18. Hirshfeld, F.L. (1977). Bonded-atom fragments for describing molecular charge densities. *Theoret. Chim. Acta* 44, 129-138. <https://doi.org/10.1007/BF00549096>.
19. Jayatilaka, D., and Dittrich, B. (2008). X-ray structure refinement using aspherical atomic density functions obtained from quantum-mechanical calculations. *Acta Crystallogr. A Found. Crystallogr.* 64, 383-393. <https://doi.org/10.1107/S0108767308005709>.
20. Capelli, S.C., Bürgi, H.-B., Dittrich, B., Grabowsky, S., and Jayatilaka, D. (2014). Hirshfeld atom refinement. *IUCrJ* 1, 361-379. <https://doi.org/10.1107/S2052252514014845>.
21. Krawczuk, A., and Genoni, A. (2024). Current developments and trends in quantum crystallography. *Acta Crystallogr. B Struct. Sci. Cryst. Eng. Mater.* 80, 249-274. <https://doi.org/10.1107/S2052520624003421>.
22. Novelli, G., McMonagle, C.J., Kleemiss, F., Probert, M., Puschmann, H., Grabowsky, S., Maynard-Casely, H.E., McIntyre, G.J., and Parsons, S. (2021). Accurate H -atom parameters for the two polymorphs of L-histidine at 5, 105 and 295 K. *Acta Crystallogr. B Struct. Sci. Cryst. Eng. Mater.* 77, 785-800. <https://doi.org/10.1107/S205252062100740X>.
23. Kleemiss, F., Dolomanov, O.V., Bodensteiner, M., Peyerimhoff, N., Midgley, L., Bourhis, L.J., Genoni, A., Malaspina, L.A., Jayatilaka, D., Spencer, J.L., et al. (2021). Accurate crystal structures and chemical properties from NoSpherA2. *Chem. Sci.* 12, 1675-1692. <https://doi.org/10.1039/D0SC05526C>.

24. Herbst-Irmer, R. (2023). In data we trust: X-ray diffraction experiments for charge density investigations. *Acta Crystallogr. B Struct. Sci. Cryst. Eng. Mater.* 79, 344-345. <https://doi.org/10.1107/S205252062300776X>.
25. Pawłędzio, S., Malinska, M., Kleemiss, F., Grabowsky, S., and Woźniak, K. (2022). Auophilic Interactions Studied by Quantum Crystallography. *Inorg. Chem.* 61, 4235-4239. <https://doi.org/10.1021/acs.inorgchem.1c03333>.
26. Niklas, J.E., Otte, K.S., Studvick, C.M., Roy Chowdhury, S.R., Vlaisavljevich, B., Bacsá, J., Kleemiss, F., Popov, I.A., and La Pierre, H.S. (2024). A tetrahedral neptunium(V) complex. *Nat. Chem.* 16, 1490-1495. <https://doi.org/10.1038/s41557-024-01529-6>.
27. Bučinský, L., Jayatilaka, D., and Grabowsky, S. (2016). Importance of Relativistic Effects and Electron Correlation in Structure Factors and Electron Density of Diphenyl Mercury and Triphenyl Bismuth. *J. Phys. Chem. A* 120, 6650-6669. <https://doi.org/10.1021/acs.jpca.6b05769>.
28. Bučinský, L., Jayatilaka, D., and Grabowsky, S. (2019). Relativistic quantum crystallography of diphenyl- and dicyanomercure. Theoretical structure factors and Hirshfeld atom refinement. *Acta Crystallogr. A Found. Adv.* 75, 705-717. <https://doi.org/10.1107/S2053273319008027>.
29. Pawłędzio, S., Malinska, M., Wońska, M., Wojciechowski, J., Andrade Malaspina, L.A., Kleemiss, F., Grabowsky, S., and Woźniak, K. (2021). Relativistic Hirshfeld atom refinement of an organo-gold(I) compound. *IUCrJ* 8, 608-620. <https://doi.org/10.1107/S2052252521004541>.
30. Boronski, J.T., Seed, J.A., Hunger, D., Woodward, A.W., Van Slageren, J., Wooles, A.J., Natrajan, L.S., Kaltsoyannis, N., and Liddle, S.T. (2021). A crystalline tri-thorium cluster with σ -aromatic metal-metal bonding. *Nature* 598, 72-75. <https://doi.org/10.1038/s41586-021-03888-3>.
31. Seed, J.A., Deng, X., Tomeček, J., Brookfield, A., Collison, D., Tuna, F., Wooles, A.J., Whitehead, G.F.S., Kaltsoyannis, N., and Liddle, S.T. (2025). Valence-Delocalized Trithorium Nanocluster Superatoms with Open-Shell Exalted Diamagnetism. *Nat. Chem.* 17, 1035-1041. <https://doi.org/10.1038/s41557-025-01790-3>.
32. Deng, X., Seed, J.A., Tomeček, J., Brookfield, A., Tuna, F., Reant, B. L.L., Wooles, A.J., Kaltsoyannis, N., and Liddle, S. (2026). Field-Induced Non-Linear Magnetic Responses of All-Metal Jellium s -Aromats. *Nat Commun.* <https://doi.org/10.1038/s41467-026-74403-3>.
33. Tomeček, J., Liddle, S.T., and Kaltsoyannis, N. (2023). Actinide-Actinide Bonding: Electron Delocalisation and σ -Aromaticity in the Tri-Thorium Cluster $[\{\text{Th}(\eta^8\text{-C}_8\text{H}_8)(\mu\text{-Cl})_2\}_3\text{K}_2]$. *ChemPhysChem* 24, e202300366. <https://doi.org/10.1002/cphc.202300366>.
34. Tomeček, J., Liddle, S.T., and Kaltsoyannis, N. (2025). Metal-Metal Bonding in Tri-Actinide Clusters: A DFT Study of $[\text{An}_3\text{Cl}_6]^z$ ($z = 1 - 6$) and $[\text{An}_3\text{Cl}_6\text{Cp}_3]^2$ ($z = -2 - +3$; An = Ac, Th, Pa, U, Np, Pu). *ChemPhysChem* 26, e202400816. <https://doi.org/10.1002/cphc.202400816>.

35. Cuyacot, B.J.R., and Foroutan-Nejad, C. (2022). $[\{\text{Th}(\text{C}_8\text{H}_8)\text{Cl}_2\}_3]^{2-}$ is stable but not aromatic. *Nature* 603, E18-E20. <https://doi.org/10.1038/s41586-021-04319-z>.
36. Boronski, J.T., Seed, J.A., Hunger, D., Woodward, A.W., Van Slageren, J., Wooles, A.J., Natrajan, L.S., Kaltsoyannis, N., and Liddle, S.T. (2022). Reply to: $[\{\text{Th}(\text{C}_8\text{H}_8)\text{Cl}_2\}_3]^{2-}$ Is Stable but Not Aromatic. *Nature* 603, E21-E22. <https://doi.org/10.1038/s41586-021-04320-6>.
37. Szczepanik, D.W. (2022). Bonding in a crystalline tri-thorium cluster: not σ -aromatic but still unique. *Angew. Chem. Int. Ed.* 61, e202204337. <https://doi.org/10.1002/anie.202204337>.
38. Lin, X., and Mo, Y. (2022). On the Bonding Nature in the Crystalline TriThorium Cluster: Core-Shell Syngenetic σ -Aromaticity. *Angew. Chem. Int. Ed.* 61, e202209658. <https://doi.org/10.1002/anie.202209658>.
39. Szczepanik, D.W. (2023). The curious case of the crystalline tri-thorium cluster: cyclic delocalization without aromatic stabilization? *RSC Adv.* 13, 34224-34229. <https://doi.org/10.1039/D3RA06603G>.
40. Badri, Z., and Foroutan-Nejad, C. (2024). On the aromaticity of actinide compounds. *Nat. Rev. Chem.* 8, 551-560. <https://doi.org/10.1038/s41570-024-00617-y>.
41. Orozco-Ic, M., Soriano-Agueda, L., Sundholm, D., Matito, E., and Merino, G. (2024). Core-electron contributions to the magnetic response of molecules with heavy elements and their significance in aromaticity assessments. *Chem. Sci.* 15, 12906-12921. <https://doi.org/10.1039/D4SC02269F>.
42. Tomeček, J., Liddle, S.T., and Kaltsoyannis, N. (2025). Computational Investigations of Metal-Metal Bonding in Molecular Thorium Compounds and Ce and Group IV Analogues. *Inorg. Chem.* 64, 14498-14512. <https://doi.org/10.1021/acs.inorgchem.5c01812>.
43. Proft, F.D., Vivas-Reyes, R., Peeters, A., Van Alsenoy, C., and Geerlings, P. (2003). Hirshfeld partitioning of the electron density: Atomic dipoles and their relation with functional group properties. *J. Comput. Chem.* 24, 463-470. <https://doi.org/10.1002/jcc.10241>.
44. Superatoms. (2022). Principles, Synthesis and Applications, P. Jena and Q. Sun, eds. (John Wiley & Sons).
45. Meindl, K., and Henn, J. (2008). Foundations of residual-density analysis. *Acta Crystallogr. A Found. Crystallogr.* 64, 404-418. <https://doi.org/10.1107/S0108767308006879>.
46. Meurer, F., Schimpf, M., Hischa, B., Hennig, C., Rehbein, J., Kleemiss, F., and Bodensteiner, M. (2025). Synthesis and quantum crystallographic evaluation of WYLID: YLID's red rival. *J. Appl. Crystallogr.* 58, 678-687. <https://doi.org/10.1107/S160057672500175X>.

47. Balmohammadi, Y., Malaspina, L.A., Nakamura, Y., Cametti, G., Siczek, M., and Grabowsky, S. (2025). A quantum crystallographic protocol for general use. *Sci. Rep.* 15, 13584. <https://doi.org/10.1038/s41598-025-96400-0>.

6.5 Supporting information

The supporting information of this work is provided as a single .pdf file with original format and page numbering starting from the next page.

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Supplemental information

Actinide-actinide bonding visualized

by Hirshfeld atom refinement

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Supplementary Materials and Methods

General Experimental Details

All manipulations were carried out using Schlenk techniques, or an MBraun UniLab glovebox, under an atmosphere of dry dinitrogen or argon. Glassware was dried by overnight storage in a 150 °C oven followed by flame-drying under vacuum (1×10^{-3} mbar). Solvents were dried by passage through activated alumina towers and degassed prior to use. All solvents were stored over potassium mirrors except for DME and THF, which were stored over activated 4 Å sieves. Deuterated solvents were distilled from potassium, degassed by three freeze-pump-thaw cycles and stored under a dinitrogen atmosphere. Glassware was silylated prior to use. The compounds $\text{ThCl}_4(\text{THF})_{3.5}$ [S1], MC_8 (M = K, Rb, Cs) [S2], $\text{C}_8\text{H}_8\text{K}_2$ [S3], $[\text{Th}(\eta^8\text{-C}_8\text{H}_8)_2]$ [S4], and $[\text{Th}(\eta^8\text{-C}_8\text{H}_8)(\text{Cl})_2(\text{THF})_2]$ [S5] were prepared by the modified procedures described below. All other reagents were purchased and used as received.

Single crystals were examined on a Rigaku XtaLAB Synergy-S diffractometer, equipped with a HyPix 6000HE photon-counting pixel array detector with mirror-monochromated Mo K α ($\lambda = 0.71073$ Å) or Cu K α radiation ($\lambda = 1.54184$ Å). For the regular IAM data sets of **1a** and **1b**, intensities were integrated from a sphere of data recorded on narrow (0.5 or 1.0°) frames by ω rotation. Cell parameters were refined from the observed positions of all strong reflections in each data set. Gaussian grid face-indexed absorption corrections with a beam profile correction were applied. The structures were solved by dual methods using SHELXT [S6]. All non-hydrogen atoms were refined by full-matrix least-squares on all unique F^2 values, with anisotropic displacement parameters, with exceptions noted in the respective cif files. Except where noted, hydrogen atoms were refined with constrained geometries and riding thermal parameters; $U_{\text{iso}}(\text{H})$ was set at 1.2 (1.5 for methyl groups) times U_{eq} of the parent atom. CrysAlisPro [S7] was used for control and integration, and SHELXL [S8] and Olex2 [S9] were employed for structure refinement. ORTEP-3 [S10] and POV-Ray [S11] were employed for molecular graphics. Details of the HAR refinements of **1a** and **1b** are given later.

^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker 400 spectrometer operating at 400 and 101 MHz, respectively or on a JEOL JNM-ECZ 400 MHz spectrometer operating at 399.78 and 100.52 MHz, respectively; chemical shifts are quoted in ppm and are relative to tetramethylsilane (^1H and ^{13}C). Samples were prepared in the glovebox and placed in J. Young PTFE 5mm screw-topped borosilicate NMR tubes.

FTIR spectra were recorded on a Bruker Alpha spectrometer with a Pt-ATR module in a glovebox.

Raman spectra were recorded on a Horiba XploRA Plus Raman microscope using a 785 nm laser with a power of 1.5 mW. The number of scans and acquisition time were varied for each complex to inhibit sample decomposition. The power was adjusted using a power filter for each complex to inhibit sample decomposition.

UV-vis-NIR spectra were recorded on a Perkin Elmer Lambda 1050 spectrometer where data were collected in 1cm path length cuvettes and were run versus the appropriate reference solvent.

Continuous-wave (c.w.) EPR spectra were measured using an X-band (9.4 GHz) Bruker EMX Plus spectrometer under 100 kHz magnetic field modulation and 2 G modulation amplitude at 293-5 K. Powdered samples were loaded into 3.9 mm (OD) quartz tubes in a glovebox under dinitrogen, and the tubes were flame sealed under vacuum using a MAPP-oxygen torch prior to experiments. Field corrections were applied to the raw data using Bruker strong pitch ($g = 2.0028$) as a reference. Spectra were simulated using the Easyspin 6.0 Software package [S12].

Variable-temperature magnetic moment data were recorded with various applied direct current (DC) external fields on a Quantum Design MPMS3 superconducting quantum interference device magnetometer using doubly recrystallized powdered samples. Measurements were performed in dc

scan mode using 40 mm scan length and 6 s scan time. Samples were carefully checked for purity and data reproducibility between several independently prepared batches for each compound examined where great care was taken to ensure accurate weighing of materials. Samples were crushed with a mortar and pestle under an argon atmosphere and immobilized in an eicosane matrix within a borosilicate glass NMR tube to prevent sample reorientation during measurements. The tube was flame-sealed under dynamic vacuum (1×10^{-3} mbar) to a length of approximately 3 cm and mounted in the center of a drinking straw, with the straw fixed to the end of an MPMS3 sample rod. Care was taken to ensure complete thermalization of the sample before each data point was measured by employing delays at each temperature point as well as cooling rate (2.5 K/min from 300 to 100 K; 1 K/min from 100 to 50 K). The sample was held for 30 minutes before isothermal magnetization measurements to account for slow thermal equilibration of the sample. Diamagnetic corrections were applied using tabulated Pascal constants [S13] and measurements were corrected for the effect of the blank sample holders (flame sealed Wilmad NMR tube and straw) and eicosane matrix. Isothermal magnetization measurements were conducted on calibrated blanks (sealed NMR tubes containing varying masses of eicosane, including no eicosane) to determine the eicosane contribution, which is defined per mg of eicosane used, in addition to the contribution from the NMR tube/straw, which is kept approximately constant from sample to sample. All samples were measured without the use of eicosane to reduce the diamagnetic contribution to the measurement [S14], reduce the likelihood of sample thermal decomposition when the eicosane is melted prior to sealing, and to remove an additional weighing error invoked when adding eicosane to the sample. However, for solely **1a**, magnetometric data were collected without eicosane and with eicosane (**1a-eico**), to confirm agreement within 6.45%, which is approximately within the measurement error of the instrument. The field was corrected for the remnant field of the superconducting magnet using a Pd reference sample under the same measurement conditions.

Elemental microanalyses were carried out by Mr Martin Jennings and Mrs Anne Davies at the Micro Analytical Laboratory, Department of Chemistry, University of Manchester.

Modified Synthesis of KC_8

A 250 mL round-bottomed Schlenk flask was charged with reagent grade (> 99.9%) graphite (5.65 g, 470.4 mmol) and dried under dynamic vacuum (1×10^{-3} mbar) at 100 °C for four hours. In an argon-filled glovebox, freshly cut potassium metal (2.299 g, 58.8 mmol) is added. The mixture was then heated under an argon atmosphere with a blowtorch whilst agitating causing the potassium metal to melt and intercalation to occur. Heating was continued until the mixture had completely changed colour from black to bronze, ~3 hours. Once the reaction was complete, it was allowed to cool to room temperature. Yield: 7.87 g, 99% [S2, S15, S16].

Modified Synthesis of $C_8H_8K_2$

A 500 mL round-bottomed Schlenk flask was charged with freshly cut potassium metal (3.12 g, 80 mmol) and suspended in THF (200 mL). At room temperature, freshly distilled 1,3,5,7-cyclooctatetraene (4.16 g, 40 mmol) was added slowly resulting in the gradual formation of a dark-brown solution. The mixture was stirred for 12 hours before being filtered. Volatiles were removed *in vacuo* to yield a pale-brown, highly pyrophoric solid. Yield: 6.80 g, 93%. 1H NMR (C_6D_6 /THF, 298 K): δ 6.47 (s, 8H, C_8H_8) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6 /THF, 298 K): δ 90.61 (s, C_8H_8) ppm. FTIR (ATR) ν/cm^{-1} : 2987 (s), 2903 (w), 2869 (m), 1457 (w), 1425 (m), 1033 (s), 918 (w), 879 (s), 762 (w), 729 (w), 703 (s), 679 (m), 668 (s), 658 (s) [S14, S17].

Modified Synthesis of $ThCl_4(THF)_{3.5}$

A 250 mL Young's ampoule was charged with $ThCl_4(DME)_2$ (22.047 g, 39.80 mmol)¹ and the solid dissolved in THF (~150 mL). Note - the volume of THF used is critical for success of the reaction: it must be a large excess. The solution was heated at 60 °C for 24 hours, then cooled to room temperature and all volatiles were removed *in vacuo*. Reaction progress was monitored by 1H NMR

spectroscopy of the solid, which is partially soluble in C₆D₆. The solid is initially a mixture of ThCl₄(DME)₂ and ThCl₄(THF)_{3.5}. Dissolution of the solid and heating in THF was repeated until the NMR spectrum of the pumped-down solid showed that all DME was removed. This usually requires 3-4 cycles. Once all DME was removed, the pale white solid was washed with hexane (2 × 30 mL), and dried *in vacuo* to give ThCl₄(THF)_{3.5} as a white powder. Yield: 24.76 g, 99.4%. ¹H NMR (C₆D₆, 298 K): δ 4.21 (s, 4H, -CH₂O), 1.39 (s, 4H, -CH₂CH₂O) ppm. ¹³C{¹H} NMR (C₆D₆, 298 K): δ 72.61 (s, -CH₂), 25.48 (s, -CH₂) ppm. FTIR (ATR) ν/cm⁻¹: 2960 (m), 2896 (m), 1465 (m), 1450 (s), 1348 (s), 1302 (w), 1252 (m), 1192 (w), 1071 (w), 1039 (m), 998 (s), 956 (m), 913 (s), 844 (w), 821 (s), 675 (s), 573 (m). Where applicable, this data matches that reported in the literature [S1, S14, S17].

Modified Synthesis of [Th(η⁸-C₈H₈)₂]

A 500 mL Young's ampoule equipped with a PTFE stirrer bar was charged with ThCl₄(THF)_{3.5} (7.675 g, 12.25 mmol) and C₈H₈K₂ (4.47 g, 24.51 mmol). The mixture was cooled to -78 °C, then THF (100 mL) was added, and the suspension was allowed to warm slowly to room temperature. The resultant yellow reaction mixture was stirred for 48 hours before solvent was removed *in vacuo* to obtain a bright yellow powder (9.11 g). Using a 500 mL Schlenk flask containing toluene (100 mL), [Th(η⁸-C₈H₈)₂] was extracted as a bright yellow microcrystalline powder *via* Soxhlet extraction for 5 days at 120 °C. Yield: 3.607 g, 67%. ¹H NMR (D₈-THF, 298 K): δ 6.58 (s, 16H, C₈H₈) ppm. ¹³C{¹H} (D₈-THF, 298 K): δ 108.06 (s, C₈H₈) ppm. FTIR (ATR) ν/cm⁻¹: 2961 (w), 1317 (w), 1261 (s), 1088 (w), 1025 (m), 964 (w), 897 (m), 856 (w), 801 (s), 743 (m), 696 (s) [S4, S14, S17].

Modified Synthesis of [Th(η⁸-C₈H₈)(Cl)₂(THF)₂]

A 500 mL Schlenk flask equipped with a PTFE stirrer bar was charged with ThCl₄(THF)_{3.5} (5.06 g, 8.08 mmol) and [Th(η⁸-C₈H₈)₂] (3.56 g, 8.08 mmol). THF (100 mL) was added at room temperature with stirring to form a yellow suspension, which was refluxed at 100 °C for four days. The resulting golden suspension was filtered hot through a Celite-packed coarse porosity frit, and the solvent removed *in vacuo* from the resulting filtrate to yield **1** as an off-white solid which was used without further purification. Yield: 8.36 g, 94%. ¹H NMR (D₈-THF, 298 K): δ 6.63 (s, 8H, C₈H₈), 3.53 (s, 8H, -CH₂), 1.68 (s, 8H, -CH₂) ppm. ¹³C{¹H} (D₈-THF, 298 K): δ 102.59 (s, C₈H₈), 68.39 (s, -CH₂), 26.53 (s, -CH₂) ppm. FTIR (ATR) ν/cm⁻¹: 2962 (s), 2900 (w), 1468 (w), 1455 (w), 1343 (w), 1209 (s), 1089 (m), 1008 (s), 904 (m), 852 (m), 797 (s), 717 (s), 669 (m) [S5, S14, S17].

Synthesis of [{Th(η⁸-C₈H₈)(μ₃-Cl)₂}₃{K(DME)₂}₂] (1a**)**

A Young's ampoule equipped with a PTFE stirrer bar was charged with a solid mixture of [Th(η⁸-C₈H₈)(Cl)₂(THF)₂] (200 mg, 0.36 mmol) and KC₈ (194 mg, 1.44 mmol). At room temperature, a 95:5 combination of benzene:THF (20 mL) was added, and the resultant suspension was stirred for three days, during which time a dark blue solid precipitated. Volatiles were removed *in vacuo* and soluble residues were extracted into DME (~10 mL) to obtain a dark blue solution. Removal of volatiles *in vacuo* yielded **1a** as a dark blue powder. Yield: 0.046 g, 23% (by Th content). Single crystals of **1a** suitable for SC-XRD were obtained by slow diffusion of pentane into a saturated DME solution at -30 °C. Compound **1a** is insoluble in aliphatic and arene solvents and sparingly soluble with limited stability in D₈-THF. Anal. Calc. for C₄₀H₆₄Cl₆K₂O₈Th₃: C, 28.94; H, 3.89. Found: C, 28.68; H, 3.58. ¹H NMR (D₈-THF, 298 K): 5.77 (s, -C₈H₈, 24H) 3.43 (s, -CH₂O), 3.27 (s, -CH₃) ppm. ¹³C{¹H} (D₈-THF, 298 K): 89.4 (s, C₈H₈), 72.82 (s, -CH₂O), 57.97 (s, -CH₃) ppm. The ¹H and ¹³C{¹H} signals for the Th-bound C₈H₈⁻ were assigned by comparison to a degraded sample of **1a**.¹⁷ ATR-IR ν/cm⁻¹: 3017 (w), 2919 (w), 2879 (w), 2810 (w), 1833 (w), 1745 (w), 1454 (w), 1366 (w), 1252 (w), 1183 (w), 1080 (m), 1020 (m), 892 (m), 848 (m), 793 (w), 744 (w), 690 (s), 493 (w), 454 (w). Raman ν/cm⁻¹ (785 nm): 51 (w), 73 (s), 87 (s), 135 (m), 200 (m), 298 (w), 330 (w), 568 (w), 742 (w), 797 (w), 1094 (w), 1365 (m), 2396 (w), 2761 (w). UV-Vis-NIR (DME): λ_{max} (ν/cm⁻¹; ε/M⁻¹cm⁻¹) = 473 (21137; 568), 545 (18335; 586), 615 (16252; 1325), 1386 (7215; 15) nm.

Synthesis of $[K(DME)_4][Th(\eta^8-C_8H_8)(\mu_3-Cl)_2]_3$ (1b**)**

A Young's ampoule equipped with a PTFE stirrer bar was charged with a solid mixture of $[Th(\eta^8-C_8H_8)(Cl)_2(THF)_2]$ (200 mg, 0.36 mmol) and KC_8 (49 mg, 0.36 mmol). At room temperature, a 95:5 combination of benzene:THF (20 mL) was added, and the resultant suspension was stirred for three days, during which time a dark blue solid precipitated. Volatiles were removed *in vacuo* and soluble residues were extracted into DME (~10 mL) to obtain a dark blue solution. Removal of volatiles *in vacuo* yielded **1b** as a dark blue powder. Yield: 0.02 g, 10.2% (by Th content). Single crystals of **1b** suitable for SC-XRD were obtained by slow diffusion of pentane into a saturated DME solution at $-30\text{ }^\circ\text{C}$. Compound **1b** is completely insoluble in aliphatic and arene solvents and sparingly soluble with limited stability in D_8 -THF. Anal. Calc. for $C_{40}H_{64}Cl_6KO_8Th_3$: C, 29.64; H, 3.98. Found: C, 30.14; H, 3.76. 1H NMR (D_8 -THF, 298 K): 3.43 (s, $-CH_2O$, 8H), 3.27 (s, $-CH_3$, 12H) ppm. $^{13}C\{^1H\}$ (D_8 -THF, 298 K): 72.9 (s, $-CH_2O$), 59.1 (s, $-CH_3$) ppm. The 1H and $^{13}C\{^1H\}$ signal for the Th-bound $C_8H_8^-$ is not observed, presumably due to the low valent nature of the thorium ions in **1b**.¹⁴ ATR-IR ν/cm^{-1} : 3027 (w), 2923 (w), 2879 (w), 2810 (w), 1750 (w), 1632 (w), 1449 (w), 1361 (w), 1257(w), 1233 (w), 1188(m), 1075 (s), 1021 (m), 902 (m), 843 (m), 798 (m), 774 (w), 700 (s), 596 (w), 488 (w). Raman ν/cm^{-1} (785 nm): 33 (m), 67 (s), 92 (s), 132 (m), 194 (m), 227 (m), 286 (w), 359 (w), 481 (w), 564 (w), 704 (w), 743 (w). UV-Vis-NIR (DME): λ_{max} (ν/cm^{-1} ; $\epsilon/M^{-1}cm^{-1}$) = 473 (21110; 900), 549 (18204; 1035), 618 (16181; 2316), 1176 (8501; 81), 1210 (8259; 121), 1374 (7278; 140), 1423 (7023; 145), 1469 (6806; 79), 1707 (5856; 810), 1737 (5756; 1022), 1797 (5562; 418), 1879 (5321; 195), 1956 (5112; 218) nm.

Hirshfeld Atom Refinement Details

Data processing was performed using CrysAlisPro [S7] analytical absorption corrections based on a Gaussian integration over a multi-faceted crystal model and semi-empirical absorption corrections were applied using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm. Four data sets were collected as follows: **1a** ($[1]^{2-}$), Cu K α , **1aCu** and Mo K α , **1aMo**; **1b** ($[1]^{1-}$), Cu K α , **1bCu** and Mo K α , **1bMo**. Discussion focusses on the **1aMo** and **1bMo** data sets.

Crystallographic modelling was performed using the Olex2 software package [S2]. The initial structure solution was found using ShelXT and olex2.refine was used as the refinement engine [S6, S9]. For the initial independent-atom model, which represents the starting point for the iterative, quantum crystallographic Hirshfeld-Atom-Refinement, all non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using a riding model. For the **1bMo** and **1bCu** data sets, two models were created. One model includes the fully modelled chelated potassium cationic moieties, to describe the presence of the cation and fully showcase the severe disorder. The second model masked the potassium cation components using the Olex2 solvent masking routine following the PLATON BYPASS algorithm [S18]. The solvent mask was used to calculate the accumulated residual density, e.g., after a solvent molecule, or in this case, the cation, removed from the model, to take into account the measured intensities instead of the calculated ones for this region of the model. Using this procedure, the model was checked to ensure the disordered part of the unit cell did not negatively affect the region of interest within the structure. Specifically, for the HAR procedure, the electron localizability maps in Olex2 were examined. The second model was therefore chosen as the starting point for the iterative Hirshfeld-Atom-Refinement procedure because the resulting quality indicator improves by applying the solvent mask, indicating a better basis for focussing on the anionic part of the structure. For the **1aMo** and **1aCu** data sets, no disorder is present in the chelated cations and therefore the full structure model for the HAR procedure was used.

As described above, the masked IAMs for $[1]^{1-}$ and full IAMs for $[1]^{2-}$ provided the starting geometries for the iterative Hirshfeld-Atom-Refinement procedure. For the same reasons stated above, the possible disorder positions of the cyclooctatetraenyl (COT) ligand were not modelled.

Differences in deformation density when masking the cation and modelling the partially disordered COT ligand in only one position were checked with no significant differences found.

For the HAR procedure, NoSpherA2 [S19] was used as the interface to the quantum chemical software package ORCA (V5) [S20]. At the start, all hydrogen atom positions were set to distances from neutron experiments [S21], since they are close or even similar to the distances freely refined after X-ray HAR [S22]. This geometry was taken for a single-point calculation in ORCA using the SARC-DKH2 [S23, S24] basis set for Th, and the def2-TZVPP [S25] was used for all other atoms (C, H, K, Cl) in $[1]^{2-}$. In $[1]^{1-}$ -def2-TZVPPD was used for all atoms except Th since the calculation was performed on the $[1]^{1-}$ anion only. For $[1]^{2-}$ including its counterions, the wavefunction was calculated using a charge of 0 and a spin-multiplicity of 1, in agreement with previous studies on $[1]^{2-}$. For $[1]^{1-}$, the wavefunction was calculated using a charge of -1 and a multiplicity of 2. For all data sets, the zeroth-order relativistic approximation (ZORA) on the all-electron basis sets was used to account for relativistic effects. NoSpherA2 [S19] was used to calculate positionally specific, non-spherical atomic form factors. These were then used in the conventional least-squares refinement by olex2.refine, and the geometry, anisotropic displacement parameters were updated using these form factors. The new geometry was then used again in the next single-point calculation. This procedure was continued until convergence was reached.

The usual strong residual electron density near the thorium atoms was partially modelled by a Gram-Charlier expansion of third order of the anisotropic displacement parameters. The output was checked to ensure physically sensible results by ensuring the resulting integrated negative probability distribution function stayed below 1%.

Topological analyses were obtained using MultiWfn [S26] on the geometries stated above with the wavefunction in .gbw format in its correspondence. Laplacian maps were obtained using a 500×500 grid in the plane defined by the three thorium atoms. The following settings were changed from the standard settings in MultiWfn: for atomic positions, steepest gradient search was used instead of the Newton algorithm; the stepsize was reduced to 0.2; the number of points was set to 480. Bader charges were obtained on a 0.10 Bohr step size onto the full density cube. Setting three was chosen with approximate refinement of basin boundaries within MultiWfn.

General DFT Calculation Details

DFT calculations on $[\{\text{Th}(\eta^8\text{-C}_8\text{H}_8)(\mu_3\text{-Cl})_2\}_3\{\text{K}(\text{THF})_2\}_2]_\infty$ ($[1]\text{K}_2$) and the $[1]^{1-}$ component of **1b** were reported previously [S14, S17]. Geometry optimization of **1a** was performed with ORCA 6.0 [S20]. Relativistic effects were treated using the zeroth-order regular approximation (ZORA) [S27]. The PBE0 hybrid exchange-correlation functional was used with Grimme's D3 dispersion with Becke-Johnson damping parameters (D3-BJ) [S28-S31]. The SARC-TZVPP basis set was used for Th [S32], and def2-TZVPP for H, C, N, O and Cl [S25]; the fitting basis SARC/J was employed to speed up the calculation of integrals using the RIJCOSX approximation [S24, S33], and the NOTRAH and TightSCF convergence settings were used. Harmonic vibrational frequency analyses confirmed the absence of imaginary frequencies and hence the geometry optimized structure of **1a** to be the true local true minimum geometry. Foster-Boys and Pipek-Mezey localization methods were also conducted with ORCA [S20].

The domain-based localized pair natural orbital variant of CCSD (DLPNO-CCSD) was employed to obtain the T_1 diagnostic value for **1a**, as implemented in ORCA using the following settings [S34, S35]: SARC-TZVP basis set for Th, def2-SVP for ligand atoms with NormalPNO thresholds and the 2nd order Douglas-Kroll-Hess Hamiltonian [S36, S37]. The fitting basis sets for RIJCOSX were generated using the AutoAux function. The calculated value for **1a** of T_1 was 0.0090, justifying the use of single-determinantal DFT approach.

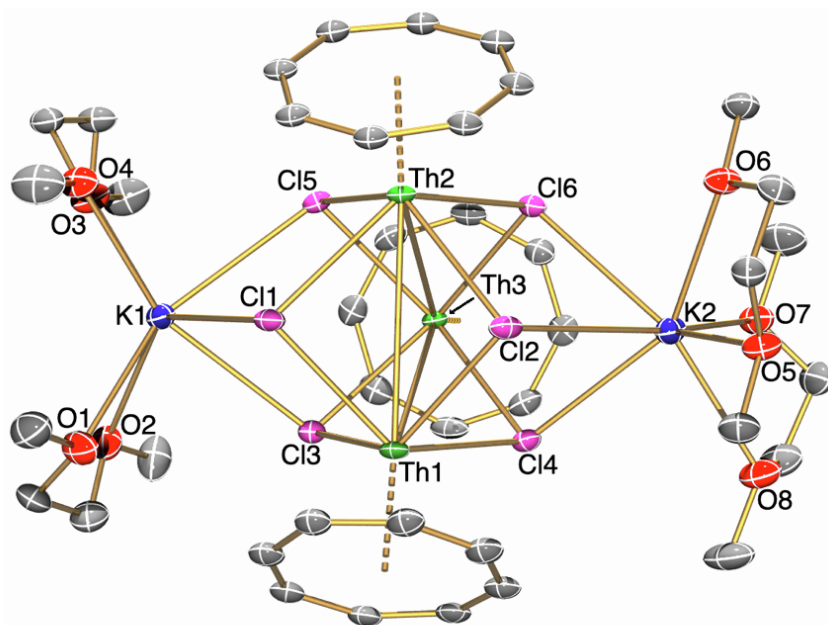
The UV-Vis-NIR spectrum of **1a** was calculated using ORCA 6.0.0 by employing time-dependent density functional theory (TD-DFT) to calculate 30 excited states. Multiple exchange-correlation functionals were tested (PBE0, CAM-B3LYP, ω -BP97X, M06-L and M06-2X); the best match with experiment was obtained with ω -BP97X.

The Raman spectrum of **1a** was calculated with Gaussian 16 [S38], revision C.01, as described previously [S17], that is using the small Stuttgart-Dresden effective core potential (ECP) [S39] and associated ECP basis set for Th [S40], cc-pVTZ for C, O, and Cl, cc-pVDZ for H [S41], and 6-311G* for K [S42], together with D3-BJ dispersion corrections. The geometry was reoptimized and the ultrafine integration grid was used. The RMSD between the ORCA and Gaussian geometries is 0.027 Å, and the Th–Th bond lengths are 4.014 and 4.017 Å, respectively. The Gaussian-reoptimized geometry was used only for the Raman and IR spectra calculations. The same settings (functional, basis set, ECP) were used when the Gaussian 16 single point calculations were needed (calculations with NBO7 [S43]). In all calculations other than the Raman spectra, the geometry from ORCA was used.

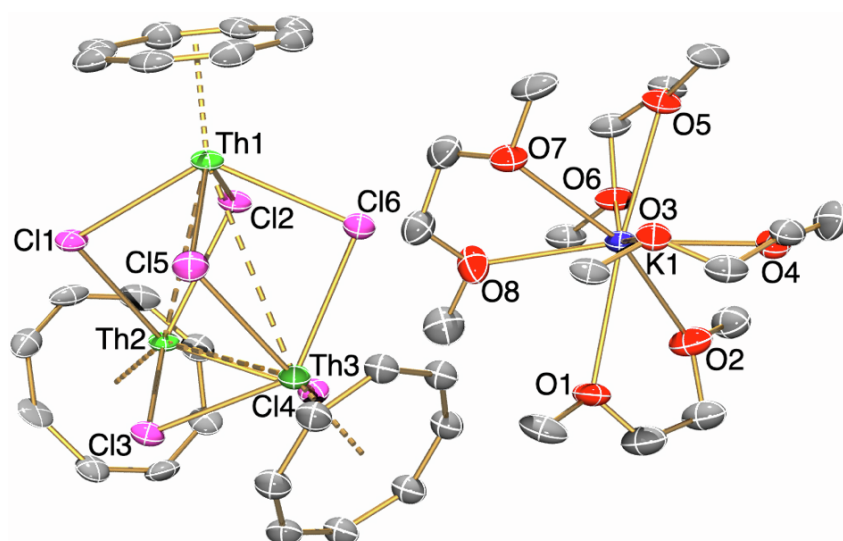
Wavefunction analyses (electron localization function (ELF), bond orders, multicenter indices) were carried out with MultiWFN 3.8 [S26] using molden input files from ORCA calculations (generated with the orca_2molden tool). QTAIM topology analysis was performed using AIMAll (version 19.02) [S44].

Adaptive natural density partitioning (AdNDP) [S45] and electron density of delocalized bonds [S46] (EDDB) analyses were performed as described in our recent publication using Gaussian 16 and NBO7 single point calculations [S14].

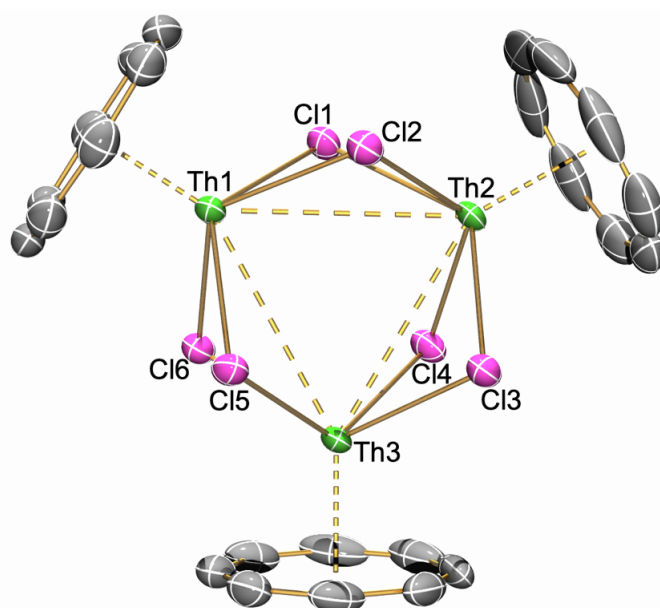
Supplementary Figures



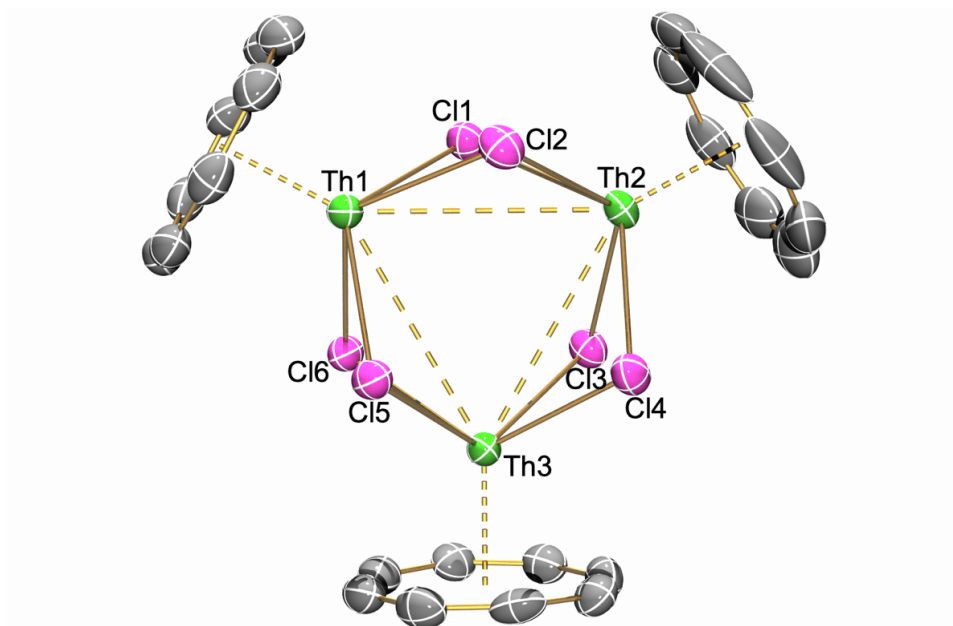
Supplementary Figure S1. Molecular structure of 1a (IAM data) at 100 K with selected atom labels. Displacement ellipsoids are set at 50% and hydrogen atoms and disorder components are omitted for clarity.



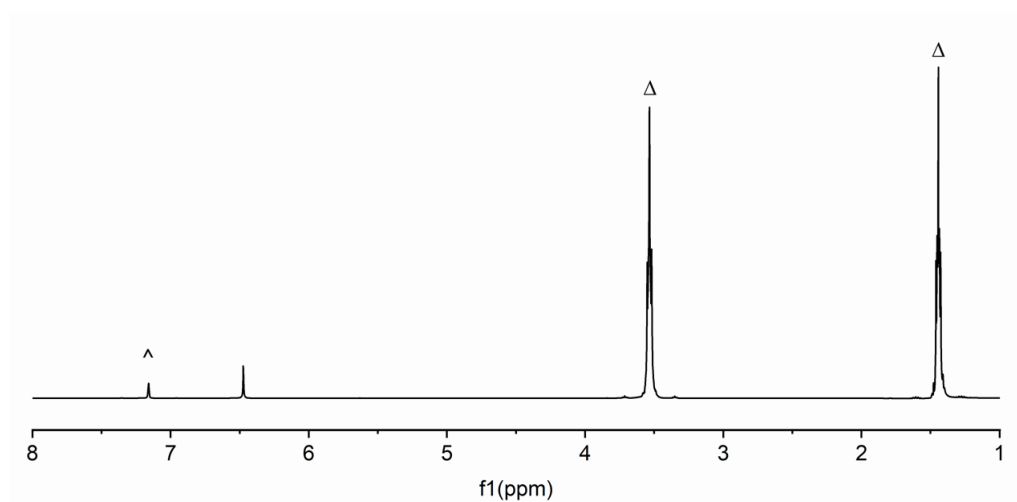
Supplementary Figure S2. Molecular structure of 1b (IAM data) at 100 K with selected atom labels. Displacement ellipsoids are set at 30% and hydrogen atoms and disorder components are omitted for clarity.



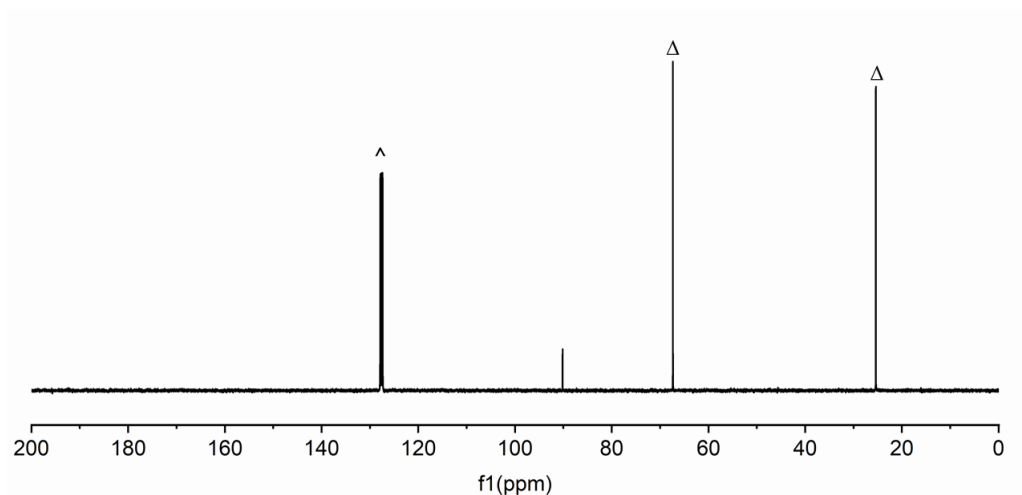
Supplementary Figure S3. Molecular structure of 1a (HAR data, 1aCu) at 155 K with selected atom labels. Displacement ellipsoids are set at 50% and $\{K(DME)_2\}^{1+}$, hydrogen atoms, and disorder components are omitted for clarity.



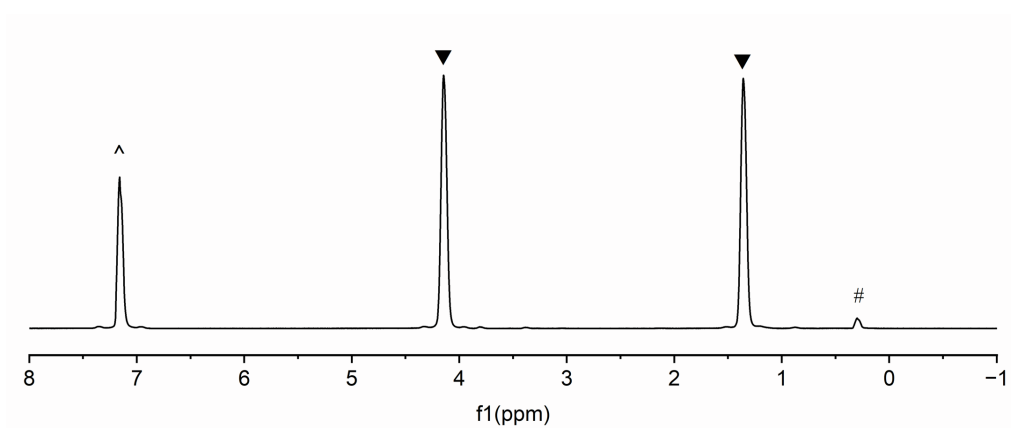
Supplementary Figure S4. Molecular structure of 1b (HAR data, 1bCu) at 100 K with selected atom labels. Displacement ellipsoids are set at 50% and $\{K(DME)_4\}^{1+}$, hydrogen atoms, and disorder components are omitted for clarity.



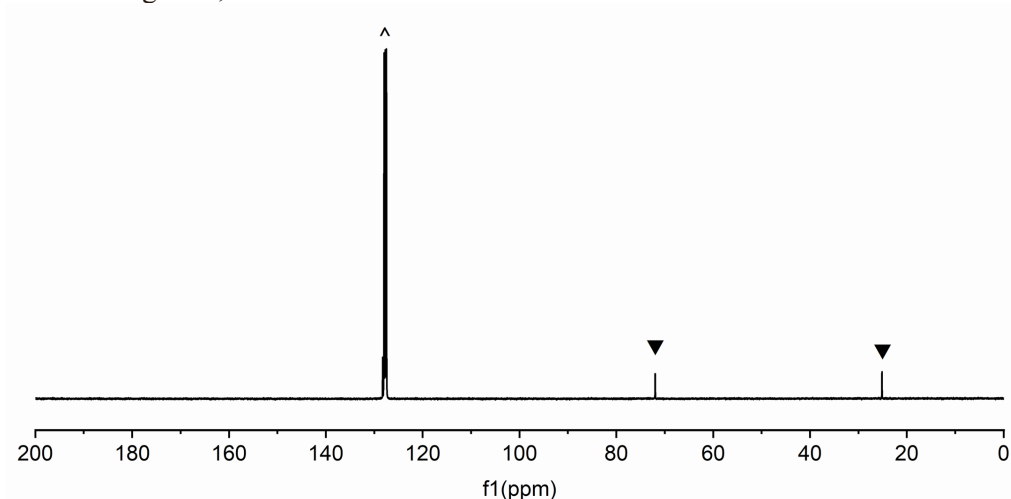
Supplementary Figure S5. 1H NMR (C_6D_6 , 298 K) spectrum of $C_8H_8K_2$. Δ = THF, a drop of which was used to aid solubility; $\wedge$ = C_6D_6 solvent.



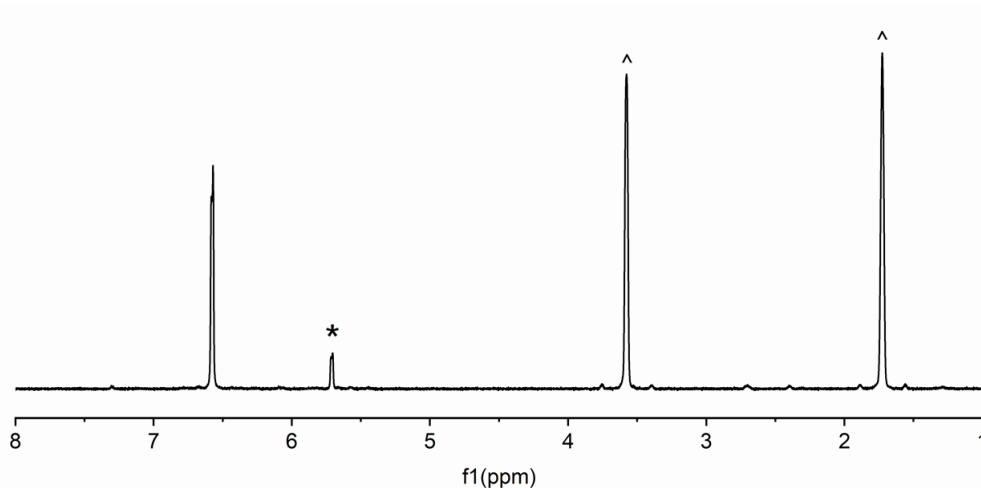
Supplementary Figure S6. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 solvent, 298 K) spectrum of $\text{C}_8\text{H}_8\text{K}_2$. Δ = THF, a drop of which was used to aid solubility; $\wedge$ = C_6D_6 solvent.



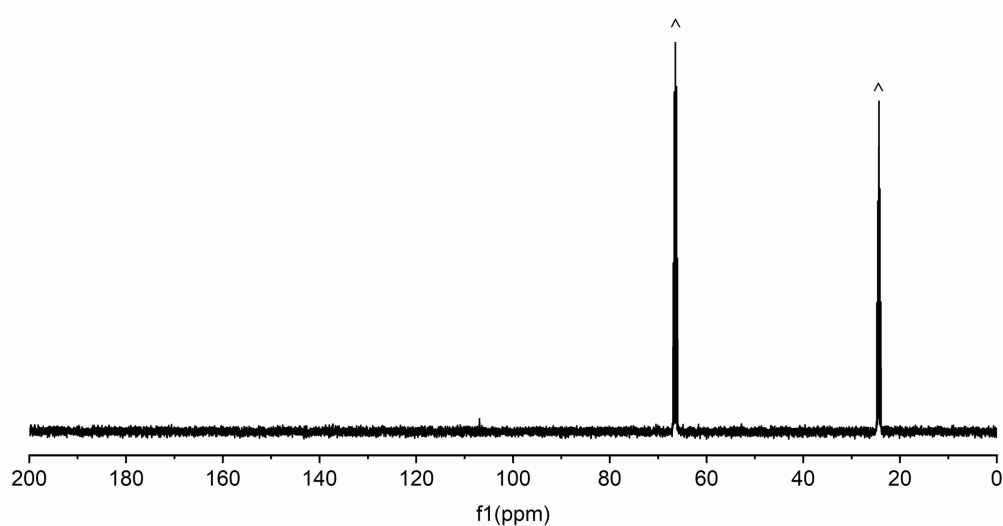
Supplementary Figure S7. ^1H NMR (C_6D_6 , 298 K) spectrum of $\text{ThCl}_4(\text{THF})_{3.5}$. $\blacktriangledown$ = coordinated THF; # = silicone grease; $\wedge$ = C_6D_6 solvent.



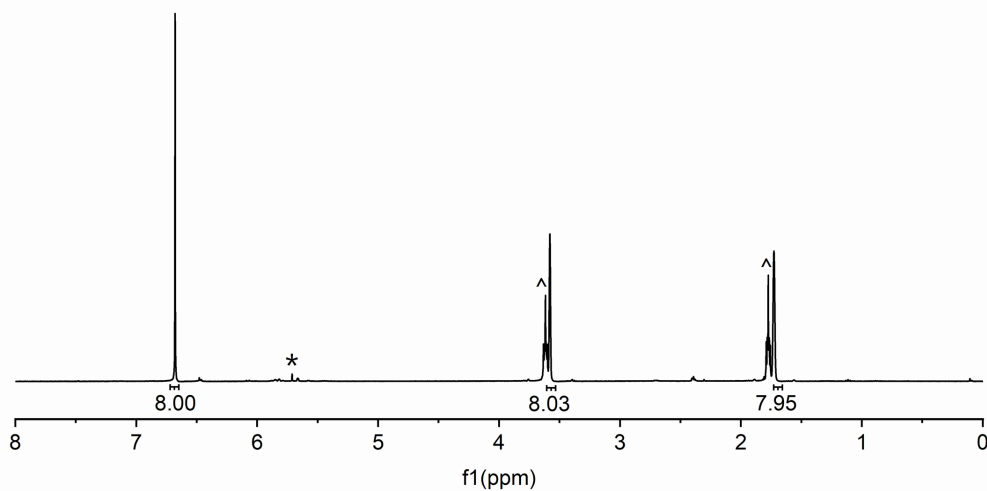
Supplementary Figure S8. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K) spectrum of $\text{ThCl}_4(\text{THF})_{3.5}$. $\blacktriangledown$ = coordinated THF; $\wedge$ = C_6D_6 solvent.



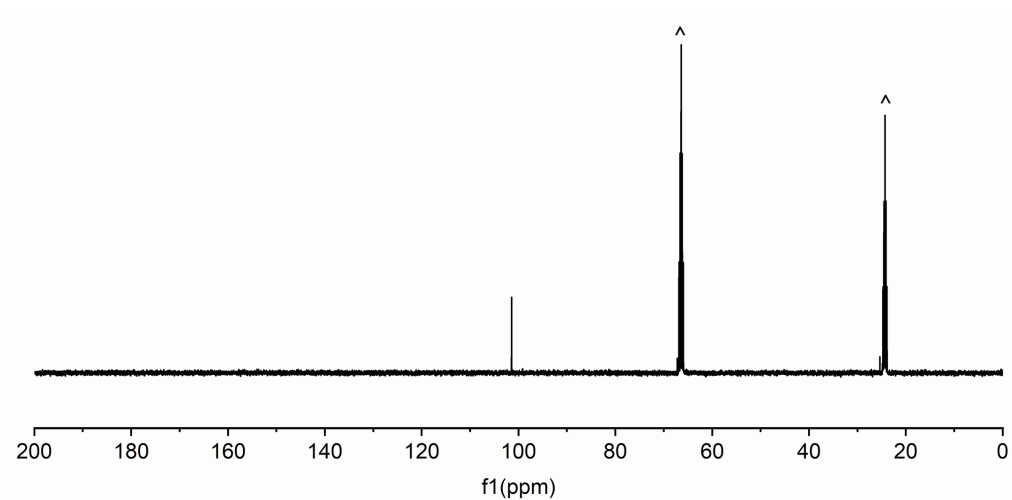
Supplementary Figure S9. ^1H NMR ($\text{D}_8\text{-THF}$, 298 K) spectrum of $[\text{Th}(\eta^8\text{-C}_8\text{H}_8)_2]$. The asterisk (*) at ~5.5 ppm denotes a trace impurity of C_8H_8 . ^ = $\text{D}_8\text{-THF}$ solvent.



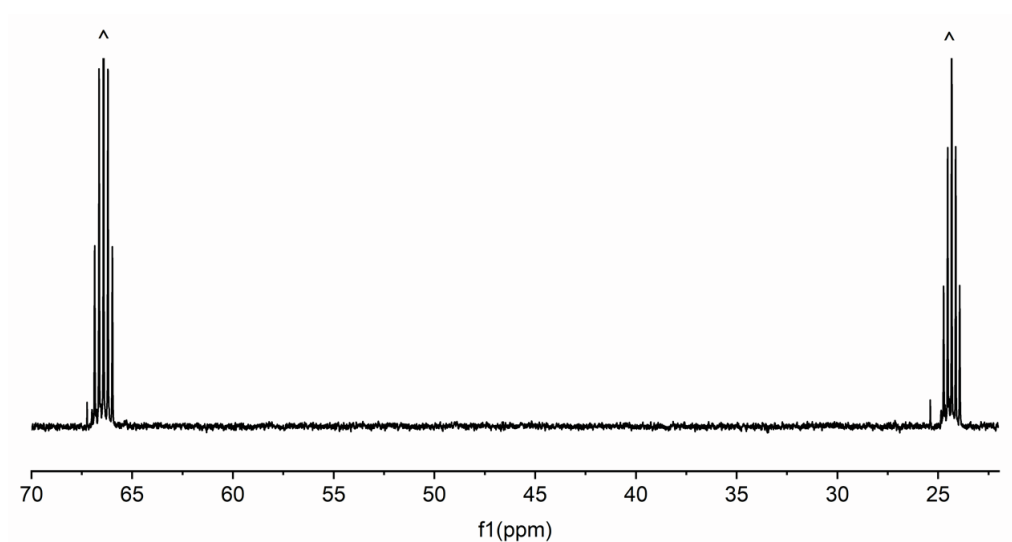
Supplementary Figure S10. $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{D}_8\text{-THF}$, 298 K) spectrum of $[\text{Th}(\eta^8\text{-C}_8\text{H}_8)_2]$. The weak nature of the signal arises from the poor solubility of $[\text{Th}(\eta^8\text{-C}_8\text{H}_8)_2]$ even in $\text{D}_8\text{-THF}$. ^ = $\text{D}_8\text{-THF}$ solvent.



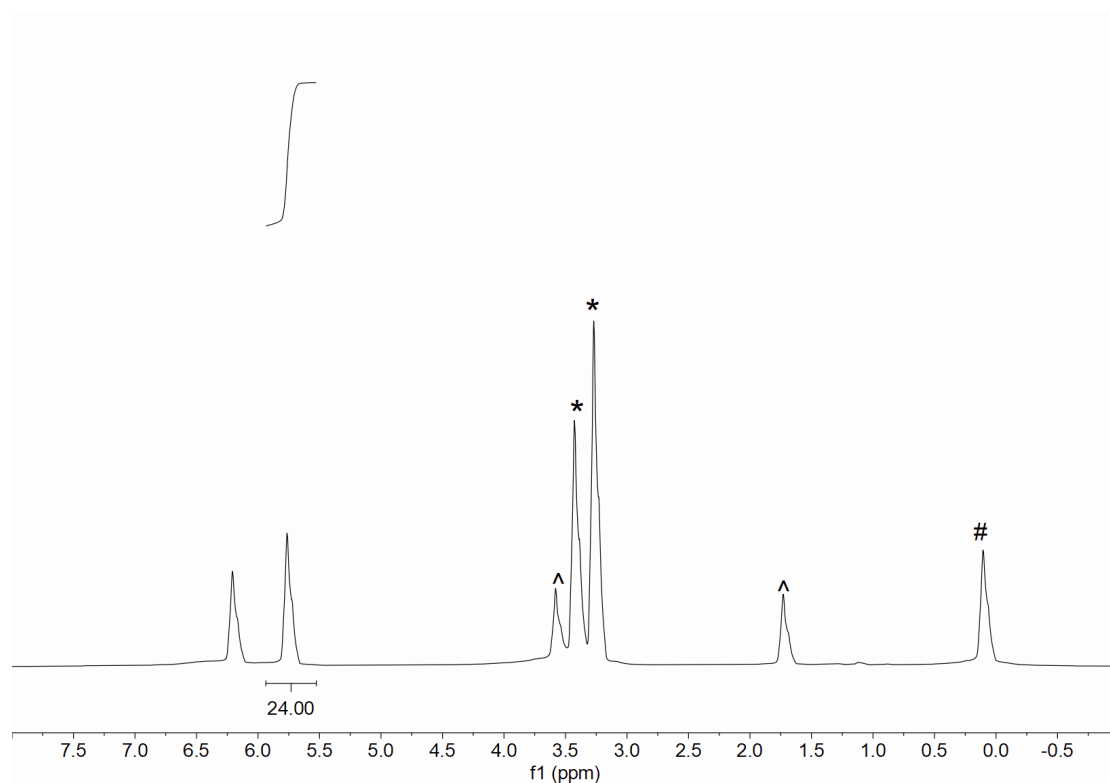
Supplementary Figure S11. ^1H NMR ($\text{D}_8\text{-THF}$, 298 K) spectrum of $[\text{Th}(\eta^8\text{-C}_8\text{H}_8)(\text{Cl})_2(\text{THF})_2]$. * = trace C_8H_8 ; ^ = $\text{D}_8\text{-THF}$ solvent.



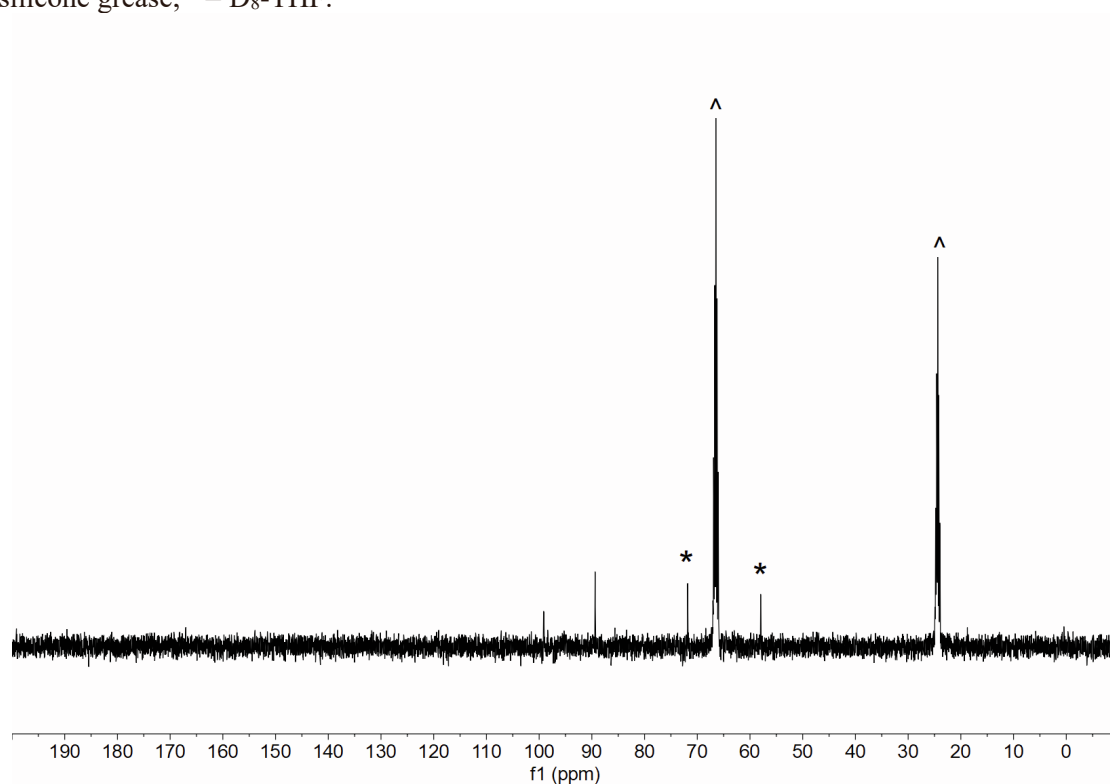
Supplementary Figure S12. $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{D}_8\text{-THF}$, 298 K) spectrum of $[\text{Th}(\eta^8\text{-C}_8\text{H}_8)(\text{Cl})_2(\text{THF})_2]$. ^ = $\text{D}_8\text{-THF}$ solvent.



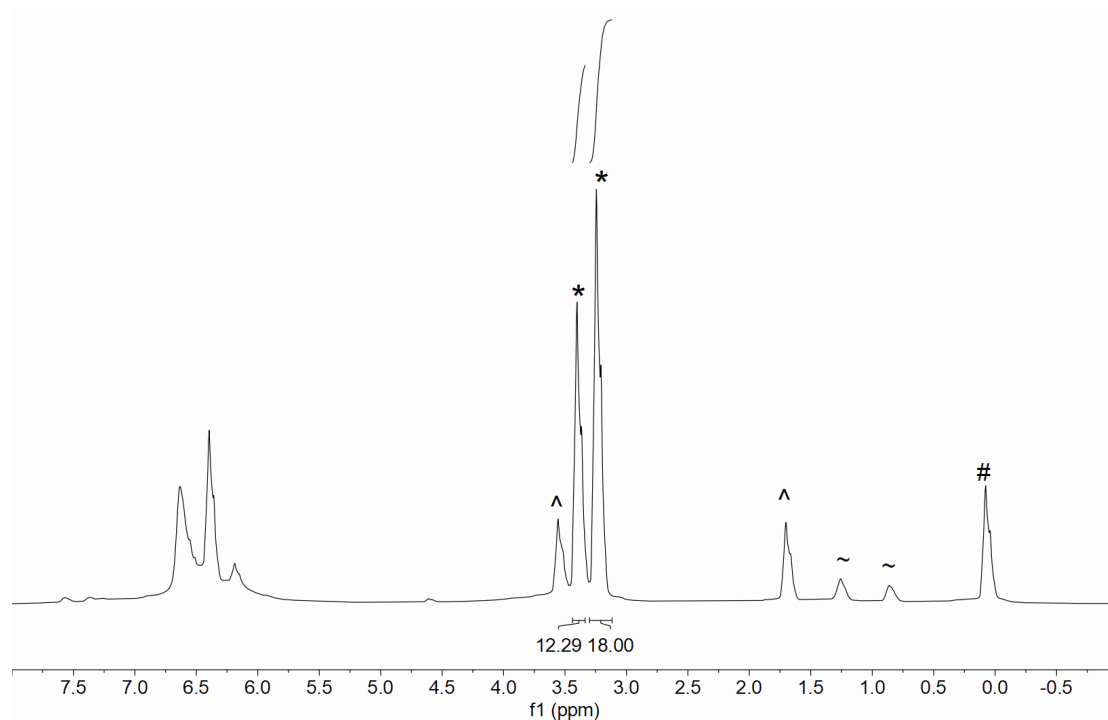
Supplementary Figure S13. Zoom-in of the $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{D}_8\text{-THF}$, 298 K) spectrum of $[\text{Th}(\eta^8\text{-C}_8\text{H}_8)(\text{Cl})_2(\text{THF})_2]$ to highlight the small resonances at 68.39 and 26.53 ppm attributed to Th-coordinated THF. ^ = $\text{D}_8\text{-THF}$ solvent.



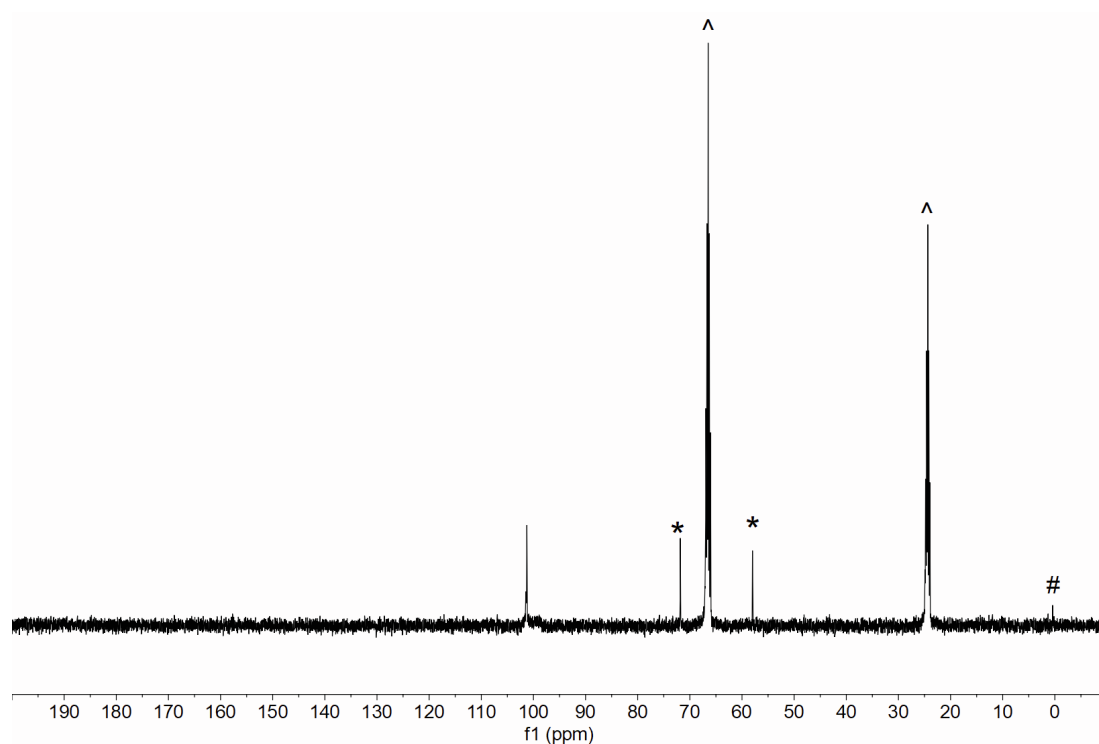
Supplementary Figure S14. ^1H NMR ($\text{D}_8\text{-THF}$, 298 K) spectrum of **1a**. * = coordinated DME; # = silicone grease; ^ = $\text{D}_8\text{-THF}$.



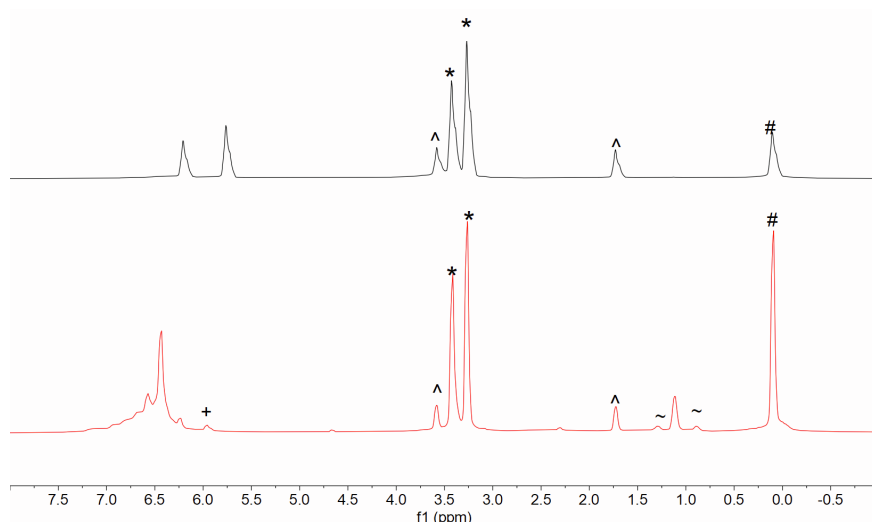
Supplementary Figure S15. $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{D}_8\text{-THF}$, 298 K) spectrum of **1a**. * = coordinated DME; ^ = $\text{D}_8\text{-THF}$.



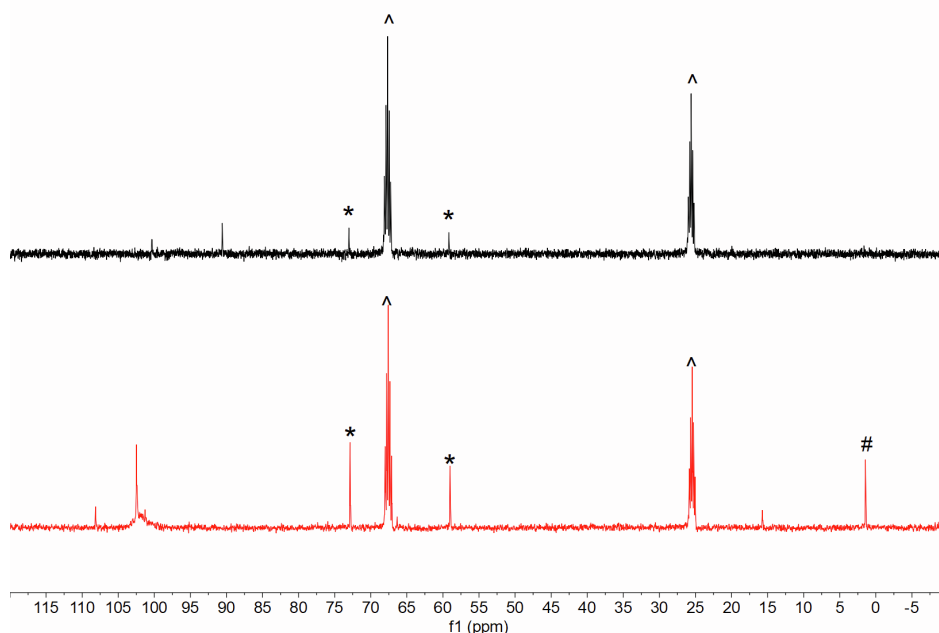
Supplementary Figure S16. ^1H NMR ($\text{D}_8\text{-THF}$, 298 K) spectrum of **1b.** Within the ^1H spectrum of **1b**, which possesses an open-shell electronic configuration, several resonances can be visualized in the region anticipated for the C_8H_8 H-atoms (6.0-7.0 ppm). However, no carbon C_8H_8 resonances could be located for **1b** in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (Supplementary Figure 15) so these resonances are assigned as diamagnetic impurities in agreement to what we have previously observed when measuring NMR spectroscopic data of open-shell trithorium nanoclusters [S14]. * = coordinated DME; # = silicone grease; ^ = $\text{D}_8\text{-THF}$; ~ = residual pentane.



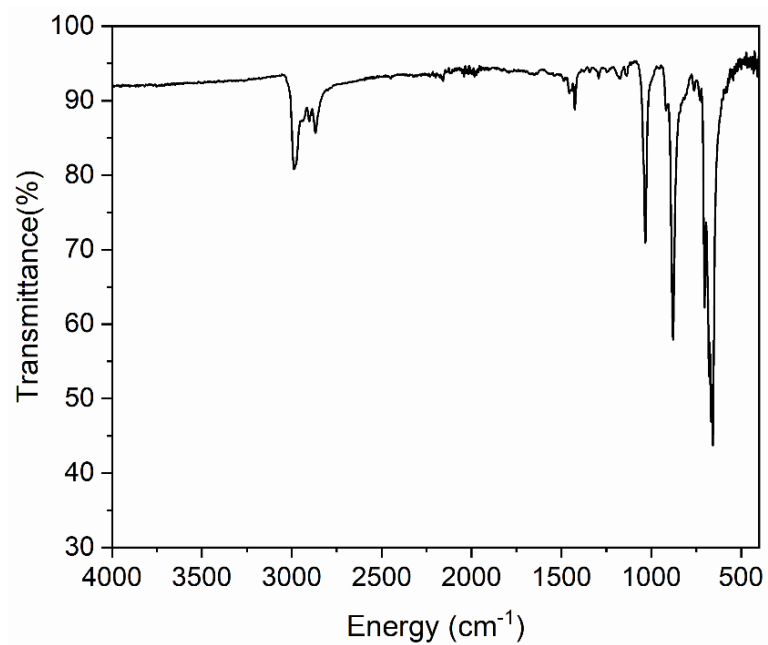
Supplementary Figure S17. $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{D}_8\text{-THF}$, 298 K) spectrum of **1b.** * = coordinated DME; ^ = $\text{D}_8\text{-THF}$; # = silicone grease.



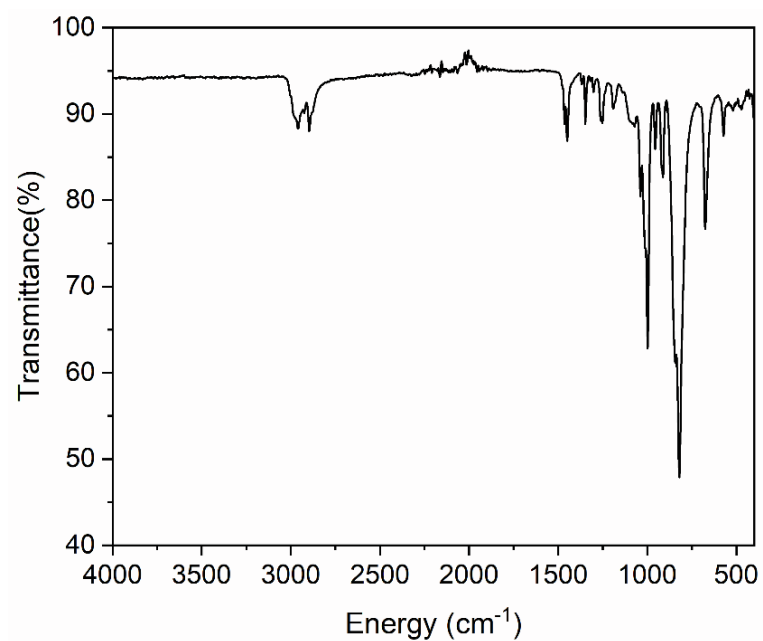
Supplementary Figure S18. Comparative ¹H NMR (D₆-benzene, 298 K) spectra of **1a (top, black) and the same sample of **1a** but intentionally degraded through excessive heating (bottom, red).** This excessive heating causes a colour change from dark blue to light brown. Upon degradation, there is the loss of the assigned C₈H₈ resonance for **1a** at ~5.77 ppm and resonances related to [Th(η⁸-C₈H₈)₂] and free 1,3,5,7-cyclooctatetraene at ~6.50 and ~5.70 ppm, respectively, which are common decomposition products, could now be observed. Whilst the chemical shift value assigned to the C₈H₈ resonance for **1a** (5.77 ppm) is very similar to that reported for free 1,3,5,7-cyclooctatetraene (5.72 ppm in D₈-THF), there is no accompanying resonance for free 1,3,5,7-cyclooctatetraene in the ¹³C{¹H} (~133 ppm) as would be expected. The ¹³C{¹H} chemical shift value of **1a** is very similar to that of K₂COT (89.4 for **1a** vs. 90.6 for K₂COT) and reflects the dianionic nature of the coordinated C₈H₈ moieties. Both of these resonances are absent when **1a** decomposes. * = coordinated DME; ^ = THF solvent; ~ = residual pentane; + = trace C₈H₈; # = silicone grease.



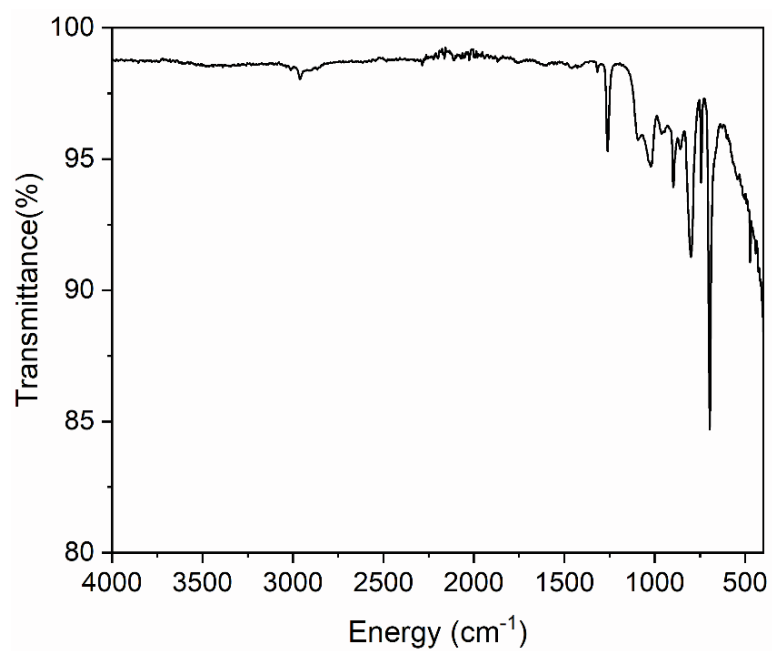
Supplementary Figure S19. Comparative ¹³C{¹H} NMR (D₆-benzene, 298 K) spectra of **1a (top, black) and the same sample of **1a** but intentionally degraded through excessive heating (bottom, red).** This excessive heating causes a colour change from dark blue to light brown. Upon degradation, there is the loss of the assigned C₈H₈ resonance for **1a** at ~89 ppm and the resonance related to [Th(η⁸-C₈H₈)₂] at ~101 ppm, which is a common decomposition product, could now be observed. * = coordinated DME; ^ = THF solvent; ~ = residual pentane; + = trace C₈H₈; # = silicone grease.



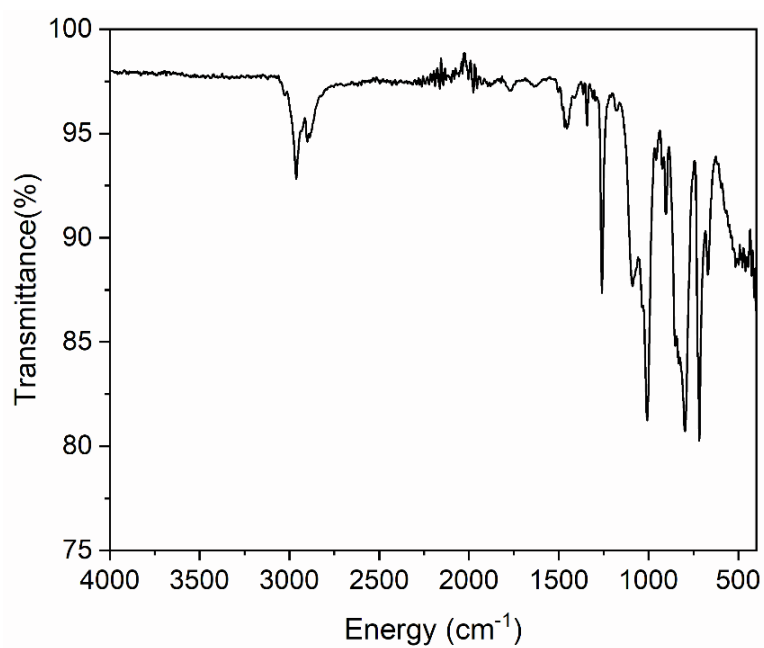
Supplementary Figure S20. ATR-IR spectrum of $C_8H_8K_2$.



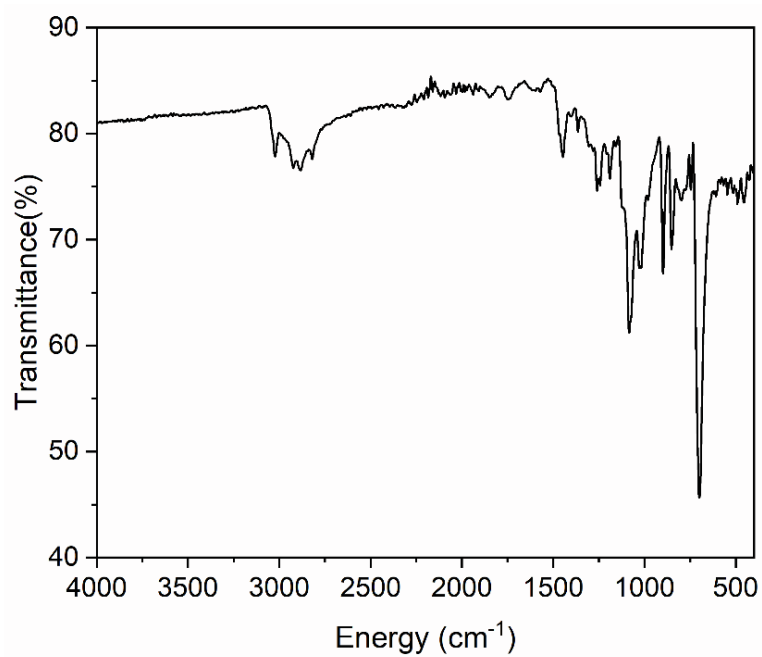
Supplementary Figure S21. ATR-IR spectrum of $ThCl_4(THF)_{3.5}$.



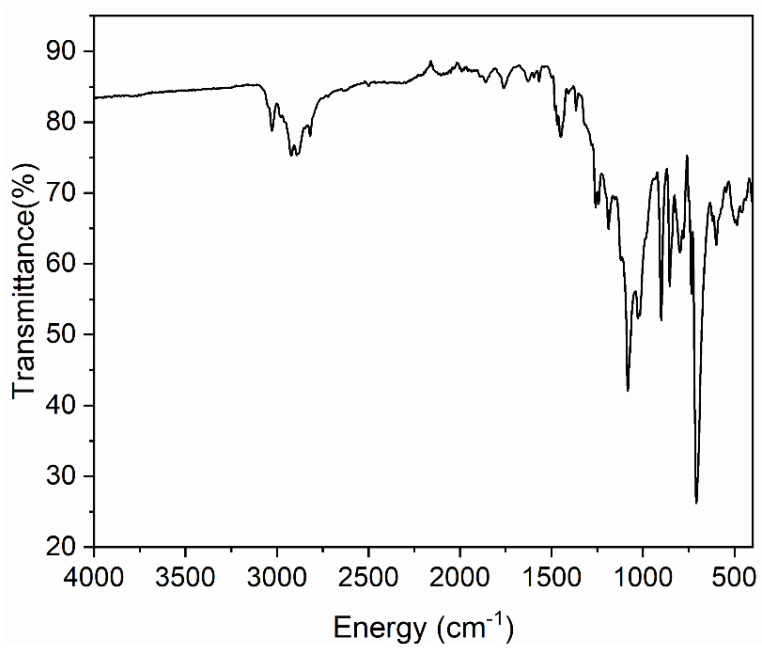
Supplementary Figure S22. ATR-IR spectrum of $[\text{Th}(\eta^8\text{-C}_8\text{H}_8)_2]$.



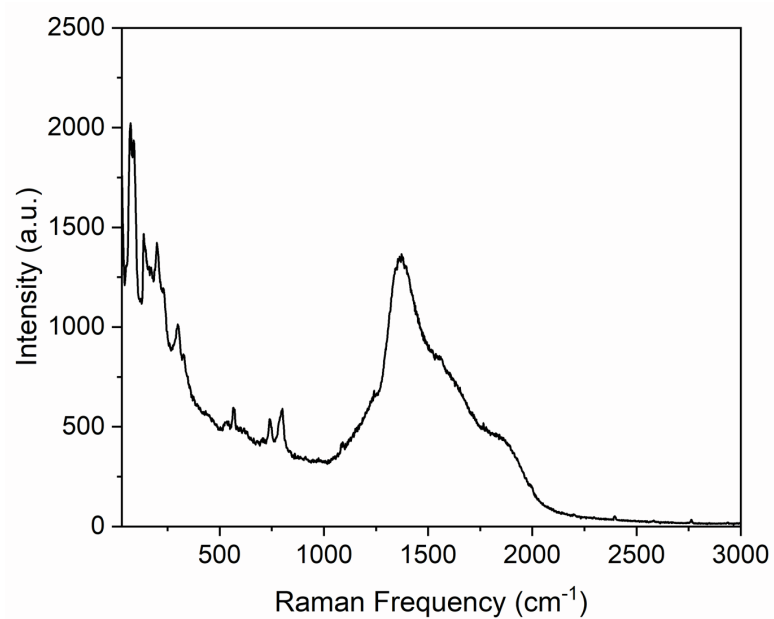
Supplementary Figure S23. ATR-IR spectrum of $[\text{Th}(\eta^8\text{-C}_8\text{H}_8)(\text{Cl})_2(\text{THF})_2]$.



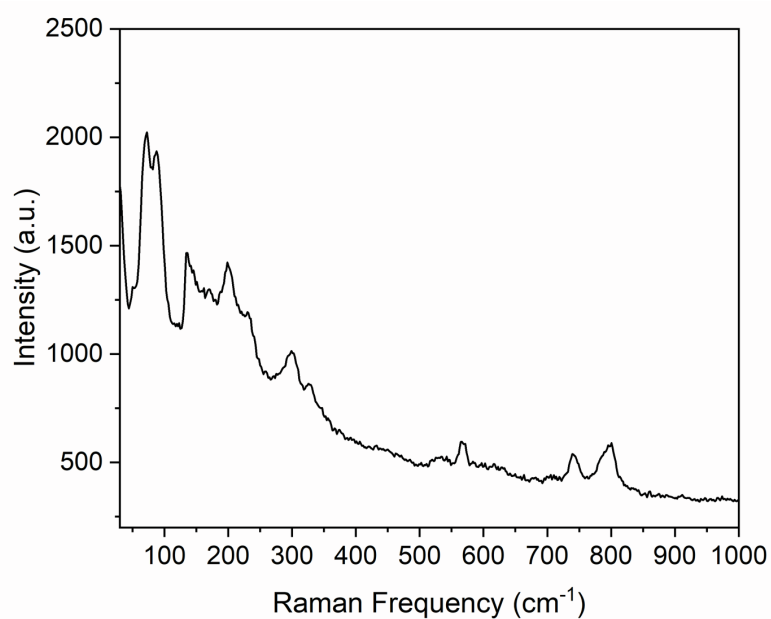
Supplementary Figure S24. ATR-IR spectrum of 1a.



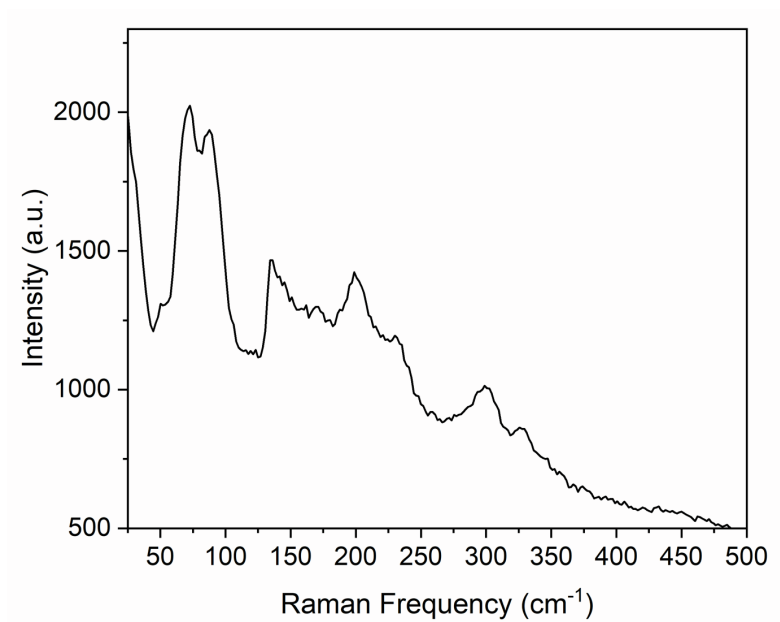
Supplementary Figure S25. ATR-IR spectrum of 1b.



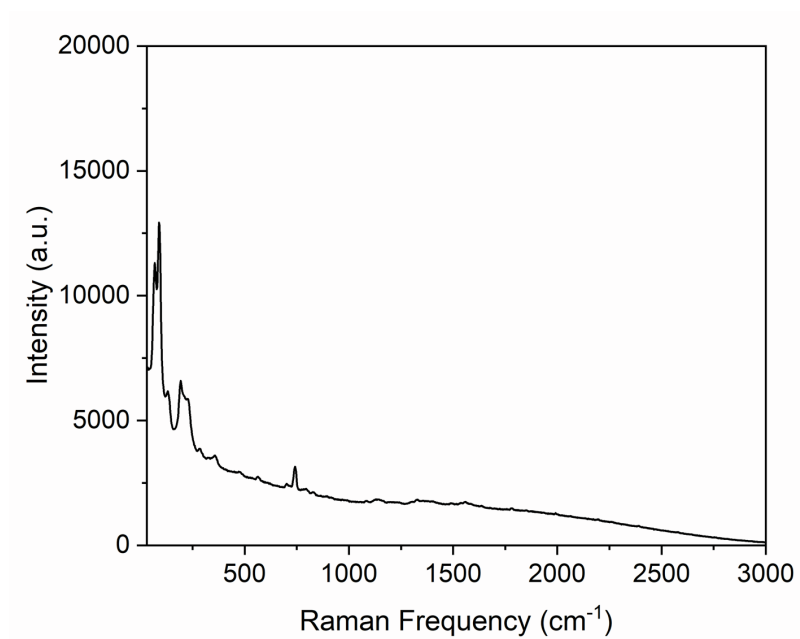
Supplementary Figure S26. Raman spectrum of 1a using a 785 nm laser over the range 30–3000 cm⁻¹. The large broad feature at ~1400 cm⁻¹ results from photoluminescence of the glass microscope slide used for the measurement [S47].



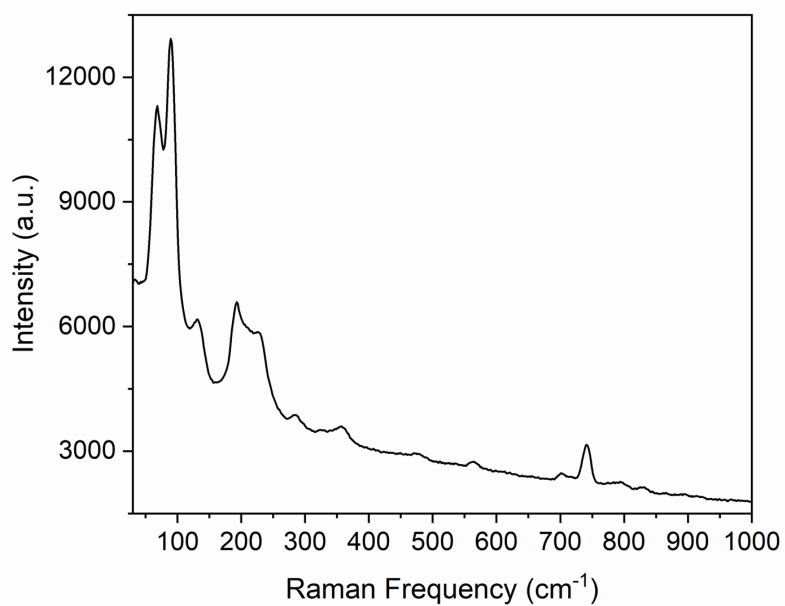
Supplementary Figure S27. Raman spectrum of 1a using a 785 nm laser zoomed in over the range 30–1000 cm⁻¹.



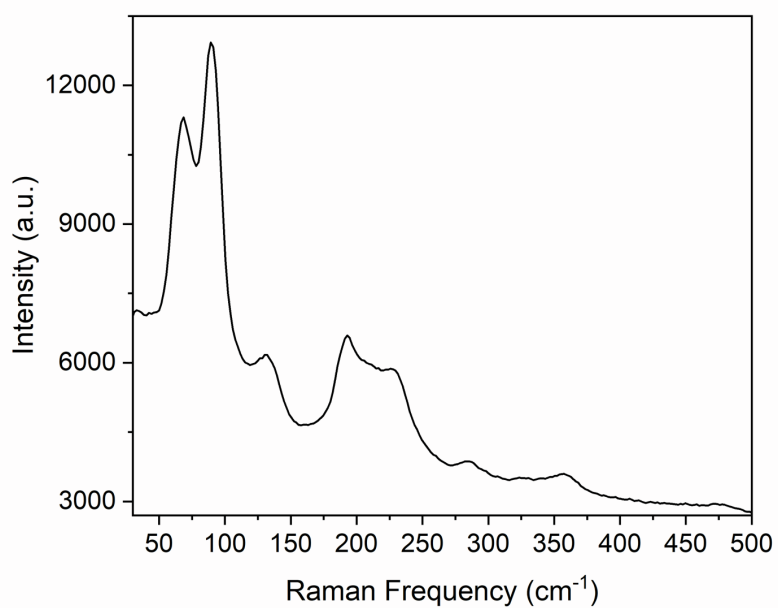
Supplementary Figure S28. Raman spectrum of 1a using a 785 nm laser zoomed in over the range 30–500 cm⁻¹.



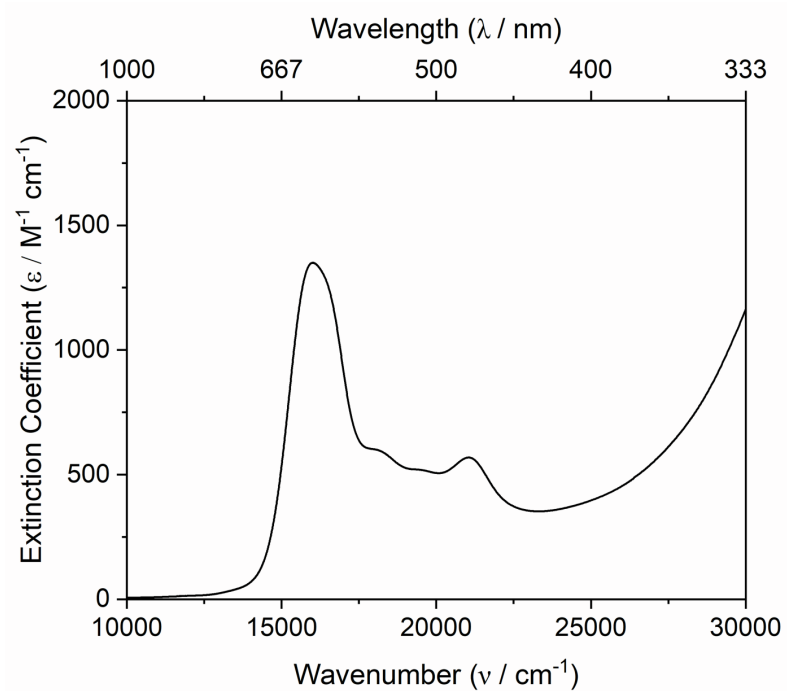
Supplementary Figure S29. Raman spectrum of 1b using a 785 nm laser over the range 30–3000 cm⁻¹.



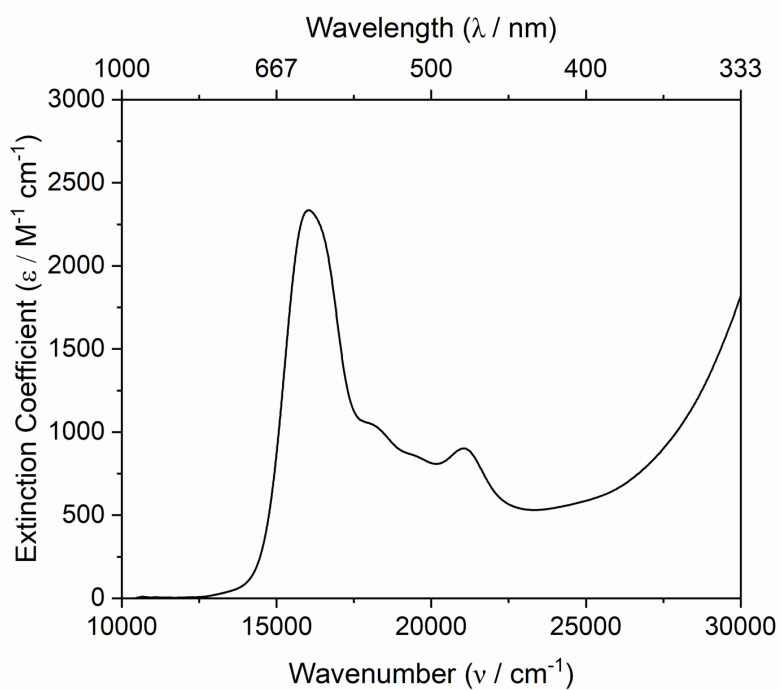
Supplementary Figure S30. Raman spectrum of 1b using a 785 nm laser zoomed in over the range 30–1000 cm⁻¹.



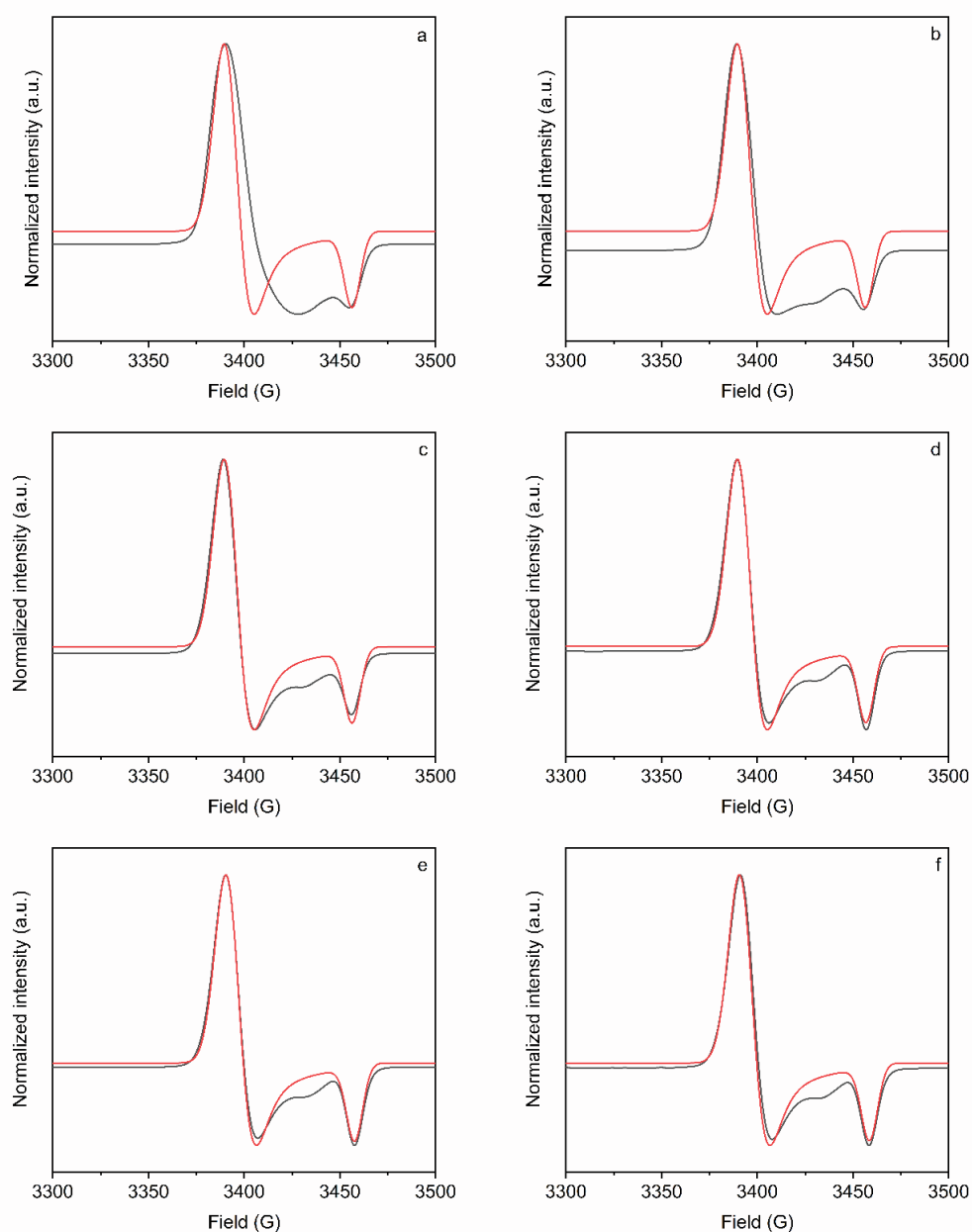
Supplementary Figure S31. Raman spectrum of 1b using a 785 nm laser zoomed in over the range 30–500 cm⁻¹.



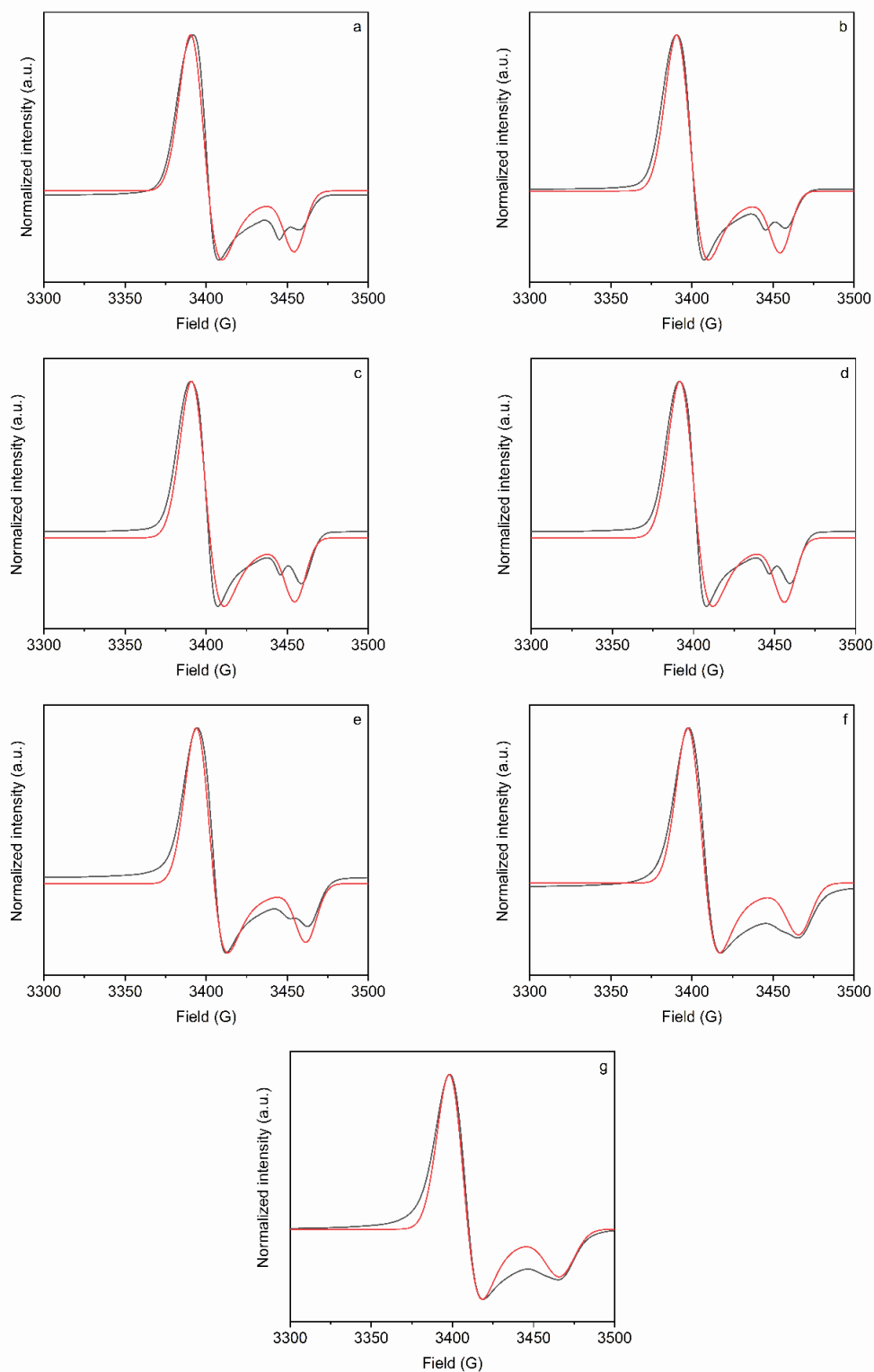
Supplementary Figure S32. UV/Vis/NIR spectrum of 1a (0.121 mM in DME).



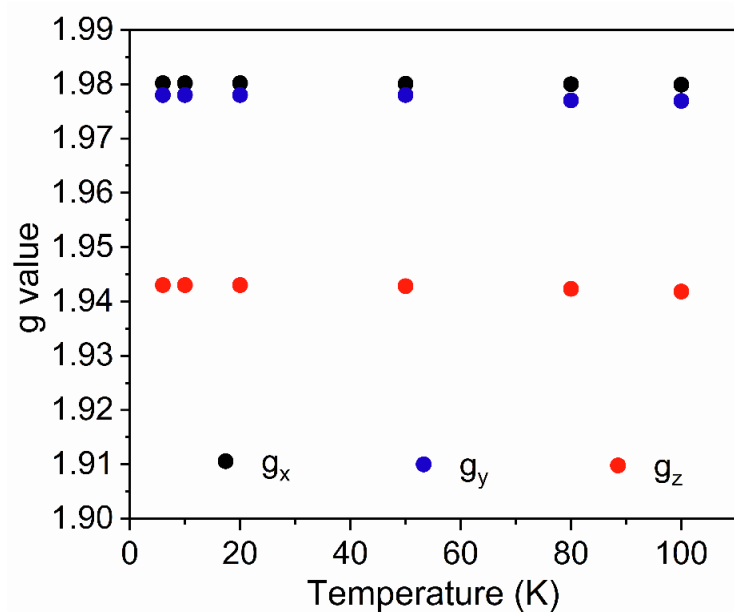
Supplementary Figure S33. UV/Vis/NIR spectrum of 1b (0.108 mM in DME).



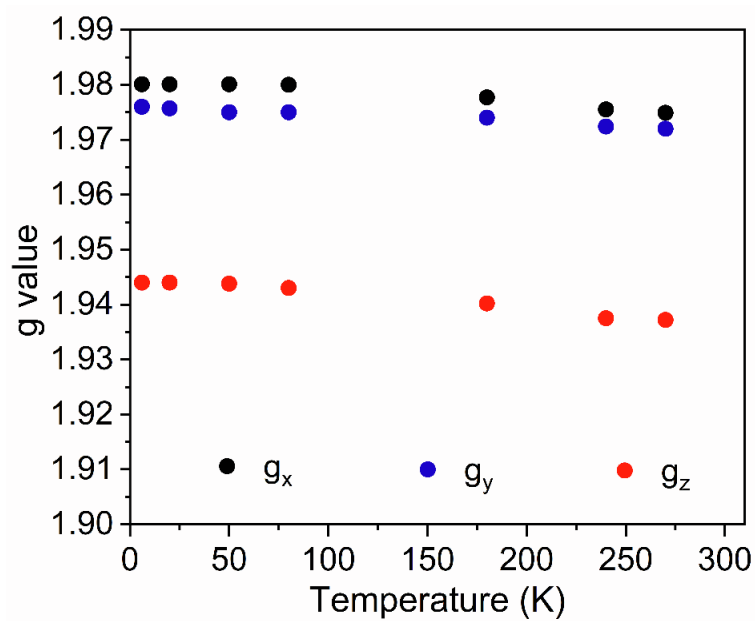
Supplementary Figure S34. X-band (9.4 GHz) EPR spectra of a frozen solution (DME:Toluene 95:5, 3mM) of 1b. Measured at 6 (a), 10 (b), 20 (c), 50 (d), 80 (e), and 100 (f) K (attenuation, 25 dB; modulation frequency, 100 kHz; modulation amplitude, 2 G).



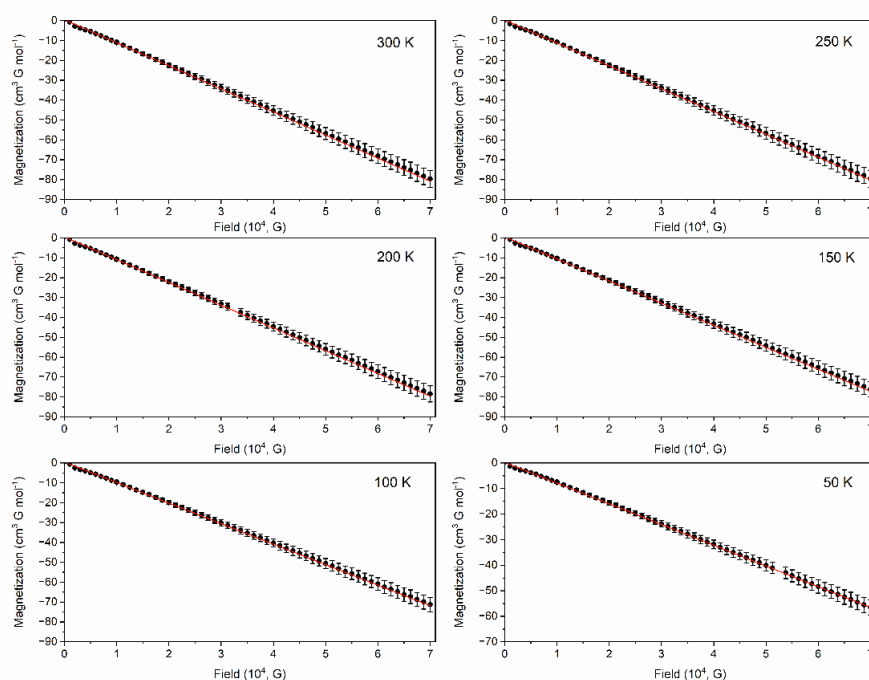
Supplementary Figure S35. X-band (9.4 GHz) EPR spectra of a powdered sample of 1b. Measured at 6 (a), 20 (b), 50 (c), 80 (d), 180 (e), 240 (f), and 270 (g) K, under modulation frequency of 100 kHz, modulation amplitude of 2 G, and microwave attenuation of 25 dB.



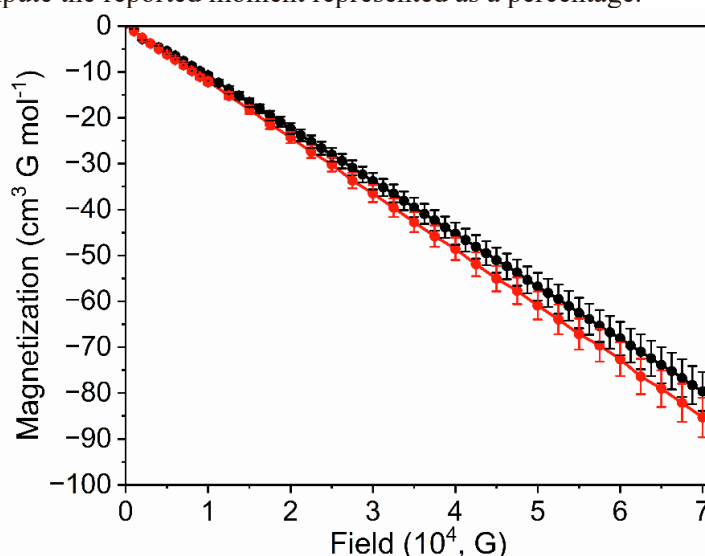
Supplementary Figure S36. Temperature dependence of the extracted g -values (g_x = black; g_y = blue; g_z = red) for a frozen solution (DME:Toluene, 95:5, 3mM) of 1b.



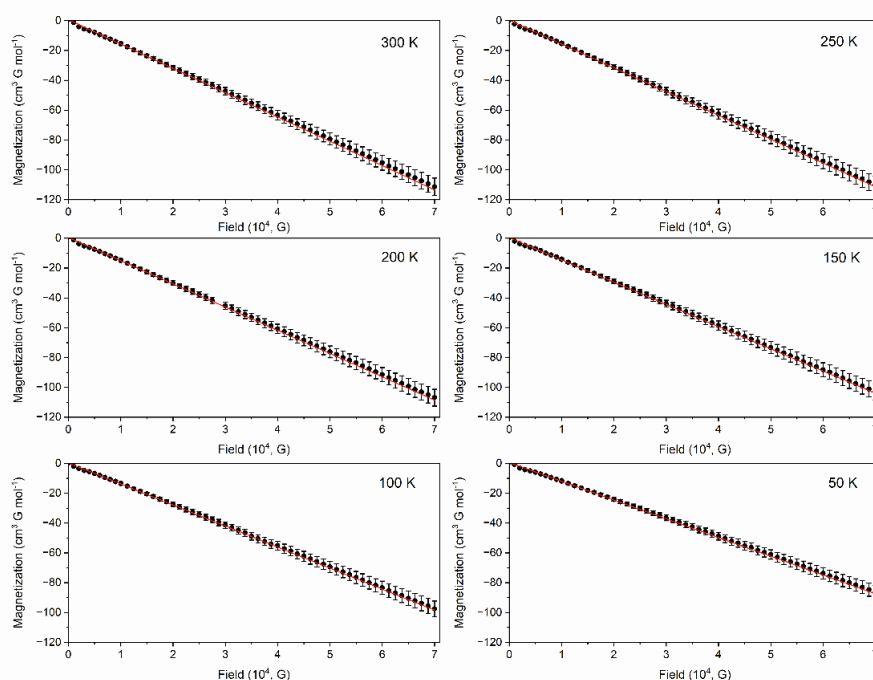
Supplementary Figure S37. Temperature dependence of the extracted g -values (g_x = black; g_y = blue; g_z = red) for a powdered sample of 1b.



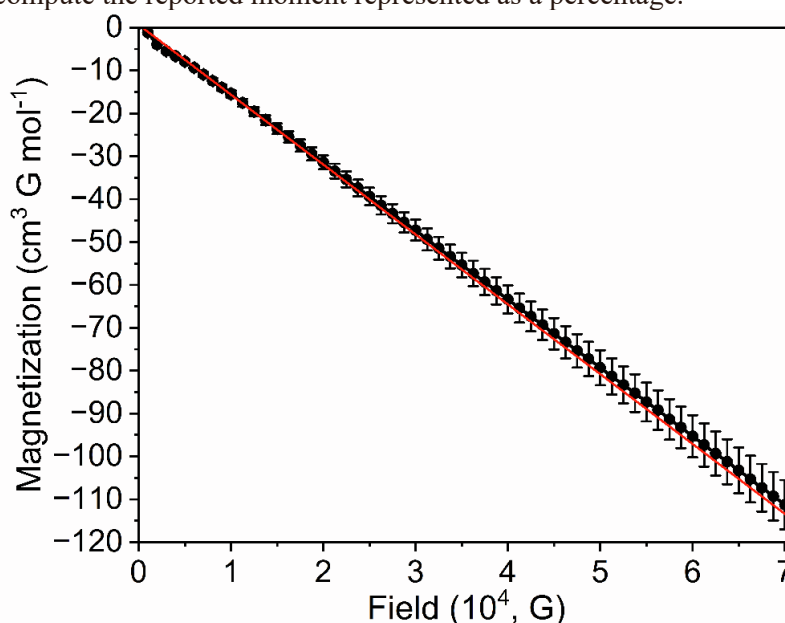
Supplementary Figure S38. Magnetization vs Field data for 1a at 300 (top left: $R^2 = 0.9999$; average error = 5.32%), 250 (top right: $R^2 = 0.9999$; average error = 5.19%), 200 (middle left: $R^2 = 0.9999$; average error = 5.14%), 150 (middle right: $R^2 = 0.9999$; average error = 5.13%), 100 (bottom left: $R^2 = 0.9999$; average error = 5.11%) and 50 (bottom right: $R^2 = 0.9999$; average error = 5.35%) K from 0-7 Tesla. The straight lines are linear regressions of the data points. Missing field measurements are due to measurement error. Errors derive from the standard deviation of the sampling distribution of the points used (sample population divided by the square root of the number of samples) to compute the reported moment represented as a percentage.



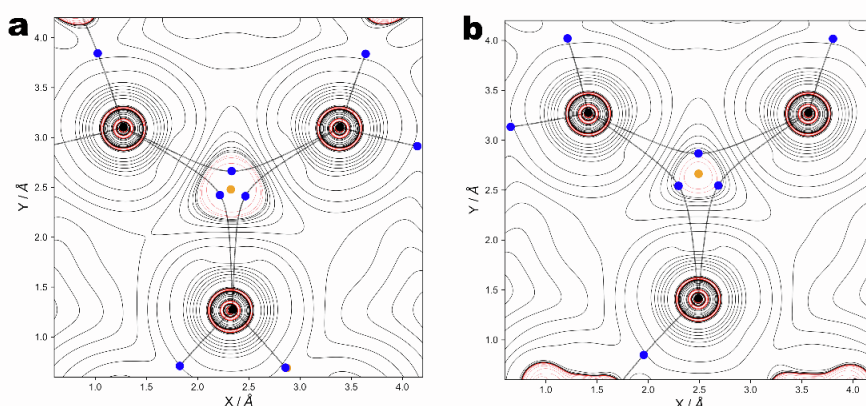
Supplementary Figure S39. Comparative Magnetization vs Field data for 1a (black: average error = 5.32%) and 1a-eico (red: average error = 5.05%) at 300 K from 0-7 Tesla. The straight lines are linear regressions of the data points. On a per molecule basis, $\chi_D = -1141.51 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ ($R^2 = 0.9999$) for **1a and $-1217.58 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ ($R^2 = 0.9999$) for **1a-eico**; this is a percentage difference of 6.45%. Errors derive from the standard deviation of the sampling distribution of the points used (sample population divided by the square root of the number of samples) to compute the reported moment represented as a percentage.**



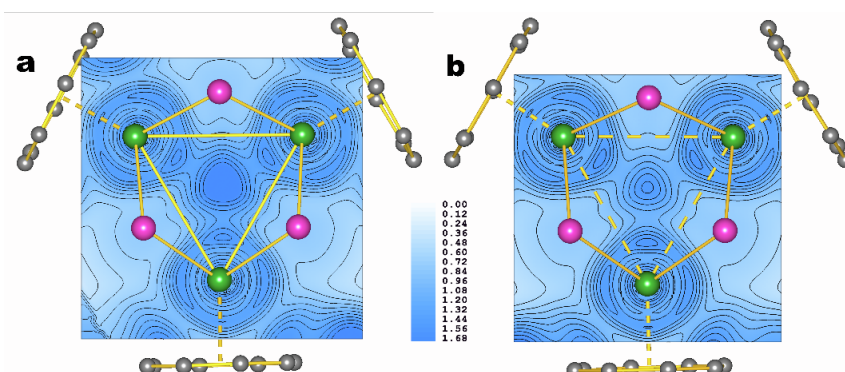
Supplementary Figure S40. Magnetization vs Field data for 1b at 300 (top left: $R^2 = 0.9999$; average error = 5.16%), 250 (top right: $R^2 = 0.9999$; average error = 5.23%), 200 (middle left: $R^2 = 0.9999$; average error = 5.23%), 150 (middle right: $R^2 = 0.9999$; average error = 5.30%), 100 (bottom left: $R^2 = 0.9999$; average error = 5.32%) and 50 (bottom right: $R^2 = 0.9999$; average error = 5.16%) K from 0-7 Tesla. The straight lines are linear regressions of the data points. Missing field measurements are due to measurement error. Errors derive from the standard deviation of the sampling distribution of the points used (sample population divided by the square root of the number of samples) to compute the reported moment represented as a percentage.



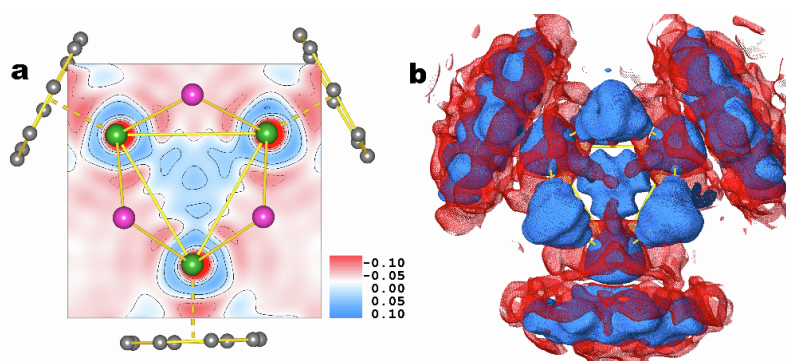
Supplementary Figure S41. Magnetization vs Field data for 1b (black: average error = 5.16%) at 300 K from 0-7 Tesla. The straight lines are linear regressions of the data points. On a per molecule basis, $\chi_D = -1591.56 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ ($R^2 = 0.9999$) for 1b. Errors derive from the standard deviation of the sampling distribution of the points used (sample population divided by the square root of the number of samples) to compute the reported moment represented as a percentage.



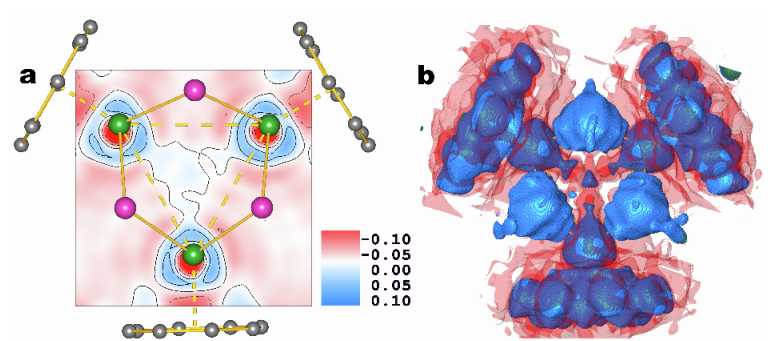
Supplementary Figure S42. Laplacian ($\nabla^2\rho(r)$) of the total electron density in the trithorium plane of a) 1aCu ($[1]^{2-}$) and b) 1bCu ($[1]^{1-}$) HAR-datasets. Red indicates negative Laplacian values and, therefore, valence shell charge concentration, black indicates positive Laplacian values and, therefore, valence shell charge depletion. The figure contains the bond paths (black lines) as well as critical points in the total electron density with the following colour scheme: Blue for covalent bond critical points, and orange for ring critical points.



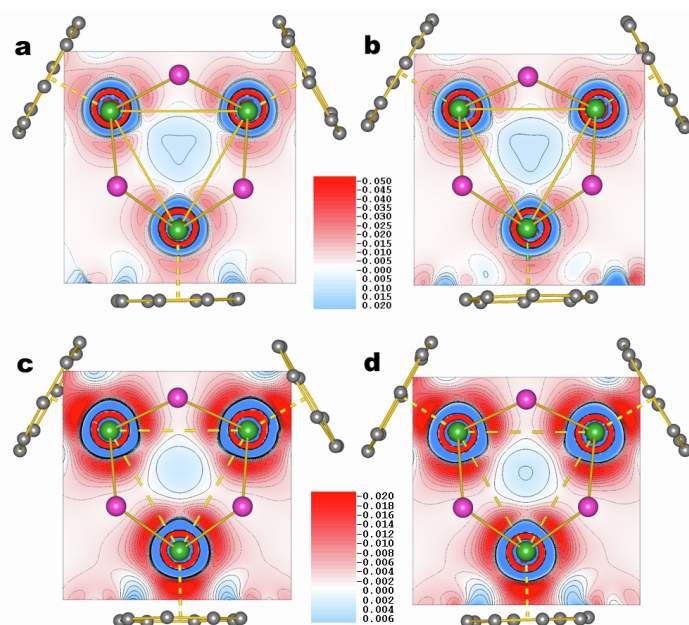
Supplementary Figure S43. Electron Localizability Index (ELI-D in a.u.) in the *cyclo*-Th₃ plane of a) 1aCu ($[1]^{2-}$) and b) 1bCu ($[1]^{1-}$). Each black line represents a 0.12 increment iso-level and a balls-and-sticks representation of each anion. Hydrogen atoms were omitted for clarity. Atom colour key: thorium, green; chloride, purple; carbon, grey.



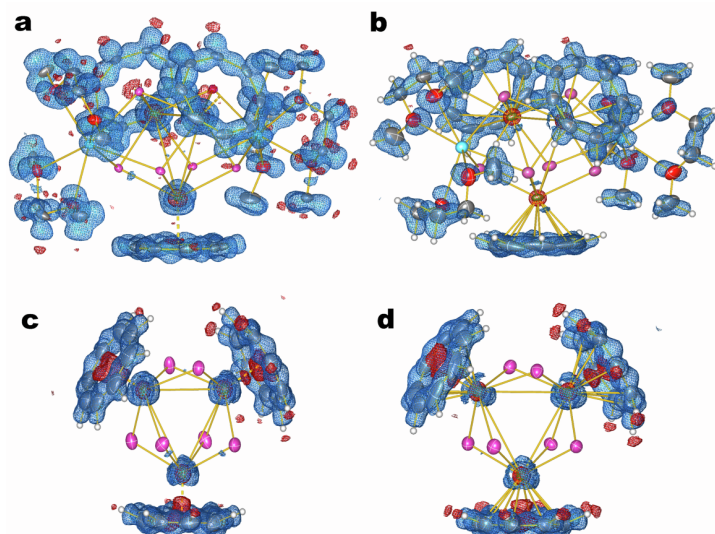
Supplementary Figure S44. HAR models of the 1aCu dataset of the dianion $[1]^{2-}$. (a) 2D and (b) 3D at the $0.02 \text{ e}\text{\AA}^{-3}$ iso-level).



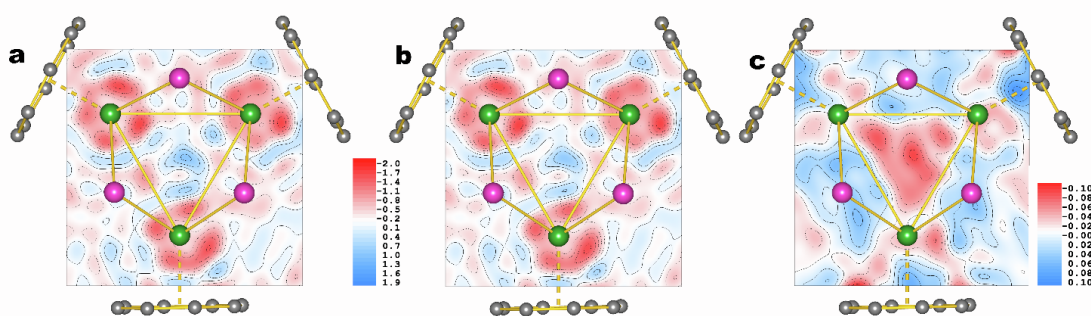
Supplementary Figure S45. HAR models of the 1bMo dataset of the monoanion $[1]^{1-}$. (a) 2D and (b) 3D at the $0.01 \text{ e}\text{\AA}^{-3}$ iso-level.



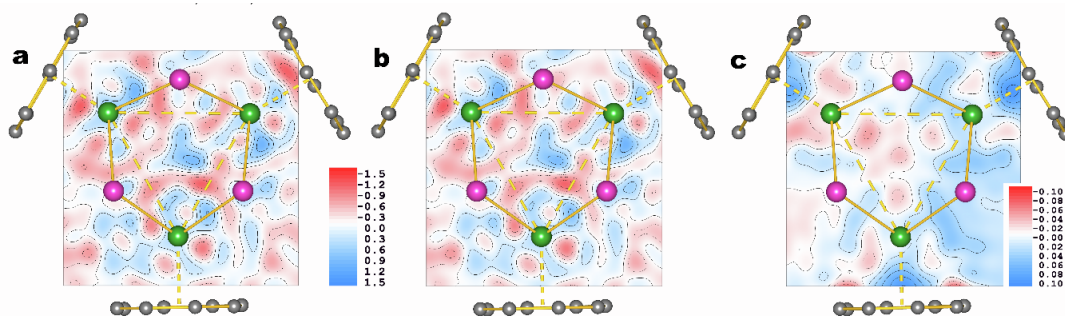
Supplementary Figure S46. 2D static deformation density maps of the HAR models of $[1]^{2-}$ and $[1]^{1-}$. (a) 1aMo, (b) 1aCu, (c) 1bMo, and (d) 1bCu.



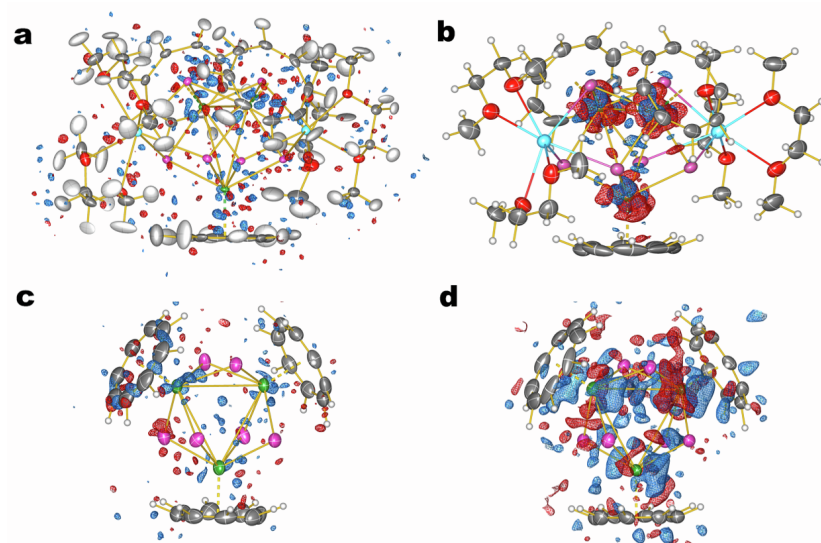
Supplementary Figure S47. 3D dynamic deformation density maps of the HAR models of $[1]^{2-}$ and $[1]^{-}$. (a) **1aMo**, (b) **1aCu**, (c) **1bMo**, (d) **1bCu**. The models of $[1]^{2-}$ (a, b) are shown at the $0.09 \text{ e}\text{\AA}^{-3}$ iso-level, models of $[1]^{-}$ (c, d) are shown at the $0.07 \text{ e}\text{\AA}^{-3}$ iso-level. Red shows negative, blue positive deformation density.



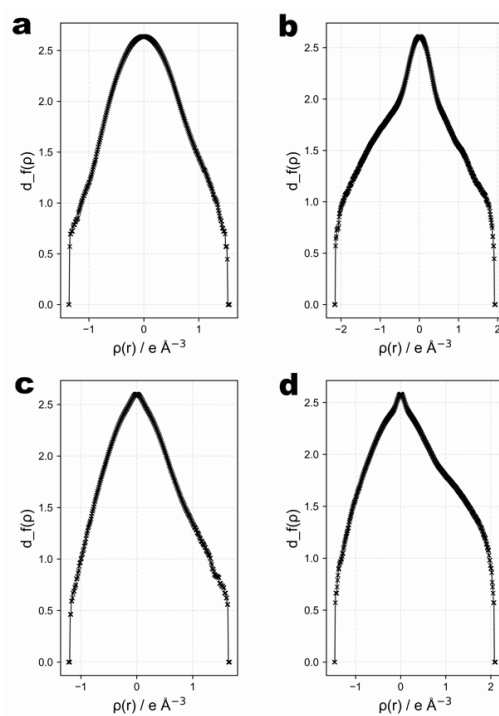
Supplementary Figure S48. Residual electron densities ($\text{e}\text{\AA}^{-3}$) for the **1aCu** dataset of $[1]^{2-}$. (a) IAM and (b) HAR models as well as their differences (c, HAR-IAM).



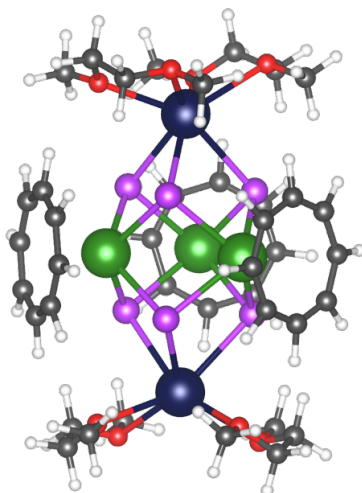
Supplementary Figure S49. Residual electron density ($\text{e}\text{\AA}^{-3}$) for the **1bCu** dataset of $[1]^{-}$. (a) IAM and (b) HAR models as well as their differences (c, HAR-IAM).



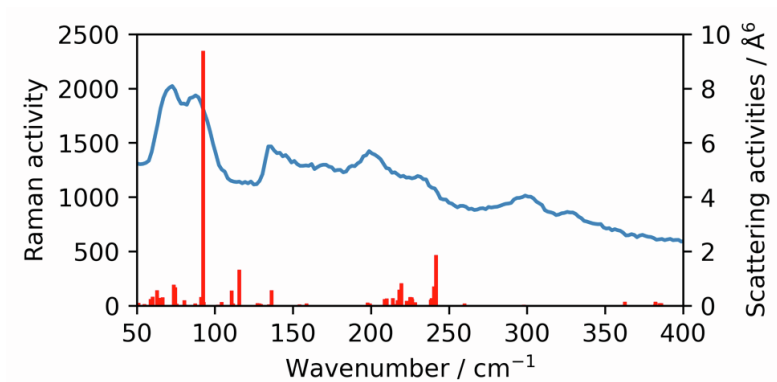
Supplementary Figure S50. 3D residual electron density maps of the HAR models of $[1]^{2-}$ and $[1]^{1-}$. (a) **1aMo**, (b) **1aCu**, (c) **1bMo**, (d) **1bCu**. All maps are shown at the $0.7 \text{ e}\text{\AA}^{-3}$ iso-level. Red shows negative, blue positive deformation density.



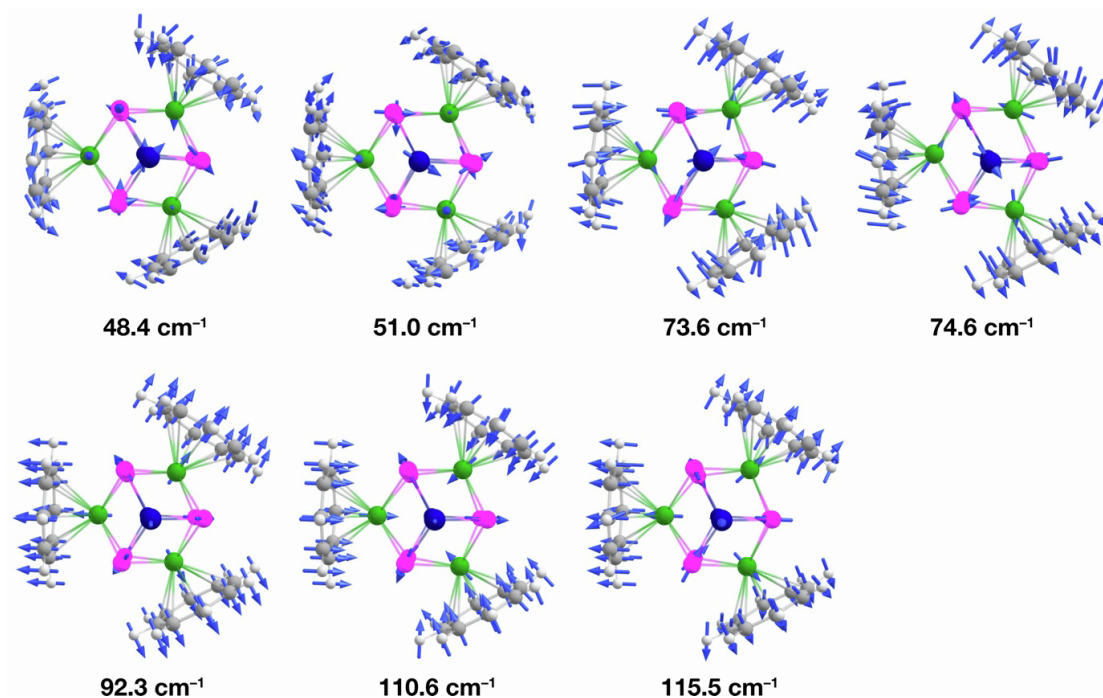
Supplementary Figure S51. Fractal dimension plots of the HAR models of $[1]^{2-}$ and $[1]^{1-}$. (a) **1aMo**, (b) **1aCu** (c), **1bMo**, (d) **1bCu** according to Meindl & Henn [S48].



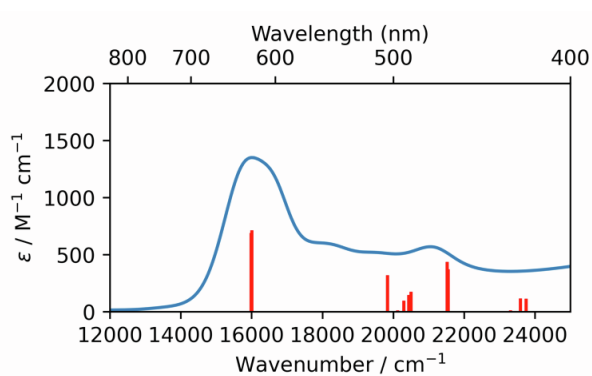
Supplementary Figure S52. The optimized geometry of 1a. Atom colour key: thorium, green; chloride, violet; potassium, blue; oxygen, red; carbon, grey.



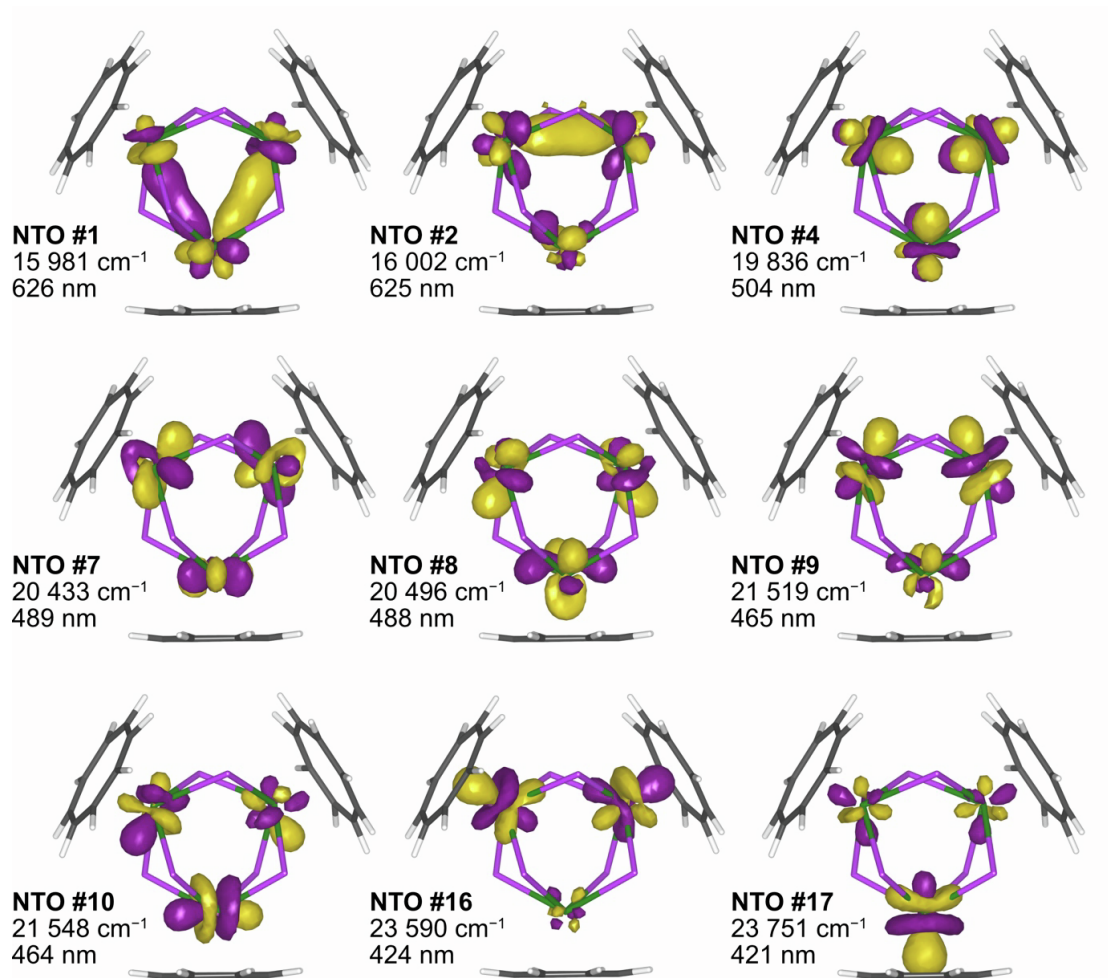
Supplementary Figure S53. Selected portion of the Raman spectrum (blue line) of 1a with DFT computed inelastic scattering bands (red sticks).



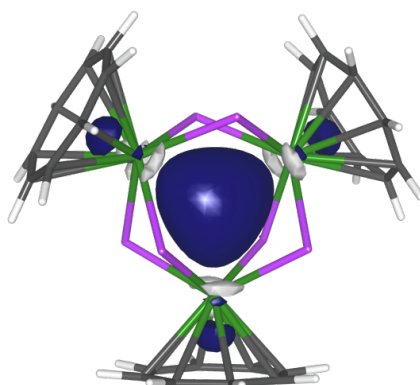
Supplementary Figure S54. Selected Raman modes of 1a including Th_3 vibrations. The DME ligands are omitted for clarity.



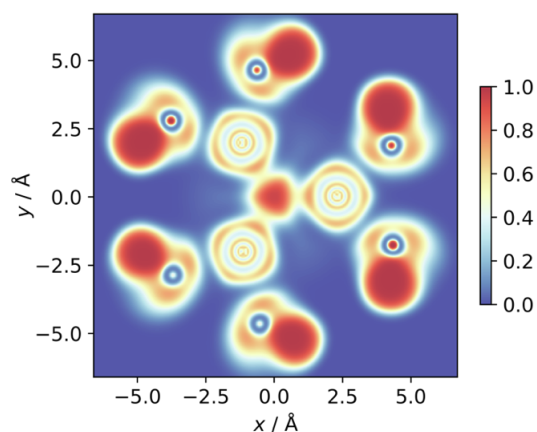
Supplementary Figure S55. The experimental UV-vis-NIR spectrum of 1a (blue line) and calculated electronic transition energies (red sticks) calculated with the ω -BP97X functional.



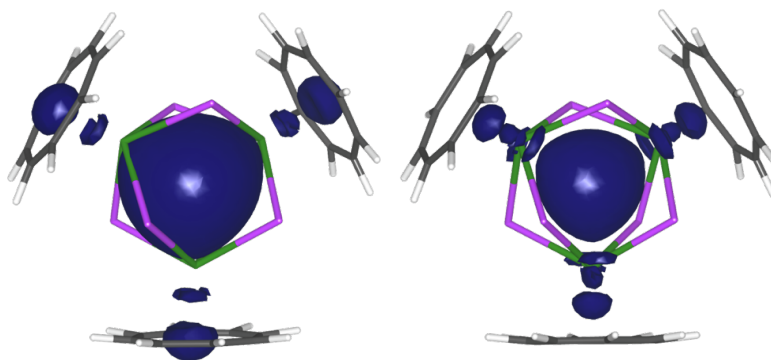
Supplementary Figure S56. Selected acceptor natural transition orbitals (NTOs) of **1a** obtained with the ω -BP97X functional. Plotted at an isovalue of 0.05 a.u. The $\{\text{K}(\text{DME})_2\}^{1+}$ components are omitted for clarity.



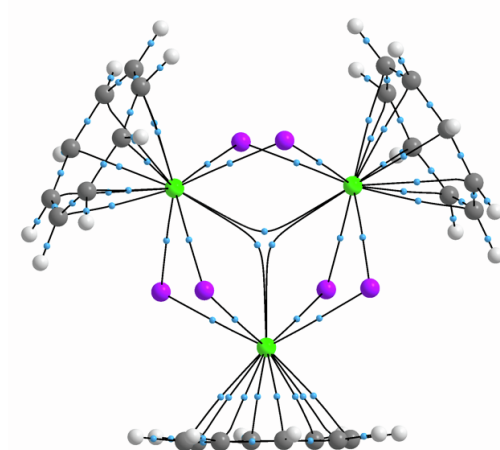
Supplementary Figure S57. HOMO (389, -2.93 eV) of **1a**. Plotted with an isovalue of 0.05 a.u. with the $\{\text{K}(\text{DME})_2\}^{1+}$ components omitted for clarity.



Supplementary Figure S58. ELF plot in the xy -plane ($z = 0$) of **1a**.



Supplementary Figure S59. AdNDP and EDDB_F plots of **1a**. Left: The 3-center Th₃-fragment MO from AdNDP (ON = 1.77) of **1a** plotted at an isovalue of 0.05 a.u. Right: EDDB_F analysis of the Th₃-fragment of **1a** plotted at an isovalue of 0.003 a.u. The {K(DME)₂}¹⁺ components are omitted for clarity.



Supplementary Figure S60. QTAIM molecular graph of the bond paths in the [1]²⁻ component of **1a**. Bond critical points are shown as light blue spheres. The {K(DME)₂}¹⁺ components are omitted for clarity.

Supplementary Tables

Supplementary Table S1. IAM crystallographic details for 1a and 1b.

	1a	1b
Formula	C ₄₀ H ₆₄ Cl ₆ K ₂ O ₈ Th ₃	C ₄₀ H ₆₄ Cl ₆ KO ₈ Th ₃
Fw, g mol ⁻¹	1659.93	1620.83
Cryst size, mm	0.18 × 0.14 × 0.05	0.18 × 0.13 × 0.11
Crystal system	monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> -1
Collection Temperature (K)	100(2)	100(2)
a, (Å)	11.5069(3)	12.1079(2)
b, (Å)	36.7998(7)	13.7978(2)
c, (Å)	13.2334(2)	17.5944(3)
α, (°)	90	107.8740(10)
β, (°)	107.501(2)	103.0260(10)
γ, (°)	90	103.109(2)
V, (Å ³)	5344.3(2)	2582.92(8)
Z	4	2
ρ _{calc} g cm ⁻³	2.063	2.084
μ, mm ⁻¹	8.826	9.050
Reflections measured	54053	52795
Unique reflections, <i>R</i> _{int}	13728, 0.0319	15546, 0.0309
Reflections with <i>F</i> ² > 2σ(<i>F</i> ²)	12177	11892
Transmission range	0.299-0.667	0.304-0.436
<i>R</i> , <i>R</i> _w ^a (<i>F</i> ² > 2σ(<i>F</i> ²))	0.0232, 0.0395	0.0368, 0.0813
<i>R</i> , <i>R</i> _w ^a (all data)	0.0307, 0.0408	0.0572, 0.0876
<i>S</i> ^a	1.025	1.019
Parameters, Restraints	613, 456	773, 1414
Max.,min. diff. map, e Å ⁻³	0.863, -0.652	2.395, -1.338

^a Conventional $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; $S = [\Sigma w(F_o^2 - F_c^2)^2/\text{no. data} - \text{no. params}]^{1/2}$ for all data.

Supplementary Table S2. IAM and HAR crystallographic details for 1a and 1b.

Species	1a ([1] ²⁻)		1b ([1] ¹⁻)	
Dataset name	1aMo	1aCu	1bMo	1bCu
Radiation Type	Mo K α	Cu K α	Mo K α	Cu K α
Wavelength / Å	0.71073	1.15184	0.71073	1.15184
Formula	C ₄₀ H ₆₄ Cl ₆ K ₂ O ₈ Th ₃	C ₄₀ H ₆₄ O ₈ Cl ₆ K ₂ Th ₃	C ₄₀ H ₆₄ Cl ₆ KO ₈ Th ₃	C ₄₀ H ₆₄ Cl ₆ KO ₈ Th ₃
D_{calc} / g cm ⁻³	2.063	2.047	2.083	2.068
μ /mm ⁻¹	8.867	30.904	9.086	31.241
Formula Weight	1659.975	1659.975	1620.877	1620.877
Colour	dark blue	dark blue	dark blue	dark blue
Shape	block	block	block	Block
Size/mm ³	0.17 × 0.10 × 0.03	0.15 × 0.11 × 0.06	0.18 × 0.14 × 0.10	0.16 × 0.13 × 0.10
T/K	100.00(10)	155(8)	100.00(10)	100.00(10)
Crystal System	monoclinic	monoclinic	triclinic	monoclinic
Space Group	$P2_1/c$	$P2_1/c$	$P-1$	$P2_1/c$
$a/\text{Å}$	11.5069(3)	11.5296(2)	12.1118(3)	14.4599(1)
$b/\text{Å}$	36.7998(7)	36.8339(4)	13.8012(3)	17.5637(2)
$c/\text{Å}$	13.2334(3)	13.2693(2)	17.5969(3)	21.2152(2)
a°	90	90	107.890(2)	90
b°	107.501(2)	107.126(2)	103.021(2)	104.911(1)
g°	90	90	103.101(2)	90
$V/\text{Å}^3$	5344.392	5385.34(15)	2584.66(11)	5206.58(9)
Z	4	4	2	4
Z'	1	1	1	1
Q_{min}°	2.21	2.40	2.42	4.04
Q_{max}°	31.00	77.68	30.51	77.54
Measured Refl.	53854	65585	52466	66918
Independent Refl.	13728	11303	14998	10946
Reflections with $I \geq 2\sigma(I)$	12172	10590	11680	10022
R_{int}	0.0330	0.0490	0.0307	0.0661
IAM Indicators				
Nr. Parameters	-	571	-	569
Nr. Restraints	-	96	-	142
Largest Peak	-	2.0589	-	3.9047
Deepest Hole	-	-1.7382	-	-1.3184
GooF	-	0.9705	-	1.0346
wR_2 (all data)	-	0.0857	-	0.1015
wR_2	-	0.0490	-	0.0993
R_I (all data)	-	0.0353	-	0.0432
R_I	-	0.0327	-	0.0396
IAM + Mask Indicators^a				
Nr. Parameters	-	-	298	298
Nr. Restraints	-	-	48	6
Largest Peak	-	-	2.2909	3.9488
Deepest Hole	-	-	-1.7211	-1.4231
GooF	-	-	0.9558	1.0103
wR_2 (all data)	-	-	0.0857	0.1017
wR_2	-	-	0.0821	0.1000
R_I (all data)	-	-	0.0430	0.0421
R_I	-	-	0.0318	0.0393
HAR Indicators^a				
Nr. Parameters	1183	571	373	328
Nr. Restraints	852	0	96	6
Largest Peak	1.2795	2.0017	1.5606	3.2412
Deepest Hole	-1.1964	-1.8210	-1.0312	-1.4500
GooF	1.0624	1.0381	0.9564	1.0147
wR_2 (all data)	0.0366	0.0795	0.0704	0.0994
wR_2	0.0353	0.0780	0.0674	0.0977
R_I (all data)	0.0300	0.0330	0.0397	0.0412
R_I	0.0225	0.0303	0.0282	0.0383

^a Conventional $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; GooF = $[\Sigma w(F_o^2 - F_c^2)^2/\text{no. data} - \text{no. params})]^{1/2}$ for all data.

Datasets of **1bMo** and **1bCu** were measured on different single crystals of the same material showing polymorphs of **1b**. We tried to index without success the other unit cells in the respective other cases and tried the Platon ADDSYM analysis on the triclinic dataset of **1bMo** without any suggestions for missed symmetry.

Supplementary Table S3. Selected experimental parameters for Raman spectroscopic measurements of 1a and 1b.

Entry	1a	1b
λ (nm)	785	785
Power (mW)	1.5	1.5
Acquisition time (s)	20	10
Accumulations	5	10
Grating (gr/mm)	600	600
Filter (%)	10	25
Slit (μm)	100	100
Hole (μm)	300	300

Supplementary Table S4. Selected UV/Vis/NIR experimental details and data for 1a and 1b.

Entry	1a	1b
Solvent	DME	DME
Molarity (mM)	0.121	0.108
ν_{max} (cm^{-1})	16252	16181
λ_{max} (nm)	615	618
ϵ_{max} ($\text{M}^{-1} \text{cm}^{-1}$)	1325	2316
$\Delta\nu_{1/2}$ (cm^{-1})	2282	2297
$\nu_{1/2}^{\circ}$ (cm^{-1})	6127	6133
$\Gamma^{\text{[a]}}$	0.63	0.63

Supplementary Table S5. Extracted g-parameters for 1b from the simulation of X-band frozen solution spectra recorded at 9.4 GHz and 6-100 K.

Temperature (K)	g_x	g_y	g_z
6	1.9802	1.978	1.943
10	1.9802	1.978	1.943
20	1.9802	1.978	1.943
50	1.9801	1.978	1.9428
80	1.98	1.977	1.9423
100	1.9799	1.9769	1.9418

Supplementary Table S6. Extracted g-parameters for 1b from the simulation of X-band powder spectra recorded at 9.4 GHz and 6-270 K.

Temperature (K)	g_x	g_y	g_z
6	1.9801	1.976	1.944
20	1.9801	1.9757	1.944
50	1.9801	1.975	1.9438
80	1.98	1.975	1.943
180	1.9777	1.974	1.9402
240	1.9755	1.9724	1.9375
270	1.9749	1.972	1.9372

Supplementary Table S7. Sample information for those used in SQUID magnetometry measurements.

Entry	1a	1a-eico	1b
Chemical formula	C ₄₀ H ₆₄ Cl ₆ K ₂ O ₈ Th ₃	C ₄₀ H ₆₄ Cl ₆ K ₂ O ₈ Th ₃	C ₄₀ H ₆₄ Cl ₆ KO ₈ Th ₃
Molecular mass (g mol ⁻¹)	1659.83	1659.83	1620.86
Sample mass (mg)	22.7	21.9	18.6
Eicosane mass (mg)	0	7.6	0

Supplementary Table S8. Selected data for the magnetic properties of 1a and 1b.

Entry	1a	1a-eico	1b
χ_D (300 K, whole molecule) ^[a]	-1141.51E-06	-1217.58E-06	-1591.56E-06
R ² value	0.9999	0.9999	0.9999
χ_D (300 K, 1/3 molecule)	-380.50E-06	-405.86E-06	-530.52E-06
χ_D (300 K, per Th)	-164.68E-06	-190.03E-06	-319.66E-06
Th Pascal's constant	-23.00E-6	-23.00E-06	-23.00E-06
Factor increase vs expected	7.160	8.262	13.898
Expected χ_D (whole molecule)	-716.48E-06	-716.48E-06	-701.58E-06
χ_D per 1/3 molecule	-238.83E-06	-215.11E-06	-233.86E-06
Expected χ_D of non-Th atoms	-647.48E-06	-647.48E-06	-632.58E-06
χ_D per 1/3 of non-Th atoms	-215.83E-06	-215.83E-06	-210.86E-06
Superatom contribution (%)	37.23	41.15	55.92
χ_D Increase vs expected (%)	59.32	69.94	126.85
$\Delta(\chi_D(\text{expected}) - \chi_D(\text{Found}))$	425.03E-06	501.10E-06	889.98E-06

^[a] χ is given in units of cm³ mol⁻¹.

Supplementary Table S9. Comparison of the calculated modes [cm⁻¹] involving the Th₃ core in [1]K₂, [1]¹⁻, and 1a [S14, S17, S49].

Mode	[1]K ₂	[1] ¹⁻	1a
bending modes	<50	51.4/51.5	48.4, 51.0
bending modes	70.8, 71.0	67.3/67.5	73.6, 74.6
symmetric breathing mode	77.2	88.7	92.3
antisymmetric breathing mode	107.4	136.0	110.6, 115.5

Supplementary Table S10. Mulliken population analyses of the HOMO of 1a and selected acceptor NTOs with strong oscillator strengths, in terms of the 6d, 5f and 7p-character (%) of MOs and Th metal contributions.

	HOMO	NTO1	NTO2	NTO4	NTO7	NTO8	NTO9	NTO10	NTO16	NTO17
6d	68	26	25	8	19	25	16	13	10	11
5f	7	65	65	85	66	61	71	74	79	79
7p	13	0	0	0	2	2	0	0	0	0
7s	1	0	0	0	1	1	1	1	1	1
Th	89	91	90	93	88	89	88	88	90	91

Supplementary Table S11. The Mulliken populations of KS HOMO of [1]K₂ and 1a, and SOMO of [1]¹⁻, given as percentages [S14, S17, S49].

	[1]K ₂	[1] ¹⁻	1a
Th 6d	64	62	68
Th 5f	7	14	7
Th 7p	20	7	13
Th 7s	1	3	1
Th total:	92	86	89

Supplementary Table S12. Selected properties at the critical points in the total electron density within $[1]^2$. Ellipt: Ellipticity; LOL: local orbital localization index. NA: BCP not found.^a

		DFT				1aMo-HAR				1aCu-HAR			
Type		$\rho(r)$	$\nabla^2\rho(r)$	Ellipt.	LOL	$\rho(r)$	$\nabla^2\rho(r)$	Ellipt.	LOL	$\rho(r)$	$\nabla^2\rho(r)$	Ellipt.	LOL
Th1	Th2	0.0224	-0.0090	0.8013	7.3868	0.0213	-0.0057	0.7404	3.7504	0.0210	-0.0052	0.7232	3.0575
Th1	Th3	0.0224	-0.0090	0.8027	8.1648	0.0213	-0.0058	0.7409	3.1179	0.0210	-0.0054	0.7313	3.1306
Th2	Th3	0.0224	-0.0090	0.8026	8.1643	0.0212	-0.0059	0.7538	5.1665	0.0208	-0.0056	0.7487	6.0622
Th1	Cl1	0.0407	0.0999	0.3234	0.0593	0.0433	0.1010	0.3365	0.0641	0.0410	0.0950	0.3323	0.0708
Th1	Cl2	0.0409	0.1005	0.3241	0.0592	0.0439	0.1019	0.3382	0.0714	0.0420	0.0971	0.3348	0.0729
Th1	Cl3	0.0409	0.1005	0.3241	0.0592	0.0417	0.0970	0.3328	0.0738	0.0438	0.1012	0.3391	0.0729
Th1	Cl4	0.0407	0.0999	0.3234	0.0593	0.0404	0.0942	0.3297	0.0715	0.0437	0.1011	0.3390	0.0629
Th2	Cl2	0.0409	0.1005	0.3241	0.0592	0.0458	0.1059	0.3430	0.0719	0.0433	0.0998	0.3384	0.0678
Th2	Cl3	0.0409	0.1005	0.3241	0.0592	0.0431	0.0999	0.3366	0.0659	0.0456	0.1047	0.3437	0.0723
Th2	Cl5	0.0407	0.0999	0.3234	0.0593	0.0426	0.0986	0.3356	0.0667	0.0440	0.1015	0.3400	0.0664
Th2	Cl6	0.0407	0.0999	0.3234	0.0593	0.0437	0.1019	0.3376	0.0684	0.0434	0.0998	0.3388	0.0650
Th3	Cl1	0.0409	0.1003	0.3240	0.0581	0.0454	0.1051	0.3422	0.0523	0.0427	0.0981	0.3372	0.0606
Th3	Cl4	0.0409	0.1003	0.3240	0.0581	0.0427	0.0986	0.3363	0.0596	0.0450	0.1035	0.3424	0.0524
Th3	Cl5	0.0409	0.1003	0.3240	0.0581	0.0438	0.1010	0.3391	0.0593	0.0441	0.1014	0.3403	0.0528
Th3	Cl6	0.0409	0.1003	0.3240	0.0581	0.0444	0.1029	0.3396	0.0533	0.0440	0.1008	0.3407	0.0592
K1	Cl3	0.0166	0.0721	0.1710	0.0106	0.0100	0.0378	0.1472	0.0055	0.0071	0.0269	0.1239	0.0111
K1	Cl4	0.0166	0.0719	0.1708	0.0105	0.0115	0.0433	0.1576	0.0086	0.0134	0.0505	0.1690	0.0174
K1	Cl5	0.0166	0.0719	0.1708	0.0105	0.0127	0.0480	0.1644	0.0090	0.0149	0.0560	0.1772	0.0278
K2	Cl1	0.0166	0.0719	0.1708	0.0105	0.0132	0.0498	0.1677	0.0181	0.0117	0.0441	0.1593	0.0071
K2	Cl2	0.0166	0.0721	0.1710	0.0106	0.0069	0.0264	0.1223	0.0133	0.0102	0.0383	0.1488	0.0062
K2	Cl6	0.0166	0.0719	0.1708	0.0105	0.0148	0.0560	0.1769	0.0278	0.0128	0.0485	0.1654	0.0079
Th1	C1	0.0450	0.1113	0.3268	9.1865	0.0435	0.1086	0.3238	46.3008	0.0420	0.1056	0.3190	12.2191
Th1	C2	0.0450	0.1110	0.3272	9.5463	0.0447	0.1077	0.3319	6.2991	NA	NA	NA	NA
Th1	C3	0.0450	0.1110	0.3272	9.5476	NA	NA	NA	NA	0.0437	0.1074	0.3264	5.9547
Th1	C4	0.0450	0.1113	0.3268	9.1854	0.0423	0.1048	0.3224	16.8814	NA	NA	NA	NA
Th1	C5	0.0450	0.1113	0.3268	9.3102	NA	NA	NA	NA	0.0429	0.1052	0.3248	6.5001
Th1	C6	0.0449	0.1109	0.3270	9.6036	0.0445	0.1062	0.3332	6.3229	NA	NA	NA	NA
Th1	C7	0.0449	0.1109	0.3270	9.6041	0.0439	0.1075	0.3274	24.0879	0.0434	0.1062	0.3265	6.3889
Th1	C8	0.0450	0.1113	0.3268	9.3096	0.0446	0.1059	0.3342	6.1307	0.0423	0.1079	0.3174	88.6402
Th2	C9	0.0450	0.1113	0.3268	9.1860	0.0443	0.1089	0.3280	7.5762	NA	NA	NA	NA
Th2	C10	0.0449	0.1109	0.3270	9.6039	0.0433	0.1058	0.3268	19.2756	0.0416	0.1052	0.3174	11.0289
Th2	C11	0.0449	0.1109	0.3270	9.6038	0.0427	0.1067	0.3219	14.2243	0.0408	0.1048	0.3132	65.0269
Th2	C12	0.0450	0.1113	0.3268	9.3099	NA	NA	NA	NA	0.0421	0.1058	0.3195	28.4251
Th2	C13	0.0450	0.1113	0.3268	9.3099	0.0443	0.1077	0.3297	12.6244	NA	NA	NA	NA
Th2	C14	0.0450	0.1110	0.3272	9.5469	NA	NA	NA	NA	0.0445	0.1099	0.3279	8.1090
Th2	C15	0.0450	0.1110	0.3272	9.5469	0.0470	0.1093	0.3419	4.5219	0.0442	0.1116	0.3237	15.5403
Th2	C16	0.0450	0.1113	0.3268	9.1860	NA	NA	NA	NA	0.0432	0.1088	0.3219	11.4247
Th3	C17	0.0450	0.1114	0.3269	9.2245	0.0431	0.1017	0.3313	5.9334	0.0418	0.1059	0.3173	32.5640
Th3	C18	0.0450	0.1111	0.3271	9.5965	NA	NA	NA	NA	0.0420	0.1040	0.3214	8.8276
Th3	C19	0.0450	0.1111	0.3271	9.5965	0.0430	0.1032	0.3289	7.0129	0.0412	0.1049	0.3149	51.8982
Th3	C20	0.0450	0.1114	0.3269	9.2245	0.0426	0.1062	0.3220	27.4903	0.0427	0.1036	0.3258	5.6135
Th3	C21	0.0450	0.1114	0.3269	9.2244	0.0434	0.1052	0.3283	7.1294	NA	NA	NA	NA
Th3	C22	0.0450	0.1111	0.3271	9.5965	0.0440	0.1054	0.3317	5.6971	0.0424	0.1049	0.3226	6.6823
Th3	C23	0.0450	0.1111	0.3271	9.5965	NA	NA	NA	NA	0.0415	0.1068	0.3144	81.2237
Th3	C24	0.0450	0.1114	0.3269	9.2245	NA	NA	NA	NA	0.0427	0.1057	0.3230	6.0418
C1	H1	0.2868	-1.0433	0.8869	0.0310	0.2645	-0.9620	0.8822	0.0418	0.2569	-0.9081	0.8822	0.0386
C2	H2	0.2879	-1.0526	0.8896	0.0296	0.2646	-0.9622	0.8819	0.0412	0.2767	-1.0599	0.8847	0.0369
C3	H3	0.2879	-1.0526	0.8896	0.0296	0.2649	-0.9644	0.8823	0.0410	0.2713	-1.0201	0.8845	0.0352
C4	H4	0.2868	-1.0433	0.8869	0.0310	0.2641	-0.9562	0.8804	0.0415	0.2522	-0.8736	0.8818	0.0376
C5	H5	0.2867	-1.0432	0.8869	0.0309	0.2646	-0.9646	0.8831	0.0416	0.3140	-1.3642	0.8835	0.0312
C6	H6	0.2879	-1.0525	0.8896	0.0295	0.2645	-0.9659	0.8836	0.0420	0.3095	-1.3270	0.8866	0.0351
C7	H7	0.2879	-1.0525	0.8896	0.0295	0.2649	-0.9692	0.8843	0.0415	0.2861	-1.1387	0.8861	0.0342
C8	H8	0.2867	-1.0432	0.8869	0.0309	0.2641	-0.9599	0.8819	0.0431	0.2750	-1.0464	0.8834	0.0340
C9	H9	0.2868	-1.0433	0.8869	0.0310	0.2646	-0.9596	0.8803	0.0410	0.2796	-1.0783	0.8809	0.0345
C10	H10	0.2879	-1.0525	0.8896	0.0295	0.2647	-0.9656	0.8833	0.0414	0.2707	-1.0151	0.8845	0.0333
C11	H11	0.2879	-1.0525	0.8896	0.0295	0.2648	-0.9649	0.8828	0.0404	0.2834	-1.1131	0.8855	0.0350
C12	H12	0.2867	-1.0432	0.8869	0.0309	0.2645	-0.9542	0.8785	0.0390	0.2836	-1.1071	0.8805	0.0349
C13	H13	0.2867	-1.0432	0.8869	0.0309	0.2636	-0.9502	0.8789	0.0425	0.2915	-1.1736	0.8825	0.0325

C14	H14	0.2879	-1.0526	0.8896	0.0296	0.2649	-0.9675	0.8837	0.0405	0.3163	-1.3869	0.8858	0.0320
C15	H15	0.2879	-1.0526	0.8896	0.0296	0.2644	-0.9629	0.8825	0.0423	0.3371	-1.5655	0.8841	0.0298
C16	H16	0.2868	-1.0433	0.8869	0.0310	0.2640	-0.9598	0.8823	0.0448	0.3160	-1.3790	0.8839	0.0332
C17	H17	0.2867	-1.0432	0.8869	0.0310	0.2631	-0.9481	0.8791	0.0447	0.2859	-1.1313	0.8839	0.0362
C18	H18	0.2879	-1.0525	0.8896	0.0295	0.2645	-0.9645	0.8832	0.0418	0.3106	-1.3382	0.8863	0.0320
C19	H19	0.2879	-1.0525	0.8896	0.0295	0.2645	-0.9654	0.8835	0.0416	0.3052	-1.2906	0.8852	0.0342
C20	H20	0.2867	-1.0432	0.8869	0.0310	0.2645	-0.9591	0.8810	0.0408	0.2765	-1.0538	0.8812	0.0376
C21	H21	0.2867	-1.0432	0.8869	0.0310	0.2650	-0.9677	0.8831	0.0426	0.3028	-1.2680	0.8839	0.0343
C22	H22	0.2879	-1.0525	0.8896	0.0295	0.2649	-0.9629	0.8816	0.0393	0.3132	-1.3593	0.8860	0.0318
C23	H23	0.2879	-1.0525	0.8896	0.0295	0.2646	-0.9666	0.8838	0.0420	0.2869	-1.1392	0.8840	0.0331
C24	H24	0.2867	-1.0432	0.8869	0.0310	0.2645	-0.9623	0.8821	0.0419	0.2729	-1.0336	0.8854	0.0358
C1	C2	0.3035	-0.8411	0.7861	0.2457	0.3056	-0.8361	0.7806	0.2387	0.3029	-0.8221	0.7818	0.2349
C1	C8	0.3004	-0.8300	0.7884	0.2335	0.2974	-0.7933	0.7815	0.2360	0.3017	-0.8173	0.7817	0.2292
C2	C3	0.3009	-0.8318	0.7880	0.2332	0.3076	-0.8495	0.7814	0.2329	0.3022	-0.8198	0.7811	0.2294
C3	C4	0.3035	-0.8411	0.7861	0.2457	0.3071	-0.8459	0.7812	0.2359	0.3049	-0.8323	0.7802	0.2364
C4	C5	0.3004	-0.8300	0.7884	0.2335	0.3010	-0.8138	0.7821	0.2325	0.2990	-0.8030	0.7820	0.2287
C5	C6	0.3035	-0.8412	0.7861	0.2456	0.2964	-0.7859	0.7803	0.2402	0.2901	-0.7517	0.7800	0.2303
C6	C7	0.3010	-0.8325	0.7880	0.2332	0.2947	-0.7772	0.7803	0.2378	0.2907	-0.7578	0.7814	0.2290
C7	C8	0.3035	-0.8413	0.7861	0.2456	0.2924	-0.7642	0.7800	0.2413	0.3022	-0.8175	0.7798	0.2347
C9	C12	0.3004	-0.8300	0.7884	0.2335	0.3216	-0.9320	0.7820	0.2259	0.3049	-0.8357	0.7819	0.2278
C9	C14	0.3035	-0.8411	0.7861	0.2457	0.3126	-0.8765	0.7816	0.2363	0.3022	-0.8172	0.7797	0.2366
C10	C11	0.3010	-0.8325	0.7880	0.2332	0.3095	-0.8620	0.7826	0.2308	0.3064	-0.8446	0.7825	0.2233
C10	C13	0.3035	-0.8413	0.7861	0.2456	0.2964	-0.7861	0.7802	0.2398	0.3068	-0.8438	0.7813	0.2301
C11	C12	0.3035	-0.8413	0.7861	0.2456	0.3182	-0.9092	0.7813	0.2327	0.3043	-0.8300	0.7814	0.2311
C13	C16	0.3004	-0.8300	0.7884	0.2335	0.2970	-0.7899	0.7810	0.2410	0.3009	-0.8128	0.7819	0.2219
C14	C15	0.3009	-0.8318	0.7880	0.2332	0.3031	-0.8227	0.7805	0.2377	0.2976	-0.7952	0.7805	0.2236
C15	C16	0.3035	-0.8411	0.7861	0.2457	0.2855	-0.7268	0.7789	0.2455	0.2997	-0.8042	0.7807	0.2299
C17	C18	0.3035	-0.8409	0.7861	0.2457	0.2917	-0.7619	0.7808	0.2405	0.3002	-0.8077	0.7807	0.2345
C17	C24	0.3004	-0.8300	0.7884	0.2336	0.2902	-0.7542	0.7809	0.2389	0.2939	-0.7757	0.7815	0.2275
C18	C19	0.3010	-0.8321	0.7880	0.2333	0.2935	-0.7719	0.7809	0.2357	0.2965	-0.7884	0.7806	0.2287
C19	C20	0.3035	-0.8409	0.7861	0.2457	0.3035	-0.8248	0.7806	0.2383	0.2966	-0.7896	0.7818	0.2322
C20	C21	0.3004	-0.8300	0.7884	0.2336	0.3027	-0.8232	0.7820	0.2327	0.2926	-0.7682	0.7817	0.2288
C21	C22	0.3035	-0.8409	0.7861	0.2457	0.3046	-0.8319	0.7810	0.2340	0.3001	-0.8074	0.7810	0.2309
C22	C23	0.3010	-0.8321	0.7880	0.2333	0.3044	-0.8308	0.7809	0.2356	0.2981	-0.7974	0.7810	0.2266
C23	C24	0.3035	-0.8409	0.7861	0.2457	0.2970	-0.7893	0.7804	0.2396	0.3045	-0.8311	0.7812	0.2315
Th ₃	RCP	0.0224	-0.0092	0.8164	-10.011	0.0211	-0.0065	0.7900	-6.8552	0.0207	-0.0061	0.7830	-7.617
COT1	RCP	0.0444	0.1122	0.3231	-9.9764	0.0437	0.1071	0.3271	-14.485	0.0423	0.1080	0.3174	-88.552
COT2	RCP	0.0444	0.1123	0.3233	-9.9877	0.0442	0.1088	0.3277	-14.558	0.0430	0.1110	0.3178	-12.164
COT3	RCP	0.0444	0.1123	0.3233	-9.9858	0.0427	0.1067	0.3216	-15.168	0.0414	0.1063	0.3146	-15.146

^a In the HAR models of [1]²⁻ and [1]⁻ some Th-C BCPs could not be located while they could be found in the purely DFT calculations. This is due to the difference in geometry of the experimental models compared to the DFT-optimized geometry. This is also reflected in the ellipticity of the HAR Th-C BCPs, which reach values up close to 100. Problems in localizing these extremely small saddle points are well-known in the literature.⁵⁰⁻⁵²

Supplementary Table S13. Selected properties at the critical points in the total electron density within [1]¹⁻. Ellipt: Ellipticity; LOL: local orbital localization index. NA: BCP not found.^a

Type		DFT				1bCu-HAR				1bMo-HAR			
		$\rho(r)$	$\nabla^2\rho(r)$	Ellipt.	LOL	$\rho(r)$	$\nabla^2\rho(r)$	Ellipt.	LOL	$\rho(r)$	$\nabla^2\rho(r)$	Ellipt.	LOL
Th1	Th2	0.0139	-0.0002	0.5824	3.7569	0.0136	-0.0004	0.6115	4.4310	0.0132	-0.0004	0.6148	4.9351
Th1	Th3	0.0138	-0.0009	0.6037	5.5925	0.0136	-0.0002	0.6055	3.7509	0.0133	0.0002	0.5961	3.6442
Th2	Th3	0.0138	-0.0010	0.6068	5.8490	0.0137	-0.0002	0.6052	3.6974	0.0133	0.0006	0.5832	3.4687
Th1	Cl1	0.0459	0.1040	0.3466	0.0301	0.0453	0.1003	0.3489	0.0260	0.0456	0.0997	0.3510	0.0271
Th1	Cl2	0.0459	0.1041	0.3463	0.0318	0.0482	0.1061	0.3555	0.0204	0.0449	0.0983	0.3497	0.0288
Th1	Cl3	0.0459	0.1041	0.3464	0.0318	0.0439	0.0963	0.3472	0.0313	0.0433	0.0957	0.3450	0.0305
Th1	Cl4	0.0459	0.1041	0.3467	0.0300	0.0442	0.0975	0.3473	0.0319	0.0443	0.0979	0.3472	0.0270
Th2	Cl2	0.0459	0.1041	0.3464	0.0319	0.0462	0.1020	0.3508	0.0286	0.0439	0.0969	0.3464	0.0309
Th2	Cl3	0.0459	0.1041	0.3464	0.0318	0.0441	0.0966	0.3476	0.0320	0.0470	0.1027	0.3541	0.0199
Th2	Cl5	0.0459	0.1040	0.3466	0.0300	0.0456	0.1002	0.3506	0.0251	0.0443	0.0978	0.3471	0.0324
Th2	Cl6	0.0459	0.1039	0.3465	0.0301	0.0457	0.1006	0.3506	0.0252	0.0457	0.1008	0.3498	0.0262

Th3	C11	0.0465	0.1052	0.3481	0.0297	0.0450	0.0992	0.3484	0.0276	0.0432	0.0956	0.3443	0.0332
Th3	C14	0.0465	0.1051	0.3479	0.0299	0.0451	0.0990	0.3493	0.0266	0.0456	0.1001	0.3504	0.0242
Th3	C15	0.0464	0.1050	0.3479	0.0298	0.0443	0.0977	0.3475	0.0292	0.0441	0.0972	0.3468	0.0344
Th3	C16	0.0465	0.1051	0.3480	0.0296	0.0439	0.0971	0.3461	0.0347	0.0466	0.1026	0.3523	0.0234
Th1	C1	0.0444	0.1072	0.3295	9.6742	0.0430	0.1029	0.3297	31.1167	0.0441	0.1059	0.3319	15.2313
Th1	C2	0.0441	0.1070	0.3279	10.5370	NA	NA	NA	NA	0.0439	0.1056	0.3310	12.2206
Th1	C3	0.0441	0.1070	0.3279	10.5148	NA	NA	NA	NA	NA	NA	NA	NA
Th1	C4	0.0444	0.1073	0.3295	9.6948	0.0477	0.1084	0.3478	3.8885	0.0455	0.1083	0.3364	9.0924
Th1	C5	0.0444	0.1073	0.3295	9.8174	NA	NA	NA	NA	0.0453	0.1082	0.3350	16.7855
Th1	C6	0.0441	0.1072	0.3280	10.3987	0.0435	0.1031	0.3324	8.9438	0.0450	0.1054	0.3375	7.8033
Th1	C7	0.0441	0.1072	0.3280	10.4006	NA	NA	NA	NA	NA	NA	NA	NA
Th1	C8	0.0444	0.1073	0.3294	9.8186	0.0440	0.1033	0.3347	6.6126	0.0447	0.1042	0.3376	6.9268
Th2	C9	0.0444	0.1073	0.3295	9.6897	0.0440	0.1036	0.3346	10.2270	0.0450	0.1021	0.3426	5.3333
Th2	C10	0.0441	0.1072	0.3280	10.3931	0.0449	0.1040	0.3392	6.5197	NA	NA	NA	NA
Th2	C11	0.0441	0.1072	0.3280	10.3856	0.0441	0.1052	0.3328	94.8762	0.0443	0.1068	0.3316	13.5871
Th2	C12	0.0444	0.1073	0.3295	9.8060	0.0438	0.1043	0.3324	11.3199	0.0440	0.1056	0.3314	23.3123
Th2	C13	0.0444	0.1073	0.3294	9.8115	0.0436	0.1059	0.3285	28.3138	0.0463	0.1086	0.3401	5.5108
Th2	C14	0.0441	0.1071	0.3280	10.5145	0.0439	0.1055	0.3314	9.9510	NA	NA	NA	NA
Th2	C15	0.0441	0.1071	0.3279	10.5428	NA	NA	NA	NA	0.0447	0.1080	0.3324	7.3525
Th2	C16	0.0444	0.1073	0.3295	9.6884	0.0440	0.1023	0.3366	7.3034	NA	NA	NA	NA
Th3	C17	0.0443	0.1070	0.3292	9.7789	0.0474	0.1051	0.3507	5.6018	0.0460	0.1055	0.3424	5.6263
Th3	C18	0.0439	0.1068	0.3276	10.5878	NA	NA	NA	NA	0.0456	0.1074	0.3378	10.1573
Th3	C19	0.0440	0.1068	0.3276	10.5557	NA	NA	NA	NA	0.0452	0.1097	0.3323	18.8215
Th3	C20	0.0443	0.1070	0.3293	9.7539	NA	NA	NA	NA	0.0467	0.1116	0.3381	26.6176
Th3	C21	0.0443	0.1070	0.3293	9.7609	NA	NA	NA	NA	0.0470	0.1120	0.3388	9.5997
Th3	C22	0.0440	0.1068	0.3276	10.5540	0.0464	0.1101	0.3384	9.6643	NA	NA	NA	NA
Th3	C23	0.0439	0.1068	0.3276	10.5906	0.0469	0.1060	0.3466	8.0371	0.0437	0.1072	0.3275	14.5864
Th3	C24	0.0443	0.1070	0.3292	9.7809	0.0476	0.1057	0.3505	6.5844	NA	NA	NA	NA
C1	H1	0.2879	-1.0506	0.8881	0.0309	0.2651	-0.9738	0.8860	0.0414	0.2651	-0.9716	0.8850	0.0415
C2	H2	0.2881	-1.0518	0.8884	0.0303	0.2646	-0.9669	0.8841	0.0406	0.2646	-0.9644	0.8830	0.0397
C3	H3	0.2881	-1.0518	0.8884	0.0303	0.2652	-0.9741	0.8857	0.0417	0.2654	-0.9765	0.8865	0.0413
C4	H4	0.2879	-1.0506	0.8881	0.0309	0.2646	-0.9671	0.8841	0.0433	0.2646	-0.9634	0.8825	0.0399
C5	H5	0.2880	-1.0506	0.8882	0.0308	0.2653	-0.9693	0.8836	0.0376	0.2653	-0.9746	0.8858	0.0417
C6	H6	0.2881	-1.0518	0.8884	0.0304	0.2648	-0.9666	0.8838	0.0419	0.2647	-0.9667	0.8838	0.0415
C7	H7	0.2881	-1.0516	0.8884	0.0304	0.2652	-0.9715	0.8849	0.0407	0.2652	-0.9728	0.8853	0.0393
C8	H8	0.2880	-1.0507	0.8882	0.0308	0.2645	-0.9664	0.8841	0.0413	0.2645	-0.9633	0.8829	0.0424
C9	H9	0.2879	-1.0506	0.8881	0.0309	0.2648	-0.9672	0.8839	0.0421	0.2644	-0.9679	0.8850	0.0445
C10	H10	0.2881	-1.0517	0.8884	0.0303	0.2649	-0.9716	0.8854	0.0423	0.2652	-0.9712	0.8846	0.0406
C11	H11	0.2881	-1.0517	0.8884	0.0303	0.2652	-0.9708	0.8843	0.0391	0.2647	-0.9645	0.8828	0.0399
C12	H12	0.2880	-1.0507	0.8882	0.0308	0.2648	-0.9706	0.8856	0.0422	0.2650	-0.9721	0.8857	0.0413
C13	H13	0.2880	-1.0508	0.8882	0.0308	0.2651	-0.9720	0.8852	0.0395	0.2648	-0.9667	0.8837	0.0415
C14	H14	0.2881	-1.0519	0.8884	0.0303	0.2648	-0.9679	0.8841	0.0404	0.2651	-0.9702	0.8843	0.0394
C15	H15	0.2881	-1.0519	0.8884	0.0303	0.2651	-0.9690	0.8841	0.0403	0.2649	-0.9650	0.8824	0.0388
C16	H16	0.2879	-1.0506	0.8881	0.0309	0.2647	-0.9681	0.8845	0.0425	0.2652	-0.9675	0.8832	0.0404
C17	H17	0.2879	-1.0505	0.8881	0.0309	0.2642	-0.9704	0.8863	0.0472	0.2647	-0.9702	0.8855	0.0453
C18	H18	0.2881	-1.0518	0.8883	0.0304	0.2653	-0.9632	0.8806	0.0363	0.2648	-0.9680	0.8841	0.0415
C19	H19	0.2881	-1.0518	0.8883	0.0304	0.2655	-0.9618	0.8799	0.0344	0.2650	-0.9712	0.8851	0.0403
C20	H20	0.2879	-1.0505	0.8881	0.0309	0.2658	-0.9586	0.8773	0.0335	0.2649	-0.9674	0.8837	0.0416
C21	H21	0.2879	-1.0505	0.8881	0.0309	0.2651	-0.9620	0.8808	0.0401	0.2649	-0.9663	0.8829	0.0396
C22	H22	0.2881	-1.0518	0.8883	0.0304	0.2651	-0.9728	0.8853	0.0410	0.2653	-0.9733	0.8856	0.0421
C23	H23	0.2881	-1.0518	0.8883	0.0303	0.2640	-0.9723	0.8875	0.0448	0.2650	-0.9641	0.8818	0.0385
C24	H24	0.2879	-1.0505	0.8881	0.0309	0.2644	-0.9785	0.8890	0.0452	0.2649	-0.9625	0.8813	0.0366
C1	C2	0.3030	-0.8378	0.7858	0.2452	0.2920	-0.7625	0.7802	0.2362	0.3096	-0.8561	0.7798	0.2392
C1	C8	0.3006	-0.8292	0.7876	0.2349	0.2968	-0.7894	0.7813	0.2353	0.2918	-0.7639	0.7812	0.2320
C2	C3	0.3010	-0.8308	0.7873	0.2356	0.2967	-0.7853	0.7792	0.2392	0.2963	-0.7876	0.7813	0.2316
C3	C4	0.3030	-0.8378	0.7858	0.2452	0.2891	-0.7468	0.7798	0.2399	0.3042	-0.8278	0.7803	0.2369
C4	C5	0.3006	-0.8292	0.7876	0.2348	0.3137	-0.8815	0.7808	0.2355	0.3043	-0.8283	0.7802	0.2366
C5	C6	0.3031	-0.8379	0.7857	0.2452	0.3098	-0.8595	0.7805	0.2342	0.2936	-0.7707	0.7800	0.2372
C6	C7	0.3010	-0.8307	0.7873	0.2357	0.2927	-0.7683	0.7810	0.2312	0.3035	-0.8249	0.7808	0.2347
C7	C8	0.3030	-0.8378	0.7857	0.2452	0.2983	-0.7951	0.7799	0.2386	0.3060	-0.8377	0.7804	0.2372
C9	C12	0.3006	-0.8291	0.7876	0.2349	0.2889	-0.7489	0.7813	0.2324	0.2886	-0.7448	0.7803	0.2382
C9	C14	0.3030	-0.8377	0.7858	0.2452	0.3012	-0.8108	0.7799	0.2388	0.2819	-0.7103	0.7798	0.2366
C10	C11	0.3010	-0.8306	0.7873	0.2357	0.2921	-0.7641	0.7803	0.2332	0.3103	-0.8635	0.7809	0.2321

C10	C13	0.3030	-0.8378	0.7857	0.2453	0.2994	-0.8008	0.7800	0.2400	0.3018	-0.8148	0.7805	0.2378
C11	C12	0.3030	-0.8378	0.7857	0.2453	0.3037	-0.8229	0.7795	0.2410	0.3004	-0.8065	0.7799	0.2387
C13	C16	0.3006	-0.8291	0.7876	0.2349	0.2975	-0.7926	0.7808	0.2351	0.3097	-0.8598	0.7809	0.2332
C14	C15	0.3010	-0.8308	0.7873	0.2356	0.3091	-0.8569	0.7811	0.2340	0.3295	-0.9736	0.7808	0.2346
C15	C16	0.3030	-0.8377	0.7858	0.2452	0.2916	-0.7609	0.7802	0.2348	0.3060	-0.8400	0.7810	0.2303
C17	C18	0.3030	-0.8377	0.7858	0.2451	0.2890	-0.7456	0.7788	0.2354	0.2775	-0.6863	0.7787	0.2416
C17	C24	0.3007	-0.8296	0.7876	0.2348	0.2561	-0.5791	0.7755	0.2562	0.3114	-0.8715	0.7822	0.2309
C18	C19	0.3009	-0.8303	0.7873	0.2355	0.3613	-1.1804	0.7820	0.2218	0.3036	-0.8227	0.7795	0.2386
C19	C20	0.3030	-0.8376	0.7858	0.2452	0.3677	-1.2272	0.7827	0.2135	0.3038	-0.8268	0.7810	0.2366
C20	C21	0.3007	-0.8295	0.7876	0.2349	0.3356	-1.0162	0.7813	0.2185	0.3114	-0.8688	0.7805	0.2347
C21	C22	0.3030	-0.8376	0.7858	0.2452	0.3171	-0.9007	0.7805	0.2357	0.3018	-0.8131	0.7794	0.2401
C22	C23	0.3009	-0.8303	0.7873	0.2355	0.2793	-0.6948	0.7787	0.2448	0.3030	-0.8263	0.7823	0.2260
C23	C24	0.3030	-0.8377	0.7858	0.2451	0.2595	-0.5944	0.7757	0.2571	0.3343	-1.0023	0.7801	0.2324
Th ₃	RCP	0.0137	-0.0036	0.6991	-7.013	0.0135	-0.0031	0.7095	-5.1907	0.0131	-0.0029	0.7077	-5.6480
COT1	RCP	0.0441	0.1068	0.3292	-13.182	0.0430	0.1031	0.3294	-29.897	0.0440	0.1050	0.3325	-15.387
COT2	RCP	0.0436	0.1084	0.3243	-10.252	0.0426	0.1035	0.3267	-13.155	0.0438	0.1080	0.3272	-12.871
COT3	RCP	0.0436	0.1061	0.3273	-12.468	0.0418	0.1119	0.3102	-14.496	0.0450	0.1091	0.3328	-17.218

^a In the HAR models of [1]²⁻ and [1]⁻ some Th-C BCPs could not be located while they could be found in the purely DFT calculations. This is due to the difference in geometry of the experimental models compared to the DFT-optimized geometry. This is also reflected in the ellipticity of the HAR Th-C BCPs, which reach values up close to 100. Problems in localizing these extremely small saddle points are well-known in the literature [S50-S52].

Supplementary Table S14. Bader charges for 1aMo ([1]²⁻)

1 (Th)	Charge:	2.016496	Volume:	146.772 Bohr ³
2 (Th)	Charge:	2.013055	Volume:	147.474 Bohr ³
3 (Th)	Charge:	2.027517	Volume:	145.840 Bohr ³
4 (K)	Charge:	0.868763	Volume:	135.971 Bohr ³
5 (Cl)	Charge:	-0.750072	Volume:	214.341 Bohr ³
6 (Cl)	Charge:	-0.744631	Volume:	207.914 Bohr ³
7 (Cl)	Charge:	-0.746351	Volume:	214.842 Bohr ³
8 (Cl)	Charge:	-0.745221	Volume:	209.867 Bohr ³
9 (Cl)	Charge:	-0.745637	Volume:	210.965 Bohr ³
10 (K)	Charge:	0.865725	Volume:	135.869 Bohr ³
11 (Cl)	Charge:	-0.742934	Volume:	204.475 Bohr ³
12 (O)	Charge:	-1.042238	Volume:	94.578 Bohr ³
13 (O)	Charge:	-1.032790	Volume:	94.398 Bohr ³
14 (O)	Charge:	-1.037219	Volume:	94.596 Bohr ³
15 (O)	Charge:	-1.057646	Volume:	92.369 Bohr ³
16 (O)	Charge:	-1.036680	Volume:	96.360 Bohr ³
17 (O)	Charge:	-1.036034	Volume:	93.313 Bohr ³
18 (O)	Charge:	-1.024357	Volume:	92.942 Bohr ³
19 (O)	Charge:	-1.045975	Volume:	98.064 Bohr ³
20 (C)	Charge:	-0.131636	Volume:	74.055 Bohr ³
21 (H)	Charge:	0.000253	Volume:	49.608 Bohr ³
22 (C)	Charge:	-0.161789	Volume:	78.377 Bohr ³
23 (H)	Charge:	-0.018737	Volume:	54.903 Bohr ³
24 (C)	Charge:	-0.127114	Volume:	75.838 Bohr ³
25 (H)	Charge:	0.000170	Volume:	46.813 Bohr ³
26 (C)	Charge:	-0.146402	Volume:	77.526 Bohr ³
27 (H)	Charge:	-0.002118	Volume:	52.865 Bohr ³
28 (C)	Charge:	-0.145222	Volume:	75.830 Bohr ³
29 (H)	Charge:	0.007143	Volume:	49.394 Bohr ³
30 (C)	Charge:	-0.128368	Volume:	75.091 Bohr ³
31 (H)	Charge:	-0.005216	Volume:	46.806 Bohr ³
32 (C)	Charge:	-0.123188	Volume:	74.366 Bohr ³
33 (H)	Charge:	-0.006734	Volume:	48.567 Bohr ³
34 (C)	Charge:	-0.134728	Volume:	74.019 Bohr ³
35 (H)	Charge:	-0.000609	Volume:	50.740 Bohr ³

36 (C)	Charge: -0.129840	Volume: 74.117 Bohr ³
37 (H)	Charge: -0.006717	Volume: 50.151 Bohr ³
38 (C)	Charge: -0.143510	Volume: 75.883 Bohr ³
39 (H)	Charge: 0.004745	Volume: 49.641 Bohr ³
40 (C)	Charge: -0.128628	Volume: 73.864 Bohr ³
41 (H)	Charge: -0.011900	Volume: 46.492 Bohr ³
42 (C)	Charge: -0.158775	Volume: 77.302 Bohr ³
43 (H)	Charge: 0.008137	Volume: 48.715 Bohr ³
44 (C)	Charge: -0.126954	Volume: 74.400 Bohr ³
45 (H)	Charge: 0.000916	Volume: 48.589 Bohr ³
46 (C)	Charge: -0.140965	Volume: 75.457 Bohr ³
47 (H)	Charge: 0.002316	Volume: 50.119 Bohr ³
48 (C)	Charge: -0.147185	Volume: 76.359 Bohr ³
49 (H)	Charge: 0.008162	Volume: 48.268 Bohr ³
50 (C)	Charge: -0.136317	Volume: 74.224 Bohr ³
51 (H)	Charge: -0.008211	Volume: 49.172 Bohr ³
52 (C)	Charge: -0.127444	Volume: 73.321 Bohr ³
53 (H)	Charge: -0.004403	Volume: 49.745 Bohr ³
54 (C)	Charge: -0.137063	Volume: 75.331 Bohr ³
55 (H)	Charge: -0.016327	Volume: 49.413 Bohr ³
56 (C)	Charge: -0.137514	Volume: 75.670 Bohr ³
57 (H)	Charge: -0.013300	Volume: 49.113 Bohr ³
58 (C)	Charge: -0.124505	Volume: 73.675 Bohr ³
59 (H)	Charge: -0.002562	Volume: 46.553 Bohr ³
60 (C)	Charge: 0.509802	Volume: 49.170 Bohr ³
61 (H)	Charge: 0.004750	Volume: 49.676 Bohr ³
62 (H)	Charge: -0.000157	Volume: 50.263 Bohr ³
63 (C)	Charge: -0.131791	Volume: 74.317 Bohr ³
64 (H)	Charge: -0.005498	Volume: 46.782 Bohr ³
65 (C)	Charge: -0.134647	Volume: 74.538 Bohr ³
66 (H)	Charge: -0.012163	Volume: 51.263 Bohr ³
67 (C)	Charge: -0.132429	Volume: 74.659 Bohr ³
68 (H)	Charge: -0.017257	Volume: 47.895 Bohr ³
69 (C)	Charge: 0.498250	Volume: 48.541 Bohr ³
70 (H)	Charge: -0.007059	Volume: 49.293 Bohr ³
71 (H)	Charge: 0.031702	Volume: 45.077 Bohr ³
72 (C)	Charge: 0.493851	Volume: 59.415 Bohr ³
73 (H)	Charge: 0.033488	Volume: 46.244 Bohr ³
74 (H)	Charge: -0.013600	Volume: 49.289 Bohr ³
75 (H)	Charge: 0.012331	Volume: 51.714 Bohr ³
76 (C)	Charge: 0.496785	Volume: 58.472 Bohr ³
77 (H)	Charge: 0.008004	Volume: 49.261 Bohr ³
78 (H)	Charge: 0.003116	Volume: 48.838 Bohr ³
79 (H)	Charge: 0.014463	Volume: 47.185 Bohr ³
80 (C)	Charge: 0.510639	Volume: 48.772 Bohr ³
81 (H)	Charge: 0.002863	Volume: 48.039 Bohr ³
82 (H)	Charge: -0.002044	Volume: 50.688 Bohr ³
83 (C)	Charge: 0.508235	Volume: 47.645 Bohr ³
84 (H)	Charge: -0.008198	Volume: 46.847 Bohr ³
85 (H)	Charge: 0.020098	Volume: 47.966 Bohr ³
86 (C)	Charge: 0.506778	Volume: 59.571 Bohr ³
87 (H)	Charge: 0.040283	Volume: 49.953 Bohr ³
88 (H)	Charge: 0.001084	Volume: 48.062 Bohr ³
89 (H)	Charge: -0.018599	Volume: 50.963 Bohr ³
90 (C)	Charge: -0.120361	Volume: 72.176 Bohr ³
91 (H)	Charge: -0.014681	Volume: 46.048 Bohr ³
92 (C)	Charge: 0.502327	Volume: 59.525 Bohr ³
93 (H)	Charge: 0.016487	Volume: 50.624 Bohr ³
94 (H)	Charge: 0.015221	Volume: 50.228 Bohr ³
95 (H)	Charge: -0.006627	Volume: 50.579 Bohr ³
96 (C)	Charge: 0.495218	Volume: 58.920 Bohr ³
97 (H)	Charge: 0.032488	Volume: 47.364 Bohr ³
98 (H)	Charge: -0.010807	Volume: 50.161 Bohr ³

99 (H)	Charge: 0.002252	Volume: 49.669 Bohr ³
100 (C)	Charge: 0.520153	Volume: 56.252 Bohr ³
101 (H)	Charge: -0.023899	Volume: 50.612 Bohr ³
102 (H)	Charge: 0.025790	Volume: 45.700 Bohr ³
103 (H)	Charge: 0.001254	Volume: 48.438 Bohr ³
104 (C)	Charge: 0.512979	Volume: 58.816 Bohr ³
105 (H)	Charge: -0.000414	Volume: 48.930 Bohr ³
106 (H)	Charge: 0.036678	Volume: 50.894 Bohr ³
107 (H)	Charge: -0.017865	Volume: 50.062 Bohr ³
108 (C)	Charge: 0.534523	Volume: 56.030 Bohr ³
109 (H)	Charge: -0.014289	Volume: 48.959 Bohr ³
110 (H)	Charge: 0.012123	Volume: 47.987 Bohr ³
111 (H)	Charge: -0.003083	Volume: 48.122 Bohr ³
112 (C)	Charge: 0.496771	Volume: 50.054 Bohr ³
113 (H)	Charge: 0.003501	Volume: 49.264 Bohr ³
114 (H)	Charge: 0.010361	Volume: 48.567 Bohr ³
115 (C)	Charge: 0.536323	Volume: 47.635 Bohr ³
116 (H)	Charge: -0.008292	Volume: 49.082 Bohr ³
117 (H)	Charge: -0.001609	Volume: 47.717 Bohr ³
118 (C)	Charge: 0.480836	Volume: 50.478 Bohr ³
119 (H)	Charge: 0.029752	Volume: 48.336 Bohr ³
120 (H)	Charge: 0.005693	Volume: 50.577 Bohr ³
121 (C)	Charge: 0.517219	Volume: 48.345 Bohr ³
122 (H)	Charge: 0.019490	Volume: 49.451 Bohr ³
123 (H)	Charge: -0.000227	Volume: 46.765 Bohr ³

Supplementary Table S15. Bader charges for 1aCu ([1]²⁻)

1 (Th)	Charge: 1.997442	Volume: 146.742 Bohr ³
2 (Th)	Charge: 2.001151	Volume: 147.542 Bohr ³
3 (Th)	Charge: 2.010374	Volume: 145.649 Bohr ³
4 (K)	Charge: 0.866251	Volume: 136.152 Bohr ³
5 (Cl)	Charge: -0.746439	Volume: 207.092 Bohr ³
6 (Cl)	Charge: -0.750646	Volume: 211.906 Bohr ³
7 (K)	Charge: 0.869751	Volume: 136.591 Bohr ³
8 (Cl)	Charge: -0.744553	Volume: 203.866 Bohr ³
9 (Cl)	Charge: -0.745675	Volume: 207.343 Bohr ³
10 (Cl)	Charge: -0.749060	Volume: 212.855 Bohr ³
11 (Cl)	Charge: -0.744049	Volume: 201.984 Bohr ³
12 (O)	Charge: -1.046773	Volume: 92.961 Bohr ³
13 (O)	Charge: -1.045117	Volume: 93.046 Bohr ³
14 (O)	Charge: -1.065605	Volume: 91.450 Bohr ³
15 (O)	Charge: -1.045063	Volume: 94.813 Bohr ³
16 (O)	Charge: -1.046993	Volume: 91.594 Bohr ³
17 (O)	Charge: -1.037221	Volume: 96.685 Bohr ³
18 (O)	Charge: -1.081236	Volume: 93.496 Bohr ³
19 (O)	Charge: -1.062539	Volume: 97.568 Bohr ³
20 (C)	Charge: -0.147834	Volume: 76.652 Bohr ³
21 (H)	Charge: 0.008315	Volume: 48.388 Bohr ³
22 (C)	Charge: -0.135450	Volume: 75.385 Bohr ³
23 (H)	Charge: -0.002774	Volume: 48.961 Bohr ³
24 (C)	Charge: -0.145217	Volume: 75.735 Bohr ³
25 (H)	Charge: 0.005678	Volume: 49.013 Bohr ³
26 (C)	Charge: -0.139032	Volume: 77.611 Bohr ³
27 (H)	Charge: 0.006326	Volume: 48.967 Bohr ³
28 (C)	Charge: -0.152388	Volume: 78.263 Bohr ³
29 (H)	Charge: -0.015639	Volume: 54.914 Bohr ³
30 (C)	Charge: -0.134759	Volume: 75.217 Bohr ³
31 (H)	Charge: 0.005712	Volume: 48.227 Bohr ³
32 (C)	Charge: -0.143788	Volume: 76.903 Bohr ³
33 (H)	Charge: 0.009319	Volume: 49.280 Bohr ³
34 (C)	Charge: -0.134201	Volume: 76.092 Bohr ³

35 (H)	Charge:	0.002527	Volume:	47.154 Bohr ³
36 (C)	Charge:	-0.135326	Volume:	75.279 Bohr ³
37 (H)	Charge:	0.001324	Volume:	48.620 Bohr ³
38 (C)	Charge:	-0.142555	Volume:	75.980 Bohr ³
39 (H)	Charge:	0.010254	Volume:	49.269 Bohr ³
40 (C)	Charge:	0.505638	Volume:	49.324 Bohr ³
41 (H)	Charge:	0.028560	Volume:	46.516 Bohr ³
42 (H)	Charge:	0.002606	Volume:	49.084 Bohr ³
43 (C)	Charge:	0.478903	Volume:	60.288 Bohr ³
44 (H)	Charge:	0.021482	Volume:	49.755 Bohr ³
45 (H)	Charge:	0.022187	Volume:	46.780 Bohr ³
46 (H)	Charge:	0.002968	Volume:	48.957 Bohr ³
47 (C)	Charge:	-0.142887	Volume:	77.020 Bohr ³
48 (H)	Charge:	0.002657	Volume:	46.272 Bohr ³
49 (C)	Charge:	-0.139690	Volume:	77.387 Bohr ³
50 (H)	Charge:	-0.003981	Volume:	51.156 Bohr ³
51 (C)	Charge:	0.515563	Volume:	48.967 Bohr ³
52 (H)	Charge:	-0.004273	Volume:	49.828 Bohr ³
53 (H)	Charge:	0.007994	Volume:	49.323 Bohr ³
54 (C)	Charge:	-0.152867	Volume:	77.073 Bohr ³
55 (H)	Charge:	0.010996	Volume:	48.986 Bohr ³
56 (C)	Charge:	0.544467	Volume:	47.985 Bohr ³
57 (H)	Charge:	0.004863	Volume:	49.532 Bohr ³
58 (H)	Charge:	-0.006363	Volume:	49.771 Bohr ³
59 (C)	Charge:	0.489494	Volume:	59.044 Bohr ³
60 (H)	Charge:	0.039076	Volume:	48.546 Bohr ³
61 (H)	Charge:	-0.014661	Volume:	51.145 Bohr ³
62 (H)	Charge:	0.010985	Volume:	49.308 Bohr ³
63 (C)	Charge:	-0.153725	Volume:	77.489 Bohr ³
64 (H)	Charge:	0.000656	Volume:	49.765 Bohr ³
65 (C)	Charge:	-0.138471	Volume:	76.286 Bohr ³
66 (H)	Charge:	0.005016	Volume:	48.787 Bohr ³
67 (C)	Charge:	0.497681	Volume:	48.881 Bohr ³
68 (H)	Charge:	0.023406	Volume:	48.303 Bohr ³
69 (H)	Charge:	0.001993	Volume:	49.023 Bohr ³
70 (C)	Charge:	-0.143580	Volume:	76.785 Bohr ³
71 (H)	Charge:	0.011884	Volume:	47.543 Bohr ³
72 (C)	Charge:	0.484994	Volume:	49.083 Bohr ³
73 (H)	Charge:	0.026376	Volume:	48.205 Bohr ³
74 (H)	Charge:	0.004429	Volume:	48.990 Bohr ³
75 (C)	Charge:	0.496639	Volume:	60.001 Bohr ³
76 (H)	Charge:	-0.009293	Volume:	51.233 Bohr ³
77 (H)	Charge:	0.036177	Volume:	51.662 Bohr ³
78 (H)	Charge:	0.009236	Volume:	48.249 Bohr ³
79 (C)	Charge:	0.505061	Volume:	58.679 Bohr ³
80 (H)	Charge:	0.018787	Volume:	45.377 Bohr ³
81 (H)	Charge:	0.016280	Volume:	51.846 Bohr ³
82 (H)	Charge:	-0.006621	Volume:	49.539 Bohr ³
83 (C)	Charge:	0.512033	Volume:	48.777 Bohr ³
84 (H)	Charge:	0.007960	Volume:	48.646 Bohr ³
85 (H)	Charge:	0.000597	Volume:	49.529 Bohr ³
86 (C)	Charge:	0.496540	Volume:	59.618 Bohr ³
87 (H)	Charge:	-0.011309	Volume:	51.222 Bohr ³
88 (H)	Charge:	0.035810	Volume:	47.725 Bohr ³
89 (H)	Charge:	0.008615	Volume:	48.894 Bohr ³
90 (C)	Charge:	0.500200	Volume:	59.671 Bohr ³
91 (H)	Charge:	0.017622	Volume:	51.681 Bohr ³
92 (H)	Charge:	0.015437	Volume:	50.475 Bohr ³
93 (H)	Charge:	-0.000519	Volume:	49.256 Bohr ³
94 (C)	Charge:	0.539565	Volume:	48.178 Bohr ³
95 (H)	Charge:	0.003680	Volume:	48.670 Bohr ³
96 (H)	Charge:	-0.002506	Volume:	49.732 Bohr ³
97 (C)	Charge:	0.516215	Volume:	59.183 Bohr ³

98 (H)	Charge: 0.027674	Volume: 48.865 Bohr ³
99 (H)	Charge: -0.010917	Volume: 50.330 Bohr ³
100 (H)	Charge: 0.009861	Volume: 49.936 Bohr ³
101 (C)	Charge: 0.510693	Volume: 58.862 Bohr ³
102 (H)	Charge: 0.017361	Volume: 49.154 Bohr ³
103 (H)	Charge: 0.017592	Volume: 49.987 Bohr ³
104 (H)	Charge: -0.005249	Volume: 49.108 Bohr ³
105 (C)	Charge: 0.517943	Volume: 48.719 Bohr ³
106 (H)	Charge: 0.018020	Volume: 51.626 Bohr ³
107 (H)	Charge: 0.000287	Volume: 48.902 Bohr ³
108 (C)	Charge: -0.139672	Volume: 76.091 Bohr ³
109 (H)	Charge: 0.008048	Volume: 48.230 Bohr ³
110 (C)	Charge: -0.126315	Volume: 75.182 Bohr ³
111 (H)	Charge: 0.006401	Volume: 48.779 Bohr ³
112 (C)	Charge: -0.128985	Volume: 74.331 Bohr ³
113 (H)	Charge: -0.006179	Volume: 48.532 Bohr ³
114 (C)	Charge: -0.148627	Volume: 77.245 Bohr ³
115 (H)	Charge: -0.011445	Volume: 49.846 Bohr ³
116 (C)	Charge: -0.164957	Volume: 76.644 Bohr ³
117 (H)	Charge: 0.007879	Volume: 48.653 Bohr ³
118 (C)	Charge: -0.138956	Volume: 74.734 Bohr ³
119 (H)	Charge: -0.001384	Volume: 47.944 Bohr ³
120 (C)	Charge: -0.144170	Volume: 77.134 Bohr ³
121 (H)	Charge: -0.000227	Volume: 50.095 Bohr ³
122 (C)	Charge: -0.128659	Volume: 74.752 Bohr ³
123 (H)	Charge: 0.008904	Volume: 48.172 Bohr ³

Supplementary Table S16. Bader charges for DFT of [1]²⁻

1 (Th)	Charge: 2.079344	Volume: 147.212 Bohr ³
2 (Cl)	Charge: -0.782753	Volume: 211.919 Bohr ³
3 (C)	Charge: -0.155570	Volume: 75.129 Bohr ³
4 (H)	Charge: 0.007882	Volume: 48.564 Bohr ³
5 (Th)	Charge: 2.079344	Volume: 147.212 Bohr ³
6 (Cl)	Charge: -0.783527	Volume: 211.630 Bohr ³
7 (C)	Charge: -0.152527	Volume: 74.652 Bohr ³
8 (H)	Charge: 0.022185	Volume: 47.482 Bohr ³
9 (Cl)	Charge: -0.783527	Volume: 211.630 Bohr ³
10 (C)	Charge: -0.152535	Volume: 74.652 Bohr ³
11 (H)	Charge: 0.022185	Volume: 47.482 Bohr ³
12 (C)	Charge: -0.155563	Volume: 75.129 Bohr ³
13 (H)	Charge: 0.007884	Volume: 48.564 Bohr ³
14 (C)	Charge: -0.157554	Volume: 75.015 Bohr ³
15 (H)	Charge: 0.007298	Volume: 48.575 Bohr ³
16 (C)	Charge: -0.152157	Volume: 74.673 Bohr ³
17 (H)	Charge: 0.022287	Volume: 47.420 Bohr ³
18 (C)	Charge: -0.152147	Volume: 74.672 Bohr ³
19 (H)	Charge: 0.022282	Volume: 47.421 Bohr ³
20 (C)	Charge: -0.157556	Volume: 75.015 Bohr ³
21 (H)	Charge: 0.007297	Volume: 48.576 Bohr ³
22 (C)	Charge: -0.155570	Volume: 75.129 Bohr ³
23 (H)	Charge: 0.007884	Volume: 48.564 Bohr ³
24 (C)	Charge: -0.152147	Volume: 74.673 Bohr ³
25 (H)	Charge: 0.022279	Volume: 47.420 Bohr ³
26 (C)	Charge: -0.152149	Volume: 74.673 Bohr ³
27 (H)	Charge: 0.022282	Volume: 47.420 Bohr ³
28 (C)	Charge: -0.157554	Volume: 75.015 Bohr ³
29 (H)	Charge: 0.007297	Volume: 48.576 Bohr ³
30 (C)	Charge: -0.157553	Volume: 75.015 Bohr ³
31 (H)	Charge: 0.007296	Volume: 48.576 Bohr ³
32 (C)	Charge: -0.152529	Volume: 74.652 Bohr ³
33 (H)	Charge: 0.022185	Volume: 47.482 Bohr ³

34 (C)	Charge: -0.152528	Volume: 74.652 Bohr ³
35 (H)	Charge: 0.022185	Volume: 47.482 Bohr ³
36 (C)	Charge: -0.155569	Volume: 75.129 Bohr ³
37 (H)	Charge: 0.007882	Volume: 48.564 Bohr ³
38 (Th)	Charge: 2.079843	Volume: 147.064 Bohr ³
39 (Cl)	Charge: -0.782752	Volume: 211.919 Bohr ³
40 (C)	Charge: -0.197173	Volume: 75.843 Bohr ³
41 (H)	Charge: 0.006741	Volume: 48.553 Bohr ³
42 (Cl)	Charge: -0.782752	Volume: 211.919 Bohr ³
43 (C)	Charge: -0.110042	Volume: 73.887 Bohr ³
44 (H)	Charge: 0.021719	Volume: 47.434 Bohr ³
45 (Cl)	Charge: -0.782752	Volume: 211.919 Bohr ³
46 (C)	Charge: -0.110042	Volume: 73.887 Bohr ³
47 (H)	Charge: 0.021720	Volume: 47.435 Bohr ³
48 (C)	Charge: -0.197172	Volume: 75.843 Bohr ³
49 (H)	Charge: 0.006740	Volume: 48.553 Bohr ³
50 (C)	Charge: -0.197173	Volume: 75.843 Bohr ³
51 (H)	Charge: 0.006741	Volume: 48.553 Bohr ³
52 (C)	Charge: -0.110043	Volume: 73.887 Bohr ³
53 (H)	Charge: 0.021721	Volume: 47.435 Bohr ³
54 (C)	Charge: -0.110044	Volume: 73.887 Bohr ³
55 (H)	Charge: 0.021722	Volume: 47.434 Bohr ³
56 (C)	Charge: -0.197173	Volume: 75.843 Bohr ³
57 (H)	Charge: 0.006741	Volume: 48.553 Bohr ³
58 (K)	Charge: 0.903587	Volume: 146.822 Bohr ³
59 (K)	Charge: 0.903582	Volume: 146.822 Bohr ³

Supplementary Table S17. Bader charges for 1bCu ([I]^{I-})

1 (Th)	Charge: 2.164345	Volume: 142.691 Bohr ³
2 (Th)	Charge: 2.165114	Volume: 142.248 Bohr ³
3 (Th)	Charge: 2.160889	Volume: 142.539 Bohr ³
4 (Cl)	Charge: -0.716868	Volume: 217.528 Bohr ³
5 (Cl)	Charge: -0.713363	Volume: 213.535 Bohr ³
6 (Cl)	Charge: -0.716438	Volume: 215.760 Bohr ³
7 (Cl)	Charge: -0.715980	Volume: 216.991 Bohr ³
8 (Cl)	Charge: -0.716223	Volume: 216.591 Bohr ³
9 (Cl)	Charge: -0.715628	Volume: 218.375 Bohr ³
10 (C)	Charge: -0.155529	Volume: 77.997 Bohr ³
11 (C)	Charge: -0.155093	Volume: 75.938 Bohr ³
12 (C)	Charge: -0.146109	Volume: 77.101 Bohr ³
13 (C)	Charge: -0.144663	Volume: 77.809 Bohr ³
14 (C)	Charge: -0.143956	Volume: 77.065 Bohr ³
15 (C)	Charge: -0.143718	Volume: 76.501 Bohr ³
16 (C)	Charge: -0.140456	Volume: 76.079 Bohr ³
17 (C)	Charge: -0.146141	Volume: 77.328 Bohr ³
18 (C)	Charge: -0.153508	Volume: 77.552 Bohr ³
19 (C)	Charge: -0.154034	Volume: 77.023 Bohr ³
20 (C)	Charge: -0.159679	Volume: 76.113 Bohr ³
21 (C)	Charge: -0.152086	Volume: 76.705 Bohr ³
22 (C)	Charge: -0.151093	Volume: 78.091 Bohr ³
23 (C)	Charge: -0.131311	Volume: 73.959 Bohr ³
24 (C)	Charge: -0.158612	Volume: 77.698 Bohr ³
25 (C)	Charge: -0.132136	Volume: 75.002 Bohr ³
26 (C)	Charge: -0.147451	Volume: 77.207 Bohr ³
27 (C)	Charge: -0.138220	Volume: 73.934 Bohr ³
28 (C)	Charge: -0.151156	Volume: 76.796 Bohr ³
29 (C)	Charge: -0.080291	Volume: 69.327 Bohr ³
30 (C)	Charge: -0.192394	Volume: 81.562 Bohr ³
31 (C)	Charge: -0.181838	Volume: 81.233 Bohr ³
32 (C)	Charge: -0.175125	Volume: 81.293 Bohr ³
33 (C)	Charge: -0.116618	Volume: 71.092 Bohr ³

34 (H)	Charge:	0.014000	Volume:	48.640 Bohr ³
35 (H)	Charge:	0.019426	Volume:	46.618 Bohr ³
36 (H)	Charge:	0.020225	Volume:	46.907 Bohr ³
37 (H)	Charge:	0.016767	Volume:	48.635 Bohr ³
38 (H)	Charge:	0.014105	Volume:	47.388 Bohr ³
39 (H)	Charge:	0.017015	Volume:	46.994 Bohr ³
40 (H)	Charge:	0.012617	Volume:	48.568 Bohr ³
41 (H)	Charge:	0.011886	Volume:	48.958 Bohr ³
42 (H)	Charge:	0.012005	Volume:	49.123 Bohr ³
43 (H)	Charge:	0.020626	Volume:	46.510 Bohr ³
44 (H)	Charge:	0.014099	Volume:	48.935 Bohr ³
45 (H)	Charge:	0.016720	Volume:	46.750 Bohr ³
46 (H)	Charge:	0.013063	Volume:	48.835 Bohr ³
47 (H)	Charge:	0.004230	Volume:	48.762 Bohr ³
48 (H)	Charge:	0.014162	Volume:	47.701 Bohr ³
49 (H)	Charge:	0.014734	Volume:	46.671 Bohr ³
50 (H)	Charge:	0.016517	Volume:	46.920 Bohr ³
51 (H)	Charge:	0.008318	Volume:	46.545 Bohr ³
52 (H)	Charge:	0.017354	Volume:	48.017 Bohr ³
53 (H)	Charge:	-0.000720	Volume:	48.730 Bohr ³
54 (H)	Charge:	0.031945	Volume:	47.202 Bohr ³
55 (H)	Charge:	0.021340	Volume:	49.106 Bohr ³
56 (H)	Charge:	0.024215	Volume:	49.330 Bohr ³
57 (H)	Charge:	0.000721	Volume:	45.590 Bohr ³

Supplementary Table S18. Bader charges for *IbMo* ([1]¹⁻)

1 (Th)	Charge:	2.165832	Volume:	143.244 Bohr ³
2 (Th)	Charge:	2.162989	Volume:	142.658 Bohr ³
3 (Th)	Charge:	2.167287	Volume:	142.520 Bohr ³
4 (Cl)	Charge:	-0.717331	Volume:	217.260 Bohr ³
5 (Cl)	Charge:	-0.719172	Volume:	218.868 Bohr ³
6 (Cl)	Charge:	-0.716515	Volume:	216.455 Bohr ³
7 (Cl)	Charge:	-0.718399	Volume:	218.071 Bohr ³
8 (Cl)	Charge:	-0.718206	Volume:	217.922 Bohr ³
9 (Cl)	Charge:	-0.714600	Volume:	213.777 Bohr ³
10 (C)	Charge:	-0.146187	Volume:	76.009 Bohr ³
11 (H)	Charge:	0.020322	Volume:	46.539 Bohr ³
12 (C)	Charge:	-0.135376	Volume:	75.712 Bohr ³
13 (H)	Charge:	0.017806	Volume:	47.118 Bohr ³
14 (C)	Charge:	-0.143644	Volume:	76.265 Bohr ³
15 (H)	Charge:	0.016271	Volume:	47.332 Bohr ³
16 (C)	Charge:	-0.153804	Volume:	76.602 Bohr ³
17 (H)	Charge:	0.009714	Volume:	48.842 Bohr ³
18 (C)	Charge:	-0.139493	Volume:	76.107 Bohr ³
19 (H)	Charge:	0.012654	Volume:	46.971 Bohr ³
20 (C)	Charge:	-0.149342	Volume:	77.026 Bohr ³
21 (H)	Charge:	0.010478	Volume:	48.944 Bohr ³
22 (C)	Charge:	-0.138393	Volume:	76.081 Bohr ³
23 (H)	Charge:	0.015277	Volume:	47.318 Bohr ³
24 (C)	Charge:	-0.158890	Volume:	78.100 Bohr ³
25 (H)	Charge:	0.010394	Volume:	49.141 Bohr ³
26 (C)	Charge:	-0.136777	Volume:	74.172 Bohr ³
27 (H)	Charge:	0.009345	Volume:	48.233 Bohr ³
28 (C)	Charge:	-0.139323	Volume:	76.004 Bohr ³
29 (H)	Charge:	0.021052	Volume:	46.499 Bohr ³
30 (C)	Charge:	-0.153689	Volume:	75.827 Bohr ³
31 (H)	Charge:	0.011928	Volume:	48.701 Bohr ³
32 (C)	Charge:	-0.144782	Volume:	76.526 Bohr ³
33 (H)	Charge:	0.009835	Volume:	48.564 Bohr ³
34 (C)	Charge:	-0.147498	Volume:	77.171 Bohr ³
35 (H)	Charge:	0.017892	Volume:	47.504 Bohr ³

36 (C)	Charge: -0.171310	Volume: 79.569 Bohr ³
37 (H)	Charge: 0.015444	Volume: 48.981 Bohr ³
38 (C)	Charge: -0.155640	Volume: 77.285 Bohr ³
39 (H)	Charge: 0.012986	Volume: 48.753 Bohr ³
40 (C)	Charge: -0.142035	Volume: 75.523 Bohr ³
41 (H)	Charge: 0.015954	Volume: 46.946 Bohr ³
42 (C)	Charge: -0.145708	Volume: 75.544 Bohr ³
43 (H)	Charge: 0.013446	Volume: 47.785 Bohr ³
44 (C)	Charge: -0.139121	Volume: 76.152 Bohr ³
45 (H)	Charge: 0.016314	Volume: 47.800 Bohr ³
46 (C)	Charge: -0.166475	Volume: 78.218 Bohr ³
47 (H)	Charge: 0.015028	Volume: 47.800 Bohr ³
48 (C)	Charge: -0.154802	Volume: 75.265 Bohr ³
49 (H)	Charge: 0.011795	Volume: 47.585 Bohr ³
50 (C)	Charge: -0.141927	Volume: 76.284 Bohr ³
51 (H)	Charge: 0.017139	Volume: 47.321 Bohr ³
52 (C)	Charge: -0.127057	Volume: 74.321 Bohr ³
53 (H)	Charge: 0.007618	Volume: 47.885 Bohr ³
54 (C)	Charge: -0.135227	Volume: 74.837 Bohr ³
55 (H)	Charge: 0.007883	Volume: 47.893 Bohr ³
56 (C)	Charge: -0.158865	Volume: 77.671 Bohr ³
57 (H)	Charge: 0.016905	Volume: 48.465 Bohr ³

Supplementary Table S19. Bader charges for DFT of [1]¹⁻

1 (Th)	Charge: 2.278510	Volume: 140.762 Bohr ³
2 (Cl)	Charge: -0.741628	Volume: 216.706 Bohr ³
3 (C)	Charge: -0.160676	Volume: 76.043 Bohr ³
4 (H)	Charge: 0.016649	Volume: 47.837 Bohr ³
5 (Th)	Charge: 2.278812	Volume: 140.755 Bohr ³
6 (Cl)	Charge: -0.742261	Volume: 217.226 Bohr ³
7 (C)	Charge: -0.155181	Volume: 75.631 Bohr ³
8 (H)	Charge: 0.016774	Volume: 47.786 Bohr ³
9 (Cl)	Charge: -0.742122	Volume: 217.193 Bohr ³
10 (C)	Charge: -0.157723	Volume: 75.700 Bohr ³
11 (H)	Charge: 0.016885	Volume: 47.790 Bohr ³
12 (C)	Charge: -0.159230	Volume: 76.039 Bohr ³
13 (H)	Charge: 0.016387	Volume: 47.830 Bohr ³
14 (C)	Charge: -0.160384	Volume: 75.976 Bohr ³
15 (H)	Charge: 0.016503	Volume: 47.820 Bohr ³
16 (C)	Charge: -0.156471	Volume: 75.615 Bohr ³
17 (H)	Charge: 0.018113	Volume: 47.798 Bohr ³
18 (C)	Charge: -0.158503	Volume: 75.662 Bohr ³
19 (H)	Charge: 0.018381	Volume: 47.796 Bohr ³
20 (C)	Charge: -0.159130	Volume: 75.966 Bohr ³
21 (H)	Charge: 0.016962	Volume: 47.825 Bohr ³
22 (C)	Charge: -0.158820	Volume: 76.032 Bohr ³
23 (H)	Charge: 0.016540	Volume: 47.826 Bohr ³
24 (C)	Charge: -0.156992	Volume: 75.634 Bohr ³
25 (H)	Charge: 0.018331	Volume: 47.786 Bohr ³
26 (C)	Charge: -0.158096	Volume: 75.660 Bohr ³
27 (H)	Charge: 0.018269	Volume: 47.781 Bohr ³
28 (C)	Charge: -0.160079	Volume: 75.969 Bohr ³
29 (H)	Charge: 0.016380	Volume: 47.829 Bohr ³
30 (C)	Charge: -0.160299	Volume: 75.957 Bohr ³
31 (H)	Charge: 0.016940	Volume: 47.825 Bohr ³
32 (C)	Charge: -0.157902	Volume: 75.702 Bohr ³
33 (H)	Charge: 0.016949	Volume: 47.791 Bohr ³
34 (C)	Charge: -0.154989	Volume: 75.632 Bohr ³
35 (H)	Charge: 0.016483	Volume: 47.791 Bohr ³
36 (C)	Charge: -0.159408	Volume: 76.055 Bohr ³
37 (H)	Charge: 0.016333	Volume: 47.831 Bohr ³

38 (Th)	Charge: 2.285477	Volume: 140.067 Bohr ³
39 (Cl)	Charge: -0.741425	Volume: 216.664 Bohr ³
40 (C)	Charge: -0.162536	Volume: 75.840 Bohr ³
41 (H)	Charge: 0.016809	Volume: 47.886 Bohr ³
42 (Cl)	Charge: -0.741622	Volume: 216.690 Bohr ³
43 (C)	Charge: -0.154532	Volume: 75.857 Bohr ³
44 (H)	Charge: 0.017486	Volume: 47.829 Bohr ³
45 (Cl)	Charge: -0.741753	Volume: 216.728 Bohr ³
46 (C)	Charge: -0.155930	Volume: 75.874 Bohr ³
47 (H)	Charge: 0.017651	Volume: 47.831 Bohr ³
48 (C)	Charge: -0.162485	Volume: 75.860 Bohr ³
49 (H)	Charge: 0.016704	Volume: 47.875 Bohr ³
50 (C)	Charge: -0.150938	Volume: 75.699 Bohr ³
51 (H)	Charge: 0.016579	Volume: 47.890 Bohr ³
52 (C)	Charge: -0.166132	Volume: 75.982 Bohr ³
53 (H)	Charge: 0.017837	Volume: 47.840 Bohr ³
54 (C)	Charge: -0.155858	Volume: 75.848 Bohr ³
55 (H)	Charge: 0.017878	Volume: 47.836 Bohr ³
56 (C)	Charge: -0.160282	Volume: 75.812 Bohr ³
57 (H)	Charge: 0.016759	Volume: 47.885 Bohr ³

Supplementary Table S20. ORCA 6.0 optimized geometry of 1a

E = -89339.301342762934 a.u.

Th	2.31926226435806	0.02388305692646	0.00200116109366
Th	-1.13290598647679	-2.02157287608206	0.00065696419682
Th	-1.18236093720007	1.99070936916371	0.00042298706447
Cl	1.10296221334440	-1.85058795915199	-1.78472464862375
Cl	1.05675453534705	1.86986886954210	-1.77134088412847
Cl	-2.14151416281490	-0.02707793800727	-1.77378688476945
Cl	1.09602089613040	-1.84868385930198	1.77381401008550
Cl	1.05029818828626	1.87388018131590	1.77417360864996
Cl	-2.15139674473740	-0.02314945354191	1.78585551852458
C	3.13377563544700	0.77090107015586	-5.63338120252758
C	2.56987225598000	2.09081911047251	-5.19103735695699
C	3.20988886291951	-1.50034517614823	-5.04808188777781
C	-2.24599163816583	-2.30554095623893	-5.65381222875555
C	-3.10506404311155	-1.16837232870565	-5.17967620779561
C	-3.26235726884768	1.15848194497164	-5.08421171033092
C	-0.30232066830311	-3.50723104064947	-5.12582795208041
C	0.62600555923505	3.38035561280885	-5.12512931005745
C	4.35178590886669	0.17194684577869	-1.80088306678316
C	-2.30048305833369	-3.67742270453703	-1.81796242630738
C	4.37641363194901	-1.15785937220898	-1.34949390517824
C	-1.17504883443927	4.33886444457584	-1.40901507077525
C	4.33870827619983	1.43289628681154	-1.18588610930622
C	-2.31551589493575	3.64676330029204	-1.84926415070435
C	-1.12794984481266	-4.34763490017225	-1.43061738952660
C	-3.37796015961078	-3.08387164808405	-1.14394598185145
C	-0.63296208484471	4.65982635626255	-0.15605782816336
C	4.36530193624906	-1.77669220283711	-0.09030943657615
C	-3.40444247886054	3.02166524747530	-1.22250681385361
C	-0.53213031270742	-4.67411158984805	-0.20375035760705
C	4.31103234878350	1.88518343746183	0.14296558863620
C	-3.71225249510327	-2.88504081002535	0.20526504338533
C	-1.02276387149597	4.45331224490345	1.17694109671037
C	4.35639459864425	-1.32397710312292	1.23828111212189
C	-3.78472786992997	2.79882370701265	0.11019599185548
C	4.31888959270126	1.26674421215198	1.40168821704761
C	-0.87568604753625	-4.49164322594661	1.14545105854969
C	-3.12405347845137	-3.22498842377914	1.43213198226600
C	4.32159625913906	-0.06316900364383	1.85376624941022

C	-2.10110629084100	3.81041057429443	1.80309452803803
C	-1.94254997491205	-3.87918288594844	1.81937107960465
C	-3.25231455078453	3.13627872202423	1.36353843406571
C	2.58002873255429	2.27236190026116	5.12464582863337
C	2.68120424569054	-2.19269548111911	5.09385948849338
C	0.60858119509177	-3.26060376501561	5.18982355602870
C	0.47399654612061	3.27453450989149	5.19877503784277
C	-2.84178821791564	-2.06933116933834	5.11992552530541
C	-2.93537251671980	1.97574749907462	5.06671886502243
C	-0.81046828329867	-3.11149800685427	5.65873929678749
C	-0.94645387844833	3.07770598159617	5.64529519363231
H	2.92611025623637	0.60357102442565	-6.69918989748808
H	4.22372770492062	0.79696168015158	-5.49871856080251
H	-2.01589857770099	-2.19152333169441	-6.72202813630660
H	3.07938616411586	2.89336299668842	-5.74178251044615
H	3.08180035428587	-1.86372254899699	-6.07519070719645
H	4.28202909670762	-1.42895137921921	-4.83048003320492
H	0.04810947244902	-3.56264674431742	-6.16387486348036
H	-4.06208822133422	-1.20370298098945	-5.71810275093560
H	-4.18797385577613	1.16369482796647	-5.67167025710023
H	1.07494217106301	4.17834010536342	-5.72809933168731
H	-2.80701767574626	-3.24103381525416	-5.52386805138912
H	-2.69873710376984	2.06280228964952	-5.31168352375052
H	-0.88891201274996	-4.40614172299267	-4.90294240863524
H	2.75818949352893	-2.20400366898495	-4.35047545566414
H	2.75469648625902	2.23645854305831	-4.11908412679314
H	-0.43984576705507	3.33178868234611	-5.34615796572418
H	0.55289340893941	-3.47208511291245	-4.45264812465337
H	-3.30885401194585	-1.27418674196601	-4.10657634553029
H	0.76327721205235	3.61050538734058	-4.06349440221972
H	-3.51223465535379	1.14860362825149	-4.01819850877591
H	4.23359175739828	0.23777649746977	-2.87643906710585
H	-2.34022941793074	-3.50766454440329	-2.88797783547956
H	-0.50610305258659	4.59472029695869	-2.22260768296535
H	4.27199862918007	-1.87214503428028	-2.15786003624725
H	-2.32448427889442	3.50998169432352	-2.92611940545583
H	-0.48117915000022	-4.56946621108219	-2.27141999870066
H	4.21377797019172	2.24154919644342	-1.89725871058347
H	-4.05314884801705	-2.56494608288368	-1.81512654047126
H	0.35146137116325	5.10827269125236	-0.23452501405379
H	-4.04546552838525	2.50046339462425	-1.92438719126358
H	4.26729118782501	-2.85457683839778	-0.16015025269358
H	0.45869822337268	-5.09821558421457	-0.32491188412401
H	4.18172343209504	2.95985282810803	0.21158934973871
H	-4.58892053744435	-2.25809675945650	0.32645874649172
H	-0.26166062525063	4.77034530889267	1.88104307824095
H	4.24554625571264	-2.13619613707890	1.94761732726958
H	-4.65266577684305	2.15333226150993	0.18976089175407
H	-0.08171749259669	-4.79922651703166	1.81673973057291
H	4.18851508876900	1.97850427091915	2.20868084452724
H	-3.64930039041960	-2.78734277688280	2.27295543609455
H	4.20862078642386	-0.13256595759083	2.93124014552722
H	-1.97499903462270	3.74787347799909	2.87794706588538
H	-1.77679162608003	-3.82487089176142	2.88938459852419
H	-3.80086512209880	2.67819991577929	2.17828282952121
H	2.70489944715154	2.50547721040929	4.06211348746663
H	2.80256819356028	-2.41193746996492	4.02791773703571
H	0.62694163188097	-3.49371230650517	4.11761695290243
H	0.50092053457605	3.51199004486251	4.12762196780392
H	3.08887468017422	1.33513480688266	5.34803047634986
H	-3.31010465210551	1.22861377808332	4.36875081840641
H	-3.30873686822000	-3.03725100808285	4.90341630012342
H	-3.25085665974268	-1.32390571100342	4.43958509547249

H	3.03262777704699	3.07053321206914	5.72461124532879
H	3.16458339650373	-1.24323707775620	5.32192505629047
H	-1.32066101582241	-4.07605706593799	5.53182072856097
H	1.07149836619311	-4.09606938064723	5.73275702456193
H	3.16295413724368	-2.98281904093118	5.68168447666245
H	0.90166821617843	4.12246202598151	5.75119878497995
H	-3.42718867032217	2.93255158754096	4.85557952505591
H	-1.48520911476558	4.02622251674243	5.51546278910455
H	-3.17532248112550	1.67492508289862	6.09403691397063
H	-3.07253248889931	-1.78941154275902	6.15521741584314
H	-0.83539725133688	-2.85043626215255	6.72563795597174
H	-0.97895924729434	2.81041722357179	6.71047216468791
K	-0.00946628246342	0.01875581757953	-4.01386053238354
K	0.02375125360375	-0.00048474304654	4.01101182410347
O	-2.45394494007795	0.05687606291224	-5.42825606748165
O	1.18477518058816	2.12836600917664	-5.44987974898093
O	2.57474876132603	-0.26134178933629	-4.85915826434908
O	-1.05856510641172	-2.34468781539173	-4.90111300813301
O	-1.54727391094075	2.06959937362108	4.87056538076639
O	-1.45522741128720	-2.11909461066021	4.89895566400908
O	1.21979399923751	2.10552404379783	5.45185763168881
O	1.32005129606495	-2.06897419400077	5.43635704834625

Supplementary Table S21. Gaussian 16 optimized geometry of 1a – used only for vibrational analyses

E = -7346.44412760 a.u.

Th	2.31615700	0.02944100	0.00085200
Th	-1.13268900	-2.02325200	0.00056600
Th	-1.18377800	1.99907300	0.00135500
Cl	1.10849200	-1.84787200	-1.79084100
Cl	1.06122900	1.87776800	-1.77626900
Cl	-2.14368400	-0.02239900	-1.77355800
Cl	1.09963700	-1.84742600	1.77623700
Cl	1.04961400	1.88302600	1.77736800
Cl	-2.14956800	-0.02063900	1.79095900
C	3.10628300	0.76272700	-5.65927500
C	2.55270800	2.08746800	-5.21960800
C	3.18952800	-1.50309600	-5.05630100
C	-2.22228700	-2.28851100	-5.66404700
C	-3.08992400	-1.15299100	-5.20306600
C	-3.24363700	1.17251200	-5.09489800
C	-0.28713000	-3.49039600	-5.10598700
C	0.61263200	3.37841800	-5.12729700
C	4.33731100	0.17385600	-1.80114300
C	-2.27714800	-3.68273800	-1.82154900
C	4.35939200	-1.15537900	-1.34949100
C	-1.16312800	4.34152800	-1.40530900
C	4.32859400	1.43476500	-1.18680700
C	-2.30267600	3.65342400	-1.85272100
C	-1.10918200	-4.35122700	-1.41902900
C	-3.36165600	-3.08643400	-1.16194300
C	-0.62574500	4.65567000	-0.14900600
C	4.34940700	-1.77350100	-0.09044300
C	-3.39659400	3.03036300	-1.23312600
C	-0.52596000	-4.67087100	-0.18452300
C	4.30419100	1.88758000	0.14167800
C	-3.71011000	-2.88113400	0.18227400
C	-1.02251800	4.44656400	1.18107300
C	4.34541200	-1.32059800	1.23769900
C	-3.78381300	2.80487400	0.09685300
C	4.31350100	1.26970500	1.40039300

C	-0.88419400	-4.48291600	1.15968300
C	-3.13550400	-3.21609000	1.41666800
C	4.31388500	-0.05986800	1.85273100
C	-2.10543400	3.80546000	1.80034100
C	-1.95811000	-3.86769500	1.81914200
C	-3.25672600	3.13696800	1.35363500
C	2.57931600	2.26398200	5.12824400
C	2.68069800	-2.17637300	5.09646700
C	0.60930100	-3.24350000	5.20522600
C	0.47217900	3.26190700	5.22012800
C	-2.83903700	-2.04820300	5.10904100
C	-2.93170400	1.95280600	5.05824000
C	-0.81092900	-3.08598200	5.66660400
C	-0.94843200	3.05251800	5.65911700
H	2.87268200	0.58480500	-6.72150400
H	4.20197400	0.78989600	-5.54831700
H	-1.96623300	-2.16535800	-6.72881800
H	3.05160500	2.88476800	-5.79351300
H	3.03294800	-1.87537200	-6.08024900
H	4.27032800	-1.43211600	-4.86617200
H	0.09269500	-3.52717600	-6.13844600
H	-4.03654400	-1.18385700	-5.76603100
H	-4.15897900	1.18431800	-5.70443800
H	1.05013700	4.17020100	-5.75275900
H	-2.78954700	-3.22635100	-5.55314500
H	-2.67129400	2.07952400	-5.30349400
H	-0.87867200	-4.39728000	-4.91368000
H	2.75168500	-2.20019500	-4.33898000
H	2.76162500	2.24523700	-4.15048300
H	-0.46098900	3.32808800	-5.32377500
H	0.55065500	-3.46213100	-4.40638400
H	-3.31786600	-1.26536600	-4.13225100
H	0.77530900	3.62119600	-4.06857000
H	-3.51684200	1.15375200	-4.03127400
H	4.22378500	0.23946300	-2.87925700
H	-2.30755700	-3.52037400	-2.89497800
H	-0.49052100	4.60352300	-2.21669700
H	4.25639400	-1.87141100	-2.15927800
H	-2.30716900	3.52002600	-2.93219900
H	-0.45453500	-4.58191100	-2.25396800
H	4.20867800	2.24539400	-1.89999700
H	-4.03331600	-2.57314100	-1.84428800
H	0.36107400	5.10489300	-0.22156300
H	-4.03925000	2.51543900	-1.94119800
H	4.25228000	-2.85359300	-0.15987500
H	0.46684400	-5.09897800	-0.29340300
H	4.18077900	2.96502300	0.21035300
H	-4.59202600	-2.25571500	0.29145200
H	-0.26385100	4.76329800	1.89119000
H	4.24009100	-2.13477200	1.94880000
H	-4.65824400	2.16396500	0.17048800
H	-0.09755500	-4.79152400	1.84243200
H	4.19016300	1.98376600	2.20920900
H	-3.67378400	-2.77853100	2.25196300
H	4.20523400	-0.12902600	2.93283000
H	-1.98575900	3.74405000	2.87811500
H	-1.80549200	-3.81268100	2.89306500
H	-3.81487300	2.68188100	2.16629400
H	2.70384500	2.52176300	4.06790700
H	2.80452000	-2.42121000	4.03295800
H	0.63061200	-3.49658400	4.13423700
H	0.49890300	3.52169700	4.15097600
H	3.08971000	1.31935900	5.33072100

H	-3.30282100	1.21673400	4.34220300
H	-3.31104200	-3.02292200	4.91809000
H	-3.24708300	-1.31667100	4.40871900
H	3.03236300	3.05083500	5.74882900
H	3.16300000	-1.21818800	5.30377200
H	-1.32184400	-4.05572200	5.55627500
H	1.07115500	-4.07049600	5.76802900
H	3.16310000	-2.95405400	5.70643300
H	0.89729400	4.10128700	5.79344300
H	-3.43073200	2.91423600	4.86817100
H	-1.49049700	4.00496400	5.54674300
H	-3.16810500	1.62721400	6.08277200
H	-3.06592600	-1.74044900	6.14123900
H	-0.83705100	-2.80272300	6.73130500
H	-0.98093700	2.76186700	6.72166700
K	-0.00918600	0.02451300	-3.99818300
K	0.02760600	0.00176500	3.99975800
O	-2.43061700	0.07175600	-5.43047500
O	1.16269000	2.12189400	-5.44922000
O	2.56378400	-0.26020000	-4.86161100
O	-1.05364200	-2.33416400	-4.88323100
O	-1.54441100	2.05904000	4.86213700
O	-1.45321600	-2.10869400	4.88567500
O	1.21909800	2.08928000	5.45138600
O	1.31850900	-2.04698000	5.43272700

Supplementary Table S22. Final coordinates for HAR refinement of 1aMo ([I]²⁻)

Th	4.0124522	13.6116572	7.3205086
Th	0.8030878	11.8219725	8.8921828
Th	1.1583418	15.7728727	9.1019035
K	4.0777385	13.4063143	11.9553511
Cl	3.6396302	11.6519943	9.3761545
Cl	2.2761723	15.7083626	6.4844657
Cl	1.0061995	13.6967384	11.0576302
Cl	1.9634620	11.9394743	6.2919978
Cl	-0.6738300	14.0213126	7.8412069
K	0.4679826	14.0876994	4.6579765
Cl	3.9480533	15.3741836	9.5577685
O	3.1059289	11.3078425	13.3958947
O	-1.0799689	11.8690395	4.3490182
O	5.7388197	11.2739867	12.5890439
O	2.0689651	13.8650606	2.4595509
O	6.1019535	15.3583965	12.4263612
O	-2.1233980	14.4928652	4.3139322
O	3.4538665	15.5070677	13.4894152
O	0.9505754	16.4189668	3.0577792
C	1.2481604	9.2051020	9.5804861
H	2.2324448	8.7399525	9.7432950
C	6.6759658	13.2622799	7.8653127
H	7.1407688	13.1375286	8.8472148
C	5.5815029	11.7347202	6.0630556
H	5.3701214	10.7013818	6.0327656
C	0.7782610	9.8016267	10.7605354
H	1.5518436	9.6599475	11.5733180
C	0.8245936	9.1738221	8.2452003
H	1.5706254	8.6847528	7.5725091
C	5.9554253	15.3650205	6.5047853
H	5.9956596	16.4053508	6.6764288
C	6.2899532	12.0578225	7.2393187
H	6.4810488	11.2018591	7.8375469
C	-0.3216193	10.6115903	11.0811049

H -0.2497104 10.9332206 12.1412562
C 4.9893094 12.4648283 5.0180493
H 4.3999608 11.8605755 4.3289510
C -0.7375339 16.7733488 10.8236396
H -1.4049979 16.2103119 11.5354555
C 6.5541249 14.6411684 7.5510536
H 6.9122652 15.2351172 8.3676225
C 4.8457874 13.8411408 4.7214594
H 4.2409304 14.0280838 3.8114962
C -1.2930567 16.9632358 9.5565064
H -2.2752371 16.4899904 9.4782572
C -0.2518178 9.6890193 7.5169773
H -0.2031048 9.5642680 6.3735285
C -1.3963431 11.1643233 10.3730753
H -2.0115019 11.8826554 10.9044131
C 0.4857306 17.0787872 11.4218678
H 0.7023394 16.7144692 12.4062940
C 5.2662251 15.0319823 5.3222118
H 4.8847322 15.9563933 4.8716475
C -0.8389647 17.5093448 8.3499533
H -1.5862448 17.2811861 7.5851299
C -1.3551069 10.5033989 7.8337606
H -2.0059543 10.8485810 7.0550543
C 1.5900496 18.3844441 8.4925689
H 2.3044759 18.7494981 7.7996843
C 3.9255164 10.1950166 13.6759514
H 3.3001549 9.2661896 13.6557580
H 4.4201510 10.2965840 14.6654259
C -1.8469990 11.1076516 9.0251687
H -2.6516031 11.7648961 8.8472148
C 0.3493951 18.0996136 7.9056995
H 0.2559687 18.2895006 6.8152582
C 1.6831232 17.6756799 10.9927590
H 2.4512021 17.6455041 11.7500099
C -2.8637213 13.3888712 4.8123295
H -3.9535237 13.4981666 4.6192305
H -2.7135224 13.3399275 5.8686945
C 7.0178769 15.6354990 11.3827432
H 6.5428751 16.1183124 10.4879251
H 7.8098698 16.2986314 11.7247682
H 7.5171680 14.7015201 11.1568300
C -2.5112707 15.7201386 4.9170826
H -1.8703430 16.4973503 4.5813680
H -3.5441186 15.9711132 4.7075765
H -2.3235833 15.7282345 5.9822822
C -2.4344595 12.1557099 4.0676995
H -3.0458672 11.3196185 4.4046761
H -2.6037019 12.3573728 2.9658994
C 4.9713255 10.0820412 12.6145380
H 5.5804943 9.2477897 12.8101612
H 4.5316988 9.9028262 11.6111806
C 2.0342271 11.4211859 14.3095180
H 1.4020413 12.2800933 13.9460375
H 1.4703120 10.5247428 14.3499047
H 2.4066295 11.5698571 15.3217100
C 2.1438510 18.2107490 9.7761092
H 3.1056737 18.5618191 9.8568826
C 6.8423554 11.1856672 11.7058369
H 6.5057633 10.8669809 10.7151003
H 7.2770047 12.1696939 11.6995265
H 7.5758452 10.4364233 12.0655311
C 2.4737940 15.2126693 14.4773752
H 1.6551931 14.7419999 13.9460375

H 2.7987278 14.5396010 15.2459849
 H 2.1197277 16.1698321 14.9178429
 C -0.6388097 10.6620061 3.7483920
 H -0.6710675 10.7087418 2.6756199
 H 0.3529868 10.5541826 4.0260507
 H -1.2433565 9.8513065 4.0891549
 C 2.0627055 12.5704437 1.8918652
 H 2.7951602 12.4493723 1.0980138
 H 2.2592124 11.8568956 2.6882407
 H 1.1001912 12.4162525 1.4009142
 C 0.9885928 17.6999678 3.6524735
 H 0.9829032 18.5029394 2.9406577
 H 0.2304834 17.7816634 4.3415719
 H 1.9161978 17.8074232 4.1775008
 C 4.5555305 16.2220878 14.0280730
 H 5.0596941 15.5663154 14.7537718
 H 4.1651788 17.1560668 14.4887340
 C 1.9109280 14.8792631 1.5119776
 H 0.9124400 14.7677597 1.0475304
 H 2.6308547 14.7787997 0.7067675
 C 5.5060821 16.5514460 12.9111280
 H 4.9332378 17.0235875 12.0529103
 H 6.3387472 17.2627862 13.2518909
 C 2.0425179 16.2173039 2.1821447
 H 2.9173579 16.2176719 2.8270701
 H 2.0508525 16.9794277 1.4513976

Supplementary Table S23. Final coordinates for HAR refinement of 1aCu ([1]²⁻)

Th 3.5281278 23.2139393 5.2946697
 Th 6.7380163 25.0017463 3.7229949
 Th 6.3773111 21.0449751 3.5147740
 K 7.0688819 22.7228329 7.9613430
 Cl 5.5732138 24.8787211 6.3252491
 Cl 3.8942600 25.1759706 3.2413731
 K 3.4429909 23.4186253 0.6554774
 Cl 5.2527518 21.1146648 6.1312308
 Cl 8.2076258 22.7976057 4.7679038
 Cl 6.5202057 23.1246908 1.5573453
 Cl 3.5794365 21.4491166 3.0571192
 O 9.6661888 22.3121349 8.3110831
 O 8.6309271 24.9266051 8.2920617
 O 5.4856849 22.9268927 10.1815206
 O 1.7578540 25.5347328 0.0050724
 O 4.0511451 21.3397200 -0.9155633
 O 1.4207900 21.4520634 0.1597797
 O 4.3880319 25.5185259 -0.8077754
 O 6.6079416 20.3816702 9.5664954
 C 2.6790467 22.9895103 7.8964166
 H 3.5383427 22.8090242 8.5875274
 C 2.5433483 24.3538380 7.5996828
 H 3.3358972 24.9512839 8.1145286
 C 6.7142413 27.6526821 4.3647769
 H 5.8572284 27.8884190 5.0432068
 C 1.2417574 24.7789012 5.3805196
 H 1.3035363 25.6153991 4.6412213
 C 0.8541236 23.5700126 4.7452049
 H 0.6801857 23.7247150 3.6521085
 C 6.2978527 27.6221099 3.0332790
 H 5.2009918 27.8302215 2.9597296
 C 1.9659952 25.0905160 6.5585782
 H 2.4263926 26.1067633 6.4862969

C 7.7882051 27.1351658 5.0888582
 H 7.5428755 27.0721798 6.1768822
 C 2.2624540 21.8041954 7.2877319
 H 2.9033276 20.9518590 7.6250447
 C 1.5881841 21.4653236 6.1084051
 H 1.8265319 20.4199775 5.7913818
 C 10.4062181 23.4024184 7.8139905
 H 11.4935082 23.2215639 7.9560170
 H 10.2118791 23.5298637 6.7272346
 C 10.0409174 21.0807776 7.7011303
 H 9.3979630 20.2733786 8.0777539
 H 9.9184527 21.1610755 6.6131062
 H 11.0885249 20.8590376 7.9382637
 C 0.9785675 22.1905831 5.0634963
 H 0.8848407 21.5607234 4.1441287
 C 6.7646032 27.0360826 1.8590247
 H 5.9328188 26.9082690 1.1235306
 C 9.9846578 24.6451942 8.5647017
 H 10.6161263 25.5045290 8.2552870
 H 10.1220917 24.4890184 9.6565300
 C 8.9309830 25.6665982 2.2445250
 H 9.3440973 24.7700611 1.7195344
 C 3.5712477 26.6054943 -1.0905602
 H 3.0866430 26.4669988 -2.0809410
 H 4.1782689 27.5355503 -1.1260668
 C 8.1848115 26.1421238 8.8829932
 H 7.1416757 26.3288717 8.5976722
 H 8.2484559 26.0636676 9.9748214
 H 8.8191695 26.9697816 8.5342675
 C 8.8904913 26.3141382 4.7743711
 H 9.2805866 25.7910968 5.6823258
 C 7.8547133 26.2205801 1.5204438
 H 7.6507509 25.6382361 0.5883953
 C 2.5258796 26.7207844 -0.0253619
 H 3.0105035 26.8813802 0.9612147
 H 1.8678376 27.5908011 -0.2358653
 C 9.3807496 25.7174290 3.5874358
 H 10.0444407 24.8481489 3.8207649
 C 2.0366517 20.2623284 -0.3309723
 H 2.6009159 19.7613873 0.4869478
 H 1.2591015 19.5551175 -0.6961832
 C 5.4909023 24.2293394 10.7445540
 H 6.4904673 24.4540262 11.1338587
 H 5.2165619 24.9623340 9.9735533
 H 4.7607639 24.2772235 11.5650104
 C 0.5077757 21.1794925 1.1958119
 H 1.0122017 20.6122504 1.9909064
 H 0.1263505 22.1224403 1.6104784
 H -0.3272682 20.5901501 0.8001668
 C 2.9646685 20.6122504 -1.4456263
 H 2.4327694 21.2236932 -2.2039461
 H 3.3330346 19.6877195 -1.9376465
 C 5.0464154 21.6214993 -1.8780461
 H 4.6329576 22.2771427 -2.6503149
 H 5.8940700 22.1187569 -1.3923664
 H 5.3884614 20.6822348 -2.3332916
 C 0.6680165 25.6327110 0.8965419
 H 0.2062349 24.6455625 1.0144746
 H 1.0231953 25.9936832 1.8691694
 H -0.0716839 26.3362385 0.4945564
 C 5.6827102 21.9198539 11.1173734
 H 4.9398893 22.0156220 11.9378298
 H 6.6993190 22.0082552 11.5561337

C	5.4636816	25.3932907	-1.7055854
H	6.0488365	24.5055937	-1.4456263
H	5.0776235	25.2938391	-2.7276686
H	6.0959189	26.2883544	-1.6358403
C	6.5790570	19.1057439	8.9717597
H	5.6801747	19.0099758	8.3567345
H	7.4711702	18.9768253	8.3440535
H	6.5639466	18.3395988	9.7541732
C	5.5315874	20.5864667	10.4516245
H	5.5177071	19.7798043	11.2188209
H	4.5728528	20.5496328	9.8923954
C	8.8073016	19.8497887	3.0649814
H	9.6498943	20.5569996	3.2602677
C	8.2722404	20.0405883	1.7930838
H	8.8026816	20.8594059	1.2465357
C	7.0680989	19.7392870	1.1996162
H	6.8999798	20.4096640	0.3233638
C	8.3312695	19.2899134	4.2506485
H	8.9029439	19.6914029	5.1230967
C	5.8861588	18.4464171	4.0363408
H	5.0629970	18.3359154	4.7845158
C	5.8766491	19.1830951	1.5901889
H	5.0460614	19.5182836	0.9219038
C	7.1419137	18.7042544	4.6830683
H	7.0401977	18.7374049	5.7951861
C	5.3727095	18.6342700	2.7466900
H	4.2551005	18.6379534	2.7479581

Supplementary Table S24. Final coordinates for purely DFT refinement of [1]²⁻

Th	2.192341	3.804566	0.000000
Cl	-2.051934	3.538022	3.392804
C	2.944557	7.741212	3.199694
H	2.166129	7.960769	5.084628
Th	2.192341	-3.804566	0.000000
Cl	4.068153	0.000000	3.397070
C	1.321520	8.679678	1.328794
H	-0.417520	9.434457	2.108551
Cl	4.068153	0.000000	-3.397070
C	1.321520	8.679678	-1.328794
H	-0.417520	9.434457	-2.108551
C	2.944557	7.741212	-3.199694
H	2.166129	7.960769	-5.084628
C	5.243969	6.404484	-3.199509
H	5.820674	5.836762	-5.084329
C	6.862137	5.457768	-1.328628
H	8.378319	4.319575	-2.108465
C	6.862137	5.457768	1.328628
H	8.378319	4.319575	2.108465
C	5.243969	6.404484	3.199509
H	5.820674	5.836762	5.084329
C	2.944557	-7.741212	-3.199694
H	2.166129	-7.960769	-5.084628
C	6.862137	-5.457768	1.328628
H	8.378319	-4.319575	2.108465
C	6.862137	-5.457768	-1.328628
H	8.378319	-4.319575	-2.108466
C	5.243969	-6.404484	-3.199509
H	5.820674	-5.836762	-5.084329
C	5.243969	-6.404484	3.199509
H	5.820674	-5.836762	5.084329
C	1.321520	-8.679678	-1.328794

H	-0.417520	-9.434457	-2.108551
C	1.321520	-8.679678	1.328794
H	-0.417520	-9.434457	2.108551
C	2.944557	-7.741212	3.199694
H	2.166129	-7.960769	5.084628
Th	-4.400937	0.000000	0.000000
Cl	-2.051934	3.538022	-3.392804
C	-8.180863	1.329860	-3.200009
H	-7.978375	2.113876	-5.084581
Cl	-2.051934	-3.538022	-3.392804
C	-8.177053	3.204407	-1.328713
H	-7.954295	5.087177	-2.108329
Cl	-2.051934	-3.538022	3.392804
C	-8.177053	3.204407	1.328713
H	-7.954295	5.087177	2.108329
C	-8.180863	1.329860	3.200009
H	-7.978375	2.113876	5.084581
C	-8.180863	-1.329860	3.200009
H	-7.978375	-2.113876	5.084581
C	-8.177053	-3.204407	1.328713
H	-7.954295	-5.087177	2.108329
C	-8.177053	-3.204407	-1.328713
H	-7.954295	-5.087177	-2.108329
C	-8.180863	-1.329860	-3.200009
H	-7.978375	-2.113876	-5.084581
K	-0.014556	0.000000	-7.248469
K	-0.014556	0.000000	7.248469

Supplementary Table S25. Final coordinates for HAR refinement of 1bMo ([I]¹⁻)

Th	3.9587693	9.1344733	5.9208195
Th	2.1675598	11.7516774	3.3517898
Th	5.5153330	9.7474926	2.1873179
Cl	1.3937876	9.3713084	4.6937662
Cl	2.8023740	9.8577677	1.3095744
Cl	4.5051960	7.5276515	3.6129585
Cl	3.4068465	11.9212930	5.9306306
Cl	6.4197095	10.1129574	4.8736362
Cl	4.7688097	12.4671827	2.5045273
C	4.0602141	6.5597954	6.8010872
H	4.0911349	5.8413889	5.9453948
C	5.8337275	8.2367108	7.7059937
H	6.8694838	8.4772393	7.3567315
C	3.9130457	9.7585970	8.5823243
H	3.8619220	10.8639170	8.7363172
C	2.7535107	6.9825574	7.0598587
H	2.0417767	6.5075435	6.3391086
C	7.3585113	11.1595797	0.7350381
H	7.3013142	12.2469722	0.9890470
C	2.6527273	9.2316846	8.3251403
H	1.8843050	10.0448240	8.3187901
C	5.7166926	9.6797814	-0.5445315
H	4.7319726	9.9116036	-1.0207981
C	5.2421359	9.3385234	8.3235528
H	5.9404105	10.2129477	8.3251403
C	6.3532812	10.8207867	-0.1714560
H	5.7416968	11.7179259	-0.4365777
C	2.1516040	8.0758064	7.6885306
H	1.0990707	8.2235853	7.3392684
C	8.0785799	10.4750880	1.7050345
H	8.4574084	11.1709451	2.4940495
C	7.5366001	7.9569083	1.7590113

H 7.5856813 7.2172115 2.5940655
 C 6.5370815 7.5944181 0.8414043
 H 6.0304925 6.6448035 1.1462150
 C 5.7656330 8.3086310 -0.1190667
 H 4.8202397 7.7670317 -0.3699004
 C 5.3456795 7.0876032 7.0725591
 H 6.1034829 6.6725797 6.3629219
 C 8.1706492 9.1380409 2.1193864
 H 8.5915060 9.0674952 3.1528849
 C 1.4498651 14.2155653 4.2149595
 H 2.1418353 14.5822433 5.0134998
 C 0.4716177 13.3662567 4.7452030
 H 0.6003322 13.2349698 5.8485540
 C -0.3402667 12.3637616 4.2038466
 H -0.6655052 11.6523942 5.0023869
 C 1.9880667 14.4149657 2.9544405
 H 2.9976861 14.8900108 3.0322307
 C 1.7990857 13.8767519 1.6732834
 H 2.6926266 14.0433641 1.0239732
 C 0.0391063 12.0268404 1.6542327
 H -0.0509395 11.1260616 0.9985723
 C 0.9717133 12.8719655 1.1573279
 H 1.4129958 12.4513771 0.2206702
 C -0.5123142 11.7700883 2.9004636
 H -0.9559330 10.7454097 2.9607908

Supplementary Table S26. Final coordinates for HAR refinement of 1bCu ([1]¹⁻)

Th 7.8510590 11.0024286 9.4961821
 Th 8.5882117 14.9669070 8.9971923
 Th 5.6504990 13.7476349 11.5202275
 Cl 5.1075125 11.7248236 9.5757253
 Cl 7.8374051 12.8299316 7.3335512
 Cl 5.7787899 15.3548891 9.1737043
 Cl 10.0780468 12.7291159 9.9718010
 Cl 8.0834607 15.1990991 11.7973985
 Cl 7.3742014 11.5881780 12.2334508
 C 6.8058854 9.0242291 7.9133142
 H 5.8686996 9.3684776 7.4089942
 C 3.0630411 13.0498291 11.9068728
 H 2.7291099 12.2998591 11.1462926
 C 8.0628152 17.2844372 7.6078521
 H 6.9624593 17.4442668 7.4827972
 C 9.7919738 9.1542004 10.0741001
 H 10.5531058 9.5634346 10.7834282
 C 6.5408896 8.5939184 9.2397169
 H 5.4561496 8.7133516 9.4795764
 C 7.9462010 9.4756161 7.2203867
 H 7.6589674 10.0762947 6.3224511
 C 7.2867419 8.4867798 10.4082633
 H 6.6272062 8.5254200 11.3102991
 C 10.8008091 15.2628553 7.3987438
 H 11.2406667 14.2669935 7.1424836
 C 8.5621256 16.3746375 6.6504641
 H 7.7494253 16.0145817 5.9718872
 C 9.5887041 17.3898194 9.7296864
 H 9.3467667 17.6163911 10.7957287
 C 10.7035463 16.5081216 9.6374327
 H 11.1068000 16.2516916 10.6481228
 C 10.0499021 9.5528964 8.7579478
 H 10.9522584 10.2115352 8.7251465
 C 8.5044505 17.7077223 8.8871029

H 7.6446409 18.0958801 9.4877768
 C 2.9986874 14.3319792 11.4046029
 H 2.6481231 14.3109028 10.3426607
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 C 11.2092158 15.6703331 8.6615940
 H 11.8793354 14.9010431 9.1208122
 C 9.7046334 15.5596818 6.5520602
 H 9.5300567 14.7254061 5.8283815
 C 5.1510734 15.5509000 13.5141367
 H 6.0532701 16.1919750 13.6719929
 C 9.2887191 9.7074570 7.5709507
 H 9.7732929 10.4310814 6.8698228
 C 4.4508458 16.0198508 12.5054966
 H 4.9224539 16.9384323 12.0811298
 C 4.7761549 12.9409342 13.9446538
 H 5.4155838 12.1347603 14.3833712
 C 5.3471321 14.2933391 14.1517120
 H 6.3205715 14.2529426 14.6990837
 C 3.7902712 12.4175359 12.9770153
 H 3.8597212 11.3092664 12.8519604
 C 3.5626717 15.5245544 11.6813639
 H 3.5534809 16.1480658 10.7547271

Supplementary Table S27. Final coordinates for purely DFT refinement of [1]¹⁻

Th 2.238584 -3.858635 -0.000238
 Cl -1.975415 -3.407209 -3.264882
 C 2.985936 -7.815609 -3.201303
 H 2.182709 -7.980400 -5.078354
 Th 2.240198 3.859198 0.000395
 Cl 3.952987 0.000318 -3.285474
 C 1.367854 -8.759023 -1.327458
 H -0.387662 -9.472936 -2.104189
 Cl 3.953100 -0.000151 3.285107
 C 1.368116 -8.758508 1.329060
 H -0.387265 -9.472031 2.106445
 C 2.986543 -7.814269 3.202169
 H 2.183668 -7.978205 5.079447
 C 5.289089 -6.486505 3.201567
 H 5.832959 -5.872527 5.078480
 C 6.915197 -5.556946 1.327889
 H 8.413782 -4.396793 2.104630
 C 6.914947 -5.557481 -1.328718
 H 8.413365 -4.397655 -2.106266
 C 5.288433 -6.487749 -3.201697
 H 5.831859 -5.874507 -5.078983
 C 2.987168 7.815073 3.202464
 H 2.184215 7.979098 5.079707
 C 6.916113 5.558130 -1.328037
 H 8.414665 4.398349 -2.105362
 C 6.916226 5.557875 1.328609
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 H 5.833733 5.873823 5.079135
 C 5.289644 6.488149 -3.201222
 H 5.833235 5.874805 -5.078408
 C 1.368664 8.758830 1.329111
 H -0.386859 9.472222 2.106309
 C 1.368596 8.759170 -1.327433
 H -0.386959 9.472772 -2.104345
 C 2.986932 7.815706 -3.201067

H 2.183861 7.980256 -5.078193
 Th -4.472214 -0.000666 -0.001950
 Cl -1.975068 -3.406536 3.263115
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 C -8.274139 1.328670 3.202432
 H -8.013887 2.107562 5.078907

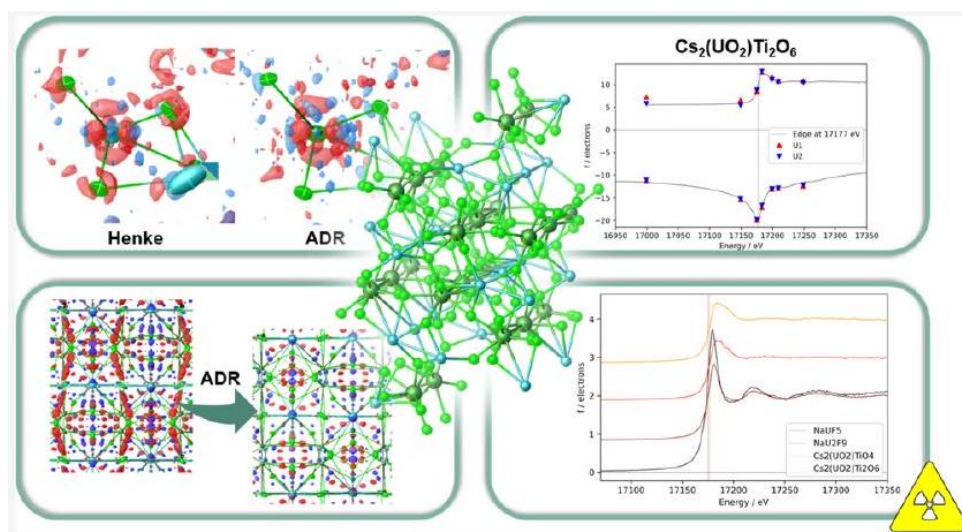
Supplementary References

- [S1] Cantat, T., Scott, B. L. & Kiplinger, J. L. (2010). Convenient access to the anhydrous thorium tetrachloride complexes $\text{ThCl}_4(\text{DME})_2$, $\text{ThCl}_4(1,4\text{-dioxane})_2$ and $\text{ThCl}_4(\text{THF})_{3.5}$ using commercially available and inexpensive starting materials. *Chem. Commun.* **46**, 919-921.
- [S2] Bergbreiter, D. E. & Killough, J. M. (1978). Reactions of potassium-graphite. *J. Am. Chem. Soc.* **100**, 2126-2134.
- [S3] Zhou, Z., Greenough, J., Wei, Z. & Petrukhina, M. A. (2017). The dinuclear scandium(III) cyclooctatetraenyl chloride complex di- μ -chlorido-bis[(η^8 -cyclooctatetraene)(tetrahydrofuran- κO) scandium(III)]. *Acta Cryst. C* **73**, 420-423.
- [S4] Avdeef, A., Raymond, K. N., Hodgson, K. O. & Zalkin, A. (1972). Two isostructural actinide π complexes. Crystal and molecular structure of bis(cyclooctatetraenyl)uranium(IV), $\text{U}(\text{C}_8\text{H}_8)_2$, and bis(cyclooctatetraenyl)thorium(IV), $\text{Th}(\text{C}_8\text{H}_8)_2$. *Inorg. Chem.* **11**, 1083-1088.
- [S5] Le Vanda, C., Solar, J. P. & Streitwieser, A. (1980). Half-sandwich cyclooctatetraenethorium compounds. *J. Am. Chem. Soc.* **102**, 2128-2136.
- [S6] Sheldrick, G. M. (2015). SHELXT – Integrated space-group and crystal-structure determination. *Acta Cryst. Sect. A* **71**, 3-8.
- [S7] CrysAlisPRO version 40.69, Oxford Diffraction/Agilent Technologies UK Ltd, Yarnton, England.
- [S8] Sheldrick, G. M. (2015). Crystal structure refinement with SHELXL. *Acta Cryst. Sect. C* **71**, 3-8.
- [S9] Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **42**, 339-341.
- [S10] Farrugia, L. J. (2012). WinGX and ORTEP for Windows: an update. *J. Appl. Cryst.* **45**, 849-854.
- [S11] Persistence of Vision (TM) Raytracer, Persistence of Vision Pty. Ltd., Williamstown, Victoria, Australia.
- [S12] Stoll, S. & Schweiger, A. (2006). Easyspin, a comprehensive software package for spectral simulation and analysis in EPR. *J. Magn. Reson.* **178**, 42-55.
- [S13] Bain, G. A. & Berry, J. F. (2008). Diamagnetic corrections and Pascal's constants. *J. Chem. Ed.* **85**, 532-536.
- [S14] Seed, J. A. *et al.* (2025). Valence-delocalized trithorium nanocluster superatoms with open-shell exalted diamagnetism. *Nat. Chem.* **17**, 1035-1041.

- [S15] Sheppard, R. F. *et al.* (2025). Uranium-stibinidiide, -stibinidene, and -stibido multiple bonds and uranium-nitride formation from multimetallic diuranium-distibene-mediated dinitrogen cleavage. *Nat. Commun.* *16*, 7136.
- [S16] Du, J., Rajeshkumar, T., Seed, J. A., Wooles, A. J., Maron, L. & Liddle, S. T. (2025). Isolable f-element diphosphene complexes by phosphinidene group transfer and coupling at uranium. *Nat. Commun.* *16*, 10445.
- [S17] Boronski, J. T., Seed, J. A., Hunger, D., Woodward, A. W., Van Slageren, J., Wooles, A. J., Natrajan, L. S., Kaltsoyannis, N. & Liddle, S. T. (2021). A crystalline tri-thorium cluster with σ -aromatic metal–metal bonding. *Nature* *598*, 72-75.
- [S18] Spek, A. L. (2015). PLATON SQUEEZE: a tool for the calculation of the disordered solvent contribution to the calculated structure factors. *Acta Cryst C* *71*, 9-18.
- [S19] Kleemiss, F. *et al.* (2021). Accurate crystal structures and chemical properties from NoSpherA2. *Chem. Sci.* *12*, 1675-1692.
- [S20] Neese, F., Wennmohs, F., Becker, U. & Riplinger, C. (2020). The ORCA quantum chemistry program package. *J. Chem. Phys.* *152*, 224108.
- [S21] Allen, F. H. & Bruno, I. J. (2010). Bond lengths in organic and metal-organic compounds revisited: $X-H$ bond lengths from neutron diffraction data. *Acta Crystallogr. B Struct. Sci.* *66*, 380-386.
- [S22] Novelli, G., McMonagle, C. J., Kleemiss, F., Probert, M., Puschmann, H., Grabowsky, S., Maynard-Casely, H. E., McIntyre, G. J. & Parsons, S. (2021). Accurate H-atom parameters for the two polymorphs of l-histidine at 5, 105 and 295 K. *Acta Cryst. B* *77*, 785-800.
- [S23] Pantazis, D. A. & Neese, F. (2012). All-electron scalar relativistic basis sets for the 6p elements. *Theor. Chem. Acc.* *131*, 1292.
- [S24] Weigend, F. (2006). Accurate Coulomb-fitting basis sets for H to Rn. *Phys. Chem. Chem. Phys.* *8*, 1057-1065.
- [S25] Weigend, F. & Ahlrichs, R. (2005). Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* *7*, 3297-3305.
- [S26] Lu, T. & Chen, F. (2012). Multiwfn: a multifunctional wavefunction analyzer. *J. Comput. Chem.* *33*, 580-592.
- [S27] Van Lenthe, E., Baerends, E. J. & Snijders, J. G. (1993). Relativistic regular two-component Hamiltonians. *J. Chem. Phys.* *99*, 4597-4610.
- [S28] Adamo, C. & Barone, V. (1999). Toward reliable density functional methods without adjustable parameters: The PBE0 model. *J. Chem. Phys.* *110*, 6158-6170.
- [S29] Grimme, S., Antony, J., Ehrlich, S. & Krieg, H. (2010). A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* *132*, 154104.
- [S30] Grimme, S., Ehrlich, S. & Goerigk, L. (2011). Effect of the damping function in dispersion corrected density functional theory. *J. Comput. Chem.* *32*, 1456-1465.
- [S31] Becke, A. D. & Johnson, E. R. (2005). A density-functional model of the dispersion interaction. *J. Chem. Phys.* *123*, 154101.
- [S32] Pantazis, D. A. & Neese, F. (2011). All-Electron Scalar Relativistic Basis Sets for the Actinides. *J. Chem. Theory Comput.* *7*, 677-684.
- [S33] Neese, F. (2003). An improvement of the resolution of the identity approximation for the formation of the Coulomb matrix. *J. Comput. Chem.* *24*, 1740-1747.
- [S34] Riplinger, C. & Neese, F. (2013). An efficient and near linear scaling pair natural orbital based local coupled cluster method. *J. Chem. Phys.* *138*, 034106.
- [S35] Saitow, M., Becker, U., Riplinger, C., Valeev, E. F. & Neese, F. (2017). A new near-linear scaling, efficient and accurate, open-shell domain-based local pair natural orbital coupled cluster singles and doubles theory. *J. Chem. Phys.* *146*, 164105.
- [S36] Douglas, M. & Kroll, N. M. (1974). Quantum electrodynamical corrections to the fine structure of helium. *Ann. Phys.* *82*, 89-155.

- [S37] Hess, B. A. (1986). Relativistic electronic-structure calculations employing a two-component no-pair formalism with external-field projection operators. *Phys. Rev. A Gen. Phys.* **33**, 3742-3748.
- [S38] Frisch, M. J. *et al.* Gaussian 16. Gaussian, Inc., Wallingford CT (2016).
- [S39] Cao, X. & Dolg, M. (2002). Segmented contraction scheme for small-core lanthanide pseudopotential basis sets. *J. Mol. Struct. THEOCHEM* **581**, 139-147.
- [S40] Küchle, W., Dolg, M., Stoll, H. & Preuss, H. (1994). Energy-adjusted pseudopotentials for the actinides. Parameter sets and test calculations for thorium and thorium monoxide. *J. Chem. Phys.* **100**, 7535-7542.
- [S41] Dunning, T. H. (1989). Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen. *J. Chem. Phys.* **90**, 1007-1023.
- [S42] Pople, J. A. & Nesbet, R. K. (1954). Self-Consistent Orbitals for Radicals. *J. Chem. Phys.* **22**, 571-572.
- [S43] Glendening, E. D.; Landis, C. R.; Weinhold, F. (2019). NBO 7.0: New vistas in localized and delocalized chemical bonding theory. *J. Comput. Chem.* **40**, 2234-2241.
- [S44] Todd, A. K. (2019). AIMAll (Version 19.10.13). TK Gristmill Software, Overland Park KS, USA.
- [S45] Zubarev, D. Y. & Boldyrev, A. I. (2008). Developing paradigms of chemical bonding: adaptive natural density partitioning. *Phys. Chem. Chem. Phys.* **10**, 5207-5217.
- [S46] Szczepanik, D. W. & Solà, M. (2021). The electron density of delocalized bonds (EDDBs) as a measure of local and global aromaticity. In *Aromaticity*, Elsevier pp 259-284.
- [S47] Tuschel, D. (2016). Selecting an Excitation Wavelength for Raman Spectroscopy. *March*.
- [S48] Meindl, K. & Henn, J. (2008). Foundations of residual-density analysis. *Acta Cryst. A* **64**, 404-418.
- [S49] Tomeček, J., Liddle, S. T. & Kaltsoyannis, N. (2023). Actinide-Actinide Bonding: Electron Delocalisation and σ -Aromaticity in the Tri-Thorium Cluster [$\{\text{Th}(\eta^8\text{-C}_8\text{H}_8)(\mu\text{-Cl})_2\}_3\text{K}_2$]. *ChemPhysChem* **24**, e202300366.
- [S50] Tassel, J. T., Kaltsoyannis, N. (2010). Covalency in AnCp_4 (An = Th-Cm): a comparison of molecular orbital, natural population and atoms-in-molecules analyses. *Dalton Trans.* **39**, 6719-6725.
- [S51] Foroutan-Nejad, C., Shahbazian, S., Marek, R. (2014). Toward a Consistent Interpretation of the QTAIM: Tortuous Link between Chemical Bonds, Interactions, and Bond/Line Paths. *Chem. Eur. J.* **20**, 10140-10152.
- [S52] Tomeček, J., Liddle, S. T., Kaltsoyannis, N. (2025). Computational Investigations of Metal-Metal Bonding in Molecular Thorium Compounds and Ce and Group IV Analogues. *Inorg. Chem.* **64**, 14489-14512.

7 Anomalous dispersion parameter refinements of uranium compounds



Preface

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Gregory Morrison – Chemical synthesis, co-writing final manuscript.

Birgit Hischa – Data acquisition, co-writing final manuscript.

Hans-Conrad zur Loye – Co-writing final manuscript.

Christoph Hennig – Conceptualisation, data acquisition, co-writing final manuscript.

Michael Bodensteiner – Conceptualisation, co-writing final manuscript.

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Abstract

Refining the anomalous dispersion parameters of the four uranium compounds NaUF_5 , NaU_2F_9 , $\text{Cs}_2(\text{UO}_2)\text{TiO}_4$, and $\text{Cs}_2(\text{UO}_2)\text{Ti}_2\text{O}_6$ gave insights into the crystallographic model improvement of very heavy atoms. We found that the values for the dispersive and absorptive parts, f' and f'' , closely followed the X-ray absorption spectra on their L_3 , L_2 , and L_1 edges. The obtained values are sensitive to the chemical environment at each crystallographically independent position. An incorrect treatment of the anomalous dispersion correction can lead to a wrong crystallographic model. The above-mentioned, already published structures were improved by this process. General guidelines were given for the crystal structure determination of very heavy compounds. When using $\text{MoK}\alpha$ radiation with uranium compounds, the proximity of its energy to the uranium L-edges causes a noticeable effect.

7.1 Introduction

In single-crystal X-ray diffraction (SC-XRD), the anomalous dispersion terms f' and f'' correct for the nonelastic behavior of a given element. They correspond directly to an X-ray absorption spectrum (XAS) and its Kramers-Kronig transformation (KKT), which contain valuable chemical information when recorded over several energies near the absorption edge of an element.^{1,2} In protein crystallography, this relation has been shown to provide valuable spatially resolved chemical information in important systems such as nitrogenase FeMoco and the FeV cofactor.^{3–5} It has received much less attention for small-molecule SC-XRD, with rare examples being presented, for instance, by Bartholomew et al.^{6,7} This is surprising as the initial research into the refinement of the anomalous dispersion correction terms goes back as early as 1978 and was well examined by L. K. Templeton and D. H. Templeton.^{8,9}

In 2022, we have described the application and implementation of anomalous dispersion refinement (ADR) within one of the most widely used crystallographic software suites Olex2.¹⁰ In this work, a good agreement was found between a recorded X-ray absorption spectrum (XAS) of the organometallic compound $\text{Mo}(\text{CO})_6$ and its KKT with the refined values for f'' and f' obtained directly from the diffraction data.

Most recently, Leinders et al. published their investigations on ADR of tetravalent uranium dioxide as well as pentavalent KUO_3 with powder diffraction.¹¹ In this study, the dispersive part of the atomic form factor f' was obtained by the transformation of refined f'' values and introduced as a parameter in the least-squares refinement procedure. In

the uranium L_3 absorption edge ($E = 17.1\text{keV}$), a significant fraction of the incoming radiation is absorbed and dispersed ($f' = -10.2e$, $f'' = 10.4e$ according to Henke et al.¹⁹). As the atomic scattering power is closely connected to the atomic position, displacement parameters, and most notably the element type, an adequate correction for these effects is essential for determining the correct structure. The quality of the structural model strongly depends on the treatment of these effects.

Herein, we present the capability and robustness of anomalous dispersion refinements (ADR) carried out at the L absorption edges of the known uranium single-crystalline compounds NaUF_5 , NaU_2F_9 , $\text{Cs}_2(\text{UO}_2)\text{TiO}_4$, and $\text{Cs}_2(\text{UO}_2)\text{Ti}_2\text{O}_6$.^{18,20} ADR was able to capture the features within the strongly pronounced L_3 edge of these compounds as well as the weaker L_2 and L_1 edges. For NaUF_5 , we present the dependency of ADR at room temperature (RT) as well as at 100 K. As ADR introduces two additional variables per resonating atom to the crystallographic model, it is important to investigate to what extent ADR improves the residual electron density and whether the correction parameters compensate for other effects.

7.2 Methods

To investigate the behavior of ADR at heavy element L-edges, SCXRD experiments were performed at various energies around the uranium L-edges ($L_3 : 17.166\text{keV}$, $L_2 : 20.948\text{keV}$, $L_1 : 21.757\text{keV}$ ²¹). Simultaneously, X-ray absorption spectra were recorded on the same single crystals in fluorescence mode in the range of these energies. All experiments were performed at the Rossendorf Beamline (BM20) at the European Synchrotron (ESRF) in Grenoble, France.²²

X-ray diffraction data were processed in CrysAlisPro²³ and evaluated in Olex2²⁴ using olex2.refine²⁵ as a refinement engine employing the serial processing module SISYPHOS.²⁶ All data were treated with only multiscan absorption correction²⁷ to avoid including the linear absorption coefficient μ . This is due to the direct proportionality between μ and f'' , the absorbing part of the dispersion correction. Especially in the edge region, the tabulated values are the most incorrect, as both the edge position and the fine structure features are individuals for each substance. Therefore, any absorption correction based on μ is also incorrect, particularly in this area.

XAS data were processed using the PyMCA²⁸ software suite, and the Kramers-Kronig transformations were performed using the kkalcc²⁹ program. Further details can be found in the Supporting Information (SI).

7.3 Results and discussion

The results from ADR together with the recorded UL_3 edge XAS data in both uranium(IV) fluorides and uranyl titanates are shown in Figure 7.1. In all cases, we observed good agreement between the XAS/KKT and the independently refined values for f''/f' obtained from SC-XRD data. The absolute values for f' and f'' follow the fine structure in the near edge region of XAS. The two crystallographically independent positions for uranium in $\text{Cs}_2(\text{UO}_2)\text{Ti}_2\text{O}_6$ (Figure 7.1) are chemically equivalent. This was reflected by very similar ADR values and underlined the sensitivity of ADR toward chemical features. Figure 7.2 shows a good agreement between f' and f'' and no significant temperature dependence for ADR of NaUF_5 at two temperatures (RT and 100 K, A). Only at the

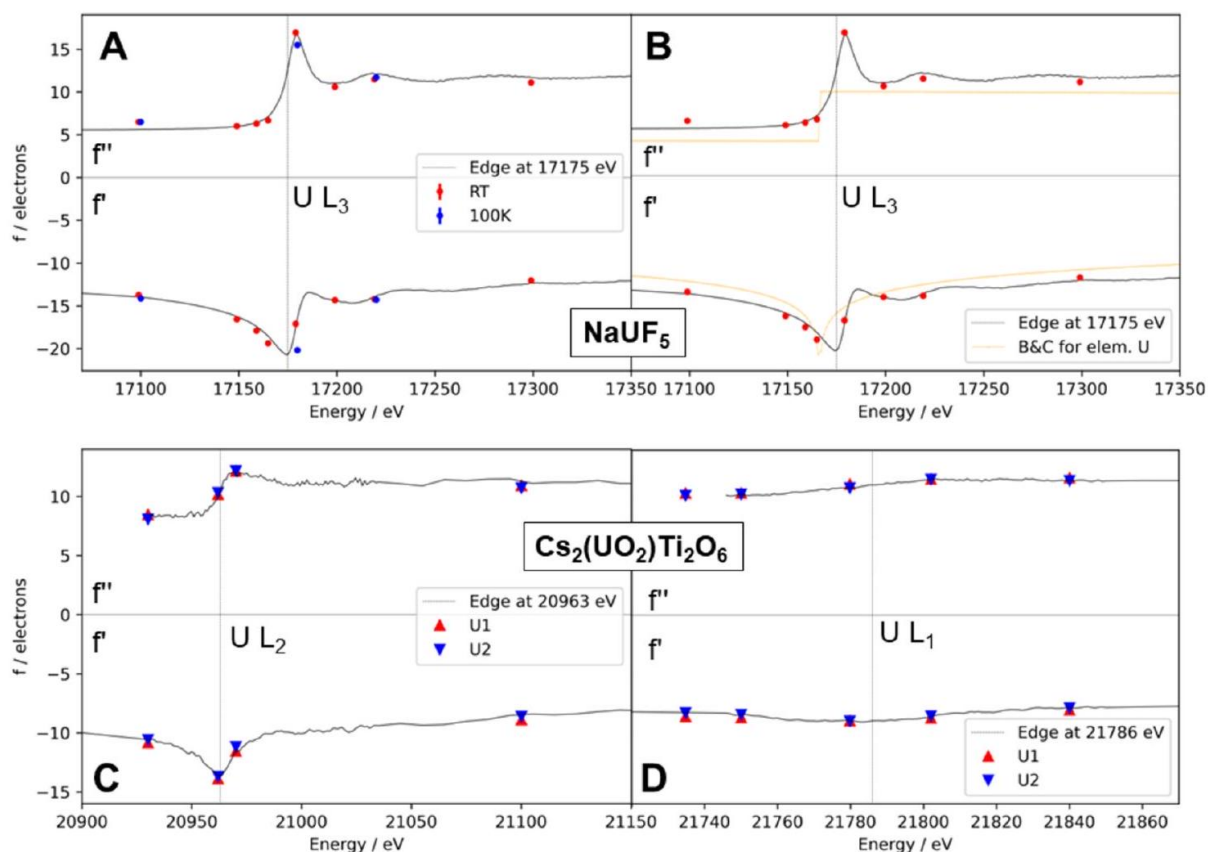


Figure 7.2: Each plot shows the recorded XAS (top) and its KKT (bottom) for NaUF_5 (A, B) and $\text{Cs}_2(\text{UO}_2)\text{Ti}_2\text{O}_6$ (C, D), together with the freely refined values for f'' (top) and f' (bottom) from XRD data at the different energies. A shows the ADR parameters at room temperature (red) as well as at 100 K (blue). (B) shows the values compared to the calculated values for uranium according to Brennan and Cowan.³⁰ Panels (C) and (D) compare the spectra to ADR values at the UL_2 and UL_1 absorption edge, respectively. The XAS and its KKT were first normalized and then fitted to the ADR parameters.

edge energy, a deviation was observed. However, this difference could be due to a small energy difference that can occur when the synchrotron beam is readjusted. For technical reasons, the low-temperature measurements were not carried out directly after the room-temperature experiments. Especially in the absorption edge, such a rather small drift in energy can already lead to a considerable deviation in absorption.

Most prominently, a large difference was observed between the refined f' and f'' values compared to the calculated dispersion correction according to Brennan and Cowan (Figure 7.2, B).³⁰ Not only was there a typical offset due to the difference in edge energy between elemental uranium and uranium embedded in a chemical environment (here by 9 eV), but there was also a shift to higher absolute values for f'' and f' . This trend was also observed for the other compounds of this study (see Figure S4 in the SI). Furthermore, a good agreement was also found at the less pronounced L_2 and L_1 edges in the respective spectra and even for the two uranium positions in the case of $\text{Cs}_2(\text{UO}_2)\text{Ti}_2\text{O}_6$.

In Figure 7.3, the residual electron density maps show the crystallographic models for three different sources of anomalous dispersion corrections above the absorption edge of uranium. In the case of NaU_2F_9 , a significant difference between the model relying on

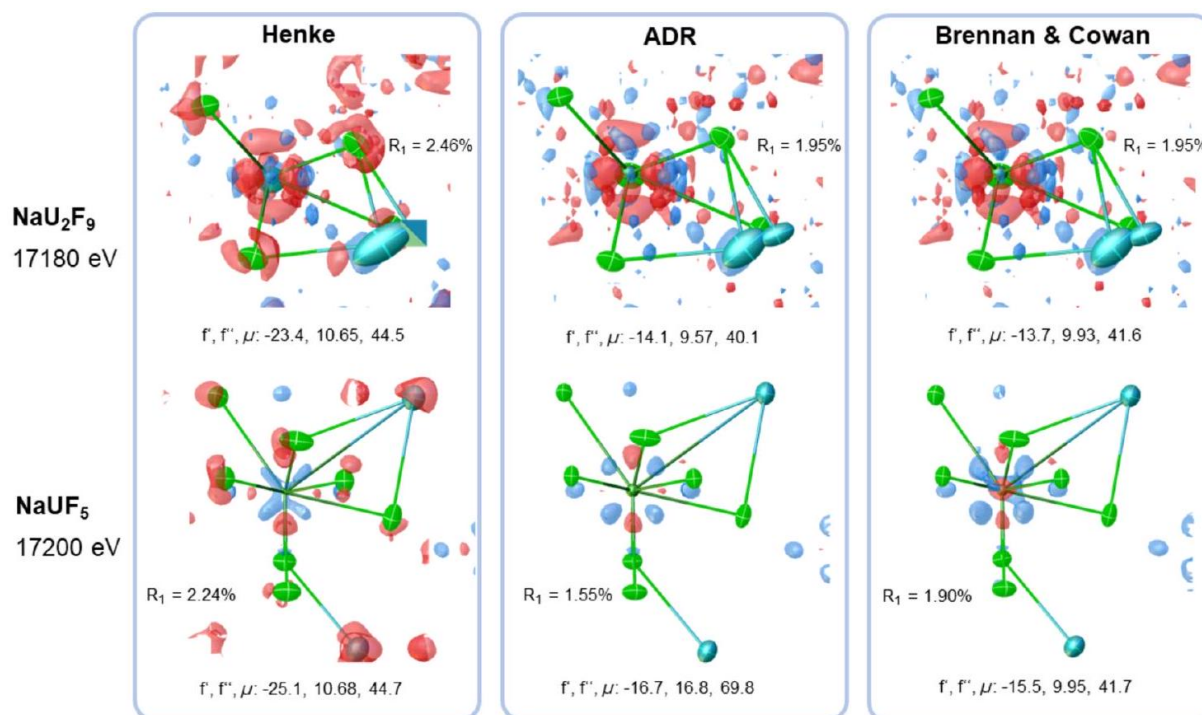


Figure 7.3: Residual electron density maps (blue: positive, red: negative) for the asymmetric units of NaU_2F_9 (top, $1.0 \text{ e} \cdot \text{\AA}^{-3}$ iso-surface) and NaUF_5 (bottom, $0.9 \text{ e} \cdot \text{\AA}^{-3}$ iso-surface) modeled according to Henke¹⁹ (left, linearly interpolated), ADR (middle), and Brennan and Cowan³⁰ (right, calculated). Ellipsoids are shown at 50% probability level, and tetrahedra indicate nonpositive definite displacement parameters. f' and f'' values are given in electrons and elemental μ in kilobarns per atom.

the Henke table¹⁹ and the one for Brennan and Cowan³⁰ was apparent. Using Henke the agreement strongly decreased and a disorder in the sodium position, far away from the uranium atom, could not be modeled properly. The values obtained from ADR closely matched those of Brennan and Cowan,³⁰ and similar agreement was obtained between measured and modeled structure factors as indicated by the crystallographic R_1 value.

In the case of NaUF_5 , ADR showed a better agreement with the measured data compared to the models using the values from Henke¹⁹ and Brennan and Cowan.³⁰ This suggests that ADR provided the most accurate values for anomalous dispersion correction in this approach, especially where pronounced spectral features dominate the XAS.

Generally, Brennan and Cowan³⁰ gave a good approximation, except for the edge region. This was particularly relevant for uranium compounds measured with $\text{MoK}\alpha$ radiation ($E_{\text{Mo K}\alpha} = 17.4 \text{ keV}$), which lies just above the U_2 edge. This was reflected very well in the work of Gianopoulos et al.,³¹ where in a charge density study of uranium, the anomalous dispersion values refined very close to those calculated by Brennan and Cowan.³⁰

^a The published structures were re-refined using *olex2.refine*²⁵ employing the recently published improved spherical model according to Thakkar.^{32,33} Additionally, for the uranyl titanate structures, the cesium atoms were refined anharmonically. Quality parameters were calculated to a resolution of $0.75 \text{ \AA}$, and f' and f'' were refined at the maximum resolution of the dataset.

Note that the resulting elemental absorption coefficient for uranium differed by more than

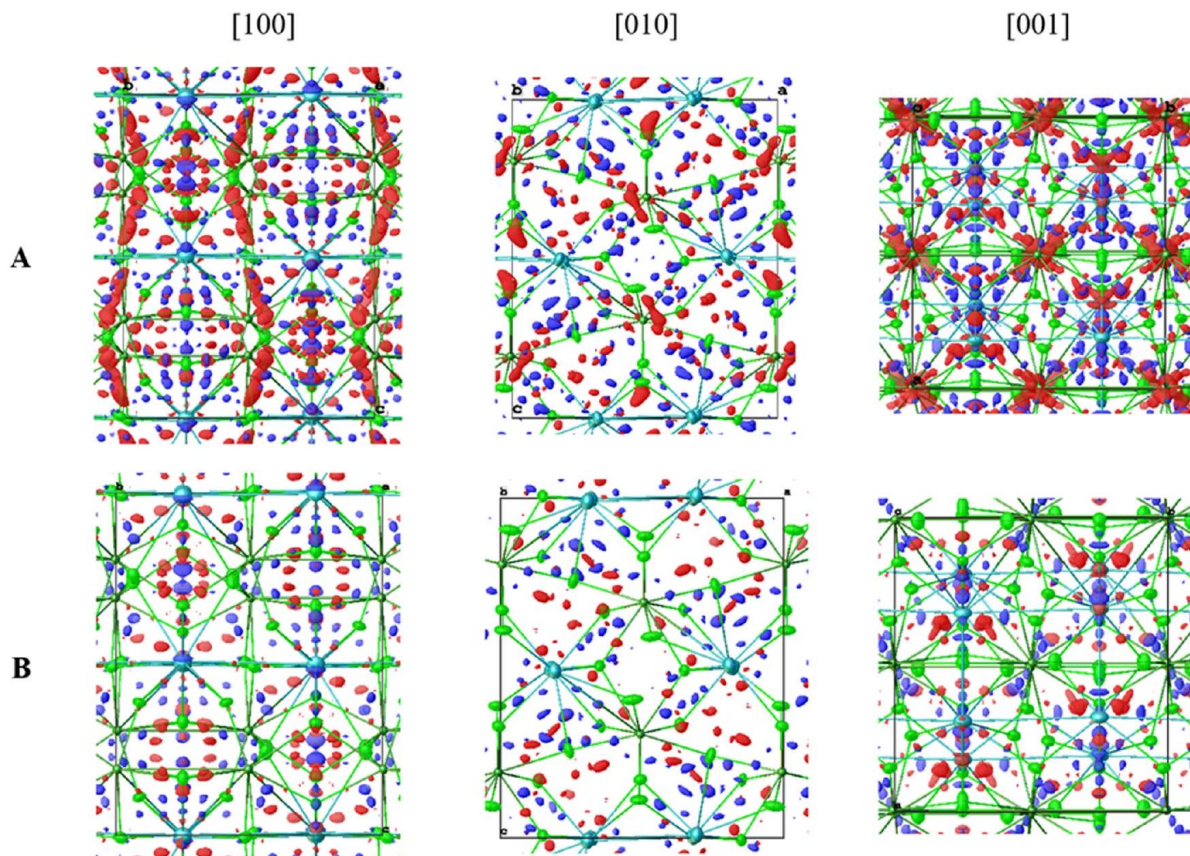


Figure 7.4: Residual electron density maps at $0.6 \text{ e} \cdot \text{\AA}^{-3}$ iso-level (blue: positive, red: negative) for the structure of NaUF_5 (CCDC 1827659)¹⁸ refined as published using Henke (A) and refined anomalous dispersion values (B) in crystallographic a , b , and c directions. Light green atoms: fluorine, dark green atoms: uranium, and cyan atoms: sodium.

50% (69.8 kilobarns per atom with ADR, 41.7 kilobarns per atom according to Brennan and Cowan³⁰). Such a difference can have a significant effect on the analytical absorption correction, which is essential for atomic structures containing heavy elements. Since f'' and μ are directly proportional to each other, their dependence is obvious. However, μ is used to correct the data, while f'' and f' are used to correct the model. Therefore, the true value of μ could potentially be found by repeatedly refining f'' and then applying the resulting μ to the absorption correction until convergence is reached.

Using the respective charged atomic form factors for uranium (U^{4+} for the fluorides and U^{6+} for the titanates) showed only a little deviation from the values obtained by using the neutral uranium atomic form factor. While the fluorides showed no significant difference, the f' obtained using charged uranium for the titanates did show lower absolute values than when using the neutral atomic form factor. This is consistent with the higher charge at the U^{6+} ion in the uranyl titanate structures. Again, the difference in f' and f'' for the two uranium positions in $\text{Cs}_2(\text{UO}_2)\text{Ti}_2\text{O}_6$ was only marginal.

As the structures of the four compounds in our study had previously been determined using Mo K α radiation, we applied ADR to these previously published datasets.^{18,20} Figure 7.4 shows the residual electron density maps of NaUF_5 with and without refined anomalous dispersion correction parameters. This map describes the observed electron

Table 7.1: Refinement indicators achieved with the Brennan and Cowan ³⁰ (B&C) anomalous dispersion values as well as by ADR for the published data of the four compounds within this study ^{a,18,20}.

Metric	NaUF ₅		NaU ₂ F ₉		Cs ₂ (UO ₂) TiO ₄		Cs ₂ (UO ₂) Ti ₂ O ₆	
	B&C	ADR	B&C	ADR	B&C	ADR	B&C	ADR
R_1, wR_2 / %	1.32, 2.64	1.26, 2.50	1.34, 3.07	1.33, 2.98	1.12, 2.52	1.08, 2.42	1.20, 2.87	1.08, 2.51
min., max. peaks / $e \text{ \AA}^{-3}$	-0.93, 1.07	-0.97, 0.97	-0.89, 1.11	-0.89, 1.03	-0.74, 0.73	-0.62, 0.67	-0.86, 1.67	-0.935, 1.53
weights	0.00, 2.91	0.00, 1.92	0.01, 0.87	0.01, 0.53	0.01, 21.0	0.00, 19.2	0.01, 11.7	0.01, 2.39
f', f'' / e	-9.7, 9.7	-11.9(3), 11.8(6)	-9.7, 9.7	-11.1(3), 9.9(6)	-9.7, 9.7	-10.2(4), 10.5(8)	-9.7, 9.7	-10.5, -11.3, 10.2, 10.1

density, which could not be completely described by the crystallographic model. Therefore, we attributed the significant reduction of this density to the improved correction by ADR for the nonelastic behavior. Even though the published structure was already of high quality, ADR improved the agreement of observed and modeled intensities even more. Subsequently, both the maximum and the minimum residual electron density peaks decreased. Table 7.1 shows the respective improvements for all four compounds with their corresponding values for the anomalous dispersion correction.

Generally, ADR improved the crystallographic model, resulting in better quality parameters, lower residuals, as well as lower weights on both the low- and high-resolution reflections. The deviation from the tabulated anomalous dispersion parameters according to Brennan and Cowan ³⁰ ($-9.7, 9.7e$) was rather large. The values by Brennan and Cowan ³⁰ differ more strongly from those of Sasaki ³⁴ ($-11.0e, 9.7e$) and Henke et al. ¹⁹ ($-10.2e, 10.4e$). In particular, f'' reached higher values in the free refinement than all tabulated sources, especially prominent for NaUF₅ with a value of 11.8 e.

Remeasurement of the crystals subject to this study on an inhouse diffractometer (Rigaku XtaLAB Synergy-DW, HyPix-Arc 150°) generally showed good agreement compared to the published structures. Further information can be found in the SI.

We are therefore confident in recommending ADR for uranium structures measured using in-house diffractometers and Mo K α radiation. However, this method should only be applied to high-quality datasets, without unresolved other issues, such as disorder, twinning, or anharmonicity. The warnings implemented in Olex2 should always be carefully considered if the values resulting from the ADR differ significantly from tabulated values.

7.4 Conclusion

In this work, we demonstrated the ability to perform anomalous dispersion refinements for very heavy elements in the energy range of their L absorption edges using four different uranium compounds as examples. The ADR's f'' and f' followed the independently recorded X-ray absorption spectra and Kramers-Kronig transformation closely, even in the delicate edge region. In the case of Cs₂ (UO₂) Ti₂O₆, which contains two crystallographically independent but chemically identical uranium positions, the deviation of f' and f'' for both positions was negligible. This underlines the benefit of refining individual dispersion parameters for spatially and chemically different elements. We have also shown that treatment of the anomalous dispersion as a free parameter leads to an improvement in the structural models of measurements with the laboratory diffractometer far away from the absorption edges. The published structures of the four compounds subject to this study, measured at an in-house diffractometer using common Mo K α radiation, could be improved by applying ADR.

7.5 References

- (1) Kramers, H. A. La Diffusion de La Lumiere Par Les Atomes. *Atti Cong. Intern. Fisica* 1927, 2, 545-557.
- (2) de L Kronig, R. On the Theory of Dispersion of X-Rays. *J. Opt. Soc. Am.* 1926, 12 (6), 547.
- (3) Einsle, O.; Andrade, S. L. A.; Dobbek, H.; Meyer, J.; Rees, D. C. Assignment of Individual Metal Redox States in a Metalloprotein by Crystallographic Refinement at Multiple X-Ray Wavelengths. *J. Am. Chem. Soc.* 2007, 129 (8), 2210-2211.
- (4) Rohde, M.; Grunau, K.; Einsle, O. CO Binding to the FeV Cofactor of CO-Reducing Vanadium Nitrogenase at Atomic Resolution. *Angew. Chem., Int. Ed.* 2020, 59 (52), 23626-23630.
- (5) Spatzal, T.; Schlesier, J.; Burger, E.-M.; Sippel, D.; Zhang, L.; Andrade, S. L. A.; Rees, D. C.; Einsle, O. Nitrogenase FeMoco Investigated by Spatially Resolved Anomalous Dispersion Refinement. *Nat. Commun.* 2016, 7 (1), No. 10902.
- (6) Bartholomew, A. K.; Musgrave, R. A.; Anderton, K. J.; Juda, C. E.; Dong, Y.; Bu, W.; Wang, S.-Y.; Chen, Y.-S.; Betley, T. A. Revealing Redox Isomerism in Trichromium Imides by Anomalous Diffraction. *Chem. Sci.* 2021, 12 (47), 15739-15749.
- (7) Bartholomew, A. K.; Teesdale, J. J.; Hernández Sánchez, R.; Malbrecht, B. J.; Juda, C. E.; Ménard, G.; Bu, W.; Iovan, D. A.; Mikhailine, A. A.; Zheng, S.-L.; Sarangi, R.; Wang, S. G.; Chen, Y.-S.; Betley, T. A. Exposing the Inadequacy of Redox Formalisms by Resolving Redox Inequivalence within Isovalent Clusters. *Proc. Natl. Acad. Sci. U.S.A.* 2019, 116 (32), 15836-15841.
- (8) Templeton, L. K.; Templeton, D. H. Cesium Hydrogen Tartrate and Anomalous Dispersion of Cesium. *Acta Crystallogr., Sect. A: Cryst. Phys., Diff., Theor. Gen. Crystallogr.* 1978, 34 (3), 368-371.
- (9) Templeton, D. H.; Templeton, L. K.; Phillips, J. C.; Hodgson, K. O. Anomalous Scattering of X-Rays by Cesium and Cobalt Measured with Synchrotron Radiation. *Acta Crystallogr., Sect. A: Cryst. Phys., Diff., Theor. Gen. Crystallogr.* 1980, 36 (3), 436-442.
- (10) Meurer, F.; Dolomanov, O. V.; Hennig, C.; Peyerimhoff, N.; Kleemiss, F.; Puschmann, H.; Bodensteiner, M. Refinement of Anomalous Dispersion Correction Parameters in Single-Crystal Structure Determinations. *IUCrJ* 2022, 9 (5), 604-609.
- (11) Leinders, G.; Grendal, O. G.; Arts, I.; Bes, R.; Prozheev, I.; Orlat, S.; Fitch, A.; Kvashnina, K.; Verwerft, M. Refinement of the Uranium Dispersion Corrections from Anomalous Diffraction. *J. Appl. Crystallogr.* 2024, 57 (2), 284.
- (12) zur Loye, H.-C.; Besmann, T.; Amoroso, J.; Brinkman, K.; Grandjean, A.; Henager, C. H.; Hu, S.; Mixture, S. T.; Phillpot, S. R.; Shustova, N. B.; Wang, H.; Koch, R. J.; Morrison, G.; Dolgoplova, E. Hierarchical Materials as Tailored Nuclear Waste Forms: A Perspective. *Chem. Mater.* 2018, 30 (14), 4475-4488.
- (13) Burns, P. C.; Ewing, R. C.; Hawthorne, F. C. The Crystal Chemistry of Hexavalent Uranium: Polyhedron Geometries, BondValence Parameters, and Polymerization of Polyhedra. *Can. Mineral.* 1997, 35, 1551-1570.
- (14) Severance, R. C.; Smith, M. D.; zur Loye, H.-C. ThreeDimensional Hybrid Framework Containing U₂O₁₃ Dimers Connected via Cation-Cation Interactions. *Inorg. Chem.* 2011, 50 (17), 7931-7933.
- (15) Balboni, E.; Burns, P. C. Cation-Cation Interactions and Cation Exchange in a Series of Isostructural Framework Uranyl Tungstates. *J. Solid State Chem.* 2014, 213, 1-8.

- (16) Read, C. M.; Yeon, J.; Smith, M. D.; Loye, H.-C. zur. Crystal Growth, Structural Characterization, Cation-Cation Interaction Classification, and Optical Properties of Uranium(VI) Containing Oxychlorides, $A_4U_5O_{16}Cl_2$ ($A = K, Rb$), $Cs_5U_7O_{22}Cl_3$, and AUO_3Cl ($A = Rb, Cs$). *CrystEngComm* 2014, 16 (31), 7259-7267.
- (17) Yeon, J.; Smith, M. D.; Tapp, J.; Möller, A.; zur Loye, H.-C. Application of a Mild Hydrothermal Approach Containing an in Situ Reduction Step to the Growth of Single Crystals of the Quaternary U(IV)-Containing Fluorides $Na_4MU_6F_{30}$ ($M = Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}$, and Zn^{2+}) Crystal Growth, Structures, and Magnetic Properties. *J. Am. Chem. Soc.* 2014, 136 (10), 3955-3963.
- (18) Klepov, V. V.; Felder, J. B.; zur Loye, H.-C. Synthetic Strategies for the Synthesis of Ternary Uranium(IV) and Thorium(IV) Fluorides. *Inorg. Chem.* 2018, 57 (9), 5597-5606.
- (19) Henke, B. L.; Lee, P.; Tanaka, T. J.; Shimabukuro, R. L.; Fujikawa, B. K. Low-Energy x-Ray Interaction Coefficients: Photoabsorption, Scattering, and Reflection: $E = 100 - 2000\text{eV}$ $Z = 1 - 94$. *At. Data Nucl. Data Tables* 1982, 27 (1), 1-144.
- (20) Morrison, G.; Christian, M. S.; Besmann, T. M.; zur Loye, H.C. Flux Growth of Uranyl Titanates: Rare Examples of TiO_4 Tetrahedra and TiO_5 Square Bipyramids. *J. Phys. Chem. A* 2020, 124 (45), 9487-9495.
- (21) Uranium. https://xdb.lbl.gov/Section1/Periodic_Table/U_Web_data.htm (accessed Feb 14, 2024).
- (22) Scheinost, A. C.; Claussner, J.; Exner, J.; Feig, M.; Findeisen, S.; Hennig, C.; Kvashnina, K. O.; Naudet, D.; Prieur, D.; Rossberg, A.; Schmidt, M.; Qiu, C.; Colomp, P.; Cohen, C.; Dettona, E.; Dyadkin, V.; Stumpf, T. ROBL-II at ESRF: A Synchrotron Toolbox for Actinide Research. *J. Synchrotron Radiat.* 2021, 28 (1), 333-349.
- (23) CrysAlis PRO; Rigaku Oxford Diffraction Ltd., 2019.
- (24) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Crystallogr.* 2009, 42 (2), 339-341.
- (25) Bourhis, L. J.; Dolomanov, O. V.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. The Anatomy of a Comprehensive Constrained, Restrained Refinement Program for the Modern Computing Environment - Olex2 Dissected. *Acta Crystallogr., Sect. A: Found. Adv.* 2015, 71 (1), 59-75.
- (26) GitHub - FlorianMeurer/plugin-SISYPHOS: SISYPHOS software for the serial modelling of crystallographic data for the same structure within Olex2. <https://github.com/FlorianMeurer/plugin-SISYPHOS> (accessed April 05, 2024).
- (27) Blessing, R. H. An Empirical Correction for Absorption Anisotropy. *Acta Crystallogr., Sect. A: Found. Crystallogr.* 1995, 51 (1), 33-38.
- (28) Solé, V.; Papillon, E.; Cotte, M.; Walter, P.; Susini, J. A Multiplatform Code for the Analysis of Energy-Dispersive X-Ray Fluorescence Spectra. *Spectrochim. Acta, Part B* 2007, 62 (1), 63-68.
- (29) Watts, B. Calculation of the Kramers-Kronig Transform of XRay Spectra by a Piecewise Laurent Polynomial Method. *Opt. Express* 2014, 22 (19), 23628-23639.
- (30) Brennan, S.; Cowan, P. L. A Suite of Programs for Calculating X-Ray Absorption, Reflection, and Diffraction Performance for a Variety of Materials at Arbitrary Wavelengths. *Rev. Sci. Instrum.* 1992, 63 (1), 850-853.
- (31) Gianopoulos, C. G.; Zhurov, V. V.; Minasian, S. G.; Batista, E. R.; Jelsch, C.; Pinkerton, A. A. Bonding in Uranium(V) Hexafluoride Based on the Experimental Electron Density Distribution Measured at 20 K. *Inorg. Chem.* 2017, 56 (4), 1775-1778.

- (32) Koga, T.; Kanayama, K.; Watanabe, T.; Imai, T.; Thakkar, A. J. Analytical Hartree-Fock Wave Functions for the Atoms Cs to Lr. *Theor. Chem. Acc.* 2000, 104 (5), 411-413.
- (33) Kleemiss, F.; Peyerimhoff, N.; Bodensteiner, M. Refinement of X-Ray and Electron Diffraction Crystal Structures Using Analytical Fourier Transforms of Slater-Type Atomic Wavefunctions in Olex2. *J. Appl. Crystallogr.* 2024, 57 (1), 161-174.
- (34) Sasaki, S. Numerical Tables of Anomalous Scattering Factors Calculated by the Cromer and Liberman's Method; Japan, 1989; p 137.

7.6 Supporting information

The supporting information of this work is provided as a single .pdf file with original format and page numbering starting from the next page.

Supporting Information

Improvement of Single-Crystal Structures of Very Heavy Element Compounds by Refining Anomalous Dispersion Parameters

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Synthesis and General Considerations

Single crystals of the four compounds were prepared using the published experimental procedures.^{1,2} Briefly, NaUF₅ and NaU₂F₉ were synthesized under mild hydrothermal conditions. For NaUF₅, 0.2500 g of UF₄, 0.0361 g of NaF, 0.25 mL of 49% HF, and 0.5 mL of distilled water were enclosed in an autoclave with a 23 mL PTFE liner. For NaU₂F₉, 0.1500 g of UF₄, 0.0108 g of NaF, 0.25 mL of 49% HF, and 1.5 mL of distilled water were enclosed in an autoclave with a 23 mL PTFE liner. Both reactions were heated to 200 °C for 36 h in a programmable oven and then allowed to cool naturally by shutting off the oven. The crystals were isolated from the mother liquor via vacuum filtration and washed with water followed by acetone. Cs₂(UO₂)TiO₄ and Cs₂(UO₂)Ti₂O₆ were grown via flux growth from a near eutectic cesium fluoride/cesium chloride melt. For Cs₂(UO₂)TiO₄ and Cs₂(UO₂)Ti₂O₆, a mixture of 1/6 mmol U₃O₈ and ½ mmol TiO₂ and a mixture of 0.5 mmol UF₄ and 1 mmol TiO₂, respectively, were layered under a mixture of 9 mmol CsF and 11 mmol CsCl in a cylindrical silver crucible. The reactions were rapidly heated to 900 °C for 12 h, cooled to 400 °C at 6 °C/h, and then allowed to cool naturally by shutting off the furnace. The flux was dissolved via sonication in water and the crystals were isolated via vacuum filtration and washed with water followed by acetone. The resulting crystals were analyzed on an in-house Bruker D8 Quest diffractometer equipped with a microfocus Mo K α X-ray source and a Photon II detector to select high-quality crystals for subsequent analysis on the beamline.

In Cs₂(UO₂)TiO₄, and Cs₂(UO₂)Ti₂O₆ the uranium ions form uranyl ions and have UO₆ square bipyramidal coordination. In Cs₂(UO₂)TiO₄, these UO₆ polyhedra corner share through two equatorial oxygens to form chains, with the other two equatorial oxygens corner-sharing to TiO₄ tetrahedra. The -yl oxygens are terminal and stick into channels occupied by the Cs cations. The UO₆ polyhedra consist of two short -yl bonds with length 1.873(2) Å, two intermediate bonds along the chains with length 2.1459(4) Å, and two longer bonds of length 2.2431(18) Å.² Cs₂(UO₂)Ti₂O₆ has two unique uranium positions, both forming uranyl ions and having UO₆ square bipyramidal coordination. The bonding environments for the two uranium positions are very similar containing two -yl oxygens with bond distances of 1.834(3) – 1.837(3) Å (U1) and 1.831(2) Å (U2) and four equatorial oxygens that corner share with TiO₅ polyhedra and have bond distances of 2.2177(18) – 2.2338(18) Å (U1) and 2.2115(19) – 2.2373(19) Å (U2).² NaUF₅ and NaU₂F₉ each have one unique uranium position, forming UF₉ polyhedra. The bond distances in NaUF₅ have a greater range, 2.134(2) – 2.486(2) Å, compared to those in NaU₂F₉, 2.24775(17) – 2.418(2) Å.¹

Experimental Procedures

All data were obtained at the Rossendorf Beamline (ROBL, BM-20) at the European Synchrotron (ESRF) in Grenoble, France.³

X-ray absorption spectroscopy data for the comparison spectra were recorded in fluorescence mode using a FalconX single-module ROI-based fluorescence detector. The energy was calibrated against the first inflection of the first derivative for an Y foil at 17.038,0 eV (see Fig. S1).

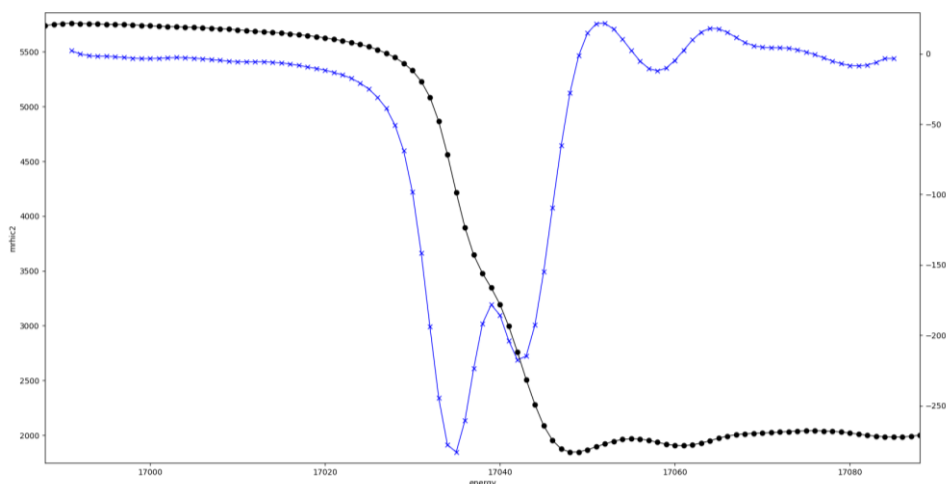


Figure S1: Absorption spectrum (transmission mode) for an Y foil for energy calibration. The minimum of the derivative was found at 17,035 eV and then set to the K absorption edge of Y at 17,038 eV.

The absorption spectra at the uranium L_3 -edge are shown in Fig. S2.

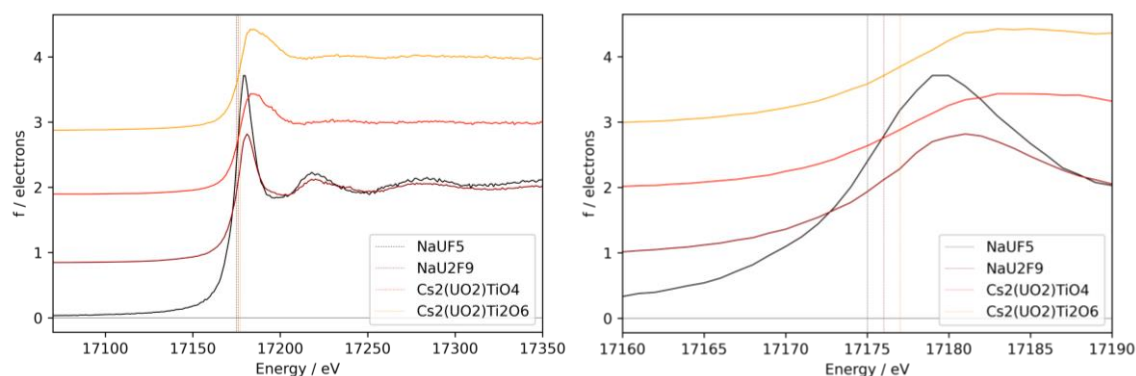


Figure S2: Absorption spectra in fluorescence mode for the compounds of this study.

Diffraction data were collected on a Huber Kappa diffractometer using a DECTRIS PILATUS3 X 2M photon counting detector for recording data. The data were processed using the SNBL toolbox⁴ and CrysAlisPro⁵. The instrument model was calibrated using an LaB_6 powder standard using *PyFAI*⁶ and the resulting instrument model was refined against an “Ylid”⁷ single-crystal dataset with 100.0% of recorded reflections indexed. Datasets were recorded at multiple energies, determined from the individual absorption spectra. For each compound and absorption edge, an initial model was obtained by a structure solution with *ShelXT*⁸ and then a refinement of positional and anisotropic parameters for all atoms using *olex2.refine*⁹ within the *Olex2*¹⁰ crystallographic suite. The initial structural model was then used as an input for serial refinement against the structure factors (.hkl files) obtained at the subsequent energies. This was done using the *Olex2*¹⁰ extension module *SISYPHOS*¹¹, which guided the serial refinement of anomalous dispersion correctional terms and the extinction correction in an automated fashion employing *olex2.refine*⁹. The output of this process can be found in .csv format containing resulting quality parameters, shift, ADPs, anomalous dispersion values, and more in the

additional supplementing material (ASM1). A .cif is also provided in a zipped folder (ASM2) for each experiment at a different wavelength.

For the cesium uranium titanates, anharmonic displacement parameters were refined for the cesium atoms, and in $\text{Cs}_2(\text{UO}_2)\text{TiO}_4$ half a molecule of water was identified at a chemically plausible position and included in the refinement with a fixed occupancy of 0.5 due to the symmetry constraint. Further information can be found in Table S1 containing the crystallographic information of the starting models.

Table S1: Crystallographic details of the starting crystal structures for the serial refinement of the studied compounds at different wavelengths.

Sample	NaUF_5	NaU_2F_9	$\text{Cs}_2(\text{UO}_2)\text{TiO}_4$	$\text{Cs}_2(\text{UO}_2)\text{Ti}_2\text{O}_6$
X-ray Energy / eV	17,100	17,100	17,000	17,000
Empirical formula	NaUF_5	NaU_2F_9	$\text{Cs}_2(\text{UO}_2)\text{TiO}_4 \cdot 0.5 \text{H}_2\text{O}$	$\text{Cs}_2(\text{UO}_2)\text{Ti}_2\text{O}_6$
CCDC Nr.	2337534	2337500	2337547	2337544
Formula weight / $\text{g}\cdot\text{mol}^{-1}$	356.011	670.033	1313.421	727.569
Crystal size / mm^3	$0.068 \times 0.049 \times 0.030$	$0.066 \times 0.050 \times 0.043$	$0.077 \times 0.049 \times 0.039$	$0.039 \times 0.028 \times 0.025$
Temperature / K	294.0(1)	293.9(1)	294.0(1)	294(1)
Space group	Pnma	Pnma	Immm	$P2_1/m$
a / Å	8.70675(4)	8.66316(8)	8.4950(2)	7.51113(10)
b / Å	8.08990(5)	11.1686(1)	13.5769(2)	16.4083(2)
c / Å	10.42316(5)	7.02070(6)	14.5795(4)	7.95961(10)
α, β, γ / °	90	90	90	90, 102.737(1), 90
V / Å ³	734.174(6)	679.29(2)	1681.54(7)	956.84(2)
ρ / $\text{g}\cdot\text{cm}^{-3}$	6.442	6.552	5.188	5.051
μ / mm^{-1}	20.494	22.016	18.881	17.441
θ -range / °	6.22 – 67.78	7.00 – 67.76	54.20 – 68.24	5.10 – 68.26
Total reflections	34779	30713	39930	45501
Data/restr./param.	1480/0/76	1355/0/61	1815/0/106	3743/0/187
Completeness / %	100	100	100	100
Resolution / Å	0.65	0.65	0.65	0.65
$R_1, wR_2, R_{\text{int}}$ (all data) / %	1.12, 3.13	1.43, 3.64	0.96, 2.41	1.38 3.24
GooF	1.047	1.031	1.060	1.038
Largest diff. peak, hole / $\text{e}\cdot\text{\AA}^{-3}$	0.89, -0.72	1.16, -1.80	0.52, -0.62	1.56, -1.30
$I/\sigma(I)$	107.3	67.6	104.2	66.4
Indices range	$-15 \leq h \leq 15$	$-15 \leq h \leq 15$	$-15 \leq h \leq 15$	$-13 \leq h \leq 13$
	$-14 \leq k \leq 14$	$-20 \leq k \leq 19$	$-24 \leq k \leq 24$	$-27 \leq k \leq 18$
	$-18 \leq l \leq 18$	$-12 \leq l \leq 12$	$-26 \leq l \leq 25$	$-14 \leq l \leq 14$
f', f'' / electrons	-13.7(1), 6.5(2)	-14.6(2), 7.0(4)	-11.09(7), 5.2(1)	U1: -12.02(7) 6.99(9) U2: -11.73(8) 5.99(10)

Labelling scheme of the starting structures of ADR

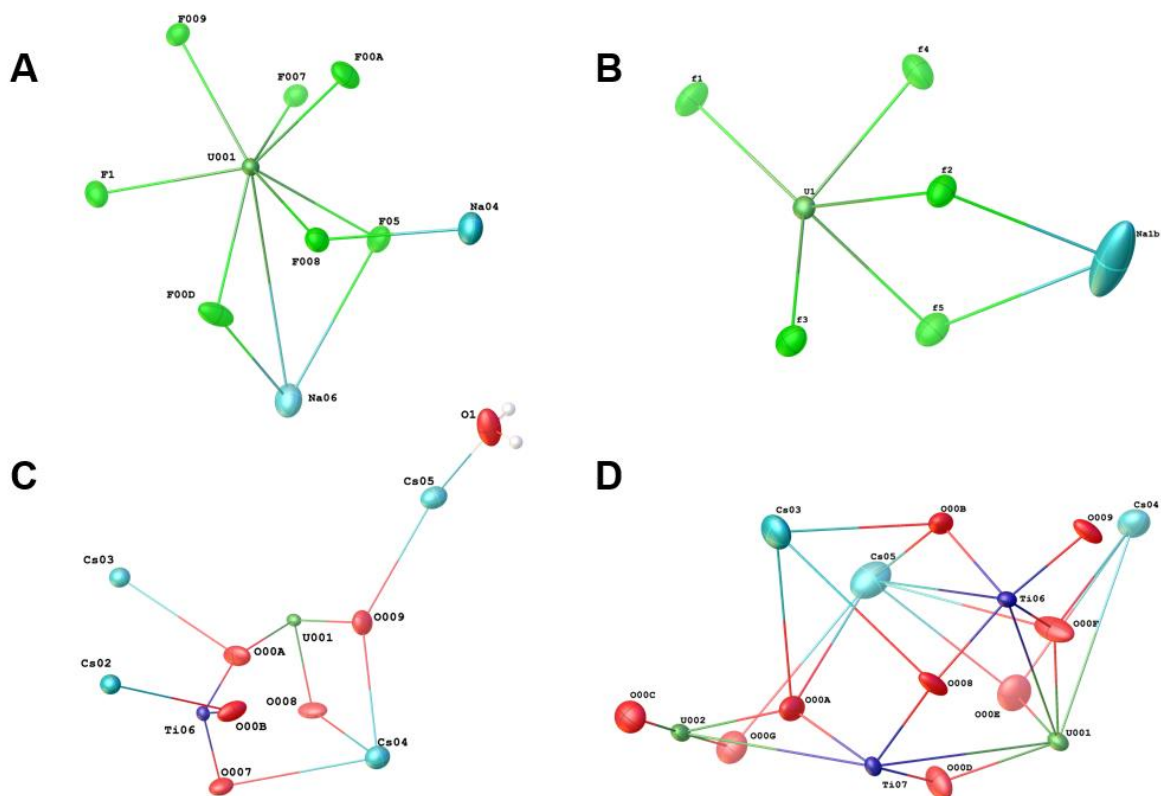


Figure S3: Labelling scheme for NaUF₅ (A), NaU₂F₉ (B), Cs₂(UO₂)TiO₄ (C), and Cs₂(UO₂)Ti₂O₆ (D) as given by the respective structure solution program.

Overlay of the starting structure models for ADR and the previously published ones.

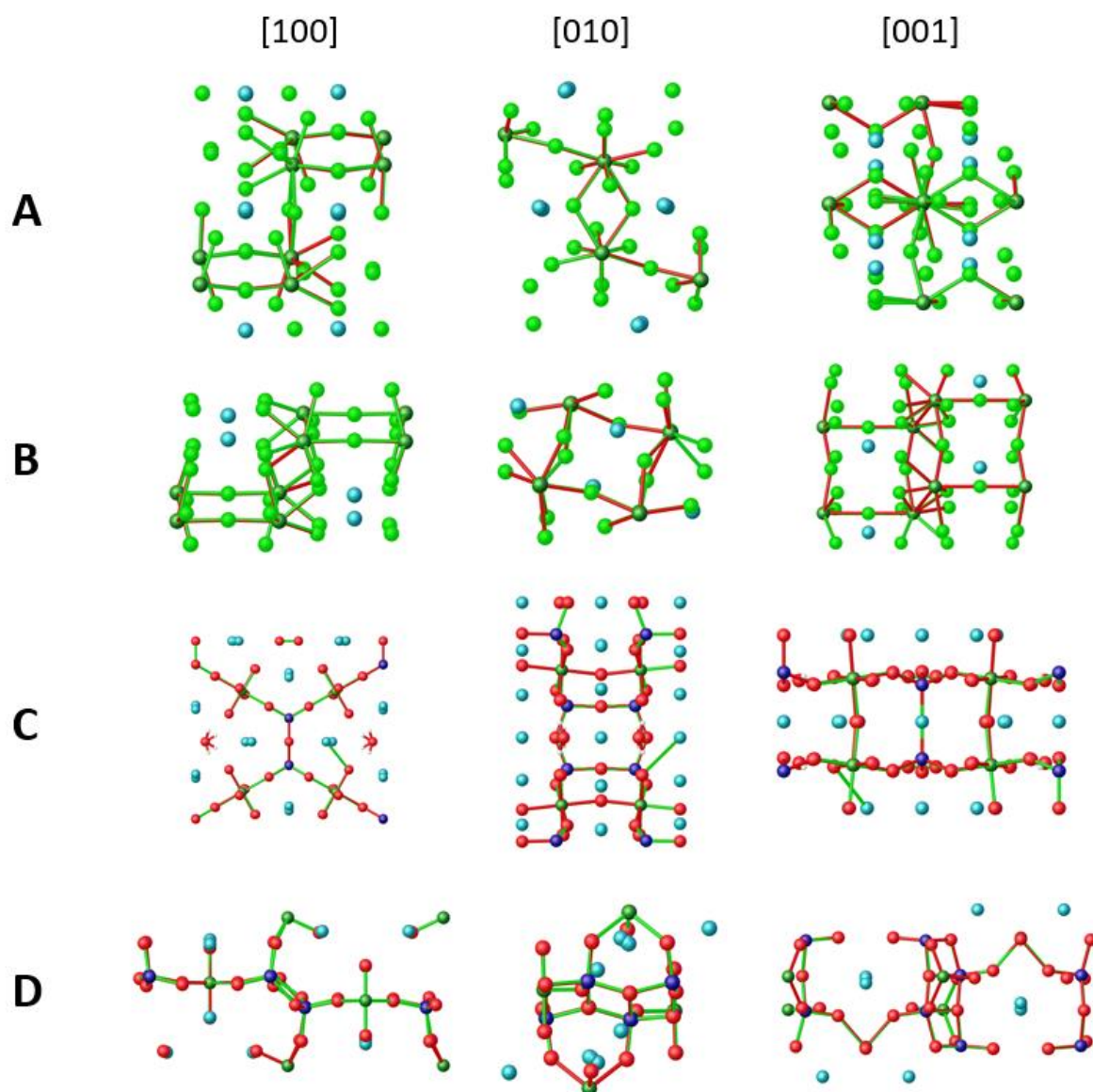


Figure S4: Structural overlay in balls-and-sticks representation of the starting models used in this study and the re-refined published structures of NaUF_5 (**A**), NaU_2F_9 (**B**), $\text{Cs}_2(\text{UO}_2)\text{TiO}_4$ (**C**), and $\text{Cs}_2(\text{UO}_2)\text{Ti}_2\text{O}_6$ (**D**).

ADR at L_2 and L_1 edges for NaUF_5 and $\text{Cs}_2(\text{UO}_2)\text{TiO}_4$

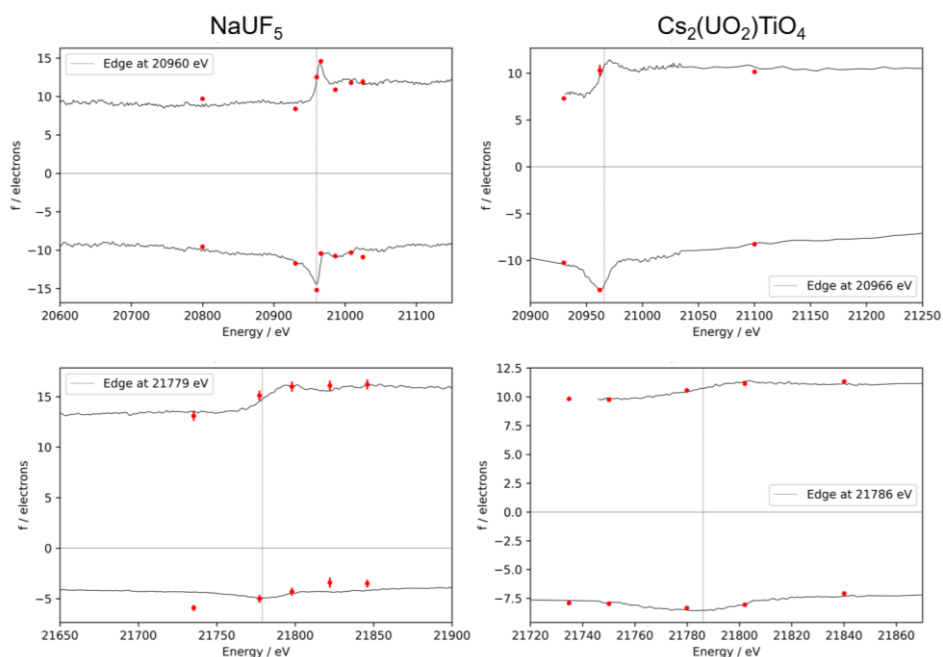


Figure S5: Each plot shows the recorded X-ray absorption spectrum and its Kramers-Kronig transformation for the L_2 (top row) and L_1 edge (bottom) of uranium in two different compounds, together with the freely refined values for f'' and f' from X-ray diffraction data at the different energies. Dispersion parameters are presented with their standard deviations for NaUF_5 and $\text{Cs}_2(\text{UO}_2)\text{TiO}_4$. Note that the X-ray absorption spectrum and its transformation were first normalized and then fitted in vertical offset and scaling to the refined anomalous dispersion parameters.

ADR at the U L_3 edges compared to the Brennan & Cowan table

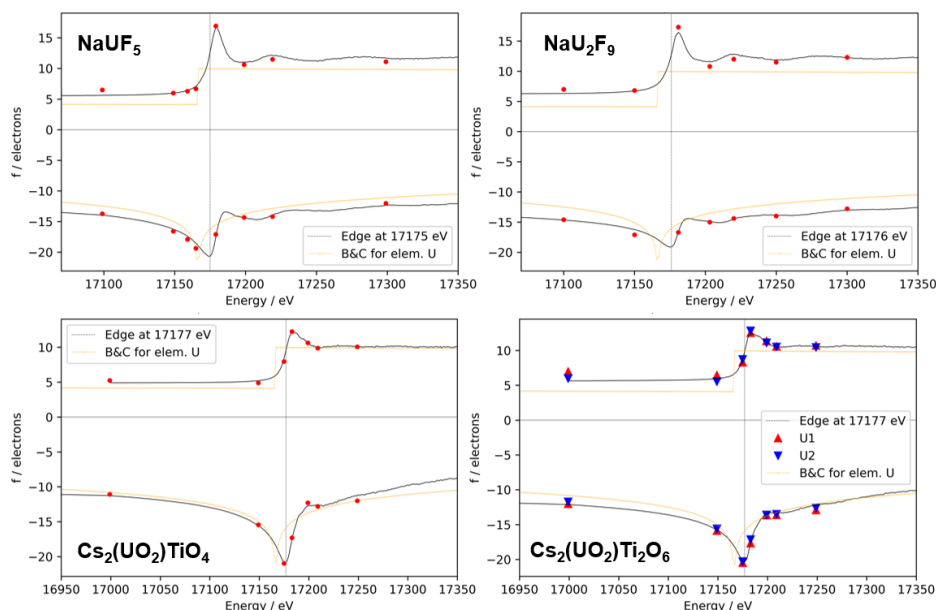


Figure S6: Each plot shows the recorded X-ray absorption spectrum (top) and its Kramers-Kronig transformation (bottom) for the L_3 edge of uranium in four different compounds, together with the freely refined values for f'' (top) and f' (bottom) from X-ray diffraction data at the different energies. Dispersion parameters

are presented with their standard deviations for NaUF₅ and Cs₂(UO₂)TiO₄. Note that the X-ray absorption spectrum as well as its transformation were first normalized and then fitted in vertical offset as well as scaling to the refined anomalous dispersion parameters.

Table S2: Values and standard deviations for f' and f'' obtained by ADR at various energies around the L₃, L₂, and L₁ absorption edges for NaUF₅ and NaUF₉.

NaUF ₅		NaUF ₉	
Energy / eV	$f', f'' / e$	Energy / eV	$f', f'' / e$
L ₃			
17,100	-13.7(1), 6.5(2)	17,100	-14.6(2), 7.0(4)
17,150	-16.6(1), 6.0(2)	17,150	-17.1(2), 6.8(3)
17,160	-17.9(1), 6.3(2)	17,181	-16.7(3), 17.3(4)
17,166	-19.4(1), 6.7(1)	17,203	-15.0(3), 10.8(4)
17,180	-17.1(2), 17.0(2)	17,220	-14.4(3), 12.0(4)
17,200	-14.3(2), 10.6(2)	17,250	-14.0(3), 11.5(4)
17,220	-14.3(2), 11.5(2)	17,300	-12.8(3), 12.3(4)
17,300	-12.0(2), 11.1(2)		
L ₂			
20,800	-9.6(1), 9.7(2)	20,800	-8.6(3), 11.4(3)
20,930	-11.7(1), 8.4(3)	20,950	-12.3(2), 10.3(3)
20,960	-15.2(1), 12.5(2)	20,965	-10.5(2), 16.8(3)
20,966	-10.4(2), 14.6(2)	20,988	-9.7(3), 12.7(3)
20,986	-10.8(2), 10.9(2)	21,200	-8.0(3), 14.4(4)
21,008	-10.3(2), 11.8(2)		
21,025	-10.9(3), 11.9(4)		
L ₁			
21,735	-5.9(3), 13.1(5)		
21,777	-5.0(4), 15.1(5)		
21,798	-4.3(4), 16.0(5)		
21,822	-3.4(5), 16.1(5)		
21,846	-3.5(4), 16.2(5)		
21,930	-3.7(4), 15.7(5)		
22,000	-4.0(4), 15.6(5)		

Table S3: Values and standard deviations for f' and f'' obtained by ADR at various energies around the L_3 , L_2 , and L_1 absorption edges for $\text{Cs}_2(\text{UO}_2)\text{TiO}_4$ and $\text{Cs}_2(\text{UO}_2)\text{Ti}_2\text{O}_6$.

$\text{Cs}_2(\text{UO}_2)\text{TiO}_4$		$\text{Cs}_2(\text{UO}_2)\text{Ti}_2\text{O}_6$		
Energy / eV	$f', f'' / e$	Energy / eV	$f', f'' / e$ (U1)	$f', f'' / e$ (U2)
L_3				
17,000	-11.1(1), 5.2(1)	17,000	-12.0(1), 7.0(1)	-11.7(1), 6.0(1)
17,150	-15.4(1), 4.9(1)	17,150	-15.9(7), 6.5(1)	-15.6(1), 5.5(1)
17,176	-21.0(2), 8.0(1)	17,176	-20.5(1), 8.3(1)	-20.3(1), 8.8(1)
17,184	-17.3(2), 12.2(1)	17,184	-17.7(1), 12.5(6)	-17.1(1), 12.8(1)
17,200	-12.3(3), 10.6(1)	17,200	-13.7(7), 11.4(1)	-13.6(7), 11.1(1)
17,210	-12.8(2), 9.9(1)	17,210	-13.6(1), 10.6(1)	-13.5(1), 10.5(1)
17,250	-12.0(2), 10.1(1)	17,250	-12.9(1), 10.7(1)	-12.6(1), 10.5(1)
L_2				
20,930	-10.2(1), 7.3(1)	20,930	-10.9(1), 8.5(1)	-10.6(1), 8.01(1)
20,962	-13.2(1), 10.3(6)	20,962	-13.9(1), 10.2(1)	-13.7(1), 10.3(1)
21,100	-8.3(1), 10.2(1)	20,970	-11.2(1), 12.1(1)	-11.2(1), 12.2(1)
		21,100	-8.9(1), 10.9(1)	-8.6(1), 10.7(1)
L_1				
21,735	-7.9(1), 9.8(1)	21,735	-8.6(1), 10.3(1)	-8.3(1), 10.1(1)
21,750	-8.0(1), 9.8(1)	21,750	-8.7(1), 10.4(1)	-8.4(1), 10.3(1)
21,780	-8.3(1), 10.6(1)	21,780	-9.0(1), 11.1(1)	-9.0(1), 10.8(1)
21,802	-8.1(1), 11.1(1)	21,802	-8.7(1), 11.5(1)	-8.6(1), 11.5(1)
21,840	-7.1(1), 11.3(1)	21,840	-8.0(1), 11.7(1)	-7.9(1), 11.4(1)

Influence of charged atomic form factors on the refinement of anomalous dispersion parameters

For uranium, the International Union for Crystallography (IUCr) has four different sets of atomic form factor parameters in its Tables¹². These are for the neutral uranium atom used in this study, as well as adaptations for the charged species U^{3+} , U^{4+} , and U^{6+} . The spherical atomic form factor is conventionally approximated by four Gaussian functions and a set of nine parameters in the form of

$$f(|Q|) = \sum_{i=1}^4 a_i \exp\left(-b_i\left(\frac{Q}{4\pi}\right)^2\right) + c_i$$

Where Q is the scattering vector and a , b , and c are the parameters fitting the Gaussian functions to the Fourier transform of the calculated atomic electron density. Table S4 shows the different parameters and Fig S6 shows the atomic form factors with increasing scattering vector.

Table S4: Fitting parameters of the four different uranium species given in reference ¹².

Species	a1	b1	a2	b2	a3	b3	a4	b4	c
U	36.0228	0.5293	23.4128	3.3253	14.9491	16.0927	4.188	100.613	13.3966
U3+	35.5747	0.52048	22.5259	3.12293	12.2165	12.7148	5.37073	26.3394	13.3092
U4+	35.3715	0.516598	22.5326	3.05053	12.0291	12.5723	4.7984	23.4582	13.2671
U6+	34.8509	0.507079	22.7584	2.8903	14.0099	13.1767	1.21457	25.2017	13.1665

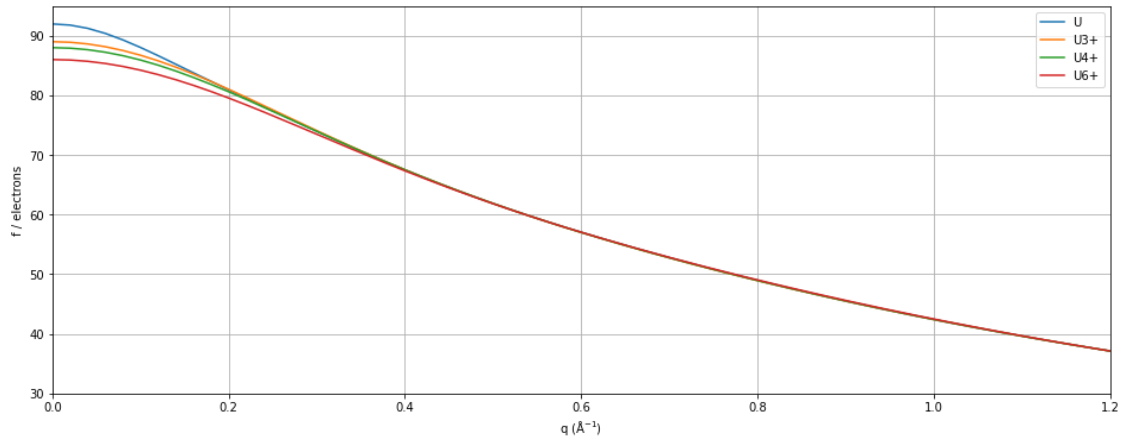


Figure S7: Atomic form factors for neutral and charged uranium species.

Fig. S6 shows, that the difference between the charged species is predominately in the low-resolution region. From about $0.3 \text{ \AA}^{-1}$, there is no significant difference between the four species.

To investigate the influence of charged atomic form factors, we took the “most suitable” charged atomic form factor for each of our ADR experiments at the L_3 absorption edge and compared it to the ADR result using the neutral atomic form factor. Fig. S7 shows the side-by-side comparison of the U^{4+} atomic form factor for the fluorides and the U^{6+} form factor for the titanate structures.

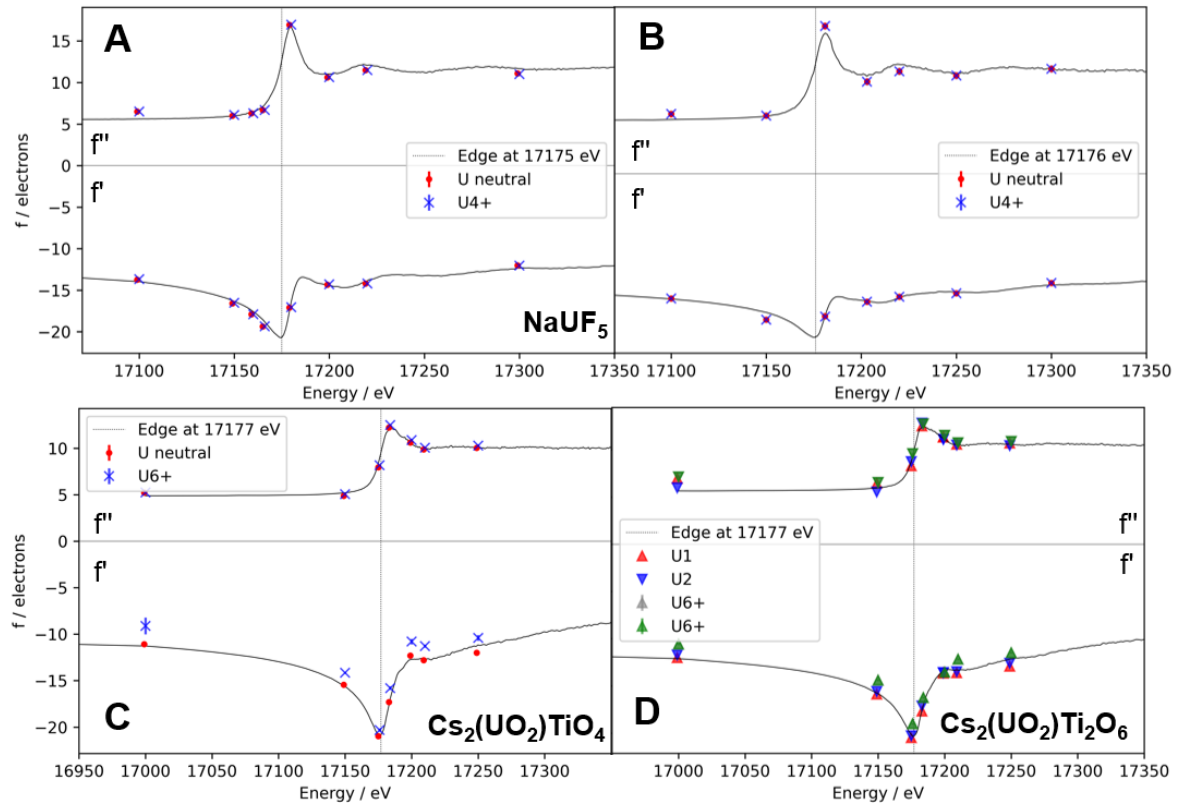


Figure S8: Comparison of ADR using neutral and charged atomic form factors. Figure according to Fig. 2 and 3 in the main text.

Generally, the change of the neutral to the respective charged atomic form factors (using tabulated anomalous dispersion correction values) did not improve the structural quality in terms of quality indicators as well as uranium ADPs (see ASM 3).

No significant difference was observed for the uranium fluorides when neutral and charged (U^{4+}) atomic form factors were used in the ADR procedure. However, for the uranyl titanates, a small difference especially in f' was observed, which is consistent with the higher charge on the metal atom and the direct correction that the real part of the anomalous dispersion correction has on the atomic form factor.

Residual density improvements of the published structures analogous to Figure 4 in the main text

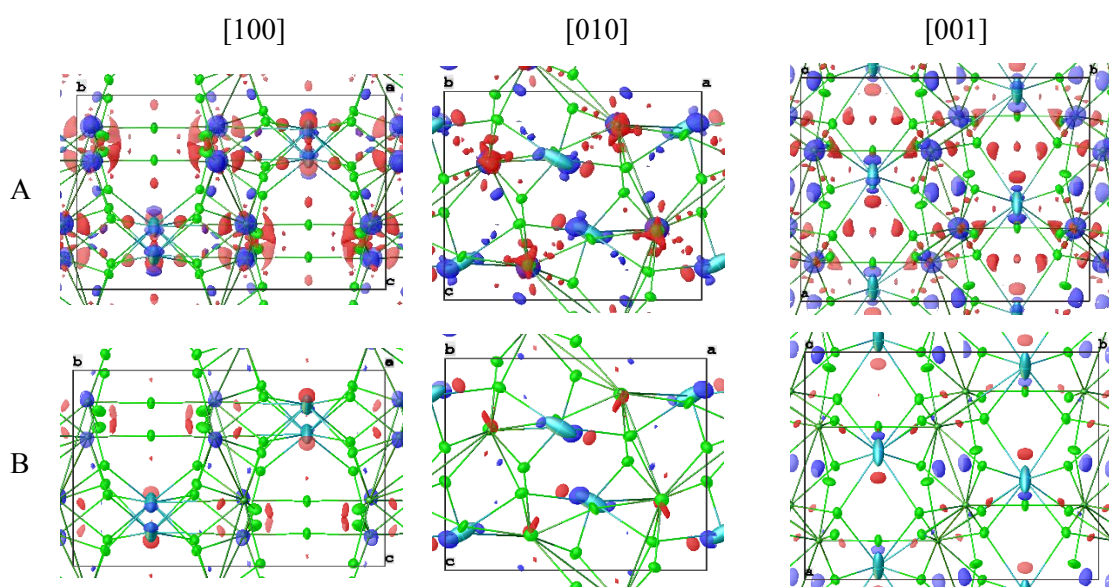


Figure S9: Residual electron density maps at $0.6 \text{ e}/\text{\AA}^3$ iso-level (blue: positive, red: negative) for the published structure of NaU_2F_9 (CCDC 1827660)¹ refined as published using Henke (A) and refined anomalous dispersion values (B) in crystallographic a, b, and c direction. Light green atoms: fluorine, dark green atoms: uranium, cyan atoms: sodium.

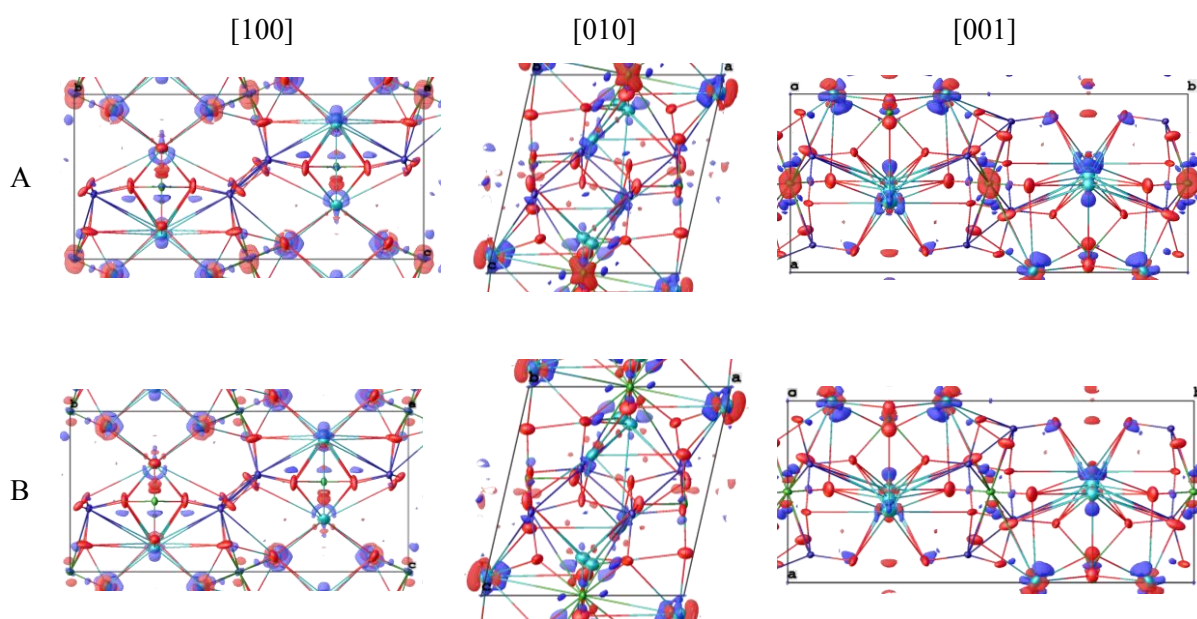
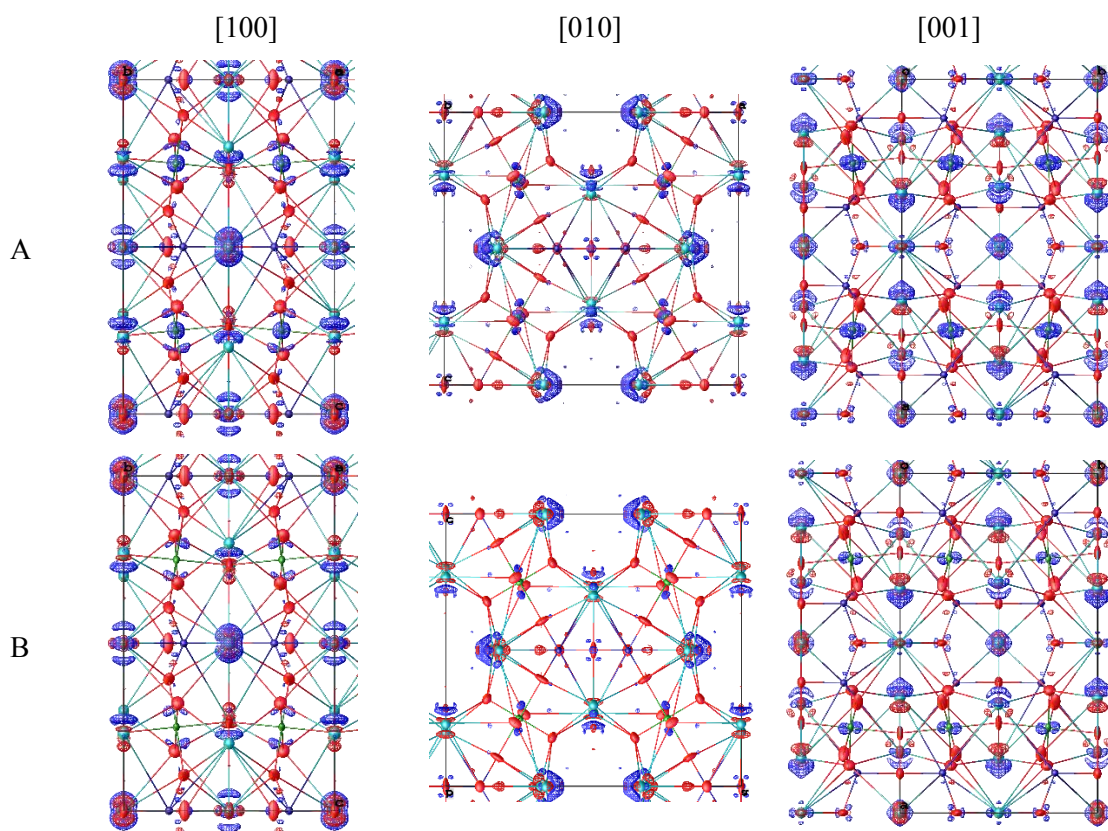


Figure S10: Residual electron density maps at $0.6 \text{ e}/\text{\AA}^3$ iso-level (blue: positive, red: negative) for the published structure of $\text{Cs}_2(\text{UO}_2)\text{Ti}_2\text{O}_8$ (CCDC 2033375) refined as published using Henke (A) and refined anomalous dispersion values (B) in crystallographic a, b, and c direction. A newly found water position was also modelled. Red atoms: oxygen, dark green atoms: uranium, dark blue atoms: titanium, cyan atoms: cesium.



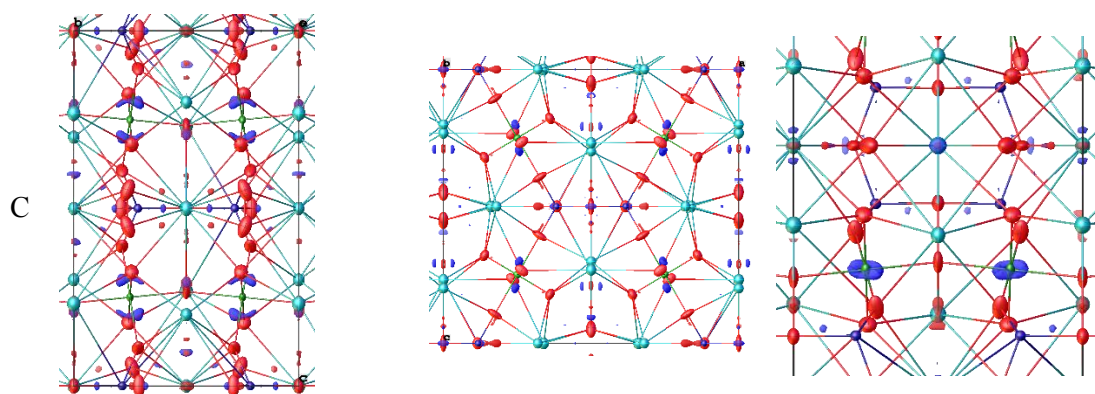


Figure S11: Residual electron density maps at $0.6 \text{ e}/\text{\AA}^3$ iso-level (blue: positive, red: negative) for the published structure of $\text{Cs}_2(\text{UO}_2)\text{Ti}_2\text{O}_6$ (CCDC 2033376) refined as published using Henke (A) and refined anomalous dispersion (B) values in crystallographic a, b, and c direction. Red atoms: oxygen, dark green atoms: uranium, dark blue atoms: titanium, cyan atoms: cesium. In C, also anharmonicity and the improved atomic form factors according to Thakkar were used.¹³

Comparison of literature ADR with a different in-house machine

The same crystals subject to this study were remeasured in the University of Regensburg X-ray department to compare the reliability of the values obtained from ADR at in-house machines. The crystals were measured using a Rigaku XtaLAB Synergy-DW rotating anode machine using a HyPix-Arc 150° photon counting detector.

The results are compared in Tab. S5 to the published structures of different crystals of the same material. The resulting .cifs can be found in the additional support material 2 (ADM2, “Synergy-DW”). In general, values for the uraniumfluorides differed more strongly than for the titanates. In the latter case, the deviation was much smaller than even between the different tables for tables for anomalous dispersion correction.

The values for the fluorides differed more significantly in the newly recorded data sets. This could be attributed to the different crystal specimens, which differed more greatly in size for these highly absorbing materials. This trend of a general shift towards higher values for f' and f'' is in accord with the main findings of our study, where a whole series of synchrotron data sets show an offset compared to the theoretical values for isolated atoms.

Table S5: Results of the comparison experiments using Mo K α radiation at inhouse devices, quality parameters determined at a common resolution of 0.75 Å.

NaUF ₅			NaU ₂ F ₉	
	ADR*	Mo K α DW	ADR*	Mo K α DW
R ₁ ,	1.26,	1.16,	1.33,	0.83,
wR ₂ / %	2.50	3.57	2.98	1.98
min., max.	-0.97,	-1.31,	-0.89,	-1.09,
peaks / eÅ ⁻³	0.97	1.00	1.03	1.07
weights	0.00,	0.02,	0.01,	0.00,
	1.92	2.83	0.53	3.50
f',	-11.9(3),	-12.7(2),	-11.1(3),	-13.6(2),
f'' / e	11.8(6)	14.1(3)	9.9(6)	14.7(3)

Cs ₂ (UO ₂)TiO ₄			Cs ₂ (UO ₂)Ti ₂ O ₆	
	ADR*	Mo K α DW	ADR*	Mo K α DW
R ₁ ,	1.08,	2.43,	1.08,	1.37,
wR ₂ / %	2.42	6.70	2.51	2.88
min., max.	-0.62, 0.67	-1.75,	-0.94	-1.66,
peaks / eÅ ⁻³		2.44	1.53	1.33
weights	0.00,	0.04,	0.01,	0.00,
	19.2	15.1	2.39	4.17
f',	-10.2(4),	-10.1(2),	-10.5(3) / -11.3(4)	-10.7(1) / -11.0(1)
f'' / e	10.5(8)	10.5(2)	10.2(4) / 10.1(5)	11.0(1) / 11.8(1)

* These data sets are re-refined from the published ones^{1,2} using olex2.refine⁹ and Thakkar IAM^{13,14} in Olex2¹⁰. Different crystals were used in the published structures. For reference, at the Mo K α wavelength, the tables of Brennen & Cowan¹⁵ (-9.7, 9.7), Henke *et al.*¹⁶ (f': -10.212 e, f'': 10.405 e) and Sasaki¹⁷ (f': -11.031 e, f'': 9.690 e) also differ strongly.

References

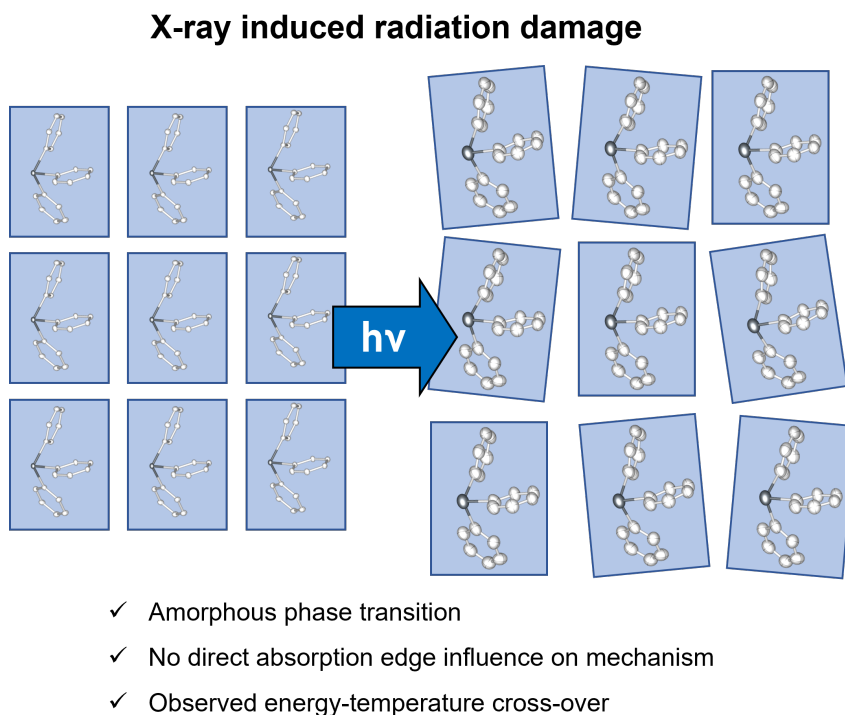
- (1) Klepov, V. V.; Felder, J. B.; zur Loye, H.-C. Synthetic Strategies for the Synthesis of Ternary Uranium(IV) and Thorium(IV) Fluorides. *Inorg. Chem.* **2018**, *57* (9), 5597–5606. <https://doi.org/10.1021/acs.inorgchem.8b00570>.
- (2) Morrison, G.; Christian, M. S.; Besmann, T. M.; zur Loye, H.-C. Flux Growth of Uranyl Titanates: Rare Examples of TiO₄ Tetrahedra and TiO₅ Square Bipyramids. *J. Phys. Chem. A* **2020**, *124* (45), 9487–9495. <https://doi.org/10.1021/acs.jpca.0c08869>.
- (3) Scheinost, A. C.; Claussner, J.; Exner, J.; Feig, M.; Findeisen, S.; Hennig, C.; Kvashnina, K. O.; Naudet, D.; Prieur, D.; Rossberg, A.; Schmidt, M.; Qiu, C.; Colomp, P.; Cohen, C.; Dettona, E.; Dyadkin, V.; Stumpf, T. ROBL-II at ESRF: A Synchrotron Toolbox for Actinide Research. *J. Synchrotron Rad* **2021**, *28* (1), 333–349. <https://doi.org/10.1107/S1600577520014265>.

- (4) Dyadkin, V.; Pattison, P.; Dmitriev, V.; Chernyshov, D. A New Multipurpose Diffractometer PILATUS@SNBL. *J Synchrotron Rad* **2016**, *23* (3), 825–829. <https://doi.org/10.1107/S1600577516002411>.
- (5) Rigaku Oxford Diffraction Ltd. CrysAlis PRO, 2019.
- (6) Ashiotis, G.; Deschildre, A.; Nawaz, Z.; Wright, J. P.; Karkoulis, D.; Picca, F. E.; Kieffer, J. The Fast Azimuthal Integration Python Library: pyFAI. *J Appl Cryst* **2015**, *48* (2), 510–519. <https://doi.org/10.1107/S1600576715004306>.
- (7) Guzei, I. A.; Bikzhanova, G. A.; Spencer, L. C.; Timofeeva, T. V.; Kinnibrugh, T. L.; Campana, C. F. Polymorphism and History of 2-Dimethylsufuranylidene-1,3-Indanedione (YLID). *Crystal Growth & Design* **2008**, *8* (7), 2411–2418. <https://doi.org/10.1021/cg701260p>.
- (8) Sheldrick, G. M. *SHELXT* – Integrated Space-Group and Crystal-Structure Determination. *Acta Crystallogr A Found Adv* **2015**, *71* (1), 3–8. <https://doi.org/10.1107/S2053273314026370>.
- (9) Bourhis, L. J.; Dolomanov, O. V.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. The Anatomy of a Comprehensive Constrained, Restrained Refinement Program for the Modern Computing Environment – *Olex2* Dissected. *Acta Crystallogr A* **2015**, *71* (1), 59–75. <https://doi.org/10.1107/S2053273314022207>.
- (10) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *OLEX2*: A Complete Structure Solution, Refinement and Analysis Program. *J Appl Cryst* **2009**, *42* (2), 339–341. <https://doi.org/10.1107/S0021889808042726>.
- (11) FlorianMeurer. FlorianMeurer/Plugin-SISYPHOS, 2023. <https://github.com/FlorianMeurer/plugin-SISYPHOS> (accessed 2024-02-14).
- (12) Brown, P. J.; Fox, A. G.; Maslen, E. N.; O’Keefe, M. A.; Willis, B. T. M. Intensity of Diffracted Intensities. In *International Tables for Crystallography, Online MRW*; John Wiley & Sons, Ltd, 2006; pp 554–595. <https://doi.org/10.1107/97809553602060000600>.
- (13) Kleemiss, F.; Peyerimhoff, N.; Bodensteiner, M. Refinement of X-Ray and Electron Diffraction Crystal Structures Using Analytical Fourier Transforms of Slater-Type Atomic Wavefunctions in *Olex2*. *J Appl Cryst* **2024**, *57* (1), 161–174. <https://doi.org/10.1107/S1600576723010981>.
- (14) Kleemiss, F.; Dolomanov, O. V.; Bodensteiner, M.; Peyerimhoff, N.; Midgley, L.; Bourhis, L. J.; Genoni, A.; Malaspina, L. A.; Jayatilaka, D.; Spencer, J. L.; White, F.; Grundkötter-Stock, B.; Steinhauer, S.; Lentz, D.; Puschmann, H.; Grabowsky, S. Accurate Crystal Structures and Chemical Properties from NoSpherA2. *Chem. Sci.* **2021**, *12* (5), 1675–1692. <https://doi.org/10.1039/D0SC05526C>.
- (15) Brennan, S.; Cowan, P. L. A Suite of Programs for Calculating X-Ray Absorption, Reflection, and Diffraction Performance for a Variety of Materials at Arbitrary Wavelengths. *Rev. Sci. Instrum.* **1992**, *63* (1), 850–853. <https://doi.org/10.1063/1.1142625>.
- (16) Henke, B. L.; Lee, P.; Tanaka, T. J.; Shimabukuro, R. L.; Fujikawa, B. K. Low-Energy x-Ray Interaction Coefficients: Photoabsorption, Scattering, and Reflection: E = 100–2000 eV Z = 1–94.

Atomic Data and Nuclear Data Tables **1982**, 27 (1), 1–144. [https://doi.org/10.1016/0092-640X\(82\)90002-X](https://doi.org/10.1016/0092-640X(82)90002-X).

- (17) Sasaki, Satoshi. *Numerical Tables of Anomalous Scattering Factors Calculated by the Cromer and Liberman's Method*; Japan, 1989; p 137.

8 Radiation damage in small-molecule compounds



Preface

The following chapter has been submitted for publication under the title:

“Radiation damage in small-molecule compounds: It’s complicated”

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Author Contributions

Florian Meurer – Conceptualisation; acquisition of ESRF and DW data; analysis and interpretation of APS, ESRF, and DW data; XAS acquisition and interpretation; XAS calculation; HAR modeling; generation of figures and tables; writing original draft; co-writing final manuscript.

Florian Kleemiss – Acquisition of APS and ESRF data; discussion of results.

Lorraine A. Malaspina – Acquisition of APS and ESRF data; sample preparation; discussion of results.

Birgit Hischa – Processing of ESRF data; prescreening for ESRF measurements.

Emanuel Hupf – Selection of compounds; crystallization of [Bi].

Yaser Balmohammadi – Crystallization of [Bi]; sample preparation; acquisition of ESRF data.

Joshua L. Dickerson – Adaptation of the RADDPOSE-3D program.

Aleksandra Zwolenik – Acquisition of ESRF data.

Angelika Hinterberger – Acquisition of ESRF data; sample preparation.

Jacob Overgaard – Original conceptualization; preliminary data acquisition at Diamond, UK.

Emil A. Klahn – Acquisition of APS data.

Pim Puylaert – Acquisition of APS data.

SuYin Wang – Beamline setup and acquisition of APS data.

Daniel Br  x – Acquisition of ESRF data.

Mathias Meyer – Processing of APS and ESRF data; software guidance.

Jeppe Christensen – Acquisition of APS data and preliminary data at Diamond, UK.

Simon J. Coles – Conceptualisation; acquisition of APS data; discussion of results.

Elsbeth F. Garman – Conceptualisation; discussion of results; guidance about absorbed dose estimations at APS.

Yu-Sheng Chen – Beamline setup and acquisition of APS data; discussion of results.

Christoph Hennig – Beamline setup and acquisition of ESRF data; guidance about XAS; discussion of results.

Michael Bodensteiner – Conceptualisation; data acquisition of ESRF data; discussion of results; funding acquisition.

Simon Grabowsky – Main conceptualisation; project supervision; acquisition of APS and ESRF data; discussion of results; writing final manuscript.

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Abstract

Radiation damage in small-molecule crystallography has been mostly ignored for several decades. Today, with new-generation synchrotrons, it is common and must be addressed, especially for quantum-crystallographic work which requires the highest possible data quality. However, it is much more complicated compared to protein crystallography because the variety of compound classes and chemical bonding leads to a large complexity of different mechanisms of X-radiation interacting with the material. Here, we focus on the radiation damage of the organo-metallic compound triphenyl bismuth BiPh₃, from which several hundred datasets across 24 crystals at three different X-ray sources were collected: the Advanced Photon Source, the European Synchrotron Radiation Facility, and a home

laboratory rotating anode X-ray generator providing Cu radiation. We empirically followed numerous correlations of properties, strictly evaluating them against the radiation dose. We find that the impact of the Bi L₃ absorption edge only increases the absorbed dose, but does not trigger different decay processes as long as the material is still crystalline. Simultaneous X-ray diffraction and X-ray absorption spectroscopy measurements show that the damage mechanism in this compound is an amorphization without covalent bond breakage or loss of the Bi coordination sphere. Only extremely long exposures (more than 10 hours) of the already amorphous material leads to oxidation of Bi from Bi(III) to Bi(V).

8.1 Introduction

In the field of experimental charge-density determination and quantum crystallography (Grabowsky et al., 2017; Genoni et al., 2018; Krawczuk & Genoni, 2024), accurate X-ray diffraction data to very high resolution are required to reconstruct small details of the valence-electron-density redistribution upon chemical bonding (Koritsánszky & Coppens, 2001; Stalke, 2011) or even of the deformation of core electron densities (Fischer et al., 2011; Bindzus et al., 2014). The breakthrough to achieve such high resolutions that enable experimental electron-density modeling in reasonable timeframes was the use of modern synchrotron facilities (Koritsánszky et al., 1998). During the last 25 years, synchrotron charge-density investigations have become indispensable for the elucidation of electronic structure (Mallinson et al., 2000; Jørgensen et al., 2014; Iversen et al., 1999; Vosegaard et al., 2023; Coppens et al., 2005). However, only during the last few years has it become obvious that there are technical and physical challenges that come with the use of synchrotron radiation that are of great importance for accurate studies. These issues include saturation of detectors with high primary beam intensities (Krause et al., 2020), insufficient anomalous dispersion correction for tunable X-ray energies (Meurer et al., 2022, 2024), and radiation damage to small-molecule crystals (Christensen et al., 2019).

Although radiation damage at synchrotron facilities is a well-known and well-studied phenomenon in macromolecular crystallography (Holton, 2009; Garman, 2010; Garman & Weik, 2018), it has been widely ignored for small-molecule and charge-density studies. It is not mentioned once in the overview articles on the use of synchrotron radiation for charge-density analysis of small-molecule crystals cited in the first paragraph. Nevertheless, from discussions with colleagues in the field and our own experience it has become clear that the phenomenon has been omnipresent during synchrotron beamtimes ever since their use for small-molecule crystallography studies. However, the effects have never been systematically investigated or reported until recently for the following reasons: i) Compounds where radiation damage was already evident in terms of reduced resolution of diffraction spots on the measured frames during the experiment were discarded for follow-up analyses. ii) Data integration and reduction software used with area detectors can mask the effects with empirical corrections, and resulting residual densities are incorporated into atomic displacement parameters or mistaken for physical effects such as anharmonic motion. iii) Only with the recent advent of third- and now fourth-generation synchrotrons (Chapman, 2023) (as well as extremely bright microfocus, metaljet, or rotating-anode sources for home lab applications (Graw et al., 2023)) have the effects become too prominent and obvious to be ignored any longer. It is of crucial importance to properly correct for or avoid the impact of radiation damage in small-molecule crystallography if any quantumcrystallographic effects beyond geometric connectivity are

to be discussed in detail.

In macromolecular crystallography, mitigation strategies and correction procedures have been worked out over many years accompanied by a rising awareness of the problem (Owen et al., 2006; Ebrahim et al., 2019). However, in small-molecule and materials crystallography, the large variety of chemical species under investigation leads to a myriad of possible interaction mechanisms of X-radiation with matter and related damage pathways which prevent generalizable conclusions. Radiation damage was first reported in 1973 for "an inorganic mixed oxide, three aromatic molecules, four metal-organic complexes, and an antibiotic" in the era of point detectors when the stability of the intensity of individual reflections was monitored over the course of long experiments (Abrahams, 1973). In the 1980s, it was described for cyclic organic crystals (Seiler & Dunitz, 1985), with the next records reported over 30 years later in 2018/2019 for brominated organic compounds (Morgan et al., 2018), Niorganic compounds (Christensen et al., 2019), and metal-organic frameworks (Widmer et al., 2019).

Recently, it was found that radiation damage (RD) can influence or even prevent phase transitions (Bogdanov et al., 2021; Poreba et al., 2022; Collings, 2021). The variability in X-ray induced effects with changing experimental parameters in a rhodium complex was studied recently (Fernando et al., 2022). Some of us have observed RD effects via residual electron-density maps in the vicinity of a spherical K^+ counter cation in a molecular salt of pharmaceutical relevance and corrected the intensities with a scaling procedure (Kleemiss et al., 2021a). We also very recently observed RD in penicillin crystal structures (Metry et al., 2026).

X-radiation-induced changes in crystal structures do not necessarily need to be seen as damage, but they can be viewed as a source of information (Boldyreva, 2024). Goodwin et al. observed a "negative X-ray expansion", which means a lattice contraction of the structure of cadmium cyanide, upon irradiation (Coates et al., 2021). The authors point out that there is "potential for exploiting X-ray exposure in the design of functional materials". Following this idea, some of us have used the heavy-atom molecular structures of $Hg(NO_3)_2(PPh_3)_2$, $Hg(CN)_2(PPh_3)_2$ and $BiPh_3$ [PPh_3 = triphenylphosphine, $P(C_6H_5)_3$; Ph = phenyl, C_6H_5] to derive a radiation-induced lattice expansivity tensor which can be seen as a measure of the material's susceptibility to radiation impact (McMonagle et al., 2024). Further, Hatcher et al. summarized how X-ray induced processes and chemical transformations can be used to trigger and design spin-crossover, linkage isomerism, photochromism and more (Lewis et al., 2025). In any case, the impact of the absorbed radiation dose on the changes in the crystal structure must be understood and well characterized.

The story behind this article began in 2012 with the ambition to monitor and detect the effect of relativity experimentally via the outer core contraction of heavy-element containing molecules, such as triphenyl bismuth $BiPh_3$, using very high-resolution X-ray diffraction data and thus brilliant synchrotron radiation. During the first experiments, the overwhelming effect of radiation damage became clear and prevented the modeling of minute electron-density effects in the heavy element's outer core region. Nevertheless, some of us worked out the theoretical background of how to observe relativity in X-ray diffraction studies (Bučinský et al., 2016; Podhorský et al., 2021) and tested it for quantum-crystallographic refinements (Bučinský et al., 2019; Malaspina et al., 2019). However, without a deep understanding of the impact of radiation damage on the outer core region of the heavy element, further experimental quantum-crystallographic investigations proved to be impossible. Therefore, we turned to the compound with the most clearly

and reliably re-occurring radiation-damage behavior that we had found, namely triphenyl bismuth BiPh_3 ($\text{Ph} = \text{phenyl}$ -, "[Bi]", Figure 8.1). This paper presents, to the best of our knowledge, the largest systematic study on small-molecule radiation damage to date. We measured a total of 24 crystals of [Bi], which yielded 330 single-crystal X-ray diffraction data sets, and tested innumerable empirical correlations, of which we present and discuss the most relevant ones here.

8.2 Experiments and methods

The experiments included in this study were performed to analyse the process of decay of smallmolecule single-crystals using the example of [Bi] (Figure 8.1). The compound BiPh_3 was obtained commercially as a crystalline powder and recrystallized from acetonitrile according to Hawley & Ferguson (1968). Radiation decay was measured as the decrease in the average intensity of all observed reflections across an entire run ($I/\sigma(I)$) for a series of single-crystal X-ray diffraction crystal structure datasets of the same single-crystal relative to the first achieved $I/\sigma(I)$ ("RelInt"). Following natural decay processes, like radioactive decay, and following previous macromolecular studies on radiation damage (Garman, 2010), as well as the existing small-molecule studies (Christensen et al., 2019; McMonagle et al., 2024), the decay was fitted with the expression $\text{RelInt} = A * \exp(-B * \text{AccDose})$. A and B are fitting parameters and "AccDose" is the accumulated absorbed dose as "average dose whole crystal" in MGy (dose=absorbed energy/irradiated sample mass = J/kg = Gy, gray), calculated by the program RADDose-3D (Fernando et al., 2021; Zeldin et al., 2013; Dickerson et al., 2024) in the smallmolecule mode and using 360° rotations with varying crystal sizes (see Table 8.1 for crystal dimensions), photon fluxes, energies, and durations. For this study, the RADDose-3D code was adapted to correctly calculate the dose for energies in fine steps between the unique L_3 and L_1 edges of Bi (Github: /GarmanGroup). An example input file for these calculations is added to the Supporting Information, subsection S1.4.

We performed three series of experiments, each with a distinct methodology and goal. For a comprehensive overview, see Table 8.1. The first series was performed at the ChemMatCARS beamline of the Advanced Photon Source (APS) synchrotron facility at the Argonne National Laboratory, IL, USA. We refer to this series as APS in the following. In this experiment, data from seven single crystals were collected. Six of these crystals were measured at temperatures of 15 K and 100 K in pairs at incident beam energies of 16.5keV, 37.5keV, and 50.0 keV, and an additional one was held at 100 K and irradiated at 70.0 keV. All datasets in this series were collected on a DECTRIS PILATUS3 S 1M CdTe detector by performing continuous 360° ω -scans, starting with a strongly attenuated beam and then gradually removing filters to increase the intensity of the primary beam. This ensured that the crystals were always fully embedded in the synchrotron beam and that no time for relaxation processes was left in between measurements. As a consequence, some of the APS datasets remain incomplete and suffer from saturation of the detector, especially those at 15 K and 16.5 keV. Even though the structural models of these measurements show strong artefacts, such as non-positive definite atomic displacement parameters, and a characteristically bent and spread F_{obs} vs F_{calc} plot (see S1.3. in the supporting information) the $I/\sigma(I)$ progression with increased absorbed dose could be used for decay modelling anyway because of the statistical dominance of unaffected reflections. The flux for the dose calculations in this series was measured in between experiments by a calibrated photodiode (Keithley 6485 picoamperemeter) (Owen et al.,

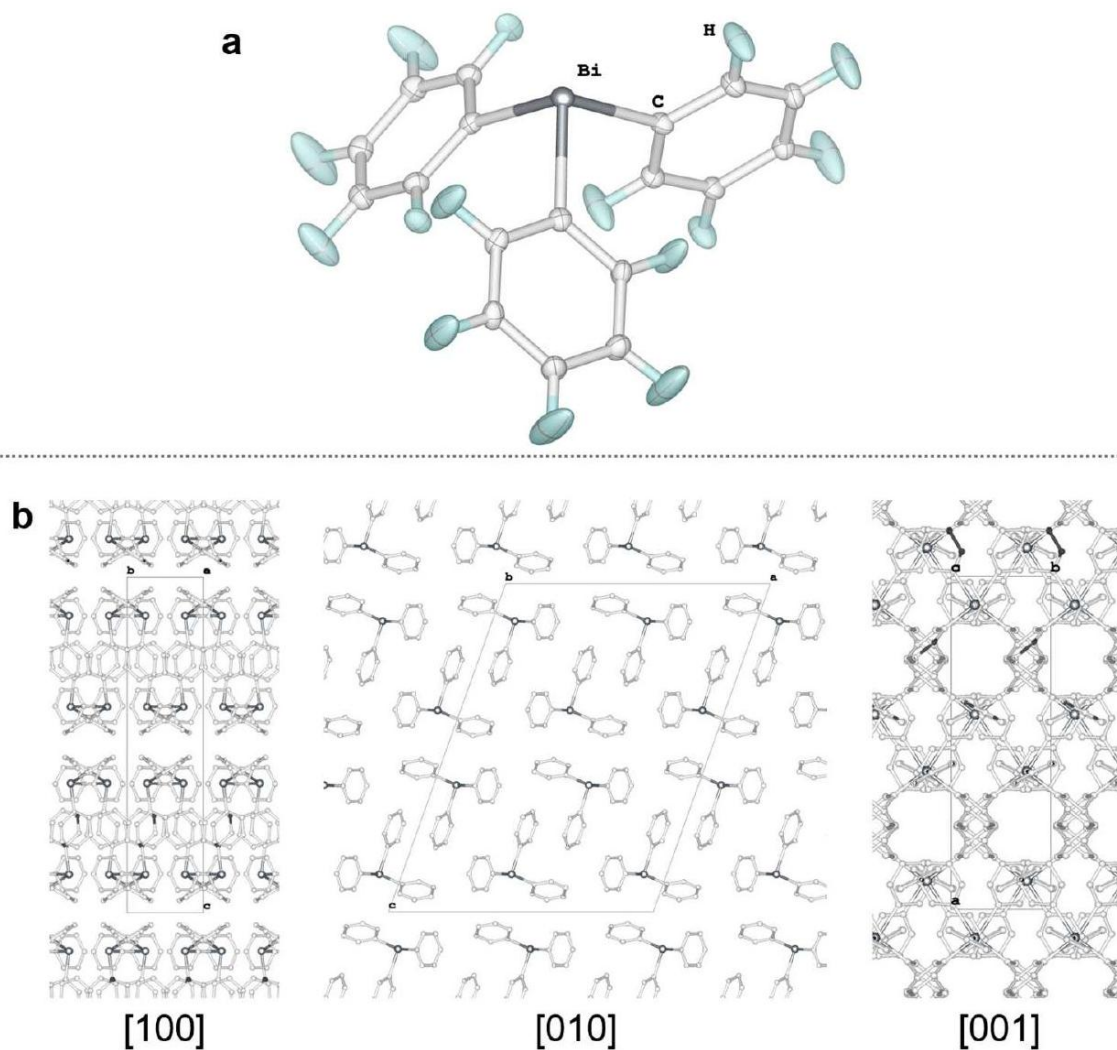


Figure 8.1: (a) Molecular structure of [Bi] after a Hirshfeld Atom Refinement (HAR, for more information see S1.2 in the supporting information) (Jayatilaka & Dittrich, 2008; Capelli et al., 2014) with anisotropic displacement parameters (ADPs) of all atoms at a 50% probability level. This HAR model serves as the best-quality reference structure, which we also deposited with the Cambridge Structural Database under CCDC2557371. (b) Crystal packing of [Bi] in the crystallographic a , b , and c directions.

2009).

The second series was performed over three different beamtimes at the Rossendorf Beamline (ROBL) (Scheinost et al., 2021) of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. In this series, ten single crystals of [Bi] were measured at 100 K around the BiL₃ absorption edge, which lies at 13.42 keV. We changed the method of measurement to an X-ray pump /X-ray probe approach. The radiation damage was inflicted in 360° scans at a given pump energy, shortly above or below the Bi L₃ absorption edge. The full intensities were then collected on a DECTRIS PLATUS3 X 2M detector with a strongly collimated beam at the probe energy of 13.35 keV - below the Bi L₃ edge. These experiments show the largest variance in decay rates, which we attribute to the unique experimental setups and the difficult nature of these measurements almost at bismuth's absorption edge. The flux was recorded on a per-frame basis by an in-line calibrated ionisation chamber, filled with 1 atm of Ar gas. The calibration took place on the same day, just before the start of the measurements.

Also at ROBL, X-ray spectroscopic measurements were performed on single-crystals and bulk material of [Bi]. X-ray absorption spectra near the BiL₃ absorption edge were recorded with a single-element Si drift detector (Vortex X90 CUBE), 1000 mm SDD, active area 50 mm² collimated to 30 mm², protected with a 25 mm Be window.

The third series of measurements was performed at 100 K on seven single crystals of [Bi] using the laboratory diffractometer Rigaku Oxford Diffraction XtaLAB Synergy-DW with a HyPix Arc 150° detector of the University of Regensburg. With the CuK α radiation of the rotating anode (8.05 keV), we could also see radiation damage in a feasible time frame. We measured this series to check on the crystals' individual variance in decay rates with the most consistent beam settings. There was no calibrated diode, but one that showed relative intensity. The relative flux was measured before each single measurement, and it was stable to the 3rd digit at 1.94 μ A for each dataset. According to instrument specifications, we estimated a flux of 10⁹ph/s for these measurements, and then adjusted the absorbed doses to the mean maximum doses in the ESRF series (14.069/5.315 = 2.647 scaling factor) to have realistic values. The beam had an approximate shape of 200 $\times$ 200 μ m, and all crystals were fully bathed in the beam.

All datasets were processed using CryAalisPro version 43 (Rigaku Oxford Diffraction Ltd, 2025). The datasets were serially refined using the olex2.refine program (Bourhis et al., 2015) inside the SISYPHOS module (Meurer, et al., 2025) in the Olex2 crystallographic software suite (Dolomanov et al., 2009). Initial structure solutions were calculated by the SHELXT software (Sheldrick, 2015).

AI-assisted coding tools (Claude in GitHub Copilot within Microsoft Visual Studio Code) were used to support data processing and figure generation. All codes and results were verified by the authors.

Hirshfeld atom refinement (HAR) was performed in the NoSpherA2 variant (Kleemiss et al., 2021b) in Olex2 using the Orca 6.1 (Neese, 2025) quantum chemical package for the wavefunction calculation.

Density functional theory (DFT) and restricted open-shell configuration interaction singles (ROCIS) calculations were performed using ORCA 6.1 on the molecular structure of the triphenyl bismuth(III) compound (BiPh₃, [Bi]). The geometry was taken directly from the HAR crystal structure without further optimization.

The ground-state wavefunction was computed using the BP86 functional with scalar relativistic corrections via the second-order Douglas-Kroll-Hess (DKH2) Hamiltonian (Wolf et al., 2002; Douglas & Kroll, 1974) on the molecular geometry obtained from HAR. Basis

sets were assigned as follows: SARC-DKH-TZVP (Pantazis & Neese, 2012) for Bi and def2-SVP (Weigend & Ahlrichs, 2005) for C and H. The auxiliary basis SARC/J was used for resolution-of-identity (RI) Coulomb fitting. Tight SCF convergence criteria were applied (TightSCF) with a DefGrid3 integration grid and up to 300 SCF iterations. X-ray absorption spectra were calculated using the generalized ROCIS (GenROCIS) (Maganas et al., 2017) module of ORCA with spin-orbit coupling (SOC) (Neese, 2005) enabled (DoSOC true, REL). A pair natural orbital (PNO) approximation was applied (DoPNO true, TCutPNO 1×10^{-11}) to reduce computational cost. 120 roots were requested (NRroots 120). The X-ray absorbing element was specified as Bi (XASElems 0). Overall ROCIS computing time: ~ 130 min (98% of total runtime of 2 h 13 min). The core hole was restricted to a single occupied molecular orbital using the OrbWin 4,4,0,250 keyword.

8.3 Results and discussion

8.3.1 Decay rates and reproducibility

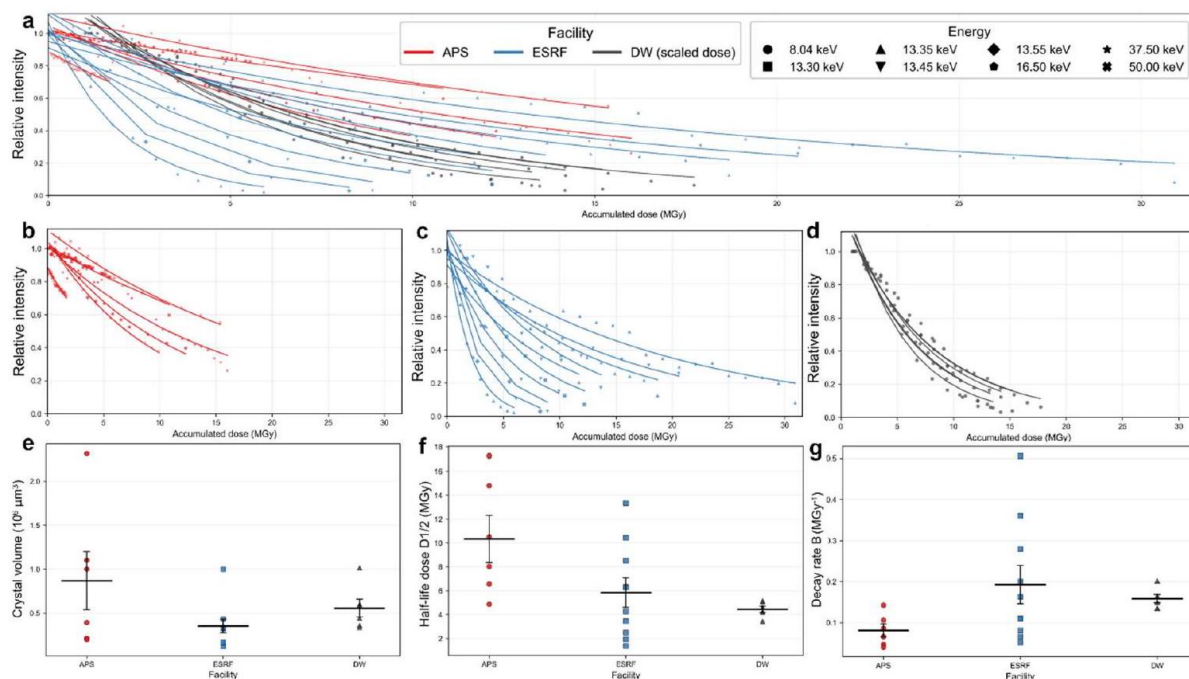


Figure 8.2: (a) Combined decay progressions for all datasets, except for 7[Bi] and 07[Bi], with their exponential fits as line plots. Each point represents a single diffraction experiment. (b–d) Experiments of the APS, ESRF, and DW series presented separately. (e–g) Distribution of crystal volumes in $10^6 \mu\text{m}^3$ (e), half-life dose (f), and decay rate (g) for each series. Doses for the DW series are adjusted to the average of ESRF doses by a factor of 2.647. Horizontal bars give the average and whiskers show the range in terms of $\pm$ standard error of the mean: $\text{SEM} = \frac{\sigma}{\sqrt{N}}$, where σ is the standard deviation and N is the number of data points.

Figure 8.2 gives a descriptive overview of the decay progressions for the three series and how crystal size, half-life dose, and decay rate were distributed. Individual data fitting (Supplementary Information, Figure S3) demonstrated that each dataset exhibited

Table 8.1: Measurement details in this study and their experimental details. For the crystallographic information, see the tables in subsection S1 of the supporting information. APS: Crystals measured at the Advanced Photon Source, Chicago, IL, in a continuous 360° rotation mode with step-wise decreased attenuation. ESRF: Crystals measured at the European Synchrotron, Grenoble, France, in a pump-and-probe protocol, inflicting radiation damage at high flux ("pump"), but collecting structural diffraction reference data at a reference energy below the absorption edge and a low flux to avoid detector saturation ("probe"). For the ESRF data, X-ray energies are given for both the probe and pump. DW: Crystals measured at the University of Regensburg home laboratory with a Rigaku Oxford Diffraction Synergy DW diffractometer. All datasets were obtained using Cu K α radiation. "No Diff." indicates whether or not the crystal still had a diffraction pattern at the end of the experiment that could be used in a refinement against the starting model. "No Diff=yes" means that no diffraction spots could be detected anymore. "No Diff=no" means that the diffraction pattern was still visible. "Nr. Exp." indicates the number of unique diffraction experiments per crystal. The "Decay Rate" is given as the parameter B in the fit of the relative signal-to-noise ratio vs. dose for the exponential fit $f(x) = A \exp(-Bx)$ with x being the accumulated dose in MGy and A, B being fitting parameters, and the coefficient of the agreement between the fitted curves and the data points being R^2 . A larger decay rate (B) means a more rapid decay. "Crystal dim." are the crystal dimensions according to the IUCr .cif definitions. " $D_{1/2}$ " indicates the half-life dose, i.e., the absorbed dose at which only half of the relative initial intensity is observed.

Name	Energy / keV	Temp. / K	No Diff.	Nr. Exp.	B / MGy $^{-1}$	R^2	Crystal dim. / mm	$D_{1/2}$ / MGy
APS								
1[Bi]	16.5	15	No	18	0.047	0.950	0.06, 0.06, 0.06	14.849
2[Bi]	16.5	100	No	21	0.086	0.959	0.07, 0.07, 0.04	8.037
3[Bi]	37.5	15	No	16	0.106	0.998	0.08, 0.07, 0.07	6.555
4[Bi]	37.5	100	Yes	34	0.066	0.966	0.11, 0.14, 0.15	10.489
5[Bi]	50.0	15	No	30	0.142	0.821	0.10, 0.10, 0.10	4.865*
6[Bi]	50.0	100	No	34	0.040	0.956	0.11, 0.10, 0.10	17.261*
7[Bi]	70.0	15	No	2	nan**	nan**	0.16, 0.16, 0.15	nan**
ESRF								
D1[Bi]	13.35, 13.30	100	Yes	8	0.163	0.941	0.04, 0.05, 0.06	4.258
D3[Bi]	13.35, 13.35	100	Yes	7	0.200	0.991	0.02, 0.08, 0.10	3.465
D4[Bi]	13.35, 13.45	100	Yes	4	0.279	0.967	0.03, 0.07, 0.08	2.481
D5[Bi]	13.35, 13.55	100	Yes	4	0.361	0.985	0.04, 0.09, 0.12	1.922
D6[Bi]	13.35, 13.45	100	Yes	10	0.111	0.926	0.11, 0.10, 0.03	6.265
D7[Bi]	13.35, 13.35	100	Yes	22	0.052	0.956	0.08, 0.08, 0.05	13.338
D20[Bi]	13.35, 13.35	100	Yes	10	0.109	0.945	0.10, 0.10, 0.10	6.337
D31[Bi]	13.35, 13.35	100	Yes	11	0.505	0.982	0.08, 0.08, 0.05	1.372
D33[Bi]	13.35, 13.45	100	Yes	9	0.066	0.985	0.08, 0.07, 0.06	10.428
D34[Bi]	13.35, 13.35	100	Yes	16	0.081	0.906	0.08, 0.07, 0.06	8.511
DW								
01[Bi]	8.04	100	Yes	9	0.434	0.962	0.11, 0.10, 0.04	1.596
02[Bi]	8.04	100	Yes	10	0.534	0.955	0.12, 0.07, 0.04	1.298
03[Bi]	8.04	100	Yes	15	0.359	0.985	0.10, 0.10, 0.06	1.928
04[Bi]	8.04	100	Yes	15	0.357	0.939	0.13, 0.13, 0.06	1.944
05[Bi]	8.04	100	Yes	12	0.398	0.945	0.09, 0.08, 0.05	1.743
06[Bi]	8.04	100	Yes	12	0.437	0.967	0.12, 0.07, 0.07	1.586

Note. * Values extrapolated; ** no damage observed; *** single-run experiment.

consistent behavior, characterized by a monotonic decrease in intensity as a function of radiation dose. However, overall, there is a large variance over all decay progressions with an average rate of $0.153 \pm 0.023 \text{ RelI MGy}^{-1}$ and an average half-life dose of $6.76 \pm 4.83 \text{ MGy}$. Although we took extreme care within each experiment that the crystals were fully bathed within an ideally double-Gaussian-shaped beam, and that uni-rotational measurements perpendicular to the primary beam ensured a consistent bathing of the crystals, fatal doses cover a large range over almost one order of magnitude. Especially the ESRF series, which was performed over three different beamtimes and which was performed close to the BiL_3 absorption edge, shows the largest variance of the three data sets. The DW series shows that when the conditions are as similar as possible, there is only a little variance in the decay progression. This series, however, was collected entirely below the absorption edge. We can still conclude that the crystal-specific variation (Figure 8.2g) in radiation decay is small and independent of crystal size. However, the half-life dose has a weak correlation with crystal-size: the bigger the crystals, the smaller the half-life dose, which means, in turn, crystals with a smaller volume survive the radiation damage for a longer time (Figure 8.2f). This could potentially be explained by photoelectric escape from the surfaces of the smallest crystals before the electron has a chance to lose energy inside the crystal (Dickerson & Garmer, 2019; Storm et al., 2021). The remaining variance is due to the varying measurement conditions.

An unexpected trend emerges from the APS datasets, for which the temperature-dependence was tested (Figure 8.3). Although the number of data points is extremely limited to one per setting, the trend describing the rate of radiation damage is captured only by the energy-temperature interaction term. Here, a crossover behavior was observed, showing a higher decay rate at 16.5 keV for the 100 K than for the 15 K data set, but an inverse trend at 50 keV, where the 15 K data set decays faster than the 100 K data set. The intermediate-energy dataset collected at 37.5 keV shows the transition between the two energies. For protein crystallography, it has been established that cryogenic temperatures help to slow down radiation damage in general (Nave & Garman, 2005; Meents et al., 2010), but, to the best of our knowledge, an energy-temperature interaction term has not been determined.

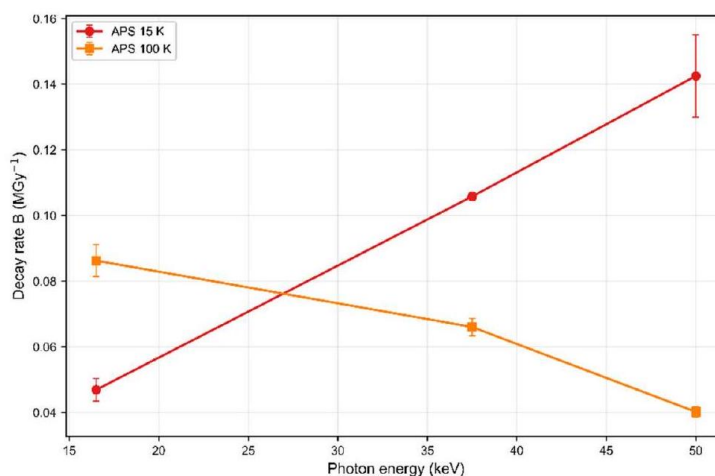


Figure 8.3: Crossover trend of the behaviour of decay rate in the APS data sets for 100 K and 15 K at energies of 16.5 keV, 37.5 keV, and 50 keV.

8.3.2 Structural changes

The change in molecular structure is represented by the Bi – C bond distances and C – C bond precision in Figure 8.4, where the precision is represented by the estimated standard uncertainty upon refinement. Figures 4a – c show that the uncertainty in bond lengths increases with dose for the C – C bonds, and the same trend is true for the Bi-C bonds (see S3.2 in the supporting information). The trend for the actual bond lengths is much weaker and only visible for the Bi-C bonds towards the end of the series of D31[Bi] and slightly for 01[Bi] (Figure 8.4e-f). In contrast, the crystal that was still diffracting towards the end of the experiment, 2[Bi], shows little to no change in the Bi – C bond lengths (Figure 8.4d). All three, however, show a consistent decrease in C – C and Bi – C bond precision with increasing radiation damage. In combination with the increase in unit cell volume (Figure 8.4g) and increase in lattice parameters (see S3.3), this means that there is little molecular change with radiation damage, but the molecular arrangements relative to each other require more space on average. In other words, the crystal periodicity is progressively lost, the mosaicity increases, but covalent bonds are not broken. This is an important finding because our hypothesis at the outset of this study was that the weak polar organometallic Bi-C bonds would be broken, and migrating radicals versus vacancies (Frenkel pairs) would destroy the crystallinity (Wirth, 2007). This mechanism cannot be confirmed, instead the average distance between molecules increases and the displacement of atoms around their resting positions increases, which can be measured as U_{eq} . The U_{eq} values for Bi (Figure 8.4h) show an exponential increase and very similar values for the same dose between the DW and ESRF dataset. The APS data set seems to have a much slower increase in the heavy Bi U_{eq} . The fact that the unit cell parameters increase upon radiation exposure is consistent with more unique reflections being measured with increased dose in the same resolution shell (Figure 8.4i).

8.3.3 Model quality as a function of decay

When the quality descriptors for the three representative datasets, which were already analysed as shown in Figure 8.4, are compared with each other (Figure 8.5), the results in the progressions of R_1 and R_{int} reflect the stage of radiation damage reliably. Especially visible in the ultimately completely diffractionless experiment of D31[Bi], both the model data agreement as per R_1 , but also the agreement of symmetrically equivalent data as per R_{int} show a strong increase shortly before the fatal dose is reached. This effect is to a similar but lesser extent also observable in 01[Bi] and 2[Bi] for the DW and APS series, respectively.

The residual electron density as a function of the process of radiation damage is visualised in Figure 8.6. There is only little but pronounced positive residual electron density in three small regions around the Bi atom and negative residual electron density on the metal position at the beginning of the experiment. This residual electron density increases towards three more pronounced regions, which merge to form a sphere of positive electron density around the Bi core, indicating a failure of the model to reproduce the smeared-out observed electron density. This might be due to an increase in positional disorder with radiation damage in [Bi]. The atomic displacement parameters also increase strongly with growing radiation damage. Shortly before the crystal becomes diffractionless, the

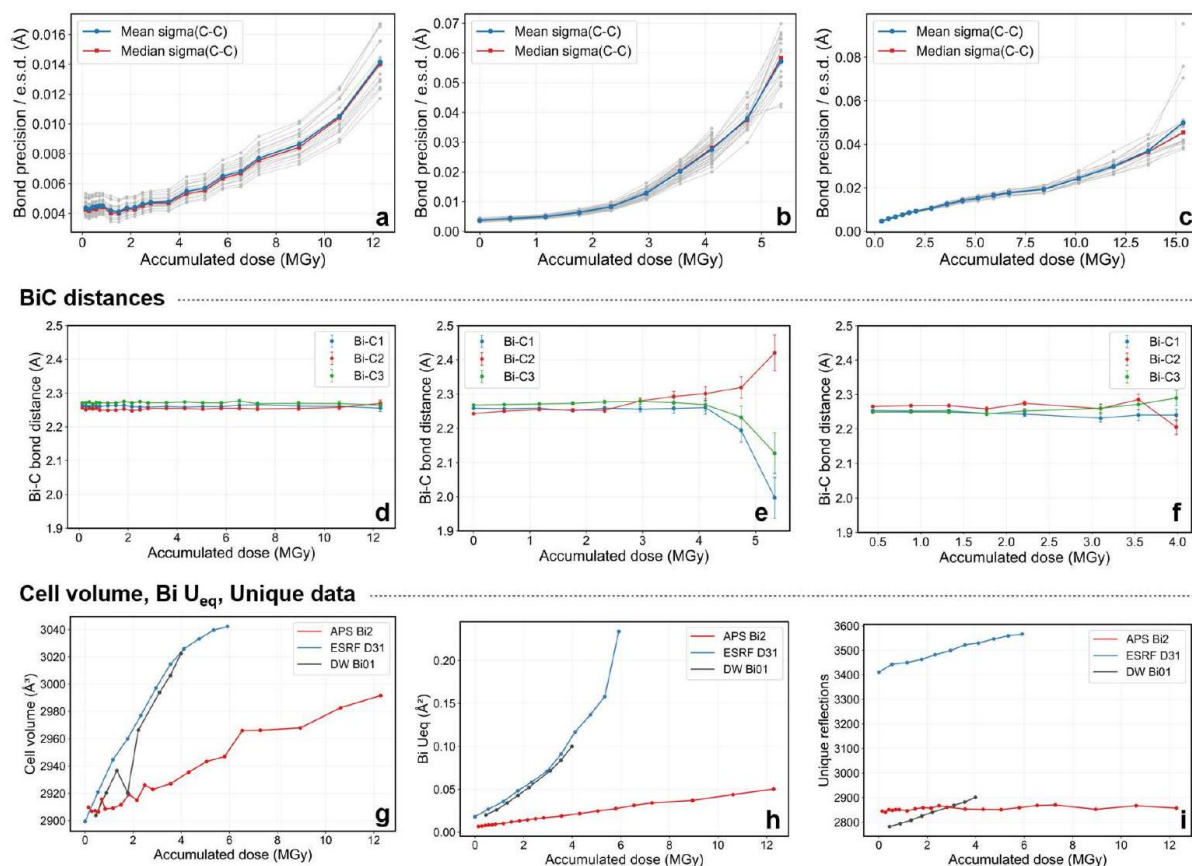


Figure 8.4: (a–c) C–C bond precision (grey are unique, blue and red show average and median, respectively), (d–f) Bi–C bond lengths, (g) cell volume, (h) U_{eq} of Bi, and (i) number of unique reflections for representative APS ((a, d), 2[Bi]), ESRF (b, e, D31[Bi]) and DW ((c, f), 01[Bi]) series.

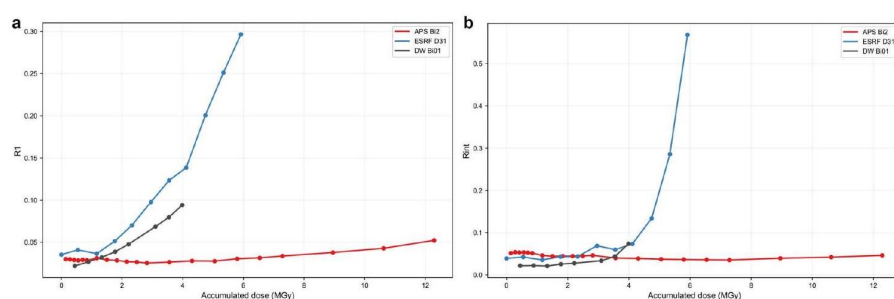


Figure 8.5: R1 (a) and Rint (b) of 2[Bi] from APS (red), D31[Bi] from ESRF (blue), and 01[Bi] from DW measurements (black).

model breaks apart and two carbon positions are lost during refinement of this diffraction dataset compared to the starting model. However, covalent bond cleavage is not observed before the crystal shows no more diffraction. The steady increase of both positive as well as negative residual electron density with accumulated dose can also be seen in the values of the minimum and maximum residual electron density peaks which are given in the caption of Figure 8.6.

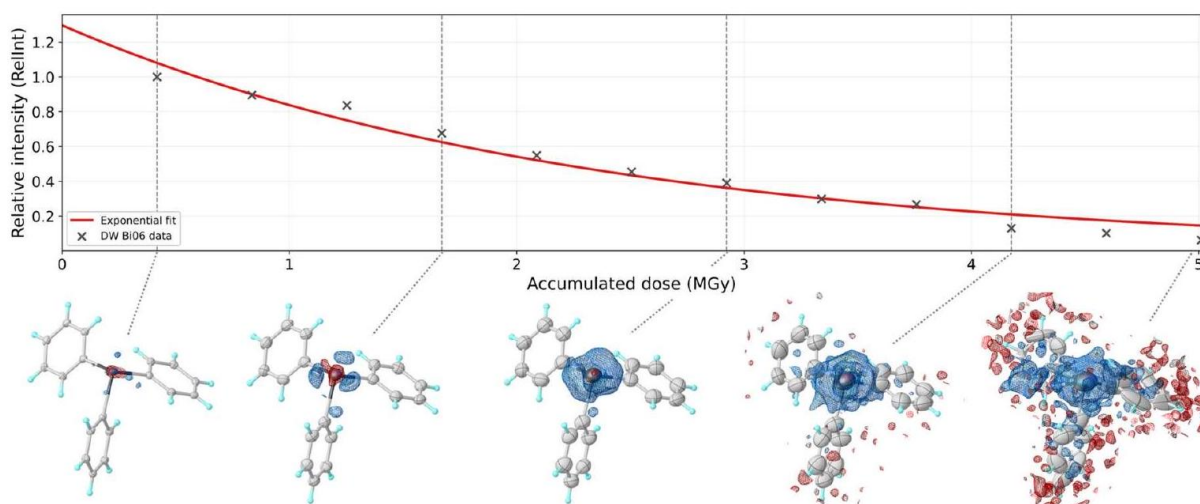


Figure 8.6: Residual electron density maps (F_{obs} minus F_{calc}) at the $0.7\text{e}/\text{\AA}^3$ iso-level for the DW 06[Bi] data set at several states of decay. An animated version is available as a separate supporting information document. Min/max peaks in $\text{e}/\text{\AA}^3$ are: $-0.7/0.8$, $-1.5/2.0$, $-0.9/2.9$, $-1.0/2.7$, and $-4.7/8.8$ for the five models, respectively.

8.3.4 Mechanism of decay

One of the main goals of this study was to determine the dependence of the process of crystalline radiation decay on absorption edges. For this purpose, the decay rates were statistically evaluated for three different data subsets: the ESRF data set (Figure 8.7a), APS combined with the ESRF data sets (Figure 8.7b), and APS combined with ESRF but only at a temperature of 100 K (Figure 8.7c). In all three cases, no significant difference (Welch test; all H_0 p-values are above 0.56) was found, indicating no difference in decay rates, whether observed below or above the Bi L_3 absorption edge. This means that while the dose per time is drastically increased above the absorption edge and thus a faster decay with respect to measurement time is still observed, there is no additional significant damage or difference in mechanism from the specific Bi 2p electronic excitations accessible above the L_3 absorption edge. Because of the faster dose accumulation and additional effects such as absorption, secondary fluorescence emission and the inaccuracy of tabulated anomalous dispersion values in the vicinity of absorption edges (Meurer et al., 2022, 2024), we would still highly recommend keeping absorption edges in mind when single crystals are measured either on laboratory devices or even more so at synchrotron facilities.

In order to inspect the local effects of radiation damage and how the process of radiation damage develops on a molecular basis, X-ray near-edge absorption spectroscopy (XANES) experiments were conducted at the Bi L_3 absorption edge on a range of different crystals of [Bi] before (fresh) and after becoming diffractionless (dead) (Figure 8.8a). In XANES, an energy shift of the rising edge to the right indicates a higher positive charge, e.g.,

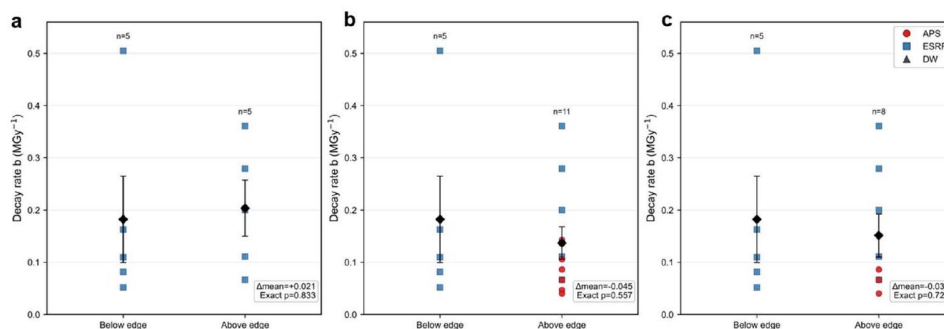


Figure 8.7: Statistical evaluation of the decay rates in dependence on the Bi L_3 absorption edge at 13.42 keV. (a) shows only the ESRF data sets (blue), (b) includes all APS data sets in addition (red), and (c) includes only 100 K APS datasets.

oxidation of the metal center. We did observe a strong change in the rising edge for one data set (Figure 8.8a, marked with *) which was left in the beam for a very long time (over night), and therefore strong oxidation of the Bi atom (presumably from Bi(III) to Bi(V)), which correlates with the increased negative residual electron density at the core region of the Bi atom (Figure 8.6). However, most "dead" single crystals showed essentially the same edge energy and the same features as fresh single crystals or bulk material. This confirms that the mechanism of radiation damage in [Bi] consists of an amorphization of the sample, prior to significant bond cleavage taking place, because the local coordination sphere seems to be identical to that of fresh [Bi].

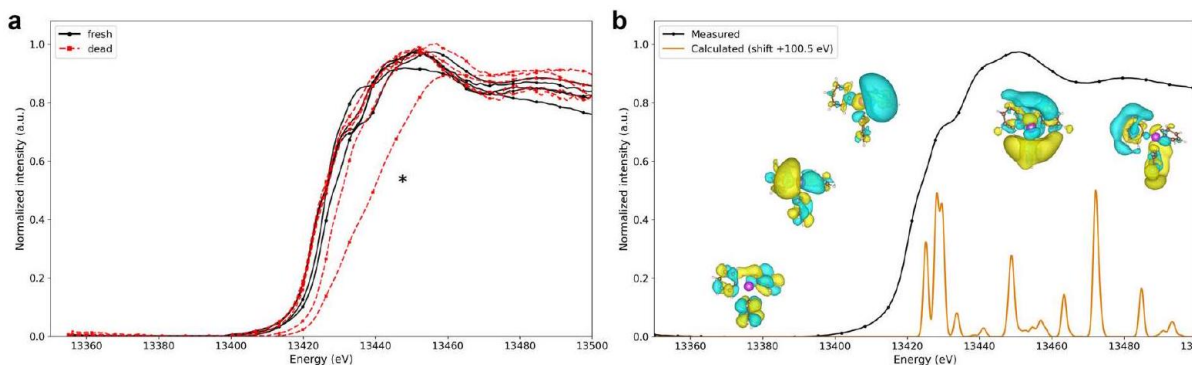


Figure 8.8: (a) Results of the XANES measurements of "fresh" and diffractionless ("dead") [Bi] crystals. * marks a crystal left overnight in the synchrotron beam inflicting damage way beyond being diffractionless. (b) The experimental bulk [Bi] XANES features compared with the electronic excitations following a DFT/ROCIS calculation. Excitations into virtual MOs, visualised at a 0.015 a.u. iso-level are numbered from left to right: 108, 110, 111, 113, and 114.

We computationally simulated the various possible excitations that occur around the absorption edge (Figure 8.8b). According to these calculations on the isolated molecule (see section 2 for details), the features in the XANES spectrum can be attributed to excitations which are mainly based on Bi 2p into either C 2p-type orbitals (108 and 110), Bi s-type (111), Bi p-type (113), or phenyl σ^* -type (114) MOs.

8.4 Conclusions

In this paper, we present the largest systematic study to date on small-molecule radiation damage, but only one system with a single heavy-element type was investigated. It is complicated to draw conclusions because we found that all observed correlations are highly dependent on the instrumental arrangements and measurement strategies. Moreover, there are various competing physical mechanisms at the molecular and crystal lattice levels concerning the interaction of the X-radiation with the sample, some of which we simulated as excitations from the Bi 2 p orbital into various molecular orbitals. Therefore, no globally generalizable recommendations can be given to help avoid or correct for radiation damage in chemical crystallography. However, we made a few important and interesting observations which are summarized below:

The mechanism of radiation damage in this compound is a loss of crystalline periodicity that leads to an X-ray induced amorphous phase transition. As long as a structure can still be determined, there is no evidence for cleavage of the covalent Bi-C bonds, or any other bond, for that matter. This finding is supported by X-ray absorption spectroscopy which shows that the coordination sphere of the Bi atom remains intact even in the amorphous state. The Bi atom is nevertheless slowly oxidized in the process, which was found for an extremely long X-ray exposure time of the already amorphous material (about 10 hours). We also found that the energy-temperature interaction term is important as there is a crossover of the impact of the inflicted damage at different energy/temperature combinations. The correlation of X-ray energy, temperature and absorbed dose for lattice contractions and expansions has also been highlighted before (Coates et al., 2021; McMonagle et al., 2024). The crystal volume has a small influence on the degree of inflicted damage, whereby there is a weak trend towards smaller crystals (less than $100\mu\text{ m}$ in each direction) being more radiation stable.

All trends and mechanisms observed in this study are strictly dose dependent. There is no indication that the Bi 2p electron excitation, the related rearrangement of valence electrons, or the related fluorescence processes are involved in the damage process. The impact of the BiL_3 absorption edge is only an increased absorption dose beyond the edge. Nevertheless, because of this faster dose accumulation and additional effects such as fluorescence and the inaccuracy of tabulated anomalous dispersion values in the vicinity of absorption edges, it is advisable to perform quantum-crystallographic experiments away from relevant absorption edge energies. However, for the understanding of physical phenomena, simultaneous X-ray diffraction and X-ray absorption spectroscopy (XANES or EXAFS) on the same crystal specimen is a very useful tool. Moreover, the X-ray/X-ray pump/probe experiment that we employed here for the ESRF measurements was a successful way of avoiding saturation of the detector, which made the analysis of the APS measurement series challenging.

8.5 References

- Abrahams, S. C. (1973). *Acta Cryst A* 29, 111-116.
 Barone, V. & Cossi, M. (1998). *J. Phys. Chem. A* 102, 1995-2001.
 Bindzus, N., Straasø, T., Wahlberg, N., Becker, J., Bjerg, L., Lock, N., Dippel, A.-C. & Iversen, B. B. (2014). *Acta Cryst A* 70, 39-48.
 Bogdanov, N. E., Zakharov, B. A., Chernyshov, D., Pattison, P. & Boldyreva, E. V.

- (2021). *Acta Cryst B* 77, 365-370.
- Boldyreva, E. V. (2024). *Acta Cryst B* 80, 1-3.
- Bourhis, L. J., Dolomanov, O. V., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2015). *Acta Cryst A* 71, 59-75.
- Bučinský, L., Jayatilaka, D. & Grabowsky, S. (2016). *J. Phys. Chem. A* 120, 6650-6669.
- Bučinský, L., Jayatilaka, D. & Grabowsky, S. (2019). *Acta Cryst A* 75, 705-717.
- Capelli, S. C., Bürgi, H.-B., Dittrich, B., Grabowsky, S. & Jayatilaka, D. (2014). *IUCrJ* 1, 361-379.
- Chapman, H. N. (2023). *IUCrJ* 10, 246-247.
- Christensen, J., Horton, P. N., Bury, C. S., Dickerson, J. L., Taberman, H., Garman, E. F. & Coles, S. J. (2019). *IUCrJ* 6, 703-713.
- Coates, C. S., Murray, C. A., Boström, H. L. B., Reynolds, E. M. & Goodwin, A. L. (2021). *Mater. Horiz.* 8, 1446-1453.
- Collings, I. E. (2021). *Acta Cryst B* 77, 307-308.
- Coppens, P., Iversen, B. & Larsen, F. K. (2005). *Coord. Chem. Rev.* 249, 179-195.
- Dickerson, J. L., & Garman, E. F. (2019). *J. Synchrotron Rad.* 26, 922-930.
- Dickerson, J. L., McCubbin, P. T. N., Brooks-Bartlett, J. C. & Garman, E. F. (2024). *Protein Science* 33, e5005.
- Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J Appl Cryst* 42, 339-341.
- Douglas, M. & Kroll, N. M. (1974). *Ann. Phys.* 82, 89-155.
- Dunning, T. H. (1989). *J. Chem. Phys.* 90, 1007-1023.
- Ebrahim, A., Moreno-Chicano, T., Appleby, M. V., Chaplin, A. K., Beale, J. H., Sherrell, D. A., Duyvesteyn, H. M. E., Owada, S., Tono, K., Sugimoto, H., Strange, R. W., Worrall, J. A. R., Axford, D., Owen, R. L. & Hough, M. A. (2019). *IUCrJ* 6, 543-551.
- Fernando, N. K., Cairns, A. B., Murray, C. A., Thompson, A. L., Dickerson, J. L., Garman, E. F., Ahmed, N., Ratcliff, L. E. & Regoutz, A. (2021). *J. Phys. Chem. A* 125, 7473-7488.
- Fernando, N. K., Boström, H. L. B., Murray, C. A., Owen, R. L., Thompson, A. L., Dickerson, J. L., Garman, E. F., Cairns, A. B. & Regoutz, A. (2022). *Phys. Chem. Chem. Phys.* 24, 28444-28456.
- Fischer, A., Tiana, D., Scherer, W., Batke, K., Eickerling, G., Svendsen, H., Bindzus, N. & Iversen, B. B. (2011). *J. Phys. Chem. A* 115, 13061-13071.
- Garman, E. F. (2010). *Acta Cryst D* 66, 339-351.
- Garman, E. F. & Weik, M. (2018). *Protein Crystallography: Challenges and Practical Solutions*, edited by K. Beis and G. Evans, pp. 88-116. London: Royal Society of Chemistry.
- GarmanGroup GitHub, <https://github.com/GarmanGroup/RADDOSE-3D/releases/tag/v4.0.1027>.
- Genoni, A., Bučinský, L., Claiser, N., Contreras-García, J., Dittrich, B., Dominiak, P. M., Espinosa, E., Gatti, C., Giannozzi, P., Gillet, J.-M., Jayatilaka, D., Macchi, P., Madsen, A. Ø., Massa, L., Matta, C. F., Merz Jr., K. M., Nakashima, P. N. H., Ott, H., Ryde, U., Schwarz, K., Sierka, M. & Grabowsky, S. (2018). *Chem. Eur. J.* 24, 10881-10905.
- Grabowsky, S., Genoni, A. & Bürgi, H.-B. (2017). *Chem. Sci.* 8, 4159-4176.
- Graw, N., Ruth, P. N., Ernemann, T., Herbst-Irmer, R. & Stalke, D. (2023). *J Appl. Cryst* 56, 13151321.
- Hawley, D. M. & Ferguson, G. (1968). *J. Chem. Soc. A* 2059-2063.
- Helmich-Paris, B., de Souza, B., Neese, F. & Izsák, R. (2021). *J. Chem. Phys.* 155, 104109.

- Holton, J. M. (2009). *J Synchrotron Rad.* 16, 133-142.
- Iversen, B. B., Larsen, F. K., Pinkerton, A. A., Martin, A., Darovsky, A. & Reynolds, P. A. (1999). *Acta Cryst B* 55, 363-374.
- Jayatilaka, D. & Dittrich, B. (2008). *Acta Cryst A* 64, 383-393.
- Jørgensen, M. R. V., Hathwar, V. R., Bindzus, N., Wahlberg, N., Chen, Y.-S., Overgaard, J. & Iversen, B. B. (2014). *IUCrJ* 1, 267-280.
- Kleemiss, F., Wieduwilt, E. K., Hupf, E., Shi, M. W., Stewart, S. G., Jayatilaka, D., Turner, M. J., Sugimoto, K., Nishibori, E., Schirmeister, T., Schmidt, T. C., Engels, B. & Grabowsky, S. (2021a). *Chem. Eur. J.* 27, 3407-3419.
- Kleemiss, F., Dolomanov, O. V., Bodensteiner, M., Peyerimhoff, N., Midgley, L., Bourhis, L. J., Genoni, A., Malaspina, L. A., Jayatilaka, D., Spencer, J. L., White, F., Grundkötter-Stock, B., Steinhauer, S., Lentz, D., Puschmann, H. & Grabowsky, S. (2021b). *Chem. Sci.* 12, 16751692.
- Koritsánszky, T., Flaig, R., Zobel, D., Krane, H.-G., Morgenroth, W. & Luger, P. (1998). *Science* 279, 356-358.
- Koritsánszky, T. S. & Coppens, P. (2001). *Chem. Rev.* 101, 1583-1628.
- Krause, L., Tolborg, K., Grønbech, T. B. E., Sugimoto, K., Iversen, B. B. & Overgaard, J. (2020). *J Appl Cryst* 53, 635-649.
- Krawczuk, A. & Genoni, A. (2024). *Acta Cryst. B* 80, 249-274.
- Lewis, S. G., Warren, M. R. & Hatcher, L. E. (2025). *Chem. Eur. J.* 31, e01711.
- Maganas, D., DeBeer, S. & Neese, F. (2017). *Inorg. Chem.* 56, 11819-11836.
- Malaspina, L. A., Wieduwilt, E. K., Bergmann, J., Kleemiss, F., Meyer, B., Ruiz-López, M. F., Pal, R., Hupf, E., Beckmann, J., Piltz, R. O., Edwards, A. J., Grabowsky, S. & Genoni, A. (2019). *J. Phys. Chem. Lett.* 10, 6973-6982.
- Mallinson, P. R., Barr, G., Coles, S. J., Guru Row, T. N., MacNicol, D. D., Teat, S. J. & Woźniak, K. (2000). *J Synchrotron Rad* 7, 160-166.
- Mardirossian, N. & Head-Gordon, M. (2014). *Phys. Chem. Chem. Phys.* 16, 9904-9924.
- McMonagle, C. J., Fuller, C. A., Hupf, E., Malaspina, L. A., Grabowsky, S. & Chernyshov, D. (2024). *Acta Cryst B* 80, 13-18.
- Meents, A., Gutmann, S., Wagner, A. & Schulze-Bries, C. (2010). *Proc. Nat. Acad. Sci. U. S. A.* 107, 1094-1099.
- Metry, E., Malaspina, L. A. & Grabowsky, S. (2026), manuscript in preparation.
- Meurer, F., Dolomanov, O. V., Hennig, C., Peyerimhoff, N., Kleemiss, F., Puschmann, H. & Bodensteiner, M. (2022). *IUCrJ* 9, 604-609.
- Meurer, F., Kleemiss, F., Hischa, B., Brück, D., Koch, A.-C. & Bodensteiner, M. (2025). *Struct. Dyn.* 12, 054102.
- Meurer, F., Morrison, G., Hischa, B., zur Loye, H.-C., Hennig, C. & Bodensteiner, M. (2024). *Inorg. Chem.* 63, 15784-15790.
- Meurer, F., Schimpf, M., Hischa, B., Hennig, C., Rehbein, J., Kleemiss, F. & Bodensteiner, M. (2025). *J Appl Cryst* 58, 678-687.
- Moncho, S. & Autschbach, J. (2010). *J. Chem. Theory Comput.* 6, 223-234.
- Morgan, L. C. F., Kim, Y., Blandy, J. N., Murray, C. A., Christensen, K. E. & Thompson, A. L. (2018). *Chem. Commun.* 54, 9849-9852.
- Nave, C. & Garman, E. F. (2005). *J. Synchrotron Rad.* 12, 257-260.
- Neese, F. (2005). *J. Chem. Phys.* 122, 034107.
- Neese, F. (2025). *WIREs Computational Molecular Science* 15, e70019.
- Owen, R. L., Rudiño-Piñera, E. & Garman, E. F. (2006). *Proc. Natl. Acad. Sci. U. S.*

A.103, 49124917.

Owen, R. L., Holton, J. M., Schulze-Briesse, C. & Garman, E. F. (2009). *J. Synchrotron Rad.* 16, 143151.

Pantazis, D. A. & Neese, F. (2012). *Theor Chem Acc* 131, 1292.

Podhorský, M., Bučinský, L., Jayatilaka, D. & Grabowsky, S. (2021). *Acta Cryst A* 77, 54-66.

Poręba, T., Świątkowski, M., Ernst, M. & Confalonieri, G. (2022). *J. Phys. Chem. C* 126, 7648-7659.

Rigaku Oxford Diffraction Ltd (2025). *CrysAlis PRO* Wroclaw, Poland: Rigaku OD.

Scheinost, A. C., Claussner, J., Exner, J., Feig, M., Findeisen, S., Hennig, C., Kvashnina, K. O., Naudet, D., Prieur, D., Rossberg, A., Schmidt, M., Qiu, C., Colomp, P., Cohen, C., Dettona, E., Dyadkin, V. & Stumpf, T. (2021). *J Synchrotron Rad* 28, 333-349.

Seiler, P. & D Dunitz, J. (1985). *Aust J Phys* 38, 405-412.

Sheldrick, G. M. (2015). *Acta Cryst A* 71, 3-8.

Stalke, D. (2011). *Chem. Eur. J.* 17, 9264-9278.

Storm, S. L. S., Axforda, D. & Owen, R. L. (2021) *IUCrJ* 8, 896-904.

Vosegaard, E. S., Ahlburg, J. V., Krause, L. & Iversen, B. B. (2023). *Acta Cryst B* 79, 380-391.

Weigend, F. & Ahlrichs, R. (2005). *Phys. Chem. Chem. Phys.* 7, 3297.

Widmer, R. N., Lampronti, G. I., Casati, N., Farsang, S., Bennett, T. D. & Redfern, S. A. T. (2019). *Phys. Chem. Chem. Phys.* 21, 12389-12395.

Wirth, B. D. (2007). *Science* 318, 923-924.

Wolf, A., Reiher, M. & Hess, B. A. (2002). *J. Chem. Phys.* 117, 9215-9226.

Zeldin, O. B., Gerstel, M. & Garman, E. F. (2013). *J Appl Cryst* 46, 1225-1230.

8.6 Supporting information

The supporting information of this work is provided as a single .pdf file with original format and page numbering starting from the next page.

Supporting information

S1. Crystallographic details

S1.1. Crystallographic information tables

In the following, the crystallographic tables of the starting models for each single-crystal decay experiment are given. The full data can be obtained in the structural folders, containing the .cif, .hkl, .res, etc. files via zenodo.org (DOI: 10.5281/zenodo.20036659).

S1.1.1. Datasets collected at the APS**Table S1** Crystallographic, measurement and refinement details of the first model for each crystal.

Name	APS_Bi1_16- 5keV_15K	APS_Bi2_16- 5keV_100K	APS_Bi3_37- 5keV_15K
Data name	1[Bi]	2[Bi]	3[Bi]
Temperature (K)	15	100	15
Crystal size (mm)	0.06, 0.06, 0.06	0.07, 0.07, 0.04	0.08, 0.07, 0.07
Radiation / λ	16.5 keV / 0.75142 Å	16.5 keV / 0.75142 Å	37.5 keV / 0.75142 Å
a (Å)	20.230(2)	20.2717(9)	20.2003(3)
b (Å)	5.7094(4)	5.7226(2)	5.69690(6)
c (Å)	26.600(2)	26.6413(12)	26.5452(3)
α (deg)	90	90	90
β (deg)	109.679(11)	109.695(5)	109.7242(15)
γ (deg)	90	90	90
V (Å ³)	2892.8(5)	2909.8(2)	2875.57(7)
Z	8	8	8
Z'	1	1	1
Rint (%)	3.43	5.14	2.28
I/ σ (I)	25.3	24.3	25.6
Measured reflections	8724	14092	48754
Independent reflections	2810	2845	16387
Reflections used	8184	13179	47135
Completeness (%)	79.74	80.78	74.4
Redundancy (Measured/Independent)	3.105	4.953	2.975
dmax (Å)	9.524	13.17	5.567
dmin (Å)	0.7559	0.7561	0.4097
μ (mm ⁻¹)	14.11	14.02	14.19
F(000)	1648	1648	1648
R1 (%)	3.23	3.00	2.78
wR2 (%)	8.99	8.28	8.82
GooF	1.03	1.02	0.977

Name	APS_Bi4_37- 5keV_100K	APS_Bi5_50keV_15K	APS_Bi6_50keV_100K
Data name	4[Bi]	5[Bi]	6[Bi]
Temperature (K)	100	15	100
Crystal size (mm)	0.11, 0.14, 0.15	0.10, 0.10, 0.10	0.11, 0.10, 0.10
Radiation / λ	37.5 keV / 0.75142 Å	50 keV / 0.75142 Å	50 keV / 0.75142 Å
a (Å)	20.2401(6)	20.18335(15)	20.2091(5)
b (Å)	5.71469(13)	5.69350(3)	5.70076(7)
c (Å)	26.5966(8)	26.5361(2)	26.5508(5)
α (deg)	90	90	90
β (deg)	109.684(3)	109.7197(8)	109.659(2)
γ (deg)	90	90	90
V (Å ³)	2896.57(15)	2870.53(4)	2880.55(10)
Z	8	8	8
Z'	1	1	1
Rint (%)	5.49	3.98	5.17
I/ σ (I)	14.3	17.3	14.5
Measured reflections	157451	97362	160756
Independent reflections	28396	28093	28010
Reflections used	161983	115339	180715
Completeness (%)	99.48	98.31	98.02
Redundancy (Measured/Independent)	5.545	3.466	5.739
dmax (Å)	6.295	4.764	4.796
dmin (Å)	0.3757	0.3757	0.3757
μ (mm ⁻¹)	14.09	14.21	14.16
F(000)	1648	1648	1648
R1 (%)	3.9	2.71	4.08
wR2 (%)	11.6	8.79	12.4
GooF	0.897	0.753	0.968

S1.1.2. Datasets collected at the ESRF

Name	ESRF_D1_13- 3keV_100K	ESRF_D20_13- 35keV_100K	ESRF_D31_13- 35keV_100K
Data name	D1[Bi]	D20[Bi]	D31[Bi]
Temperature (K)	100	100	100
Crystal size (mm)	0.04, 0.05, 0.06	0.10, 0.10, 0.10	0.08, 0.08, 0.05
Radiation / λ	13.3 keV / 0.93222 Å	13.35 keV / 0.92872 Å	13.35 keV / 0.93227 Å
a (Å)	20.2587(9)	20.2944(4)	20.2539(3)
b (Å)	5.7151(2)	5.7293(1)	5.71351(6)
c (Å)	26.6029(15)	26.6488(4)	26.6043(7)
α (deg)	90	90	90
β (deg)	109.702(5)	109.649(2)	109.655(2)
γ (deg)	90	90	90
V (Å ³)	2899.8(3)	2918.1(1)	2899.29(10)
Z	8	8	8
Z'	1	1	1
Rint (%)	6.47	7.68	3.89
I/ σ (I)	16.9	11.7	42.7
Measured reflections	22472	10944	10180
Independent reflections	4000	3421	3411
Reflections used	21339	10441	9662
Completeness (%)	96.48	87.52	87.87
Redundancy (Measured/Independent)	5.618	3.199	2.984
dmax (Å)	13.18	13.21	13.27
dmin (Å)	0.7147	0.731	0.7349
μ (mm ⁻¹)	6.326	6.281	10.28
F(000)	1648	1648	1648
R1 (%)	2.82	5.04	3.52
wR2 (%)	8.05	15.1	12.3
GooF	0.977	0.945	1.02

Name	ESRF_D33_13- 45keV_100K	ESRF_D34_13- 35keV_100K	ESRF_D3_13- 45keV_100K
Data name	D33[Bi]	D34[Bi]	D3[Bi]
Temperature (K)	100	100	100
Crystal size (mm)	0.08, 0.07, 0.06	0.08, 0.07, 0.06	0.04, 0.07, 0.06
Radiation / λ	13.45 keV / 0.92872 Å	13.35 keV / 0.93227 Å	13.45 keV / 0.93227 Å
a (Å)	20.2648(6)	20.5295(6)	20.3770(5)
b (Å)	5.7157(2)	5.78716(8)	5.7441(1)
c (Å)	26.6036(9)	26.9557(5)	26.7236(7)
α (deg)	90.0	90	90.0
β (deg)	109.655(4)	109.670(3)	109.618(3)
γ (deg)	90.0	90	90.0
V (Å ³)	2901.88(19)	3015.65(12)	2946.37(13)
Z	8	8	8
Z'	1	1	1
Rint (%)	10.9	4.22	5.22
I/ σ (I)	15.9	9.37	14.8
Measured reflections	10317	5928	22545
Independent reflections	3583	3109	4093
Reflections used	9480	5581	21151
Completeness (%)	89.91	78.04	98.01
Redundancy (Measured/Independent)	2.879	1.907	5.508
dmax (Å)	13.19	13.27	13.27
dmin (Å)	0.7244	0.7284	0.717
μ (mm ⁻¹)	6.316	9.883	10.12
F(000)	1648	1648	1648
R1 (%)	8.94	4.45	3.34
wR2 (%)	28	12.3	10.4
GooF	1.230	1.000	0.998

Name	ESRF D4 13- 45keV_100K	ESRF D5 13- 55keV_100K	ESRF D6 13- 45keV_100K
Data name	D4[Bi]	D5[Bi]	D6[Bi]
Temperature (K)	100	100	100
Crystal size (mm)	0.03, 0.07, 0.10	0.04, 0.09, 0.12	0.11, 0.10, 0.03
Radiation / λ	13.45 keV / 0.93227 Å	13.55 keV / 0.93227 Å	13.45 keV / 0.93227 Å
a (Å)	20.2846(5)	20.1608(11)	20.2623(12)
b (Å)	5.72222(7)	5.6817(2)	5.7137(2)
c (Å)	26.6333(4)	26.4856(17)	26.614(3)
α (deg)	90	90.0	90.0
β (deg)	109.646(2)	109.719(7)	109.688(8)
γ (deg)	90	90.0	90.0
V (Å ³)	2911.44(10)	2856.0(3)	2901.1(4)
Z	8	8	8
Z'	1	1	1
Rint (%)	5.03	4.7	2.37
I/ σ (I)	16.8	18.7	36.1
Measured reflections	22886	22488	11706
Independent reflections	4071	4035	3536
Reflections used	21722	21334	11222
Completeness (%)	97.91	97.94	84.86
Redundancy (Measured/Independent)	5.622	5.573	3.311
dmax (Å)	13.27	18.38	13.27
dmin (Å)	0.718	0.7129	0.7177
μ (mm ⁻¹)	10.24	6.423	10.27
F(000)	1648	1648	1648
R1 (%)	2.61	2.53	2.06
wR2 (%)	7.21	7.75	6.52
GooF	1.01	0.961	0.993

Name	ESRF_D7_13- 35keV_100K
Data name	D7[Bi]
Temperature (K)	100
Crystal size (mm)	0.08, 0.08, 0.05
Radiation / λ	13.35 keV / 0.93227 Å
a (Å)	20.2415(7)
b (Å)	5.70885(18)
c (Å)	26.5836(9)
α (deg)	90
β (deg)	109.657(4)
γ (deg)	90
V (Å ³)	2892.86(17)
Z	8
Z'	1
Rint (%)	2.70
I/ σ (I)	40.0
Measured reflections	12025
Independent reflections	3990
Reflections used	11295
Completeness (%)	95.82
Redundancy (Measured/Independent)	3.014
dmax (Å)	18.56
dmin (Å)	0.7178
μ (mm ⁻¹)	10.3
F(000)	1648
R1 (%)	2.40
wR2 (%)	14.9
GooF	0.965

S1.1.3. Datasets collected on a Rigaku Oxford Diffraction Synergy DW

Name	DW_Bi01_8-04keV_100K	DW_Bi02_8-04keV_100K	DW_Bi03_8-04keV_100K
Data name	01[Bi]	02[Bi]	03[Bi]
Temperature (K)	100	100	100
Crystal size (mm)	0.11, 0.10, 0.04	0.12, 0.07, 0.04	0.10, 0.10, 0.06
Radiation / λ	8.04 keV / 1.5418 Å	8.04 keV / 1.5418 Å	8.04 keV / 1.5418 Å
a (Å)	20.2709(5)	20.2506(5)	20.2436(5)
b (Å)	5.71409(14)	5.71386(11)	5.71053(12)
c (Å)	26.6167(7)	26.6034(6)	26.5984(6)
α (deg)	90	90	90
β (deg)	109.630(3)	109.697(2)	109.687(3)
γ (deg)	90	90	90
V (Å ³)	2903.83(13)	2898.15(11)	2895.09(12)
Z	8	8	8
Z'	1	1	1
Rint (%)	2.16	1.93	1.73
I/ σ (I)	35.8	44.3	51.4
Measured reflections	8826	10938	11438
Independent reflections	2782	2771	2787
Reflections used	8118	10008	10413
Completeness (%)	95.8	95.22	95.77
Redundancy (Measured/Independent)	3.173	3.947	4.104
dmax (Å)	18.5	13.23	18.5
dmin (Å)	0.8066	0.8064	0.8064
μ (mm ⁻¹)	23.78	23.82	23.85
F(000)	1648	1648	1648
R1 (%)	2.18	1.91	1.97
wR2 (%)	6.2	6.17	5.48
GooF	1.05	1.02	1.05

Name	DW_Bi04_8-04keV_100K	DW_Bi05_8-04keV_100K	DW_Bi06_8-04keV_100K
Data name	04[Bi]	05[Bi]	06[Bi]
Temperature (K)	100	100	100
Crystal size (mm)	0.13, 0.13, 0.06	0.09,0.08, 0.05	0.12, 0.07, 0.07
Radiation / λ	8.04 keV / 1.5418 Å	8.04 keV / 1.5418 Å	8.04 keV / 1.5418 Å
a (Å)	20.2489(4)	20.2559(6)	20.2456(5)
b (Å)	5.70955(10)	5.71171(16)	5.71546(12)
c (Å)	26.5858(5)	26.6087(8)	26.5903(6)
α (deg)	90	90	90
β (deg)	109.635(2)	109.665(3)	109.667(3)
γ (deg)	90	90	90
V (Å ³)	2894.91(10)	2898.98(16)	2897.35(13)
Z	8	8	8
Z'	1	1	1
Rint (%)	2.02	1.99	1.63
I/ σ (I)	47.6	31.5	49.7
Measured reflections	8941	9814	10847
Independent reflections	2795	2844	2784
Reflections used	8230	9130	10031
Completeness (%)	96.38	96.67	95.67
Redundancy (Measured/Independent)	3.199	3.451	3.896
dmax (Å)	18.5	18.5	18.5
dmin (Å)	0.807	0.804	0.8064
μ (mm ⁻¹)	23.85	23.82	23.83
F(000)	1648	1648	1648
R1 (%)	2.25	1.94	1.77
wR2 (%)	6.46	5.15	4.96
GooF	1.07	1.04	1.03

S1.2. Hirshfeld Atom Refinement of D7[Bi]**S1.2.1. Crystallographic information table**

Name	ESRF_D7_IAM	ESRF_D7_HAR
Data name	D7[Bi]	
Temperature (K)	100	
Crystal size (mm)	0.08, 0.08, 0.05	
Radiation / λ	13.35 keV / 0.93227 Å	
a (Å)	20.2415(7)	
b (Å)	5.70885(18)	
c (Å)	26.5836(9)	
α (deg)	90	
β (deg)	109.657(4)	
γ (deg)	90	
V (Å ³)	2892.86(17)	
Z	8	
Z'	1	
Rint (%)	2.70	
I/ σ (I)	40.0	
Measured reflections	12025	
Independent reflections	3990	
Reflections used	11295	
Completeness (%)	95.82	
Redundancy (Measured/Independent)	3.014	
dmax (Å)	18.56	
dmin (Å)	0.7178	
μ (mm ⁻¹)	10.3	
F(000)	1648	
R1 (%)	2.40	2.14
wR2 (%)	14.9	13.86
GooF	0.965	0.952
Min, max peaks eÅ ⁻³	-1.28, 1.34	-1.28, 1.16

S1.2.2. HAR procedure description

HAR was performed using NoSpherA2 (Kleemiss *et al.*, 2021b) via olex2.refine (Bourhis *et al.*, 2015) in the Olex2 crystallographic software suite (Dolomanov *et al.*, 2009). The molecular wavefunction for [Bi] was calculated using ORCA6.1 (Neese, 2025). The ω B97X-V functional (Mardirossian & Head-Gordon, 2014) and cc-pVQZ basis sets (Dunning, 1989) for C and H, the SARC-DKH2 basis set (Pantazis & Neese, 2012) for Bi, the zeroth-order relativistic approximation (ZORA) (Moncho & Autschbach, 2010), a water implicit solvation model (CPCM) (Barone & Cossi, 1998), resolution of identity coulomb integrals and COSX numerical integration of the Hartree-Fock exchange (RIJCOSX) (Helmich-Paris *et al.*, 2021) were applied. Standard SCF convergence criteria (“NormalConv”) were set. The HAR converged after seven cycles of wavefunction calculation (SCF), partitioning, and crystallographic refinement of positional, and atomic displacement parameters.

S1.3. Detector saturation in the APS measurements

The 15K, 16.5 keV dataset of the APS series (1[Bi]) is affected by oversaturation of the detector. This resulted in a typical bent bouquet-like shape of the Fobs/Fcalc plot. For the first datasets, the refined model shows non-positive definite (NPD) atomic displacement parameters for all atoms. For other APS series, 2[Bi], 3[Bi], and 4[Bi], there is also a visible spread in the Fobs/Fcalc. However, in these cases improper use of the extinction correction can provide a sensible structural model, while NPDs appear when EXTI is not used. We also noticed the same phenomenon in a previous study, which was measuring WYLID and YLID (Meurer *et al.*, 2025) at ROBL at the ESRF. In contrast to that study and in contrast to series 2[Bi], 3[Bi], and 4[Bi], the effect of detector saturation cannot be mitigated for 1[Bi] by employing an extinction correction.

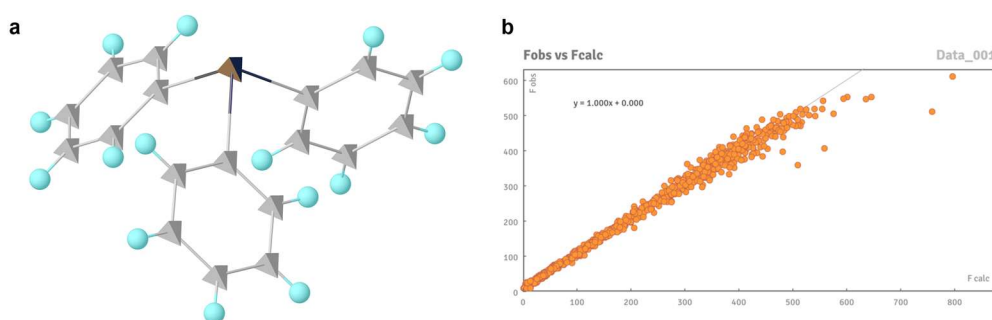


Figure S1 Structural model of the first measurement in the 1[Bi] APS series. **a** Pyramids show unphysical, negative values for the atomic displacement parameters. **b** shows the comparison of the calculated (Fcalc) and measured (Fobs) structure factors. A dent and spread (“bouquet-like”) shape shows the oversaturation of the detector.

S1.4. Example input file for the RADDOS-3D calculations

```
#####
#                               #
#                               #
#####

Crystal

Type cuboid                # Choices are: Cuboid, Cylinder, Spherical, Polyhedron (would need
                               wireframe mesh)

Dimensions 100 80 20 # Dimensions of the crystal in X,Y,Z in µm.

PixelsPerMicron 1.0    # The computational resolution

AbsCoefCalc SmallMole  # Tells RADDOS-3D how to calculate the Absorption coefficients
```

```

SmallMoleAtoms C 18 H 15 Bi 1 # Elemental content in the unit cell (needs to be integer numbers)
NumMonomers 4          # Number of this formulas repeated in the unit cell (Z in crystallographic)

AngleP 0.0             # in Degree corresponding to point 2.6
AngleL 0.0             # in Degree corresponding to point 2.7

CalculatePEEscape FALSE # Whether or not Photoelectron escape should be used in the calculation

UnitCell 20.271 5.7251 26.604 # unit cell size: a, b, c
          90 109.68 90      # alpha, beta and gamma angles

#####
#                               Beam Block                               #
#####
Beam

# Type Experimentalpgm # If we have it we can provide the beam profile in an ASCII File
# File beam.pgm       # Name of the file with beam profile
# Pixelsize X Y       # Pixelsize of the beamprofile

Type Gaussian          # Gaussian profile beam
Flux 1.31E+10          # in photons per second (2e12 = 2 * 10^12)
Energy 13.35 keV       # in keV
FWHM 250 300          # in micro-m, vertical by horizontal for a Gaussian beam
Collimation Rectangular 250 250 # Vertical/Horizontal collimation of the beam
                                # For 'uncollimated' Gaussians, 3xFWHM recommended

#####
#                               Wedge Block                               #
#####

Wedge 0 360           # Start and End rotational angle of the crystal
                      # Start < End
ExposureTime 719.9    # Total time for entire angular range in seconds

AngularResolution 0.5 # Only change from the defaults when using very
                      # small wedges, e.g 5 Degree.

```


S2. Data plotted in the main section**S2.1. Figure 2 – Relative Intensity vs. dose in MGy****S2.1.1. APS (1-3)**

APS_Bi1_16-5keV_15K_fin		APS_Bi2_16-5keV_100K_fin		APS_Bi3_37-5keV_15K_fin	
AccDose	RelInt	AccDose	RelInt	AccDose	RelInt
0.3428	1.000	0.1401	1.000	0.6208	1.000
0.6856	1.040	0.2801	0.9652	1.242	0.9354
1.028	1.068	0.4202	0.9629	1.862	0.8659
1.371	1.178	0.5603	0.987	2.483	0.8100
1.714	0.9999	0.7003	0.9915	3.104	0.7466
2.057	1.0450	0.8404	0.9738	3.725	0.7137
2.830	0.9999	1.170	0.9562	4.345	0.6623
3.603	0.9550	1.500	0.9725	4.966	0.6184
4.376	0.9101	1.829	0.9491	5.587	0.5776
5.148	0.8652	2.159	0.938	6.208	0.5435
5.921	0.8204	2.489	0.9448	6.828	0.5123
6.694	0.7755	2.818	0.8244	7.449	0.4775
8.428	0.7306	3.563	0.7039	8.070	0.4483
10.16	0.6857	4.307	0.6819	8.691	0.4334
11.89	0.6408	5.052	0.6674	9.311	0.4029
13.63	0.5959	5.796	0.604	9.932	0.3827
15.36	0.5511	6.54	0.5698		
		7.285	0.5249		
		8.952	0.4799		
		10.62	0.427		
		12.29	0.3974		

S2.1.2. APS (4-6)

APS_Bi4_37-5keV_100K_fin		APS_Bi5_50keV_15K_fin		APS_Bi6_50keV_100K_fin	
AccDose	RelInt	AccDose	RelInt	AccDose	RelInt
0.1966	1.000	0.05224	1.000	0.126	1.000
0.3931	0.9731	0.1045	0.8664	0.252	1.011
0.5897	0.9506	0.1567	0.8482	0.5039	0.9877
0.7862	0.9745	0.2090	0.8568	0.6299	0.9987
0.9828	0.9630	0.2612	0.8468	0.8819	0.9606
1.179	0.9271	0.3134	0.8585	1.134	0.9620
1.376	0.8566	0.3657	0.8385	1.260	0.9613
1.572	0.9187	0.4179	0.8235	1.386	0.9487
1.769	0.8200	0.4702	0.8245	1.512	0.9537
1.966	0.8904	0.5224	0.8263	1.638	0.9488
2.162	0.8728	0.5746	0.8065	1.764	0.9475

2.359	0.8792	0.6324	0.7868	1.89	0.9638
2.555	0.8582	0.6902	0.7767	2.016	0.9461
2.752	0.8653	0.748	0.7782	2.142	0.9202
2.948	0.8482	0.8058	0.7732	2.268	0.9354
3.48	0.8745	0.8636	0.7749	2.394	0.9345
4.151	0.7952	0.9214	0.7755	2.520	0.9301
4.487	0.7956	0.9792	0.7682	2.646	0.9238
4.823	0.8123	1.037	0.7648	2.898	0.9149
7.171	0.7243	1.095	0.7475	3.150	0.8852
7.507	0.6999	1.153	0.7415	3.276	0.8985
9.664	0.5716	1.210	0.7552	3.401	0.8961
10.24	0.5097	1.268	0.7519	3.527	0.8888
10.81	0.4965	1.326	0.7331	3.653	0.8935
11.39	0.4793	1.384	0.7318	3.779	0.8898
11.97	0.4524	1.442	0.7407	3.905	0.8812
12.54	0.4465	1.499	0.7364	4.031	0.8836
13.12	0.4200	1.557	0.7291	4.787	0.8517
13.69	0.4059	1.615	0.7215	4.913	0.8492
14.27	0.3848	1.673	0.7118	5.039	0.8433
14.84	0.3350			5.165	0.8420
15.42	0.3120			5.417	0.8299
15.99	0.2604			5.543	0.8281
				10.83	0.5973

S2.1.3. ESRF (1-3)

ESRF_D1_13-3keV_100K		ESRF_D20_13-35keV_100K		ESRF_D31_13-35keV_100K	
AccDose	RelInt	AccDose	RelInt	AccDose	RelInt
0.000	1.000	0.000	1.000	0.000	1.000
1.720	0.9499	0.592	0.832	0.5433	0.8573
3.446	0.7579	1.16	0.7427	1.167	0.6742
5.270	0.4808	1.70	0.7748	1.763	0.4424
6.943	0.3638	3.46	0.5396	2.326	0.3572
8.700	0.2174	4.91	0.5253	2.956	0.2260
10.43	0.1253	6.69	0.4455	3.552	0.1333
12.18	0.07031	8.42	0.4200	4.115	0.09403
		10.1	0.3674	4.746	0.05976
		11.7	0.2046	5.342	0.03370
				5.918	0.02248

S2.1.4. ESRF (4-6)

ESRF_D33_13-45keV_100K		ESRF_D34_13-35keV_100K		ESRF_D3_13-45keV_100K	
AccDose	RelInt	AccDose	RelInt	AccDose	RelInt
0.000	1.0000	0.000	0.7832	0.000	1.0000
2.489	0.7474	1.193	1.000	1.607	0.7629
5.201	0.6637	2.497	0.8812	3.295	0.5418
7.800	0.5609	3.719	0.8244	4.921	0.3580
10.23	0.4651	4.875	0.8307	6.575	0.2220
12.96	0.4099	6.174	0.6322	8.299	0.2272
15.51	0.3441	7.395	0.5297	9.915	0.1495
17.90	0.3073	8.624	0.5145		
20.57	0.2570	9.920	0.4435		
		11.13	0.4022		
		12.41	0.3555		
		13.69	0.3248		
		14.89	0.2569		
		16.22	0.2409		
		17.49	0.2173		
		18.68	0.1259		

S2.1.5. ESRF (7-9)

ESRF_D4_13-45keV_100K		ESRF_D5_13-55keV_100K		ESRF_D6_13-45keV_100K	
AccDose	RelInt	AccDose	RelInt	AccDose	RelInt
0.000	1.000	0.000	1.0000	0.000	1.000
2.991	0.5429	2.679	0.3312	1.132	1.027
6.121	0.1069	5.524	0.2093	2.296	0.9608
8.899	0.02937	8.259	0.02956	3.606	0.8975
				5.014	0.6934
				6.617	0.4995
				8.356	0.3453
				10.13	0.3370
				11.89	0.3654
				13.65	0.1717

S2.1.6. ESRF (10)**ESRF_D7_13-35keV_100K**

AccDose	RelInt
0.000	1.000
1.472	0.9583
2.944	0.7987
4.416	0.7566
5.888	0.7096
7.360	0.6364
8.832	0.5508
10.30	0.6370
11.78	0.6040
13.25	0.5665
14.72	0.5492
16.19	0.5111
17.66	0.3728
19.14	0.3490
20.61	0.2986
22.08	0.3156
23.55	0.3207
25.02	0.2461
26.50	0.2351
27.97	0.2342
29.44	0.1990
30.91	0.08264

S2.1.7. DW (1-3)

DW_Bi01_8-04keV_100K		DW_Bi02_8-04keV_100K		DW_Bi03_8-04keV_100K	
AccDose	RelInt	AccDose	RelInt	AccDose	RelInt
1.172	1.000	1.349	1.000	1.182	1.000
2.345	0.9208	2.697	0.8958	2.363	0.9144
3.517	0.8227	4.046	0.8080	3.545	0.8588
4.690	0.6435	5.394	0.5005	4.726	0.6776
5.862	0.5120	6.743	0.3448	5.908	0.5873
7.035	0.4438	8.091	0.2328	7.090	0.4988
8.207	0.3261	9.440	0.1656	8.271	0.4086
9.380	0.2322	10.79	0.1226	9.453	0.3131
10.55	0.1368	12.14	0.09841	10.63	0.2779
		13.49	0.05815	11.82	0.2653
				13.00	0.2345
				14.18	0.1752
				15.36	0.1371
				16.54	0.08873
				17.72	0.06293

S2.1.8. DW (4-6)

DW_Bi04_8-04keV_100K		DW_Bi05_8-04keV_100K		DW_Bi06_8-04keV_100K	
AccDose	RelInt	AccDose	RelInt	AccDose	RelInt
1.014	1.000	1.181	1.000	1.105	1.000
2.028	0.9218	2.363	0.9327	2.211	0.8948
3.042	0.8630	3.544	0.8497	3.316	0.8366
4.056	0.7655	4.726	0.7495	4.422	0.6759
5.070	0.7199	5.907	0.5811	5.527	0.5490
6.084	0.6170	7.088	0.4945	6.632	0.4536
7.098	0.5675	8.270	0.4600	7.738	0.3894
8.112	0.4764	9.451	0.3084	8.843	0.2986
9.126	0.4135	10.63	0.2204	9.948	0.2666
10.14	0.3092	11.81	0.1777	11.05	0.1299
11.15	0.2836	13.00	0.07879	12.16	0.1013
12.17	0.06806	14.18	0.03172	13.26	0.06183
13.18	0.1652				
14.2	0.1232				
15.21	0.03959				

S2.2. Figure 4 – C-C and Bi-C standard uncertainties and bond lengths in Å vs. dose in MGy**S2.2.1. a – c**

2[Bi]		D31[Bi]		01[Bi]	
AccDose	mean_sigma_cc	AccDose	mean_sigma_cc	AccDose	mean_sigma_cc
0.1401	0.0044	0.0000	0.0037	0.4429	0.0046
0.2801	0.0043	0.5433	0.0043	0.8859	0.0058
0.4202	0.0044	1.1669	0.0050	1.3288	0.0069
0.5603	0.0044	1.7632	0.0064	1.7717	0.0083
0.7003	0.0045	2.3258	0.0083	2.2147	0.0097
0.8404	0.0045	2.9564	0.0129	3.1005	0.0165
1.1701	0.0042	3.5517	0.0202	3.5435	0.0215
1.4998	0.0041	4.1146	0.0275	3.9864	0.0281
1.8294	0.0044	4.7463	0.0380		
2.1591	0.0044	5.3422	0.0572		
2.4888	0.0046				
2.8185	0.0047				
3.5629	0.0048				
4.3072	0.0055				
5.0516	0.0057				
5.7959	0.0065				
6.5403	0.0068				
7.2846	0.0077				
8.9523	0.0086				
10.6200	0.0105				
12.2877	0.0141				

S2.2.2. d

2[Bi]			
AccDose	Bi-C1	Bi-C2	Bi-C3
0.1401	2.2644	2.2566	2.2713
0.2801	2.2614	2.2511	2.2715
0.4202	2.2598	2.2547	2.2738
0.5603	2.2633	2.2533	2.2677
0.7003	2.2613	2.2549	2.2721
0.8404	2.2606	2.2501	2.2715
1.1701	2.2625	2.2494	2.2708
1.4998	2.2632	2.2500	2.2707
1.8294	2.2637	2.2529	2.2751
2.1591	2.2600	2.2481	2.2713
2.4888	2.2587	2.2508	2.2746
2.8185	2.2584	2.2544	2.2714
3.5629	2.2605	2.2547	2.2718
4.3072	2.2581	2.2542	2.2738
5.0516	2.2602	2.2529	2.2715

5.7959	2.2598	2.2550	2.2709
6.5403	2.2642	2.2548	2.2767
7.2846	2.2656	2.2532	2.2687
8.9523	2.2617	2.2545	2.2698
10.6200	2.2609	2.2577	2.2692
12.2877	2.2554	2.2697	2.2644

S2.2.3. e**D31[Bi]**

AccDose	Bi-C1	Bi-C2	Bi-C3
0.0000	2.2585	2.2431	2.2679
0.5433	2.2574	2.2501	2.2694
1.1669	2.2586	2.2552	2.2711
1.7632	2.2521	2.2535	2.2731
2.3258	2.2588	2.2528	2.2772
2.9564	2.2563	2.2798	2.2785
3.5517	2.2578	2.2930	2.2753
4.1146	2.2607	2.3013	2.2688
4.7463	2.1938	2.3194	2.2326
5.3422	1.9969	2.4206	2.1272

S2.2.4. f**01[Bi]**

AccDose	Bi-C1	Bi-C2	Bi-C3
0.4429	2.2532	2.2657	2.2493
0.8859	2.2524	2.2680	2.2496
1.3288	2.2528	2.2682	2.2492
1.7717	2.2456	2.2583	2.2448
2.2147	2.2434	2.2748	2.2524
3.1005	2.2318	2.2592	2.2604
3.5435	2.2407	2.2857	2.2716
3.9864	2.2405	2.2056	2.2902

S2.2.5. g-i**2[Bi]**

AccDose	Cell Volume	Bi Ueq	Unique reflections
0.140065	2909.8	0.00661	2845
0.280130	2906.8	0.00703	2840
0.420195	2907.3	0.00781	2851
0.560260	2906.4	0.00830	2848
0.700325	2915.6	0.00839	2851
0.840390	2908.5	0.00931	2851

1.17007	2909.1	0.01015	2846
1.49976	2911.6	0.01192	2854
1.82944	2919.1	0.01306	2859
2.15913	2915.0	0.01436	2857
2.48882	2926.0	0.01556	2867
2.81850	2922.8	0.01664	2861
3.56286	2927.1	0.01870	2853
4.30722	2935.4	0.02153	2852
5.05157	2943.2	0.02453	2851
5.79593	2946.9	0.02733	2859
6.54029	2965.9	0.03112	2868
7.28465	2966.1	0.03403	2870
8.95233	2967.9	0.03690	2852
10.6200	2982.6	0.04375	2867
12.2877	2991.6	0.05020	2857

D31[Bi]

AccDose	Cell Volume	Bi Ueq	Unique reflections
0.0000	2899.29	0.01784	3411
0.543346	2920.94	0.02665	3443
1.16691	2944.75	0.03559	3450
1.76315	2959.84	0.04824	3463
2.32583	2977.1	0.05816	3482
2.95644	2997.3	0.0708	3499
3.55175	3014.6	0.0911	3522
4.11457	3025.8	0.1167	3529
4.74630	3033.1	0.1368	3546
5.34224	3039.5	0.1580	3559
5.91798	3042.2	0.2340	3566

01[Bi]

AccDose	Cell Volume	Bi Ueq	Unique reflections
0.442934	2903.83	0.02010	2782
0.885867	2920.4	0.02584	2794
1.32880	2936.6	0.03408	2808
1.77173	2920.4	0.04289	2825
2.21467	2966.2	0.05211	2840
2.65760	2920.4	0.1420	2496
3.10054	2994.0	0.0715	2868
3.54347	3006.2	0.0840	2882
3.98640	3022.4	0.0999	2901

S2.3. Figure 5 – R1, Rint and Goof vs dose in MGy**2[Bi]**

AccDose	R1	Rint	Goof
0.1401	0.03	0.05143	1.017
0.2801	0.0296	0.05359	1.014
0.4202	0.0289	0.05295	1.023
0.5603	0.0284	0.05314	1.024
0.7003	0.0290	0.05250	1.018
0.8404	0.0285	0.05128	1.026
1.1700	0.0310	0.04583	1.024
1.500	0.0291	0.04389	1.028
1.829	0.0284	0.04423	1.034
2.159	0.0268	0.04425	1.027
2.489	0.0264	0.04441	1.028
2.818	0.0252	0.04605	1.029
3.563	0.0263	0.03968	1.027
4.307	0.0278	0.03874	1.028
5.052	0.0275	0.03690	1.029
5.796	0.0303	0.03621	1.013
6.540	0.0314	0.03558	1.023
7.285	0.0335	0.03503	1.014
8.952	0.0377	0.03924	1.025
10.62	0.0427	0.04175	1.004
12.29	0.0521	0.04604	0.9771

D31[Bi]

AccDose	R1	Rint	Goof
0.0000	0.0352	0.03895	1.024
0.5433	0.0408	0.04204	1.026
1.167	0.0363	0.03531	1.023
1.763	0.0512	0.04280	1.016
2.326	0.0699	0.04326	0.9973
2.956	0.0978	0.06878	0.9891
3.552	0.1234	0.05952	1.060
4.115	0.1384	0.07319	1.052
4.746	0.2006	0.1338	1.103
5.342	0.2510	0.2860	1.052
5.918	0.2964	0.5675	0.9873

01[Bi]

AccDose	R1	Rint	GooF
0.4429	0.0218	0.02156	1.048
0.8859	0.0266	0.02204	1.035
1.329	0.0319	0.02091	1.027
1.772	0.0386	0.02536	1.024
2.215	0.0475	0.02750	1.014
2.658	0.7680	0.03041	18.200
3.101	0.0683	0.03350	0.9912
3.543	0.0794	0.04343	0.9733
3.986	0.0940	0.07355	0.9525

S3. Additional material

S3.1. Unique decay plots

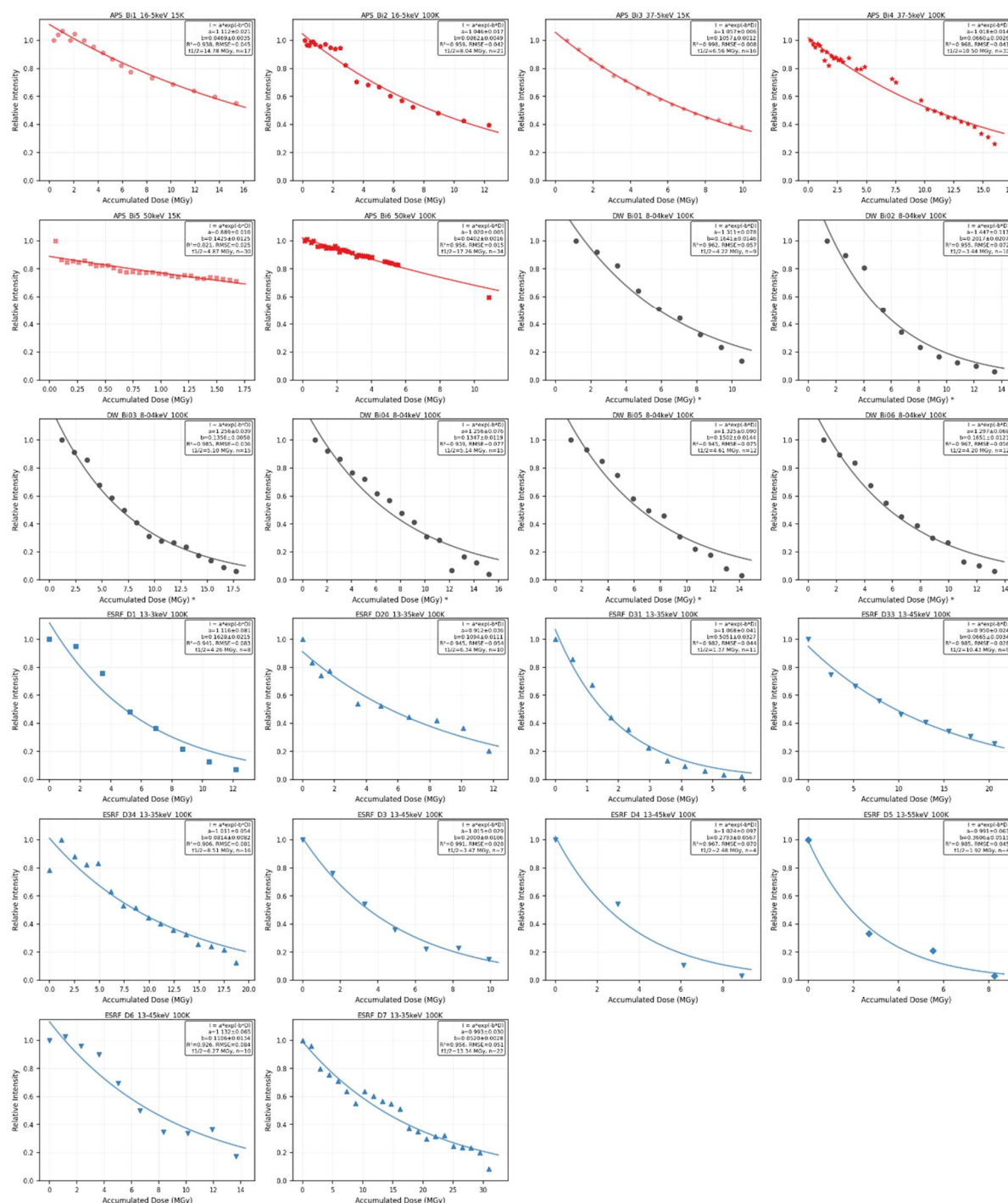


Figure S2 Unique decay progressions and fits for the 22 datasets used in the decay description.

S3.2. Bi-C bond precision

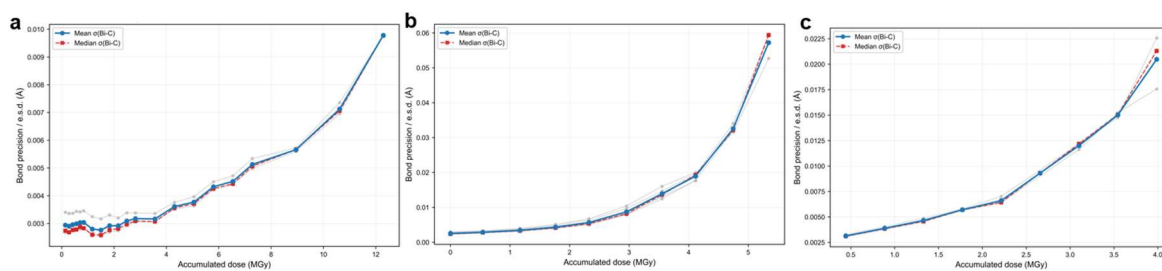


Figure S3 Bi-C bond precision (a-c, grey are unique, blue and red show average and median, respectively) for representative APS (a, 2[Bi]), ESRF (b, D31[Bi]) and DW (c, 01[Bi]) series.

S3.3. Cell parameters

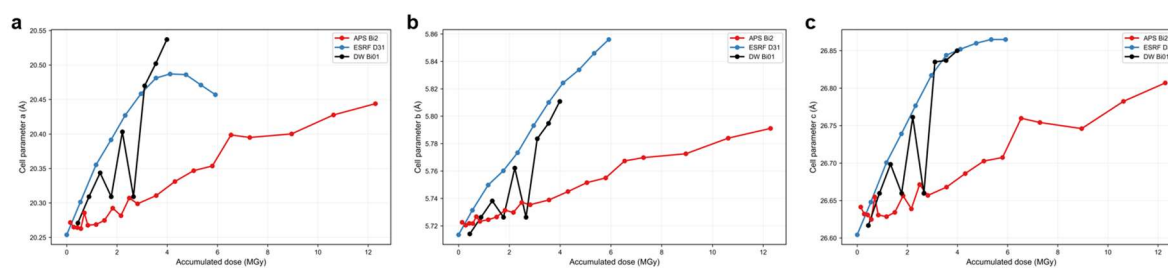
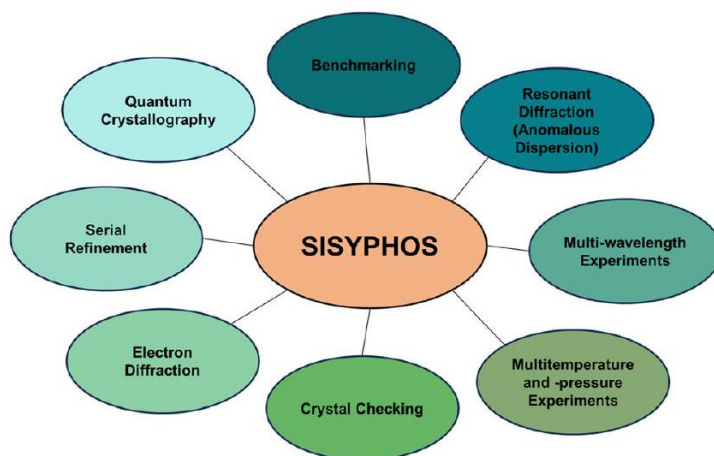


Figure S4 Lattice parameters a (a), b (b), and c (c) of 2[Bi] (red), D31[Bi] (blue), and 01[Bi] (black).

9 SISYPHOS: Serial refinement in Olex2



Preface

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"SISYPHOS: An automatic procedure for the serial refinement of single-crystal diffraction data in Olex2"

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Florian Kleemiss – Programming, software testing, co-writing final manuscript.

Birgit Hischa – Data acquisition, co-writing final manuscript.

Daniel Brück – Programming, software testing, co-writing final manuscript.

Ann-Cathrin Koch – Data acquisition, crystallisation, statistical analysis, co-writing final manuscript.

Michael Bodensteiner – Conceptualisation, co-writing final manuscript.

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Abstract

A program for serial handling of crystallographic data is presented within Olex2. Especially for small molecule electron and x-ray diffraction, the handling of several datasets of the same structure can be tedious and prone to errors, which can affect comparability. The program SISYPHOS allows for the individual refinement of a starting model against several recorded datasets (in ".hkl" format) with adaptation to changes in the unit cell, wavelength, among other parameters. The program was tested for resonant diffraction (also known as anomalous dispersion), investigations on radiation damage, the benchmarking of different configurations for quantum crystallographic modeling, electron diffraction data, and for testing several datasets from the same measurement using various settings to identify the most suitable dataset.

9.1 Introduction

With the steady improvement of x-ray diffraction devices, small molecule crystallography is no longer heavily dependent on measurement time but instead has an abundance of data. Especially with the latest innovations of rotating and metal-jet anode devices,¹ using photon-counting detectors,^{2,3} as well as the recent introduction of the first commercial electron diffractometers,^{4,5} the time for data collection is significantly reduced. At the same time, the improved datasets reveal more of the imperfections of the average crystal structure model. These include disorder, anharmonicity, absorption effects, and others. Often, several datasets of the same compound are collected-either at different wavelengths⁶ or from different crystals to be able to find the best crystallographic model of the compound at hand.

When complete datasets are collected in minutes rather than formerly days or even weeks, an automatic procedure becomes feasible and maybe even necessary. Especially for chemical crystallography in synchrotron facilities, it is common to record multiple datasets-either for obtaining a complete dataset despite angular restrictions, radiation damage, varying wavelengths (e.g., resonant diffraction), or at different temperatures and pressure conditions.

This, however, leads to the problem that less time is spent on the modeling and refinement per structure model, increasing "avoidable" errors in published structures. As recently described in a review by Raymond and Girolami,⁷ who categorize the different origins of "pathological crystal structures." According to the authors, there are causes intrinsic to the method of crystallography, such that the time spent per crystal structure has an impact. Thomson has already reported that the number of publications with multiple datasets of the same structure has increased significantly since the turn of the millennium, and has developed CX-ASAP, a high-throughput tool for the serial refinement and analysis

of crystallography data collected under different conditions.⁸ However, the program relies on the ShelXL⁹ refinement engine and is therefore limited to its functionality regarding non-spherical atomic form factors,^{10,11} the modeling of anharmonic motion,^{12,13} and anomalous dispersion.¹⁴

In this work, the software module SISYPHOS, as part of the crystallographic software suite Olex2,¹⁵ is introduced. SISYPHOS aims to make the refinement of different datasets of the same or very similar crystal structures easily accessible and convenient to a wide range of crystallographers. An overview of the fields in which the software can be applied can be found in Figure 9.1. The use cases include crystal checking, multitemperature and multi-pressure series, quantum crystallographic benchmarking, analysis of radiation damage, and resonant diffraction experiments. The general principle is to refine the same crystallographic starting model either against several datasets of the same structure or with a series of different settings against the same dataset, or both. Direct communication with the established quantum crystallographic software NoSpherA2¹⁶ enables serial use of quantum crystallography for a variety of scenarios. SISYPHOS collects resulting data and model parameters, alongside refinement indicators, and provides the user with a formatted .csv file for easy comparison of the different models. Each generated model is stored in a separate location for further investigation. Fully written in Python 3,¹⁷ SISYPHOS can be adjusted for user-specific applications. Especially with the advent of high-level, commercial electron diffractometers, the program offers a pathway for a smoother and optimized structure elucidation process.

9.2 Implementation

9.2.1 Architecture and workflow

In the following, the typical workflow (see the workflow below) within SISYPHOS is explained. The program searches for all uniquely named *.hkl* files in the chosen data directory recursively and creates a new directory in the parent output directory for each structure, copying any identically named *.ins* files for later reference, and the template model *.ins* along with the *.hkl* file into it. Differences in unit cells, wavelength, temperature, etc., are read from the respective *.ins* file. The program automatically ignores *.hkl* files within its output directory and increments output folder names with integer numbers to enable multiple runs on the same dataset. SISYPHOS proceeds to refine each structure in its new directory, leaving all old models unchanged. It checks automatically if extinction correction is required and compares the extinction factor to its standard uncertainty, omitting the extinction correction if the value is smaller than 3σ . During the refinement, the different modes are applied individually. For anomalous dispersion refinement,¹⁸ the corresponding parameters for all atoms of one or many element types as selected during the setup are included in the least squares refinement of *olex2.refine*. If NoSpherA2 is used, the settings for the quantum chemical calculation, currently only supporting ORCA,^{19–22} can either be set from the NoSpherA2 GUI or a benchmark file ("Benchmark Mode").

Once the refinement is complete, the information extraction process begins. This involves built-in Olex2 functions as well as parsing of the resulting *.cif*. SISYPHOS extracts all bond lengths and uncertainty from the model, using the variance-covariance matrix. Where defined, uncertainties of derived values are collected as well. All results are first appended to a *.txt* output file, which is subsequently converted into a *.csv* file for convenient

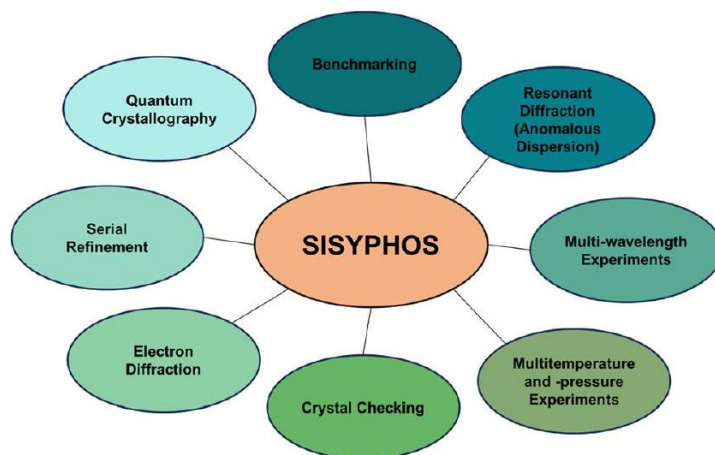


Figure 9.1: Overview of the different areas of application for SISYPHOS.

data handling and visualization.

9.2.2 User interface

Figure 9.2 shows the graphical user interface of SISYPHOS as implemented in Olex2. The blue button labeled "DIR" allows the user to select the main directory for the data. The routine will search through all subfolders for uniquely named .hkl files (including .hklf4 and .hklf5 files). On the right side of the directory textfield, the .ins button allows the user to select the starting model against which each dataset is refined. By default, it will open the current structure folder. The settings in the following rows depend on the selected mode, which are changeable using the tickboxes in the row labeled "Mode options." By default, the user can apply corrections to the incoming x-ray energy and restrict the outer resolution limit for all datasets, which is helpful for comparison purposes, for example, where datasets show different maximum resolution, but should be refined using the same cutoff.

In "Use NoSpherA2" mode, a Hirshfeld Atom Refinement ^{10,23} will be performed on each dataset, using the settings as shown in the GUI that is imported from the NoSpherA2 software. In combination with the benchmark mode, the user can select a text file containing a dictionary of each combination of settings for the HAR procedure they want to perform on the structure. An example of the layout of this benchmark file is given in the program folder. Finally, the user can perform a refinement of anomalous dispersion parameters by enabling the mode "DISP refinement." In an additional line of the GUI, the element (or elements, white space separated) can be entered. Additionally, if there is more than one position for the selected element, the values for anomalous dispersion can be constrained to be equal or individual, by the checkbox "Individual DISP." For comparison, the structures can be refined

9.3 SISYPHOS

Additionally, the user is able to only include CrysAlisPro ²⁷ style "struct" folders for the search of datasets, and, therefore, exclude datasets within the main experiment folder, or whether the weighting scheme used by the refinement should be updated ("Update

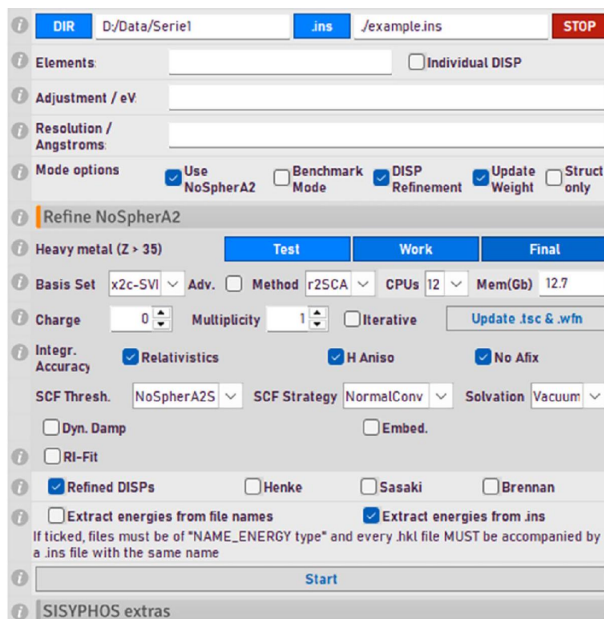


Figure 9.2: Graphical user interface of SISYPHOS in Olex2 showing settings for a refinement of anomalous dispersion parameters while employing a Hirshfeld Atom Refinement within NoSpherA2 using ORCA. Using the tabulated values according to Henke et al.,²⁴ Sasaki,²⁵ or Brennan and Cowan.²⁶

Weight"). Finally, the user can tell the program where to find the correct energy. By default, the x-ray energy from the template .ins file is used, but alternatively, an .ins file corresponding to each dataset can be used to ensure the correct energy matches the model. Additionally, for synchrotron applications, it is possible to read the energy from the dataset name if it adheres to the naming scheme of "NAME_ENERG.hkl," where NAME can be anything and ENERG is the energy in integer eV. The gray "Start" button at the bottom will start the serial refinement, which can be stopped using the red "STOP" button.

9.4 Applications and discussion

9.4.1 Crystal screening

A possible scenario for crystal screening on different x-ray diffractometers would be to measure some visually selected crystals on various devices. The aim is to find the best combination of diffractometer and wavelength for each crystal. To emulate this scenario, we measured a total of three different sucrose crystals at various x-ray sources: a Rigaku Oxford Diffraction SuperNova equipped with an Ag K α source, a Rigaku Oxford Diffraction SuperNova equipped with CuK α and CuK β sources, and a Rigaku Oxford Diffraction Synergy DW with CuK α and MoK α rotating anode sources.

Figure 9.5 compares the R1, wR2, Rint, I/ σ (I), cell volume, and unique reflections for a total of eleven different measurements of two different sucrose single crystals at the in-house diffractometers of the University of Regensburg.

9.4.2 Multitemperature experiments

To demonstrate the application of SISYPHOS for serial measurements, we investigated the well-known YLID^{6,28} structure at temperatures ranging from 250 to 110 K in 20 K increments as a small test case. Figure 9.3 displays selected parameters of the crystal structures as generated by CrysAlisPro automatic data reduction routine. As expected, quality indicators exhibit a negative correlation with temperature, showing lower residuals at lower temperatures due to reduced atomic motion.

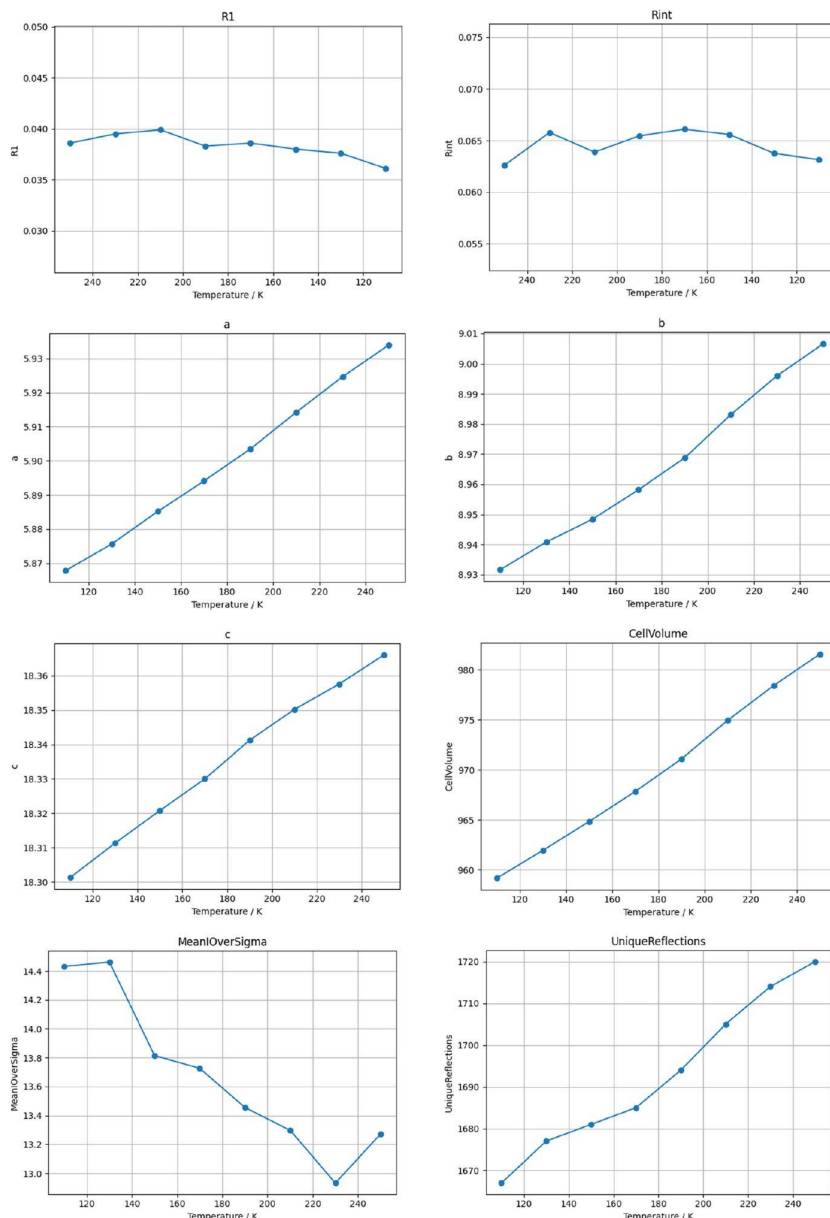


Figure 9.3: Selected data for the multi-temperature run of YLID from the SISYPHOS output.csv file. Plots were created by a simple Python script employing the Pandas²⁹ and Matplotlib³⁰ modules.

For the same reason, the signal-to-noise ratio increases with lower temperatures. All three cell dimensions increase with rising temperature, also resulting in more unique reflections based on the larger cell volume at a fixed wavelength. The steady R_{int} statistics indicate

a low dependency of the agreement of systematically equivalent reflections at different temperatures.

For this dataset, all data processing and refinement steps, except for the initial model, were automated using CrysAlisPro (data processing, reduction, and multi-scan absorption correction) and SISYPHOS (model refinement and information extraction). This way, the required manual software interaction time for creating this data series was drastically reduced, allowing the processing to be performed unsupervised. The last refinement shift in the output.csv file also gives an overview of model convergence.

9.4.3 Anomalous dispersion refinements

Resonant single-crystal diffraction is a powerful technique that allows probing spatially resolved x-ray absorption spectra of crystalline materials. The chemical applications as well as the crystallographic implications can be found in a variety of publications by the Betley and Chen groups, who pioneered this field for the single-crystal community using data from the APS synchrotron facility.^{31–33} We recently reported on the implementation of ADR in Olex2 and the effect of using tabulated values for AD in the vicinity of absorption edges,¹⁸ as well as structural improvements by ADR for heavy element structures.^{34,35}

SISYPHOS can be used to efficiently evaluate resonant diffraction data, e.g., from a serial synchrotron experiment. For example, see Refs. 18 and 34, where the program was used to efficiently analyze a large amount of synchrotron datasets measured at the Rossendorf Beamline at the ESRF.³⁶

9.4.4 Quantum crystallographic benchmarking

Quantum Crystallography is at the forefront of analyzing and understanding diffraction data.³⁰ The independent atom model has been the default model for structural refinement over the last 50 years.³⁷ With the advance of new x-ray generation and detection technologies, its inadequacies become more and more obvious. With NoSpherA2, there is already a powerful tool to make the Hirshfeld Atom Refinement available for daily use, and, by being able to employ the state-of-the-art quantum chemical program ORCA,^{19–22} it can be performed faster than ever. SISYPHOS fully supports the use of NoSpherA2, to enable efficient serial quantum crystallographic analyses.

Using the example of the Olex2 shipped structure "SuperSugar," the application of SISYPHOS for quantum crystallographic benchmarking is evaluated. For this, a single structure is chosen, alongside the "Benchmark file," which contains the desired settings for the quantum chemical calculation conducted by NoSpherA2 and the ORCA software suite. For this assessment, the Hartree-Fock (HF) method was compared to density functionals of various levels of accuracy on Jacobs ladder: PBE, PBE0, B3LYP, and r2SCAN.^{38–40} They were applied during an HAR procedure within NoSpherA2, employing ORCA5 for the underlying quantum chemical calculation using either only the split-valence or the triple-zeta Ahlrichs basis sets def2-SVP or def2-TZVP, respectively.⁴¹ For comparison, SISYPHOS also generates the results from the independent atom model (IAM). This allows for convenient benchmarking of the shown (see Sec. S3 for more details) settings options for performing a HAR.

Figure 9.4 shows selected model indicators for each of the IAM and HAR models of the "SuperSugar" sucrose dataset.

As expected, every HAR model surpassed the quality indicators of the IAM. The differences between the HAR models show a clear preference for the triple-zeta basis sets compared to the split-valence ones. For functionals, the meta-GGA r2SCAN performed best in terms of R1, wR2, and negative residual density peaks, while, surprisingly, HF, together with B3LYP, had the lowest positive residual electron density.

A more thorough testing of the various settings for HAR is explored in another paper within this special issue.⁴²

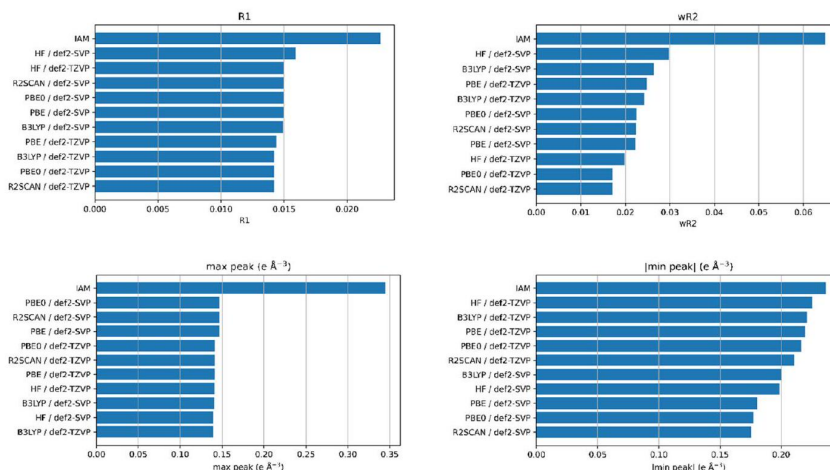


Figure 9.4: Quality indicators of the IAM and HAR models created by SISYPHOS employing ORCA and NoSpherA2 on the Olex2 internal "SuperSugar" dataset.

In summary, SISYPHOS was used to successively refine several thousand models by varying the level of theory underlying the quantum chemical calculations. This approach allowed them to obtain information about the performance of the various NoSpherA2 settings, as illustrated in Figure 9.4. The authors discussed trends regarding the different parameters and noted that even DFT methods that do not belong to the highest class of functionals, such as the aforementioned R2SCAN, can produce decent refinement outcomes. The refinement results were then evaluated using classical crystallographic indicators such as R1 and wR2, as well as the position of hydrogen atoms relative to neutron reference structures. A SISYPHOS run provides the necessary parameters for all of this, enabling the results to be extracted using lightweight Python scripts. As executing several thousand refinements successively in a reasonable time frame on a single computer is hardly achievable, a SISYPHOS run can also be parallelized using subprocesses and a headless version of Olex2. Therefore, an initial generated set of method files from predefined parameter sets can be distributed on independent Olex2 headless executions across multiple CPU cores. This procedure can also be transferred to the cluster capacities offered by high-performance computing facilities. By distributing the method files across an array of jobs via a batch script, automated, high throughput exploration of settings can be enabled with SISYPHOS.

9.4.5 Mixed-position structures

Our final example is the application of SISYPHOS to a crystallization study. The group VI hexacarbonyls $M(CO)_6$ ($M = Cr, Mo, W$) can be co-crystallized from a stoichiometric solution mixture of two or all three of them. To statistically evaluate the reproducibility

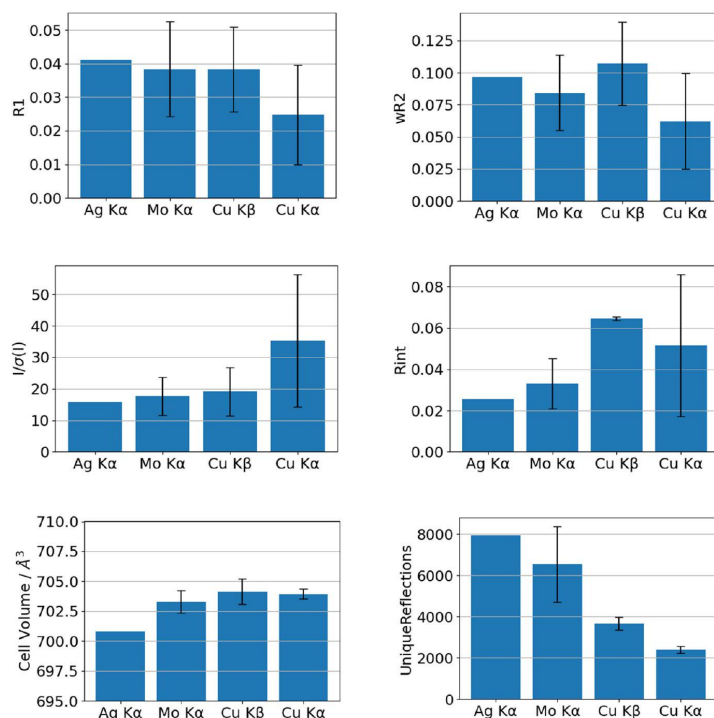


Figure 9.5: Bar diagrams of eleven datasets and crystallographic model indicators as average values for each wavelength, and, where applicable, one standard deviation of two sucrose single crystals measured on different devices of the central analytics x-ray department of the University of Regensburg. Device configuration and further information for each wavelength can be found in Sec. S4 of the supplementary material.

of this crystallization method, eight crystals of a 1:1 stoichiometric mixture of $\text{Cr}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ were measured using a $\text{MoK}\alpha$ rotating anode and modeled using SISYPHOS with an EXYZ and EADP constrained central metal position and freely refined occupancy of the metal position, constrained to add up to 1. Table 9.1 shows the results of these datasets, making it easy to spot outliers (such as Nr. 6) and calculate statistical indicators for larger datasets (such as mean, median, accuracy).

9.5 Conclusion

In this work, we introduced the Olex2 plugin SISYPHOS and demonstrated the applications it was designed to address. SISYPHOS can be used to refine a structural model against several datasets of the same structure or refine different modeling approaches for the same dataset, collecting the model and data information in the .csv format. The applications for crystal screening, benchmarking quantum crystallography, anomalous dispersion refinements, multitemperature studies, as well as crystallization studies were described.

Table 9.1: Agreement statistic R1 of measured and modeled structure factors and the refined occupancies [Occu(Cr/W)] for Cr and W at the central metal position. Nr. 9 and Nr. 8 are data from the same crystal (with 10 and 7, respectively), using different data processing strategies.

Nr	R1	Occu(Cr)	Occu(W)
1	0.0135	0.495	0.505
2	0.0195	0.496	0.504
3	0.0124	0.467	0.533
4	0.0192	0.466	0.534
5	0.0231	0.454	0.546
6	0.0697	0.448	0.552
7	0.0128	0.472	0.528
8	0.0127	0.472	0.528
9	0.0161	0.504	0.496
10	0.0166	0.504	0.496
Avg.	0.0216	0.4778	0.5222
SD	0.0164	0.0194	0.0194

9.6 References

- ¹ W. R. Gray, "A new hot cathode tube with rotating anode," Br. J. Radiol. 3(28), 171-177 (1930).
- ² C. Broennimann, E. F. Eikenberry, B. Henrich, R. Horisberger, G. Huelsen, E. Pohl, B. Schmitt, C. Schulze-Briesse, M. Suzuki, T. Tomizaki, H. Toyokawa, and A. Wagner, "The PILATUS 1M detector," J. Synchrotron Rad. 13(2), 120-130 (2006).
- ³ C. Gemme, "The ATLAS pixel detector," Nucl. Instrum. Methods Phys. Res., Sect. A 501(1), 87-92 (2003).
- ⁴ Rigaku, see <https://rigaku.com/products/crystallography/electron-diffraction/xtalab-synergy-ed> for "XtaLAB Synergy-ED" (Accessed 29 September 2025).
- ⁵ ELDICO, see <https://www.eldico-scientific.com/product/> for "Product - ELDICO Scientific AG" (Accessed 29 September 2025).
- ⁶ N. Graw, P. N. Ruth, T. Ernemann, R. Herbst-Irmer, and D. Stalke, "Indium $K\alpha$ radiation from a MetalJet X-ray source: The long way to a successful charge-density investigation," J. Appl. Crystallogr. 56(5), 1315-1321 (2023).
- ⁷ K. N. Raymond and G. S. Girolami, "Pathological crystal structures," Acta Crystallogr. C 79(11), 445-455 (2023).
- ⁸ A. J. Thompson, K. M. L. Smith, J. K. Clegg, and J. R. Price, "CX-ASAP: A high-throughput tool for the serial refinement and analysis of crystallographic data collected under varying conditions," J. Appl. Crystallogr. 56(Pt 2), 558-564 (2023).
- ⁹ G. M. Sheldrick, "SHELXT - Integrated space-group and crystal-structure determination," Acta Crystallogr. A 71(1), 3-8 (2015).
- ¹⁰ S. C. Capelli, H.-B. Bürgi, B. Dittrich, S. Grabowsky, and D. Jayatilaka, "Hirshfeld atom refinement," IUCrJ 1(5), 361-379 (2014).
- ¹¹ N. K. Hansen and P. Coppens, "Testing aspherical atom refinements on smallmolecule data sets," Acta Crystallogr. A 34(6), 909-921 (1978).
- ¹² W. F. Kuhs, "The anharmonic temperature factor in crystallographic structure analysis," Aust. J. Phys. 41, 369-382 (1988).

- ¹³ H. B. Bürgi, S. C. Capelli, and H. Birkedal, "Anharmonicity in anisotropic displacement parameters," *Acta Crystallogr. A* 56(5), 425-435 (2000).
- ¹⁴ F. Meurer, C. Von Essen, C. Kühn, H. Puschmann, and M. Bodensteiner, "The benefits of CuK β radiation for the single-crystal X-ray structure determination of crystalline sponges," *IUCrJ* 9(3), 349-354 (2022).
- ¹⁵ O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, and H. Puschmann, "OLEX2: A complete structure solution, refinement and analysis program," *J. Appl. Crystallogr.* 42(2), 339-341 (2009).
- ¹⁶ F. Kleemiss, O. V. Dolomanov, M. Bodensteiner, N. Peyerimhoff, L. Midgley, L. J. Bourhis, A. Genoni, L. A. Malaspina, D. Jayatilaka, J. L. Spencer, F. White, B. Grundkötter-Stock, S. Steinhauer, D. Lentz, H. Puschmann, and S. Grabowsky, "Accurate crystal structures and chemical properties from NoSpherA2," *Chem. Sci.* 12(5), 1675-1692 (2021).
- ¹⁷ G. van Rossum and F. L. Drake, *The Python Language Reference*, Release 3.0.1 [Repr.] (Python Software Foundation, Hampton, NH, 2010).
- ¹⁸ F. Meurer, O. V. Dolomanov, C. Hennig, N. Peyerimhoff, F. Kleemiss, H. Puschmann, and M. Bodensteiner, "Refinement of anomalous dispersion correction parameters in single-crystal structure determinations," *IUCrJ* 9(5), 604609 (2022).
- ¹⁹ F. Neese, "An improvement of the resolution of the identity approximation for the formation of the Coulomb matrix," *J. Comput. Chem.* 24(14), 1740-1747 (2003).
- ²⁰ F. Neese, F. Wennmohs, U. Becker, and C. Riplinger, "The ORCA quantum chemistry program package," *J. Chem. Phys.* 152(22), 224108 (2020).
- ²¹ F. Neese, "Software update: The ORCA program system-Version 5.0," *WIREs Comput. Mol. Sci.* 12(5), e1606 (2022).
- ²² F. Neese, "The SHARK integral generation and digestion system," *J. Comput. Chem.* 44(3), 381-396 (2023).
- ²³ F. L. Hirshfeld, "Bonded-atom fragments for describing molecular charge densities," *Theoret. Chim. Acta* 44(2), 129-138 (1977).
- ²⁴ B. L. Henke, P. Lee, T. J. Tanaka, R. L. Shimabukuro, and B. K. Fujikawa, "Low-energy x-ray interaction coefficients: Photoabsorption, scattering, and reflection: $E = 100 - 2000\text{eV}$ $Z = 1 - 94$," *At. Data Nucl. Data Tables* 27(1), 1-144 (1982).
- ²⁵ S. Sasaki, "Numerical tables of anomalous scattering factors calculated by the Cromer and Liberman's method," Report No. KEK-88-14 of the National Laboratory for High Energy Physics, Tsukuba, Ibaraki (1989), p. 137.
- ²⁶ S. Brennan and P. L. Cowan, "A suite of programs for calculating x-ray absorption, reflection, and diffraction performance for a variety of materials at arbitrary wavelengths," *Rev. Sci. Instrum.* 63(1), 850-853 (1992).
- ²⁷ Rigaku Oxford Diffraction Ltd., "CrysAlis PRO" (2025).
- ²⁸ I. A. Guzei, G. A. Bikzhanova, L. C. Spencer, T. V. Timofeeva, T. L. Kinnibrugh, and C. F. Campana, "Polymorphism and history of 2-dimethylsufuranylidene-1,3-indanedione (YLID)," *Cryst. Growth Des.* 8(7), 2411-2418 (2008).
- ²⁹ W. McKinney, "Data structures for statistical computing in python," in *Scipy* (2010).
- ³⁰ J. D. Hunter, "Matplotlib: A 2D graphics environment," *Comput. Sci. Eng.* 9(3), 90-95 (2007).
- ³¹ A. K. Bartholomew, J. J. Teesdale, R. Hernández Sánchez, B. J. Malbrecht, C. E. Juda, G. Ménard, W. Bu, D. A. Iovan, A. A. Mikhailine, S.-L. Zheng, R. Sarangi, S. G. Wang, Y.-S. Chen, and T. A. Betley, "Exposing the inadequacy of redox formalisms by resolving redox inequivalence within isovalent clusters," *Proc. Natl. Acad. Sci. U. S. A.* 116(32),

15836-15841 (2019).

³² A. K. Bartholomew, R. A. Musgrave, K. J. Anderton, C. E. Juda, Y. Dong, W. Bu, S.Y. Wang, Y.-S. Chen, and T. A. Betley, "Revealing redox isomerism in trichromium imides by anomalous diffraction," *Chem. Sci.* 12(47), 15739-15749 (2021).

³³ C. E. Juda, C. E. Casaday, J. J. Teesdale, A. K. Bartholomew, B. Lin, K. M. Carsch, R. A. Musgrave, S.-L. Zheng, X. Wang, C. M. Hoffmann, S. Wang, Y. S. Chen, and T. A. Betley, "Composition determination of heterometallic trinuclear clusters via anomalous x-ray and neutron diffraction," *J. Am. Chem. Soc.* 146, 30320 (2024).

³⁴ F. Meurer, G. Morrison, B. Hischa, H.-C. zur Loye, C. Hennig, and M. Bodensteiner, "Improvement of single-crystal structures of very heavy element compounds by refining anomalous dispersion parameters," *Inorg. Chem.* 63(34), 15784-15790 (2024).

³⁵ G. Leinders, O. G. Grendal, I. Arts, R. Bes, I. Prozheev, S. Orlat, A. Fitch, K. Kvashnina, and M. Verwerft, "Refinement of the uranium dispersion corrections from anomalous diffraction," *J. Appl. Crystallogr.* 57(2), 284 (2024).

³⁶ A. C. Scheinost, J. Claussner, J. Exner, M. Feig, S. Findeisen, C. Hennig, K. O. Kvashnina, D. Naudet, D. Prieur, A. Rossberg, M. Schmidt, C. Qiu, P. Colomp, C. Cohen, E. Dettona, V. Dyadkin, and T. Stumpf, "ROBL-II at ESRF: A synchrotron toolbox for actinide research," *J. Synchrotron Rad.* 28(1), 333-349 (2021).

³⁷ A. H. Compton, "The distribution of the electrons in atoms," *Nature* 95(2378), 343-344 (1915).

³⁸ C. Adamo, M. Cossi, and V. Barone, "An accurate density functional method for the study of magnetic properties: The PBE0 model," *J. Mol. Struct.* 493(1), 145-157 (1999).

³⁹ J. W. Furness, A. D. Kaplan, J. Ning, J. P. Perdew, and J. Sun, "Accurate and numerically efficient r^2 SCAN meta-generalized gradient approximation," *J. Phys. Chem. Lett.* 11(19), 8208-8215 (2020).

⁴⁰ C. Lee, W. Yang, and R. G. Parr, "Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density," *Phys. Rev. B* 37(2), 785-789 (1988).

⁴¹ F. Weigend and R. Ahlrichs, "Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn : Design and assessment of accuracy," *Phys. Chem. Chem. Phys.* 7(18), 3297 (2005).

⁴² D. Brück, F. Meurer, and F. Kleemiss, "Benchmarking crystal structure refinement: A systematic study on Hirshfeld atom refinement," *Struct. Dyn.* 12(5), 054101 (2025).

9.7 Supporting information

The supporting information of this work is provided as a single .pdf file with original format and page numbering starting from the next page.

Supplementary Material

S1 Crystal Screening

Each single crystal chosen for this section were obtained from a package of commercial sugar (sucrose). All experiments were conducted at 100K temperature. The following devices were used for this section:

1. Rigaku XTaLAB Synergy-DW with an Arc150° curved hybrid photon counting detector device and Mo K α and Cu K α sources
2. Rigaku Oxford Diffraction SuperNova with an Atlas S2 CCD detector and Cu K α and Cu K β sources
3. Rigaku Oxford Diffraction SuperNova with an Atlas S2 CCD detector and Mo K α and Ag K α sources

Table S1: Overview of the experiments in section “Crystal Screening”

Name	Device Nr.	Wavelength
F_Zucker_long_GV_Cu_beta_auto	2	Cu K β
F_Zucker_long_GV_Cu_alpha_auto	2	Cu K α
F_Zucker2_MO_Mo_auto	3	Mo K α
F_Zucker2_DW_Mo_auto	1	Mo K α
F_Zucker2_DW_Cu_auto	1	Cu K α
F_Zucker1_MO_Ag_auto	3	Ag K α
F_Zucker1_GV_Cu_beta_auto	2	Cu K β
F_Zucker1_GV_Cu_alpha_auto	2	Cu K α
F_Zucker1_DW_Mo_auto	1	Mo K α
F_Zucker1_DW_Cu_auto	1	Cu K α
F-Zucker1_MO_Mo_auto	3	Mo K α

Table S2: Crystallographic information of F_Zucker_long_GV_Cu_beta_auto

Parameter	Value	Parameter	Value	Parameter	Value
Dataset	F_Zucker_long_GV_Cu_beta_auto	a (Å)	7.72037(6)	b (Å)	8.66673(9)
c (Å)	10.81214(8)	α (°)	90	β (°)	103.0026(8)
γ (°)	90	Volume (Å ³)	704.894(11)	Wavelength (Å)	1.39222
μ (mm ⁻¹)	0.928	GoF	1.0951	Z	2
Z'	1	R1	0.0294	R_int	0.0652173
R $_{\sigma}$	0.03021	wR2	0.0839715	RMS residual (e·Å ⁻³)	0.0427664
Max peak (e·Å ⁻³)	0.246648	Max hole (e·Å ⁻³)	-0.168815	Completeness	0.965543
Total reflections	19836	Unique reflections	3895	Friedel merged	0
Friedel pairs	3064	Datacount	3895	Diis	0.01
F000	365.267	Filemaxindices	(10, 12, 15)	Fileminindices	(-10, -11, -15)
Filteredoff	0	Inconsistentequivalents	26	Intensitytransformed	0
Limdmax	100	Limdmin	0.69611	Maxd	10.5349
Maxindices	(10, 12, 15)	Max Har Cycles	10	Meanioversigma	24.5634
Mind	0.716668	Minindices	(-10, -11, 0)	Nr. Npd	14
Orca Damp	False	Orca Scf Conv	NoSpherA2 SCF	Orca Strategy	Scf NormalConv
Orca Solvation	Vacuum	Omittedbyuser	0	Omittedreflections	0
R1 All	0.0297256	R1 Gt	0.0294294	R All	0.0297
Redundancy	(1333, 2035, 1674, 996, 517, 274, 123, 32, 9)	Reflectionapomax	15	Relativistic	False
Systematicabsencesremoved	27	Weight	True	Basis Name	def2-TZVP
Becke Accuracy	Normal	Charge	0	Cluster Grow	True
Cluster Radius	0	Full Har	False	H Afix	True
H Aniso	True	Hooft Str	0.02(6)	Last Shift	-0.0008
Max Shift Over Esd	-0.000809596	Mem	8	Method	r2SCAN
Multiplicity	1	Ncpus	2	Pyscf Damping	0.6
Tot Reflins	19809				

Table S3: Crystallographic information of F_Zucker_long_GV_Cu_alpha_auto

Parameter	Value	Parameter	Value	Parameter	Value
Dataset	F_Zucker_long_GV_Cu_alpha_auto	a (Å)	7.71431(6)	b (Å)	8.66023(9)
c (Å)	10.80644(8)	α (°)	90	β (°)	103.0004(8)
γ (°)	90	Volume (Å³)	703.449(10)	Wavelength (Å)	1.54184
μ (mm⁻¹)	1.267	GoF	1.1355	Z	2
Z'	1	R1	0.0201	R_int	0.0796949
R_σ	0.0157804	wR2	0.0516963	RMS residual (e·Å⁻³)	0.030539
Max peak (e·Å⁻³)	0.13743	Max hole (e·Å⁻³)	-0.129516	Completeness	0.997202
Total reflections	75437	Unique reflections	2495	Friedel merged	0
Friedel pairs	2298	Datacount	2495	Diis	0.01
F000	365.615	Filemaxindices	(9, 10, 12)	Fileminindices	(-9, -10, -12)
Filteredoff	0	Inconsistentequivalents	26	Intensitytransformed	0
Limdmax	100	Limdmin	0.77092	Maxd	10.5295
Maxindices	(8, 10, 12)	Max Har Cycles	10	Meanoversigma	50.8262
Mind	0.839244	Minindices	(-9, -10, 0)	Nr. Npd	2
Orca Damp	False	Orca Scf Conv	NoSpherA2 SCF	Orca Strategy	Scf NormalConv
Orca Solvation	Vacuum	Omittedbyuser	0	Omittedreflections	0
R1 All	0.0201598	R1 Gt	0.0200974	R All	0.0202
Redundancy	(144, 206, 220, 233, 236, 273, 226, 270, 225, 191, 131, 96, 73, 54, 69, 64, 49, 61, 97, 109, 138, 146, 171, 136, 102, 94, 80, 74, 69, 57, 88, 78, 98, 92, 82, 88, 65, 40, 28, 16, 14, 4, 4, 1)	Reflectionaportmax	75	Relativistic	False
Systematicabsencesremoved	75	Weight	True	Basis Name	def2-TZVP
Becke Accuracy	Normal	Charge	0	Cluster Grow	True
Cluster Radius	0	Full Har	False	H Afix	True
H Aniso	True	Hooft Str	0.06(4)	Last Shift	-0.0006
Max Shift Over Esd	-0.000609784	Mem	8	Method	r2SCAN
Multiplicity	1	Ncpus	2	Pyscf Damping	0.6
Tot Reflins	75362				

Table S4: Crystallographic information of F_Zucker2_MO_Mo_auto

Parameter	Value	Parameter	Value	Parameter	Value
Dataset	F_Zucker2_MO_Mo_auto	a (Å)	7.71854(6)	b (Å)	8.65807(9)
c (Å)	10.81167(8)	α (°)	90	β (°)	102.9731(8)
γ (°)	90	Volume (Å ³)	704.076(11)	Wavelength (Å)	0.71073
μ (mm ⁻¹)	0.144	GoF	1.0604	Z	2
Z'	1	R1	0.0528	R_int	0.0444445
R $_{\sigma}$	0.0718686	wR2	0.1109	RMS residual (e·Å ⁻³)	0.103172
Max peak (e·Å ⁻³)	0.499629	Max hole (e·Å ⁻³)	-0.400873	Completeness	0.798119
Total reflections	14002	Unique reflections	7381	Friedel merged	0
Friedel pairs	3837	Datacount	7381	Diis	0.01
F000	364.337	Filemaxindices	(14, 15, 19)	Fileminindices	(-14, -8, -19)
Filteredoff	0	Inconsistentequivalents	3	Intensitytransformed	0
Limdmax	100	Limdmin	0.355365	Maxd	7.52152
Maxindices	(13, 15, 19)	Max Har Cycles	10	Meanioversigma	10.7389
Mind	0.542134	Minindices	(-14, -8, 0)	Nr. Npd	0
Orca Damp	False	Orca Scf Conv	NoSpherA2SCF	Orca Scf Strategy	NormalConv
Orca Solvation	Vacuum	Omittedbyuser	0	Omittedreflections	0
R All	0.0706	Redundancy	(9456, 2094, 118, 1)	Reflectionapotmax	5
Relativistic	False	Systematicabsencesremoved	11	Weight	True
Basis Name	def2-TZVP	Becke Accuracy	Normal	Charge	0
Cluster Grow	True	Cluster Radius	0	Full Har	False
H Afix	True	H Aniso	True	Hoof Str	-0.5(5)
Last Shift	-3.7498	Max Shift Over Esd	-3.74977	Mem	8
Method	r2SCAN	Multiplicity	1	Ncpus	2
Pyscf Damping	0.6	Tot Reflins	13991		

Table S5: Crystallographic information of F_Zucker2_DW_Mo_auto

Parameter	Value	Parameter	Value	Parameter	Value
Dataset	F_Zucker2_DW_Mo_auto	a (Å)	7.71039(6)	b (Å)	8.65700(9)
c (Å)	10.80319(8)	α (°)	90	β (°)	102.9702(8)
γ (°)	90	Volume (Å ³)	702.703(10)	Wavelength (Å)	0.71073
μ (mm ⁻¹)	0.145	GoF	1.0199	Z	2
Z'	1	R1	0.0404	R_int	0.0373125
R $_{\sigma}$	0.0493553	wR2	0.0904	RMS residual (e·Å ⁻³)	0.0789935
Max peak (e·Å ⁻³)	0.439959	Max hole (e·Å ⁻³)	-0.273617	Completeness	0.825754
Total reflections	17477	Unique reflections	6246	Friedel merged	0
Friedel pairs	3461	Datacount	6246	Diis	0.01
F000	364.337	Filemaxindices	(12, 13, 16)	Fileminindices	(-13, -14, -18)
Filteredoff	0	Inconsistentequivalents	0	Intensitytransformed	0
Limdmax	100	Limdmin	0.355365	Maxd	8.657
Maxindices	(12, 13, 18)	Max Har Cycles	10	Meanioversigma	17.243
Mind	0.579527	Minindices	(-13, -14, 0)	Nr. Npd	0
Orca Damp	False	Orca Scf Conv	NoSpherA2SCF	Orca Scf Strategy	NormalConv
Orca Solvation	Vacuum	Omittedbyuser	0	Omittedreflections	0
R All	0.0525	Redundancy	(3913, 3121, 1434, 472, 188, 32)	Reflectionapotmax	9
Relativistic	False	Systematicabsencesremoved	28	Weight	True
Basis Name	def2-TZVP	Becke Accuracy	Normal	Charge	0
Cluster Grow	True	Cluster Radius	0	Full Har	False
H Afix	True	H Aniso	True	Hooft Str	0.3(3)
Last Shift	-7.6322	Max Shift Over Esd	-7.63221	Mem	8
Method	r2SCAN	Multiplicity	1	Ncpus	2
Pyscf Damping	0.6	Tot Reflins	17449		

Table S6: Crystallographic information of F_Zucker2_DW_Cu_auto

Parameter	Value	Parameter	Value	Parameter	Value
Dataset	F_Zucker2_DW_Cu_auto	a (Å)	7.71638(6)	b (Å)	8.66549(9)
c (Å)	10.81114(8)	α (°)	90	β (°)	102.9782(8)
γ (°)	90	Volume (Å ³)	704.433(11)	Wavelength (Å)	1.54184
μ (mm ⁻¹)	1.265	GoF	1.3343	Z	2
Z'	1	R1	0.0212	R_int	0.0291019
R_ σ	0.0310863	wR2	0.0467017	RMS residual (e·Å ⁻³)	0.029822
Max peak (e·Å ⁻³)	0.111161	Max hole (e·Å ⁻³)	-0.127524	Completeness	0.863824
Total reflections	7938	Unique reflections	2512	Friedel merged	0
Friedel pairs	1355	Datacount	2512	Diis	0.01
F000	365.615	Filemaxindices	(9, 10, 13)	Fileminindices	(-9, -10, -13)
Filteredoff	0	Inconsistentequivalents	3	Intensitytransformed	0
Limdmax	100	Limdmin	0.77092	Maxd	10.535
Maxindices	(9, 10, 13)	Max Har Cycles	10	Meanioversigma	23.5261
Mind	0.79821	Minindices	(-9, -10, 0)	Nr. Npd	15
Orca Damp	False	Orca Scf Conv	NoSpherA2S CF	Orca Scf Strategy	NormalConv
Orca Solvation	Vacuum	Omittedbyuser	0	Omittedreflections	0
R1 All	0.0230137	R1 Gt	0.0211942	R All	0.023
Redundancy	(1737, 1100, 581, 346, 110, 37, 10, 4)	Reflectionapotmax	12	Relativistic	False
Systematicabsencesremoved	18	Weight	True	Basis Name	def2-TZVP
Becke Accuracy	Normal	Charge	0	Cluster Grow	True
Cluster Radius	0	Full Har	False	H Afix	True
H Aniso	True	Hooft Str	0.19(9)	Last Shift	0.0308
Max Shift Over Esd	0.0307713	Mem	8	Method	r2SCAN
Multiplicity	1	Ncpus	2	Pyscf Damping	0.6
Tot Reflins	7920				

Table S7: Crystallographic information of F_Zucker1_MO_Ag_auto

Parameter	Value	Parameter	Value	Parameter	Value
Dataset	F_Zucker1_MO_Ag_auto	a (Å)	7.70467(6)	b (Å)	8.65050(9)
c (Å)	10.79200(8)	α (°)	90	β (°)	103.0095(8)
γ (°)	90	Volume (Å ³)	700.817(10)	Wavelength (Å)	0.56087
μ (mm ⁻¹)	0.087	GoF	1.053	Z	2
Z'	1	R1	0.041	R_int	0.0253828
R _{σ}	0.0465378	wR2	0.0967	RMS residual (e ⁻ Å ⁻³)	0.0750581
Max peak (e ⁻ Å ⁻³)	0.394249	Max hole (e ⁻ Å ⁻³)	-0.254217	Completeness	0.741107
Total reflections	14907	Unique reflections	7938	Friedel merged	0
Friedel pairs	2522	Datacount	7938	Diis	0.01
F000	364.159	Filemaxindices	(12, 12, 20)	Fileminindices	(-14, -16, -20)
Filteredoff	0	Inconsistentequivalents	0	Intensitytransformed	0
Limdmax	100	Limdmin	0.280435	Maxd	6.88661
Maxindices	(13, 12, 20)	Max Har Cycles	10	Meanioversigma	15.8587
Mind	0.515508	Minindices	(-14, -16, 0)	Nr. Npd	0
Orca Damp	False	Orca Scf Conv	NoSpherA2SCF	Orca Scf Strategy	NormalConv
Orca Solvation	Vacuum	Omittedbyuser	0	Omittedreflections	0
R All	0.0489	Redundancy	(6881, 2935, 631, 57, 7)	Reflectionapotmax	9
Relativistic	False	Systematicabsencesremoved	9	Weight	True
Basis Name	def2-TZVP	Becke Accuracy	Normal	Charge	0
Cluster Grow	True	Cluster Radius	0	Full Har	False
H Afix	True	H Aniso	True	Hoof Str	0.2(4)
Last Shift	-7.8774	Max Shift Over Esd	-7.87739	Mem	8
Method	r2SCAN	Multiplicity	1	Ncpus	2
Pyscf Damping	0.6	Tot Reflins	14898		

Table S8: Crystallographic information of F_Zucker1_GV_Cu_beta_auto

Parameter	Value	Parameter	Value	Parameter	Value
Dataset	F_Zucker1_GV_Cu_beta_auto	a (Å)	7.71280(6)	b (Å)	8.65985(9)
c (Å)	10.80659(8)	α (°)	90	β (°)	102.9577(8)
γ (°)	90	Volume (Å ³)	703.411(10)	Wavelength (Å)	1.39222
μ (mm ⁻¹)	0.93	GoF	1.0715	Z	2
Z'	1	R1	0.0472	R_int	0.0639284
R $_{\sigma}$	0.0607562	wR2	0.129929	RMS residual (e·Å ⁻³)	0.0643111
Max peak (e·Å ⁻³)	0.288072	Max hole (e·Å ⁻³)	-0.300157	Completeness	0.860529
Total reflections	6783	Unique reflections	3449	Friedel merged	0
Friedel pairs	720	Datacount	3449	Diis	0.01
F000	365.267	Filemaxindices	(9, 12, 15)	Fileminindices	(-10, -11, -11)
Filteredoff	0	Inconsistentequivalents	33	Intensitytransformed	0
Limdmax	100	Limdmin	0.69611	Maxd	10.5314
Maxindices	(10, 12, 15)	Max Har Cycles	10	Meanioversigma	13.6396
Mind	0.717149	Minindices	(-10, -11, 0)	Nr. Npd	17
Orca Damp	False	Orca Scf Conv	NoSpherA2S CF	Orca Strategy	Scf NormalConv
Orca Solvation	Vacuum	Omittedbyuser	0	Omittedreflections	0
R1 All	0.0478715	R1 Gt	0.0472143	R All	0.0479
Redundancy	(2316, 1263, 362, 127, 44, 20, 1)	Reflectionapotmax	7	Relativistic	False
Systematicabsencesremoved	9	Weight	True	Basis Name	def2-TZVP
Becke Accuracy	Normal	Charge	0	Cluster Grow	True
Cluster Radius	0	Full Har	False	H Afix	True
H Aniso	True	Hooft Str	-0.07(15)	Last Shift	0.0023
Max Shift Over Esd	0.00228012	Mem	8	Method	r2SCAN
Multiplicity	1	Ncpus	2	Pyscf Damping	0.6
Tot Reflins	6774				

Table S9: Crystallographic information of F_Zucker1_GV_Cu_alpha_auto

Parameter	Value	Parameter	Value	Parameter	Value
Dataset	F_Zucker1_GV_Cu_alpha_auto	a (Å)	7.71308(6)	b (Å)	8.66152(9)
c (Å)	10.80960(8)	α (°)	90	β (°)	102.9481(8)
γ (°)	90	Volume (Å ³)	703.795(10)	Wavelength (Å)	1.54184
μ (mm ⁻¹)	1.266	GoF	1.0707	Z	2
Z'	1	R1	0.0461	R_int	0.0820446
R $_{\sigma}$	0.0690598	wR2	0.117085	RMS residual (e·Å ⁻³)	0.0740435
Max peak (e·Å ⁻³)	0.25582	Max hole (e·Å ⁻³)	-0.311709	Completeness	0.863818
Total reflections	6227	Unique reflections	2163	Friedel merged	0
Friedel pairs	709	Datacount	2163	Diis	0.01
F000	365.615	Filemaxindices	(9, 10, 9)	Fileminindices	(-9, -10, -12)
Filteredoff	0	Inconsistentequivalents	9	Intensitytransformed	0
Limdmax	100	Limdmin	0.77092	Maxd	10.5347
Maxindices	(8, 10, 12)	Max Har Cycles	10	Meanioversigma	11.8971
Mind	0.838884	Minindices	(-9, -10, 0)	Nr. Npd	26
Orca Damp	False	Orca Scf Conv	NoSpherA2S CF	Orca Strategy	Scf NormalConv
Orca Solvation	Vacuum	Omittedbyuser	0	Omittedreflections	0
R1 All	0.0531586	R1 Gt	0.0461385	R All	0.0531
Redundancy	(1408, 796, 343, 150, 99, 65, 37, 35, 16, 3)	Reflectionapotmax	10	Relativistic	False
Systematicabsencesremoved	7	Weight	True	Basis Name	def2-TZVP
Becke Accuracy	Normal	Charge	0	Cluster Grow	True
Cluster Radius	0	Full Har	False	H Afix	True
H Aniso	True	Hoofst Str	-0.2(2)	Last Shift	1.176
Max Shift Over Esd	1.17596	Mem	8	Method	r2SCAN
Multiplicity	1	Ncpus	2	Pyscf Damping	0.6
Tot Reflins	6220				

Table S10: Crystallographic information of F_Zucker1_DW_Mo_auto

Parameter	Value	Parameter	Value	Parameter	Value
Dataset	F_Zucker1_DW_Mo_auto	a (Å)	7.70736(6)	b (Å)	8.65458(9)
c (Å)	10.80400(8)	α (°)	90	β (°)	102.9793(8)
γ (°)	90	Volume (Å ³)	702.257(10)	Wavelength (Å)	0.71073
μ (mm ⁻¹)	0.145	GoF	1.024	Z	2
Z'	1	R1	0.0415	R_int	0.0344061
R $_{\sigma}$	0.0491644	wR2	0.0936	RMS residual (e·Å ⁻³)	0.0791129
Max peak (e·Å ⁻³)	0.516944	Max hole (e·Å ⁻³)	-0.312835	Completeness	0.927301
Total reflections	25265	Unique reflections	8393	Friedel merged	0
Friedel pairs	4513	Datacount	8393	Diis	0.01
F000	364.337	Filemaxindices	(13, 15, 16)	Fileminindices	(-13, -15, -19)
Filteredoff	0	Inconsistentequivalents	0	Intensitytransformed	0
Limdmax	100	Limdmin	0.355365	Maxd	8.65458
Maxindices	(13, 15, 19)	Max Har Cycles	10	Meanioversigma	17.1551
Mind	0.545665	Minindices	(-13, -15, 0)	Nr. Npd	0
Orca Damp	False	Orca Scf Conv	NoSpherA2SCF	Orca Scf Strategy	NormalConv
Orca Solvation	Vacuum	Omittedbyuser	0	Omittedreflections	0
R All	0.0521	Redundancy	(5537, 3428, 1814, 1141, 434, 102, 12)	Reflectionapotmax	11
Relativistic	False	Systematicabsencesremoved	26	Weight	True
Basis Name	def2-TZVP	Becke Accuracy	Normal	Charge	0
Cluster Grow	True	Cluster Radius	0	Full Har	False
H Afix	True	H Aniso	True	Hooft Str	-0.5(2)
Last Shift	-7.1943	Max Shift Over Esd	-7.19434	Mem	8
Method	r2SCAN	Multiplicity	1	Ncpus	2
Pyscf Damping	0.6	Tot Reflins	25239		

Table S11: Crystallographic information of F_Zucker1_DW_Cu_auto

Parameter	Value	Parameter	Value	Parameter	Value
Dataset	F_Zucker1_DW_Cu_auto	a (Å)	7.71400(6)	b (Å)	8.66486(9)
c (Å)	10.81035(8)	α (°)	90	β (°)	102.9683(8)
γ (°)	90	Volume (Å ³)	704.143(11)	Wavelength (Å)	1.54184
μ (mm ⁻¹)	1.265	GoF	0.9811	Z	2
Z'	1	R1	0.0118	R_int	0.0152184
R _{σ}	0.0141109	wR2	0.0334328	RMS residual (e·Å ⁻³)	0.0214273
Max peak (e·Å ⁻³)	0.0792047	Max hole (e·Å ⁻³)	-0.0841425	Completeness	0.86721
Total reflections	7713	Unique reflections	2449	Friedel merged	0
Friedel pairs	855	Datacount	2449	Diis	0.01
F000	365.615	Filemaxindices	(9, 10, 10)	Fileminindices	(-9, -10, -13)
Filteredoff	0	Inconsistentequivalents	4	Intensitytransformed	0
Limdmax	100	Limdmin	0.77092	Maxd	10.5346
Maxindices	(9, 10, 13)	Max Har Cycles	10	Meanoversigma	55.1956
Mind	0.805724	Minindices	(-9, -10, 0)	Nr. Npd	6
Orca Damp	False	Orca Scf Conv	NoSpherA2S CF	Orca Scf Strategy	NormalConv
Orca Solvation	Vacuum	Omittedbyuser	0	Omittedreflections	0
R1 All	0.012332	R1 Gt	0.0117607	R All	0.0123
Redundancy	(1283, 972, 404, 324, 172, 64, 36, 26, 15, 6, 6, 0, 1)	Reflectionapotmax	15	Relativistic	False
Systematicabsencesremoved	10	Weight	True	Basis Name	def2-TZVP
Becke Accuracy	Normal	Charge	0	Cluster Grow	True
Cluster Radius	0	Full Har	False	H Afix	True
H Aniso	True	Hooft Str	0.21(4)	Last Shift	-0.0005
Max Shift Over Esd	-0.000477065	Mem	8	Method	r2SCAN
Multiplicity	1	Ncpus	2	Pyscf Damping	0.6
Tot Reflins	7703				

Table S12: Crystallographic information of F-Zucker1_MO_Mo_auto

Parameter	Value	Parameter	Value	Parameter	Value
Dataset	F-Zucker1_MO_Mo_auto	a (Å)	7.71651(6)	b (Å)	8.66456(9)
c (Å)	10.80648(8)	α (°)	90	β (°)	102.9633(8)
γ (°)	90	Volume (Å ³)	704.108(11)	Wavelength (Å)	0.71073
μ (mm ⁻¹)	0.144	GoF	1.0832	Z	2
Z'	1	R1	0.019	R_int	0.0160189
R $_{\sigma}$	0.0276254	wR2	0.0421848	RMS residual (e·Å ⁻³)	0.0323209
Max peak (e·Å ⁻³)	0.159634	Max hole (e·Å ⁻³)	-0.127868	Completeness	0.798484
Total reflections	7152	Unique reflections	4109	Friedel merged	0
Friedel pairs	1420	Datacount	4109	Diis	0.01
F000	364.337	Filemaxindices	(11, 13, 15)	Fileminindices	(-10, -11, -16)
Filteredoff	0	Inconsistentequivalents	2	Intensitytransformed	0
Limdmax	100	Limdmin	0.355365	Maxd	7.51984
Maxindices	(11, 13, 16)	Max Har Cycles	10	Meanioversigma	25.4559
Mind	0.659312	Minindices	(-11, -11, 0)	Nr. Npd	7
Orca Damp	False	Orca Scf Conv	NoSpherA2S CF	Orca Scf Strategy	NormalConv
Orca Solvation	Vacuum	Omittedbyuser	0	Omittedreflections	0
R1 All	0.0200219	R1 Gt	0.0190117	R All	0.02
Redundancy	(4119, 1187, 176, 29, 3)	Reflectionapotmax	7	Relativistic	False
Systematicabsencesremoved	3	Weight	True	Basis Name	def2-TZVP
Becke Accuracy	Normal	Charge	0	Cluster Grow	True
Cluster Radius	0	Full Har	False	H Afix	True
H Aniso	True	Hooft Str	0.4(3)	Last Shift	-0.0006
Max Shift Over Esd	-0.000558635	Mem	8	Method	r2SCAN
Multiplicity	1	Ncpus	2	Pyscf Damping	0.6
Tot Reflins	7149				

S2 Multitemperature Experiments

Each suitable YLID calibration single crystal was chosen for this section. All experiments were performed on device Nr. 2 using Cu K α radiation. The experiment temperatures are as follows:

Table S13: Overview of the experiments in section “Crystal Screening”

Name	Temperature (K)
ylid_multitempm_8_110_00_auto	110
ylid_multitempm_8_130_00_auto	130
ylid_multitempm_8_150_00_auto	150
ylid_multitempm_8_170_00_auto	170
ylid_multitempm_8_190_00_auto	190
ylid_multitempm_8_210_00_auto	210
ylid_multitempm_8_230_00_auto	230
ylid_multitempm_8_250_00_auto	250

Table S14: Crystallographic information of ylid_multitepm_8_110_00_auto

Parameter	Value	Parameter	Value	Parameter	Value
Dataset	ylid_multitepm_8_110_00_auto	a (Å)	5.8678(3)	b (Å)	8.9316(4)
c (Å)	18.3013(8)	α (°)	90	β (°)	90
γ (°)	90	Volume (Å ³)	959.15(8)	Wavelength (Å)	1.54184
μ (mm ⁻¹)	2.742	GoF	1.0726	Z	4
Z'	1	R1	0.0361	R_int	0.0631286
R $_{\sigma}$	0.0559487	wR2	0.0933	RMS residual (e·Å ⁻³)	0.0607982
Max peak (e·Å ⁻³)	0.25259	Max hole (e·Å ⁻³)	-0.331993	Completeness	0.989318
Total reflections	5375	Unique reflections	1667	Friedel merged	0
Friedel pairs	772	Datacount	1667	F000	434.643
Filemaxindices	(6, 9, 20)	Fileminindices	(-6, -10, -21)	Filteredoff	0
Inconsistentequivalents	0	Intensitytransformed	0	Limdmax	100
Limdmin	0.77092	Maxd	9.15063	Maxindices	(6, 10, 21)
Meanioversigma	14.4315	Mind	0.839588	Minindices	(-6, 0, 0)
Nr. Npd	0	Omittedbyuser	0	Omittedreflections	0
R All	0.0381	Redundancy	(2163, 971, 286, 84, 14, 1)	Reflectionapotmax	10
Systematicabsencesremoved	31	Weight	True	Hooft Str	0.022(17)
Last Shift	0.0004	Max Shift Over Esd	0.000363975	Tot Reflins	5344

Table S15: Crystallographic information of ylid_multitepm_7_130_00_auto

Parameter	Value	Parameter	Value	Parameter	Value
Dataset	ylid_multitepm_7_130_00_auto	a (Å)	5.8756(3)	b (Å)	8.9408(4)
c (Å)	18.3113(8)	α (°)	90	β (°)	90
γ (°)	90	Volume (Å ³)	961.94(8)	Wavelength (Å)	1.54184
μ (mm ⁻¹)	2.734	GoF	1.0492	Z	4
Z'	1	R1	0.0376	R_int	0.0637462
R $_{\sigma}$	0.0528091	wR2	0.0991	RMS residual (e·Å ⁻³)	0.0629118
Max peak (e·Å ⁻³)	0.20973	Max hole (e·Å ⁻³)	-0.367986	Completeness	0.990549
Total reflections	5373	Unique reflections	1677	Friedel merged	0
Friedel pairs	770	Datacount	1677	F000	434.643
Filemaxindices	(7, 9, 20)	Fileminindices	(-6, -10, -21)	Filteredoff	0
Inconsistentequivalents	3	Intensitytransformed	0	Limdmax	100
Limdmin	0.77092	Maxd	9.15566	Maxindices	(6, 10, 21)
Meanioversigma	14.4624	Mind	0.83937	Minindices	(-6, 0, 0)
Nr. Npd	0	Omittedbyuser	0	Omittedreflections	0
R All	0.0393	Redundancy	(2165, 977, 280, 82, 16, 1)	Reflectionapotmax	10
Systematicabsencesremoved	32	Weight	True	Hooft Str	0.018(18)
Last Shift	0.0006	Max Shift Over Esd	0.000569433	Tot Reflins	5341

Table S16: Crystallographic information of ylid_multitepm_6_150_00_auto

Parameter	Value	Parameter	Value	Parameter	Value
Dataset	ylid_multitepm_6_150_00_auto	a (Å)	5.8852(3)	b (Å)	8.9484(4)
c (Å)	18.3208(8)	α (°)	90	β (°)	90
γ (°)	90	Volume (Å ³)	964.83(8)	Wavelength (Å)	1.54184
μ (mm ⁻¹)	2.726	GoF	1.0567	Z	4
Z'	1	R1	0.038	R_int	0.0655807
R $_{\sigma}$	0.0571131	wR2	0.0992	RMS residual (e·Å ⁻³)	0.0612675
Max peak (e·Å ⁻³)	0.239119	Max hole (e·Å ⁻³)	-0.34754	Completeness	0.986502
Total reflections	5405	Unique reflections	1681	Friedel merged	0
Friedel pairs	772	Datacount	1681	F000	434.643
Filemaxindices	(7, 9, 20)	Fileminindices	(-6, -10, -21)	Filteredoff	0
Inconsistentequivalents	0	Intensitytransformed	0	Limdmax	100
Limdmin	0.77092	Maxd	9.16038	Maxindices	(7, 10, 21)
Meanioversigma	13.8153	Mind	0.839299	Minindices	(-6, 0, 0)
Nr. Npd	0	Omittedbyuser	0	Omittedreflections	0
R All	0.0398	Redundancy	(2174, 964, 298, 77, 19, 1)	Reflectionapotmax	10
Systematicabsencesremoved	32	Weight	True	Hooft Str	0.013(18)
Last Shift	-0.0002	Max Shift Over Esd	-0.000158852	Tot Reflins	5373

Table S17: Crystallographic information of ylid_multitepm_5_170_00_auto

Parameter	Value	Parameter	Value	Parameter	Value
Dataset	ylid_multitepm_5_170_00_a uto	a (Å)	5.8941(3)	b (Å)	8.9582(4)
c (Å)	18.3300(8)	α (°)	90	β (°)	90
γ (°)	90	Volume (Å ³)	967.84(8)	Wavelength (Å)	1.54184
μ (mm ⁻¹)	2.717	GoF	1.0625	Z	4
Z'	1	R1	0.0386	R_int	0.066086 2
R $_{\sigma}$	0.0557729	wR2	0.099	RMS residual (e·Å ⁻³)	0.060364 2
Max peak (e·Å ⁻³)	0.219788	Max hole (e·Å ⁻³)	-0.28602	Completeness	0.990012
Total reflections	5395	Unique reflections	1685	Friedel merged	0
Friedel pairs	776	Datacount	1685	F000	434.643
Filemaxindices	(7, 9, 20)	Fileminindices	(-6, -10, -21)	Filteredoff	0
Inconsistentequivalents	1	Intensitytransform ed	0	Limdmax	100
Limdmin	0.77092	Maxd	9.16501	Maxindices	(7, 10, 21)
Meanioversigma	13.7268	Mind	0.84015 9	Minindices	(-6, 0, 0)
Nr. Npd	0	Omittedbyuser	0	Omittedreflectio ns	0
R All	0.0404	Redundancy	(2199, 964, 293, 77, 15, 1)	Reflectionapotm ax	10
Systematicabsencesremo ved	30	Weight	True	Hoofst Str	0.024(18)
Last Shift	0.0001	Max Shift Over Esd	5.46158 e-05	Tot Reflins	5365

Table S18: Crystallographic information of ylid_multitepm_4_190_00_auto

Parameter	Value	Parameter	Value	Parameter	Value
Dataset	ylid_multitepm_4_190_00_auto	a (Å)	5.9034(3)	b (Å)	8.9687(4)
c (Å)	18.3412(8)	α (°)	90	β (°)	90
γ (°)	90	Volume (Å ³)	971.09(8)	Wavelength (Å)	1.54184
μ (mm ⁻¹)	2.708	GoF	1.0681	Z	4
Z'	1	R1	0.0383	R_int	0.0654506
R $_{\sigma}$	0.0569449	wR2	0.1003	RMS residual (e·Å ⁻³)	0.0584412
Max peak (e·Å ⁻³)	0.219842	Max hole (e·Å ⁻³)	-0.256389	Completeness	0.988331
Total reflections	5424	Unique reflections	1694	Friedel merged	0
Friedel pairs	784	Datacount	1694	F000	434.643
Filemaxindices	(7, 9, 20)	Fileminindices	(-6, -10, -21)	Filteredoff	0
Inconsistentequivalents	1	Intensitytransformed	0	Limdmax	100
Limdmin	0.77092	Maxd	9.1706	Maxindices	(7, 10, 21)
Meanioversigma	13.4554	Mind	0.839582	Minindices	(-6, 0, 0)
Nr. Npd	0	Omittedbyuser	0	Omittedreflections	0
R All	0.0406	Redundancy	(2210, 959, 302, 76, 16, 1)	Reflectionapotmax	10
Systematicabsencesremoved	32	Weight	True	Hooft Str	0.001(18)
Last Shift	-0.0001	Max Shift Over Esd	-0.000110607	Tot Reflins	5392

Table S19: Crystallographic information of ylid_multitepm_3_210_00_auto

Parameter	Value	Parameter	Value	Parameter	Value
Dataset	ylid_multitepm_3_210_00_auto	a (Å)	5.9143(3)	b (Å)	8.9831(4)
c (Å)	18.3502(8)	α (°)	90	β (°)	90
γ (°)	90	Volume (Å ³)	974.93(8)	Wavelength (Å)	1.54184
μ (mm ⁻¹)	2.698	GoF	1.0544	Z	4
Z'	1	R1	0.0399	R_int	0.0638732
R $_{\sigma}$	0.0545126	wR2	0.1049	RMS residual (e·Å ⁻³)	0.0587645
Max peak (e·Å ⁻³)	0.211432	Max hole (e·Å ⁻³)	-0.277484	Completeness	0.98669
Total reflections	5469	Unique reflections	1705	Friedel merged	0
Friedel pairs	802	Datacount	1705	F000	434.643
Filemaxindices	(7, 10, 21)	Fileminindices	(-6, -9, -21)	Filteredoff	0
Inconsistentequivalents	0	Intensitytransformed	0	Limdmax	100
Limdmin	0.77092	Maxd	9.1751	Maxindices	(7, 10, 21)
Meanioversigma	13.2969	Mind	0.838831	Minindices	(-6, 0, 0)
Nr. Npd	0	Omittedbyuser	0	Omittedreflections	0
R All	0.0428	Redundancy	(2240, 968, 296, 81, 15, 1)	Reflectionapotmax	10
Systematicabsencesremoved	31	Weight	True	Hooft Str	0.005(19)
Last Shift	0.0008	Max Shift Over Esd	0.000796237	Tot Reflins	5438

Table S20: Crystallographic information of ylid_multitepm_2_230_00_auto

Parameter	Value	Parameter	Value	Parameter	Value
Dataset	ylid_multitepm_2_230_00_a uto	a (Å)	5.9247(3)	b (Å)	8.9960(4)
c (Å)	18.3576(8)	α (°)	90	β (°)	90
γ (°)	90	Volume (Å ³)	978.43(8)	Wavelength (Å)	1.54184
μ (mm ⁻¹)	2.688	GoF	1.0256	Z	4
Z'	1	R1	0.0395	R_int	0.0657724
R $_{\sigma}$	0.0580049	wR2	0.1005	RMS residual (e·Å ⁻³)	0.0596221
Max peak (e·Å ⁻³)	0.213718	Max hole (e·Å ⁻³)	-0.227774	Completeness	0.991898
Total reflections	5502	Unique reflections	1714	Friedel merged	0
Friedel pairs	805	Datacount	1714	F000	434.643
Filemaxindices	(7, 10, 21)	Fileminindices	(-6, -9, -21)	Filteredoff	0
Inconsistentequivalents	0	Intensitytransformed	0	Limdmax	100
Limdmin	0.77092	Maxd	9.17879	Maxindices	(7, 10, 21)
Meanioversigma	12.9335	Mind	0.839237	Minindices	(-6, 0, 0)
Nr. Npd	0	Omittedbyuser	0	Omittedreflections	0
R All	0.0428	Redundancy	(2252, 974, 305, 74, 17, 1)	Reflectionapotmax	10
Systematicabsencesremoved	31	Weight	True	Hooft Str	0.007(19)
Last Shift	-0.0001	Max Shift Over Esd	-8.5911e-05	Tot Reflins	5471

Table S21: Crystallographic information of ylid_multitepm_1_250_00_auto

Parameter	Value	Parameter	Value	Parameter	Value
Dataset	ylid_multitepm_1_250_00_auto	a (Å)	5.9340(3)	b (Å)	9.0066(4)
c (Å)	18.3661(8)	α (°)	90	β (°)	90
γ (°)	90	Volume (Å ³)	981.57(8)	Wavelength (Å)	1.54184
μ (mm ⁻¹)	2.679	GoF	1.0326	Z	4
Z'	1	R1	0.0386	R_int	0.0626117
R $_{\sigma}$	0.0535067	wR2	0.1012	RMS residual (e·Å ⁻³)	0.0530178
Max peak (e·Å ⁻³)	0.177669	Max hole (e·Å ⁻³)	-0.21546	Completeness	0.992499
Total reflections	5511	Unique reflections	1720	Friedel merged	0
Friedel pairs	809	Datacount	1720	F000	434.643
Filemaxindices	(7, 10, 21)	Fileminindices	(-6, -9, -21)	Filteredoff	0
Inconsistentequivalents	1	Intensitytransformed	0	Limdmax	100
Limdmin	0.77092	Maxd	9.18304	Maxindices	(7, 10, 21)
Meanioversigma	13.2709	Mind	0.839672	Minindices	(-7, 0, 0)
Nr. Npd	0	Omittedbyuser	0	Omittedreflections	0
R All	0.0409	Redundancy	(2254, 975, 304, 76, 17, 1)	Reflectionapotmax	11
Systematicabsencesremoved	31	Weight	True	Hooft Str	0.014(19)
Last Shift	0.0004	Max Shift Over Esd	0.000413802	Tot Reflins	5480

S3 Quantum Crystallographic Benchmarking

Table S22: Crystallographic information of SuperSugar_B3LYP_def2-TZVP

Parameter	Value	Parameter	Value	Parameter	Value
Dataset	SuperSugar_B3LYP_def2-TZVP	a (Å)	7.71885(3)	b (Å)	8.66642(4)
c (Å)	10.81599(5)	α (°)	90	β (°)	102.9649(4)
γ (°)	90	Volume (Å ³)	705.089(5)	Wavelength (Å)	0.71073
μ (mm ⁻¹)	0.144	GoF	1.2065	Z	1
Z'	0.5	R1	0.0142	R_int	0.0209291
R $_{\sigma}$	0.0123296	wR2	0.0241789	RMS residual (e·Å ⁻³)	0.0354195
Max peak (e·Å ⁻³)	0.139145	Max hole (e·Å ⁻³)	-0.221183	Completeness	0.82989
Total reflections	229342	Unique reflections	23500	Friedel merged	0
Friedel pairs	17803	Datacount	23500	Diis	0.01
F000	364.337	Filemaxindices	(20, 21, 27)	Fileminindices	(-20, -20, -27)
Filteredoff	0	Inconsistentequivalents	14	Intensitytransformed	0
Limdmax	100	Limdmin	0.355365	Maxd	8.66642
Maxindices	(19, 21, 27)	Max Har Cycles	10	Meanioversigma	57.7497
Mind	0.373692	Minindices	(-20, -20, 0)	Nr. Npd	0
Orca Damp	False	Orca Scf Conv	NoSpherA2S CF	Orca Scf Strategy	NormalConv
Orca Scnl	False	Orca Solvation	Vacuum	Omittedbyuser	0
Omittedreflections	0	R1 All	0.0165634	R1 Gt	0.0141911
R All	0.0166	Redundancy	(9277, 6454, 3961, 3597, 2916, 2248, 1822, 1634, 1515, 1465, 1245, 1123, 1002, 863, 672, 507, 362, 255, 234, 165, 128, 91, 42, 49, 25, 26, 14, 12, 7, 9, 0, 7, 3, 2, 1)	Reflectionapotmax	67
Relativistic	False	Systematicabsencesremoved	60	Weight	True
Basis Name	def2-TZVP	Becke Accuracy	Normal	Charge	0
Cluster Grow	True	Cluster Radius	0	Exact Formula	{'O': 11.0, 'C': 12.0, 'H': 22.0}
Full Har	True	H Afix	True	H Aniso	True
Hooft Str	0.05(3)	Last Shift	0.0003	Max Shift Over Esd	0.000327237
Mem	75	Method	B3LYP	Multiplicity	0
Ncpus	18	Pyscf Damping	0.6	Tot Reflins	229282

Table S23: Crystallographic information of SuperSugar_R2SCAN_def2-TZVP

Parameter	Value	Parameter	Value	Parameter	Value
Dataset	SuperSugar_R2SCAN_def2-TZVP	a (Å)	7.71885(3)	b (Å)	8.66642(4)
c (Å)	10.81599(5)	α (°)	90	β (°)	102.9649(4)
γ (°)	90	Volume (Å ³)	705.089(5)	Wavelength (Å)	0.71073
μ (mm ⁻¹)	0.144	GoF	1.5985	Z	1
Z'	0.5	R1	0.0142	R_int	0.0209291
R $_{\sigma}$	0.0123296	wR2	0.0172116	RMS residual (e·Å ⁻³)	0.0358491
Max peak (e·Å ⁻³)	0.141237	Max hole (e·Å ⁻³)	-0.210705	Completeness	0.82989
Total reflections	229342	Unique reflections	23500	Friedel merged	0
Friedel pairs	17803	Datacount	23500	Diis	0.01
F000	364.337	Filemaxindices	(20, 21, 27)	Fileminindices	(-20, -20, -27)
Filteredoff	0	Inconsistentequivalents	14	Intensitytransformed	0
Limdmax	100	Limdmin	0.355365	Maxd	8.66642
Maxindices	(19, 21, 27)	Max Har Cycles	10	Meanioversigma	57.7497
Mind	0.373692	Minindices	(-20, -20, 0)	Nr. Npd	0
Orca Damp	False	Orca Scf Conv	NoSpherA2S CF	Orca Scf Strategy	NormalConv
Orca Scnl	False	Orca Solvation	Vacuum	Omittedbyuser	0
Omittedreflections	0	R1 All	0.0165372	R1 Gt	0.014165
R All	0.0165	Redundancy	(9277, 6454, 3961, 3597, 2916, 2248, 1822, 1634, 1515, 1465, 1245, 1123, 1002, 863, 672, 507, 362, 255, 234, 165, 128, 91, 42, 49, 25, 26, 14, 12, 7, 9, 0, 7, 3, 2, 1)	Reflectionapotmax	67
Relativistic	False	Systematicabsencesremoved	60	Weight	True
Basis Name	def2-TZVP	Becke Accuracy	Normal	Charge	0
Cluster Grow	True	Cluster Radius	0	Exact Formula	{'O': 11.0, 'C': 12.0, 'H': 22.0}
Full Har	True	H Afix	True	H Aniso	True
Hooft Str	0.05(3)	Last Shift	-0.0004	Max Shift Over Esd	-0.000427887
Mem	75	Method	R2SCAN	Multiplicity	0
Ncpus	18	Pyscf Damping	0.6	Tot Reflins	229282

Table S24: Crystallographic information of SuperSugar_PBE0_def2-TZVP

Parameter	Value	Parameter	Value	Parameter	Value
Dataset	SuperSugar_PBE0_def2-TZVP	a (Å)	7.71885(3)	b (Å)	8.66642(4)
c (Å)	10.81599(5)	α (°)	90	β (°)	102.9649(4)
γ (°)	90	Volume (Å ³)	705.089(5)	Wavelength (Å)	0.71073
μ (mm ⁻¹)	0.144	GoF	1.5973	Z	1
Z'	0.5	R1	0.0142	R_int	0.0209291
R _{σ}	0.0123296	wR2	0.0171985	RMS residual (e·Å ⁻³)	0.0360759
Max peak (e·Å ⁻³)	0.14176	Max hole (e·Å ⁻³)	-0.216359	Completeness	0.82989
Total reflections	229342	Unique reflections	23500	Friedel merged	0
Friedel pairs	17803	Datacount	23500	Diis	0.01
F000	364.337	Filemaxindices	(20, 21, 27)	Fileminindices	(-20, -20, -27)
Filteredoff	0	Inconsistentequivalents	14	Intensitytransformed	0
Limdmax	100	Limdmin	0.355365	Maxd	8.66642
Maxindices	(19, 21, 27)	Max Har Cycles	10	Meanioversigma	57.7497
Mind	0.373692	Minindices	(-20, -20, 0)	Nr. Npd	0
Orca Damp	False	Orca Scf Conv	NoSpherA2S CF	Orca Scf Strategy	NormalConv
Orca Scnl	False	Orca Solvation	Vacuum	Omittedbyuser	0
Omittedreflections	0	R1 All	0.0165543	R1 Gt	0.0141818
R All	0.0166	Redundancy	(9277, 6454, 3961, 3597, 2916, 2248, 1822, 1634, 1515, 1465, 1245, 1123, 1002, 863, 672, 507, 362, 255, 234, 165, 128, 91, 42, 49, 25, 26, 14, 12, 7, 9, 0, 7, 3, 2, 1)	Reflectionapotmax	67
Relativistic	False	Systematicabsencesremoved	60	Weight	True
Basis Name	def2-TZVP	Becke Accuracy	Normal	Charge	0
Cluster Grow	True	Cluster Radius	0	Exact Formula	{'O': 11.0, 'C': 12.0, 'H': 22.0}
Full Har	True	H Afix	True	H Aniso	True
Hooft Str	0.05(3)	Last Shift	0.0004	Max Shift Over Esd	0.000395206
Mem	75	Method	PBE0	Multiplicity	0
Ncpus	18	Pyscf Damping	0.6	Tot Reflins	229282

Table S25: Crystallographic information of SuperSugar_PBE_def2-TZVP

Parameter	Value	Parameter	Value	Parameter	Value
Dataset	SuperSugar_PBE_def2-TZVP	a (Å)	7.71885(3)	b (Å)	8.66642(4)
c (Å)	10.81599(5)	α (°)	90	β (°)	102.9649(4)
γ (°)	90	Volume (Å ³)	705.089(5)	Wavelength (Å)	0.71073
μ (mm ⁻¹)	0.144	GoF	1.2273	Z	1
Z'	0.5	R1	0.0144	R_int	0.0209291
R _{σ}	0.0123296	wR2	0.0248094	RMS residual (e·Å ⁻³)	0.0359278
Max peak (e·Å ⁻³)	0.141174	Max hole (e·Å ⁻³)	-0.219591	Completeness	0.82989
Total reflections	229342	Unique reflections	23500	Friedel merged	0
Friedel pairs	17803	Datacount	23500	Diis	0.01
F000	364.337	Filemaxindices	(20, 21, 27)	Fileminindices	(-20, -20, -27)
Filteredoff	0	Inconsistentequivalents	14	Intensitytransformed	0
Limdmax	100	Limdmin	0.355365	Maxd	8.66642
Maxindices	(19, 21, 27)	Max Har Cycles	10	Meanioversigma	57.7497
Mind	0.373692	Minindices	(-20, -20, 0)	Nr. Npd	0
Orca Damp	False	Orca Scf Conv	NoSpherA2S CF	Orca Scf Strategy	NormalConv
Orca Scnl	False	Orca Solvation	Vacuum	Omittedbyuser	0
Omittedreflections	0	R1 All	0.0167781	R1 Gt	0.0144088
R All	0.0168	Redundancy	(9277, 6454, 3961, 3597, 2916, 2248, 1822, 1634, 1515, 1465, 1245, 1123, 1002, 863, 672, 507, 362, 255, 234, 165, 128, 91, 42, 49, 25, 26, 14, 12, 7, 9, 0, 7, 3, 2, 1)	Reflectionapotmax	67
Relativistic	False	Systematicabsencesremoved	60	Weight	True
Basis Name	def2-TZVP	Becke Accuracy	Normal	Charge	0
Cluster Grow	True	Cluster Radius	0	Exact Formula	{'O': 11.0, 'C': 12.0, 'H': 22.0}
Full Har	True	H Afix	True	H Aniso	True
Hooft Str	0.05(3)	Last Shift	0.0002	Max Shift Over Esd	0.000194882
Mem	75	Method	PBE	Multiplicity	0
Ncpus	18	Pyscf Damping	0.6	Tot Reflins	229282

Table S26: Crystallographic information of SuperSugar_HF_def2-TZVP

Parameter	Value	Parameter	Value	Parameter	Value
Dataset	SuperSugar_HF_def2-TZVP	a (Å)	7.71885(3)	b (Å)	8.66642(4)
c (Å)	10.81599(5)	α (°)	90	β (°)	102.9649(4)
γ (°)	90	Volume (Å ³)	705.089(5)	Wavelength (Å)	0.71073
μ (mm ⁻¹)	0.144	GoF	1.8448	Z	1
Z'	0.5	R1	0.015	R_int	0.0209291
R $_{\sigma}$	0.0123296	wR2	0.0198625	RMS residual (e $\cdot$ Å ⁻³)	0.038459
Max peak (e $\cdot$ Å ⁻³)	0.141108	Max hole (e $\cdot$ Å ⁻³)	-0.225396	Completeness	0.82989
Total reflections	229342	Unique reflections	23500	Friedel merged	0
Friedel pairs	17803	Datacount	23500	Diis	0.01
F000	364.337	Filemaxindices	(20, 21, 27)	Fileminindices	(-20, -20, -27)
Filteredoff	0	Inconsistentequivalents	14	Intensitytransformed	0
Limdmax	100	Limdmin	0.355365	Maxd	8.66642
Maxindices	(19, 21, 27)	Max Har Cycles	10	Meanioversigma	57.7497
Mind	0.373692	Minindices	(-20, -20, 0)	Nr. Npd	0
Orca Damp	False	Orca Scf Conv	NoSpherA2S CF	Orca Scf Strategy	NormalConv
Orca Scnl	False	Orca Solvation	Vacuum	Omittedbyuser	0
Omittedreflections	0	R1 All	0.0173741	R1 Gt	0.0150023
R All	0.0174	Redundancy	(9277, 6454, 3961, 3597, 2916, 2248, 1822, 1634, 1515, 1465, 1245, 1123, 1002, 863, 672, 507, 362, 255, 234, 165, 128, 91, 42, 49, 25, 26, 14, 12, 7, 9, 0, 7, 3, 2, 1)	Reflectionapotmax	67
Relativistic	False	Systematicabsencesremoved	60	Weight	True
Basis Name	def2-TZVP	Becke Accuracy	Normal	Charge	0
Cluster Grow	True	Cluster Radius	0	Exact Formula	{'O': 11.0, 'C': 12.0, 'H': 22.0}
Full Har	True	H Afix	True	H Aniso	True
Hooft Str	0.05(3)	Last Shift	0.0002	Max Shift Over Esd	0.000249284
Mem	75	Method	HF	Multiplicity	0
Ncpus	18	Pyscf Damping	0.6	Tot Reflins	229282

Table S27: Crystallographic information of SuperSugar_B3LYP_def2-SVP

Parameter	Value	Parameter	Value	Parameter	Value
Dataset	SuperSugar_B3LYP_def2-SVP	a (Å)	7.71885(3)	b (Å)	8.66642(4)
c (Å)	10.81599(5)	α (°)	90	β (°)	102.9649(4)
γ (°)	90	Volume (Å ³)	705.089(5)	Wavelength (Å)	0.71073
μ (mm ⁻¹)	0.144	GoF	1.2906	Z	1
Z'	0.5	R1	0.0149	R_int	0.0209291
R _{σ}	0.0123296	wR2	0.026405	RMS residual (e ⁻ Å ⁻³)	0.0371716
Max peak (e ⁻ Å ⁻³)	0.14096	Max hole (e ⁻ Å ⁻³)	-0.200089	Completeness	0.82989
Total reflections	229342	Unique reflections	23500	Friedel merged	0
Friedel pairs	17803	Datacount	23500	Diis	0.01
F000	364.337	Filemaxindices	(20, 21, 27)	Fileminindices	(-20, -20, -27)
Filteredoff	0	Inconsistentequivalents	14	Intensitytransformed	0
Limdmax	100	Limdmin	0.355365	Maxd	8.66642
Maxindices	(19, 21, 27)	Max Har Cycles	10	Meanioversigma	57.7497
Mind	0.373692	Minindices	(-20, -20, 0)	Nr. Npd	0
Orca Damp	False	Orca Scf Conv	NoSpherA2S CF	Orca Scf Strategy	NormalConv
Orca Scnl	False	Orca Solvation	Vacuum	Omittedbyuser	0
Omittedreflections	0	R1 All	0.017289	R1 Gt	0.0149346
R All	0.0173	Redundancy	(9277, 6454, 3961, 3597, 2916, 2248, 1822, 1634, 1515, 1465, 1245, 1123, 1002, 863, 672, 507, 362, 255, 234, 165, 128, 91, 42, 49, 25, 26, 14, 12, 7, 9, 0, 7, 3, 2, 1)	Reflectionapotmax	67
Relativistic	False	Systematicabsencesremoved	60	Weight	True
Basis Name	def2-SVP	Becke Accuracy	Normal	Charge	0
Cluster Grow	True	Cluster Radius	0	Exact Formula	{'O': 11.0, 'C': 12.0, 'H': 22.0}
Full Har	True	H Afix	True	H Aniso	True
Hooft Str	0.05(3)	Last Shift	0.0004	Max Shift Over Esd	0.000429736
Mem	75	Method	B3LYP	Multiplicity	0
Ncpus	18	Pyscf Damping	0.6	Tot Reflins	229282

Table S28: Crystallographic information of SuperSugar_R2SCAN_def2-SVP

Parameter	Value	Parameter	Value	Parameter	Value
Dataset	SuperSugar_R2SCAN_def2-SVP	a (Å)	7.71885(3)	b (Å)	8.66642(4)
c (Å)	10.81599(5)	α (°)	90	β (°)	102.9649(4)
γ (°)	90	Volume (Å ³)	705.089(5)	Wavelength (Å)	0.71073
μ (mm ⁻¹)	0.144	GoF	1.3211	Z	1
Z'	0.5	R1	0.015	R_int	0.0209291
R $_{\sigma}$	0.0123296	wR2	0.0224032	RMS residual (e·Å ⁻³)	0.0365722
Max peak (e·Å ⁻³)	0.146596	Max hole (e·Å ⁻³)	-0.175391	Completeness	0.82989
Total reflections	229342	Unique reflections	23500	Friedel merged	0
Friedel pairs	17803	Datacount	23500	Diis	0.01
F000	364.337	Filemaxindices	(20, 21, 27)	Fileminindices	(-20, -20, -27)
Filteredoff	0	Inconsistentequivalents	14	Intensitytransformed	0
Limdmax	100	Limdmin	0.355365	Maxd	8.66642
Maxindices	(19, 21, 27)	Max Har Cycles	10	Meanioversigma	57.7497
Mind	0.373692	Minindices	(-20, -20, 0)	Nr. Npd	0
Orca Damp	False	Orca Scf Conv	NoSpherA2S CF	Orca Scf Strategy	NormalConv
Orca Scnl	False	Orca Solvation	Vacuum	Omittedbyuser	0
Omittedreflections	0	R1 All	0.0173296	R1 Gt	0.014972
R All	0.0173	Redundancy	(9277, 6454, 3961, 3597, 2916, 2248, 1822, 1634, 1515, 1465, 1245, 1123, 1002, 863, 672, 507, 362, 255, 234, 165, 128, 91, 42, 49, 25, 26, 14, 12, 7, 9, 0, 7, 3, 2, 1)	Reflectionapotmax	67
Relativistic	False	Systematicabsencesremoved	60	Weight	True
Basis Name	def2-SVP	Becke Accuracy	Normal	Charge	0
Cluster Grow	True	Cluster Radius	0	Exact Formula	{'O': 11.0, 'C': 12.0, 'H': 22.0}
Full Har	True	H Afix	True	H Aniso	True
Hooft Str	0.05(3)	Last Shift	-0.0005	Max Shift Over Esd	-0.000512492

Mem	75	Method	R2SCAN	Multiplicity	0
Ncpus	18	Pyscf Damping	0.6	Tot Reflins	229282

Table S29: Crystallographic information of SuperSugar_PBE0_def2-SVP

Parameter	Value	Parameter	Value	Parameter	Value
Dataset	SuperSugar_PBE0_def2-SVP	a (Å)	7.71885(3)	b (Å)	8.66642(4)
c (Å)	10.81599(5)	α (°)	90	β (°)	102.9649(4)
γ (°)	90	Volume (Å ³)	705.089(5)	Wavelength (Å)	0.71073
μ (mm ⁻¹)	0.144	GoF	1.3216	Z	1
Z'	0.5	R1	0.015	R_int	0.0209291
R_ σ	0.0123296	wR2	0.0225497	RMS residual (e·Å ⁻³)	0.0367637
Max peak (e·Å ⁻³)	0.146842	Max hole (e·Å ⁻³)	-0.176977	Completeness	0.82989
Total reflections	229342	Unique reflections	23500	Friedel merged	0
Friedel pairs	17803	Datacount	23500	Diis	0.01
F000	364.337	Filemaxindices	(20, 21, 27)	Fileminindices	(-20, -20, -27)
Filteredoff	0	Inconsistentequivalents	14	Intensitytransformed	0
Limdmax	100	Limdmin	0.355365	Maxd	8.66642
Maxindices	(19, 21, 27)	Max Har Cycles	10	Meanioversigma	57.7497
Mind	0.373692	Minindices	(-20, -20, 0)	Nr. Npd	0
Orca Damp	False	Orca Scf Conv	NoSpherA2S CF	Orca Scf Strategy	NormalConv
Orca Scnl	False	Orca Solvation	Vacuum	Omittedbyuser	0
Omittedreflections	0	R1 All	0.0173877	R1 Gt	0.0150303
R All	0.0174	Redundancy	(9277, 6454, 3961, 3597, 2916, 2248, 1822, 1634, 1515, 1465, 1245, 1123, 1002, 863, 672, 507, 362, 255, 234, 165, 128, 91, 42, 49, 25, 26, 14, 12, 7, 9, 0, 7, 3, 2, 1)	Reflectionapotmax	67
Relativistic	False	Systematicabsencesremoved	60	Weight	True
Basis Name	def2-SVP	Becke Accuracy	Normal	Charge	0
Cluster Grow	True	Cluster Radius	0	Exact Formula	{'O': 11.0, 'C': 12.0, 'H': 22.0}
Full Har	True	H Afix	True	H Aniso	True

Hooft Str	0.05(3)	Last Shift	-0.0006	Max Shift Over Esd	-0.000587011
Mem	75	Method	PBE0	Multiplicity	0
Ncpus	18	Pyscf Damping	0.6	Tot Reflins	229282

Table S30: Crystallographic information of SuperSugar_PBE_def2-SVP

Parameter	Value	Parameter	Value	Parameter	Value
Dataset	SuperSugar_PBE_def2-SVP	a (Å)	7.71885(3)	b (Å)	8.66642(4)
c (Å)	10.81599(5)	α (°)	90	β (°)	102.9649(4)
γ (°)	90	Volume (Å ³)	705.089(5)	Wavelength (Å)	0.71073
μ (mm ⁻¹)	0.144	GoF	1.3234	Z	1
Z'	0.5	R1	0.015	R_int	0.0209291
R _{σ}	0.0123296	wR2	0.0222635	RMS residual (e·Å ⁻³)	0.0364393
Max peak (e·Å ⁻³)	0.14662	Max hole (e·Å ⁻³)	-0.180271	Completeness	0.82989
Total reflections	229342	Unique reflections	23500	Friedel merged	0
Friedel pairs	17803	Datacount	23500	Diis	0.01
F000	364.337	Filemaxindices	(20, 21, 27)	Fileminindices	(-20, -20, -27)
Filteredoff	0	Inconsistentequivalents	14	Intensitytransformed	0
Limdmax	100	Limdmin	0.355365	Maxd	8.66642
Maxindices	(19, 21, 27)	Max Har Cycles	10	Meanioversigma	57.7497
Mind	0.373692	Minindices	(-20, -20, 0)	Nr. Npd	0
Orca Damp	False	Orca Scf Conv	NoSpherA2S CF	Orca Scf Strategy	NormalConv
Orca Scnl	False	Orca Solvation	Vacuum	Omittedbyuser	0
Omittedreflections	0	R1 All	0.0173162	R1 Gt	0.0149579
R All	0.0173	Redundancy	(9277, 6454, 3961, 3597, 2916, 2248, 1822, 1634, 1515, 1465, 1245, 1123, 1002, 863, 672, 507, 362, 255, 234, 165, 128, 91, 42, 49, 25, 26, 14, 12, 7, 9, 0, 7, 3, 2, 1)	Reflectionapotmax	67
Relativistic	False	Systematicabsencesremoved	60	Weight	True
Basis Name	def2-SVP	Becke Accuracy	Normal	Charge	0
Cluster Grow	True	Cluster Radius	0	Exact Formula	{'O': 11.0, 'C': 12.0, 'H': 22.0}
Full Har	True	H Afix	True	H Aniso	True

Hooft Str	0.05(3)	Last Shift	0.0006	Max Esd	Shift Over	0.0005936 08
Mem	75	Method	PBE	Multiplicity		0
Ncpus	18	Pyscf Damping	0.6	Tot Reflins		229282

Table S31: Crystallographic information of SuperSugar_HF_def2-SVP

Parameter	Value	Parameter	Value	Parameter	Value
Dataset	SuperSugar_HF_def2-SVP	a (Å)	7.71885(3)	b (Å)	8.66642(4)
c (Å)	10.81599(5)	α (°)	90	β (°)	102.9649(4)
γ (°)	90	Volume (Å ³)	705.089(5)	Wavelength (Å)	0.71073
μ (mm ⁻¹)	0.144	GoF	1.3478	Z	1
Z'	0.5	R1	0.0159	R_int	0.0209291
R _{σ}	0.0123296	wR2	0.0297916	RMS residual (e·Å ⁻³)	0.0390636
Max peak (e·Å ⁻³)	0.139293	Max hole (e·Å ⁻³)	-0.198574	Completeness	0.82989
Total reflections	229342	Unique reflections	23500	Friedel merged	0
Friedel pairs	17803	Datacount	23500	Diis	0.01
F000	364.337	Filemaxindices	(20, 21, 27)	Fileminindices	(-20, -20, -27)
Filteredoff	0	Inconsistentequivalents	14	Intensitytransformed	0
Limdmax	100	Limdmin	0.355365	Maxd	8.66642
Maxindices	(19, 21, 27)	Max Har Cycles	10	Meanioversigma	57.7497
Mind	0.373692	Minindices	(-20, -20, 0)	Nr. Npd	0
Orca Damp	False	Orca Scf Conv	NoSpherA2S CF	Orca Scf Strategy	NormalConv
Orca Scnl	False	Orca Solvation	Vacuum	Omittedbyuser	0
Omittedreflections	0	R1 All	0.0182816	R1 Gt	0.0159374
R All	0.0183	Redundancy	(9277, 6454, 3961, 3597, 2916, 2248, 1822, 1634, 1515, 1465, 1245, 1123, 1002, 863, 672, 507, 362, 255, 234, 165, 128, 91, 42, 49, 25, 26, 14, 12, 7, 9, 0, 7, 3, 2, 1)	Reflectionapotmax	67
Relativistic	False	Systematicabsencesremoved	60	Weight	True
Basis Name	def2-SVP	Becke Accuracy	Normal	Charge	0
Cluster Grow	True	Cluster Radius	0	Exact Formula	{'O': 11.0, 'C': 12.0, 'H': 22.0}
Full Har	True	H Afix	True	H Aniso	True
Hoofst Str	0.05(3)	Last Shift	-0.0007	Max Shift Over Esd	-0.000711943
Mem	75	Method	HF	Multiplicity	0
Ncpus	18	Pyscf Damping	0.6	Tot Reflins	229282

Table S32: Crystallographic information of SuperSugar_IAM

Parameter	Value	Parameter	Value	Parameter	Value
Dataset	SuperSugar_IAM	a (Å)	7.71885(3)	b (Å)	8.66642(4)
c (Å)	10.81599(5)	α (°)	90	β (°)	102.9649(4)
γ (°)	90	Volume (Å ³)	705.089(5)	Wavelength (Å)	0.71073
μ (mm ⁻¹)	0.144	GoF	1.1724	Z	1
Z'	0.5	R1	0.0226	R_int	0.0209291
R $_{\sigma}$	0.0123296	wR2	0.0649717	RMS residual (e·Å ⁻³)	0.0590861
Max peak (e·Å ⁻³)	0.345036	Max hole (e·Å ⁻³)	-0.236503	Completeness	0.82989
Total reflections	229342	Unique reflections	23500	Friedel merged	0
Friedel pairs	17803	Datacount	23500	F000	364.337
Filemaxindices	(20, 21, 27)	Fileminindices	(-20, -20, -27)	Filteredoff	0
Inconsistentequivalents	14	Intensitytransformed	0	Limdmax	100
Limdmin	0.355365	Maxd	8.66642	Maxindices	(19, 21, 27)
Meanioversigma	57.7497	Mind	0.373692	Minindices	(-20, -20, 0)
Nr. Npd	0	Omittedbyuser	0	Omittedreflections	0
R1 All	0.0248877	R1 Gt	0.0225674	R All	0.0249
Redundancy	(9277, 6454, 3961, 3597, 2916, 2248, 1822, 1634, 1515, 1465, 1245, 1123, 1002, 863, 672, 507, 362, 255, 234, 165, 128, 91, 42, 49, 25, 26, 14, 12, 7, 9, 0, 7, 3, 2, 1)	Reflectionapotmax	67	Systematicabsencesremoved	60
Weight	True	Exact Formula	{'O': 11.0, 'C': 12.0, 'H': 22.0}	Hoofst Str	0.05(3)
Last Shift	0.0048	Max Shift Over Esd	0.00484218	Tot Reflins	229282

S4 Mixed Metal Position

Table S33: Crystallographic information of ACK001_Kristmeth_evap_08_auto_fin

Parameter	Value	Parameter	Value	Parameter	Value
Dataset	ACK001_Kristmeth_evap_08_auto_fin	a (Å)	11.6160(3)	b (Å)	11.0826(2)
c (Å)	6.2802(3)	α (°)	90	β (°)	90
γ (°)	90	Volume (Å ³)	808.49(5)	Wavelength (Å)	0.71073
μ (mm ⁻¹)	7.445	GoF	1.029	Z	4
Z'	0.5	R1	0.0135	R_int	0.0170228
R $_{\sigma}$	0.0154927	wR2	0.0290486	RMS residual (e·Å ⁻³)	0.113257
Max peak (e·Å ⁻³)	0.697988	Max hole (e·Å ⁻³)	-0.776371	Completeness	0.904026
Total reflections	8595	Unique reflections	1931	Friedel merged	1
Friedel pairs	1415	Datacount	1931	F000	510.334
Filemaxindices	(18, 18, 10)	Fileminindices	(-17, -18, -9)	Filteredoff	0
Inconsistentequivalents	0	Intensitytransformed	0	Limdmax	100
Limdmin	0.355365	Maxd	8.01854	Maxindices	(18, 18, 10)
Meanoversigma	45.7133	Mind	0.590981	Minindices	(0, 0, 0)
Nr. Npd	0	Omittedbyuser	0	Omittedreflections	0
R1 All	0.017157	R1 Gt	0.013505	R All	0.0172
Redundancy	(5681, 1457)	Reflectionapotmax	10	Systematicabsencesremoved	563
Weight	True	Exact Formula	{'W': 0.2526027496101694, 'O': 3.0, 'C': 3.0, 'Cr': 0.24739725038998303}	Last Shift	-0.0003
Max Shift Over Esd	-0.000291254	Tot Reflins	8032		

Table S34: Crystallographic information of ACK001_Kristmeth_evap_07_auto_fin

Parameter	Value	Parameter	Value	Parameter	Value
Dataset	ACK001_Kristmeth_evap_07_auto_fin	a (Å)	11.6121(3)	b (Å)	11.0836(2)
c (Å)	6.2790(3)	α (°)	90	β (°)	90
γ (°)	90	Volume (Å ³)	808.14(5)	Wavelength (Å)	0.71073
μ (mm ⁻¹)	7.448	GoF	1.0377	Z	4
Z'	0.5	R1	0.0195	R_int	0.0224145
R $_{\sigma}$	0.0243487	wR2	0.0504723	RMS residual (e·Å ⁻³)	0.155364
Max peak (e·Å ⁻³)	0.855029	Max hole (e·Å ⁻³)	-0.823403	Completeness	0.897882
Total reflections	4961	Unique reflections	1908	Friedel merged	1
Friedel pairs	287	Datacount	1908	F000	510.334
Filemaxindices	(17, 18, 10)	Fileminindices	(-19, -18, -9)	Filteredoff	0
Inconsistentequivalents	10	Intensitytransformed	0	Limdmax	100
Limdmin	0.355365	Maxd	8.01761	Maxindices	(19, 18, 10)
Meanoversigma	30.6865	Mind	0.592139	Minindices	(0, 0, 0)
Nr. Npd	0	Omittedbyuser	0	Omittedreflections	0
R1 All	0.0230432	R1 Gt	0.0194771	R All	0.023
Redundancy	(3911, 525)	Reflectionapotmax	8	Systematicabsencesremoved	337
Weight	True	Exact Formula	{'W': 0.2521142302778679, 'O': 3.0, 'C': 3.0, 'Cr': 0.2478857697221321}	Last Shift	-0.0004
Max Shift Over Esd	-0.000396424	Tot Reflins	4624		

Table S35: Crystallographic information of ACK001_Kristmeth_evap_06_auto_fin

Parameter	Value	Parameter	Value	Parameter	Value
Dataset	ACK001_Kristmeth_evap_06_auto_fin	a (Å)	11.6218(3)	b (Å)	11.0891(2)
c (Å)	6.2851(3)	α (°)	90	β (°)	90
γ (°)	90	Volume (Å ³)	809.99(5)	Wavelength (Å)	0.71073
μ (mm ⁻¹)	7.431	GoF	1.0502	Z	4
Z'	0.5	R1	0.0124	R_int	0.0173456
R $_{\sigma}$	0.0139599	wR2	0.0255277	RMS residual (e·Å ⁻³)	0.11038
Max peak (e·Å ⁻³)	0.559944	Max hole (e·Å ⁻³)	-0.556311	Completeness	0.859616
Total reflections	8610	Unique reflections	1837	Friedel merged	1
Friedel pairs	1396	Datacount	1837	F000	510.334
Filemaxindices	(19, 14, 10)	Fileminindices	(-19, -15, -9)	Filteredoff	0
Inconsistentequivalents	0	Intensitytransformed	0	Limdmax	100
Limdmin	0.355365	Maxd	8.02289	Maxindices	(19, 15, 10)
Meanoversigma	49.0468	Mind	0.591085	Minindices	(0, 0, 0)
Nr. Npd	0	Omittedbyuser	0	Omittedreflections	0
R1 All	0.0159951	R1 Gt	0.0123873	R All	0.016
Redundancy	(5679, 1464, 1)	Reflectionapotmax	10	Systematicabsencesremoved	468
Weight	True	Exact Formula	{'W': 0.2662663692034129, 'O': 3.0, 'C': 3.0, 'Cr': 0.2337336307965871}	Last Shift	-0.0004
Max Shift Over Esd	-0.000354231	Tot Reflins	8142		

Table S36: Crystallographic information of ACK001_Kristmeth_evap_05_auto_fin

Parameter	Value	Parameter	Value	Parameter	Value
Dataset	ACK001_Kristmeth_evap_05_auto_fin	a (Å)	11.6119(3)	b (Å)	11.0852(2)
c (Å)	6.2803(3)	α (°)	90	β (°)	90
γ (°)	90	Volume (Å ³)	808.40(5)	Wavelength (Å)	0.71073
μ (mm ⁻¹)	7.446	GoF	0.9741	Z	4
Z'	0.5	R1	0.0192	R_int	0.0347486
R $_{\sigma}$	0.0293595	wR2	0.0363416	RMS residual (e·Å ⁻³)	0.228453
Max peak (e·Å ⁻³)	0.94637	Max hole (e·Å ⁻³)	-0.93273	Completeness	0.937589
Total reflections	8559	Unique reflections	1983	Friedel merged	1
Friedel pairs	1401	Datacount	1983	F000	510.334
Filemaxindices	(18, 18, 8)	Fileminindices	(-18, -18, -10)	Filteredoff	0
Inconsistent equivalents	0	Intensitytransformed	0	Limdmax	100
Limdmin	0.355365	Maxd	8.01813	Maxindices	(18, 18, 10)
Meanoversigma	25.1457	Mind	0.593184	Minindices	(0, 0, 0)
Nr. Npd	0	Omittedbyuser	0	Omittedreflections	0
R1 All	0.0311174	R1 Gt	0.0192434	R All	0.0311
Redundancy	(5732, 1412, 1)	Reflectionapomax	9	Systematicabsencesremoved	500
Weight	True	Exact Formula	{'W': 0.267112097549075, 'O': 3.0, 'C': 3.0, 'Cr': 0.232887902450925}	Last Shift	-0.0001
Max Shift Over Esd	-0.000120221	Tot Reflins	8059		

Table S37: Crystallographic information of ACK001_Kristmeth_evap_04_auto_fin

Parameter	Value	Parameter	Value	Parameter	Value
Dataset	ACK001_Kristmeth_evap_04_auto_fin	a (Å)	11.6265(3)	b (Å)	11.0919(2)
c (Å)	6.2858(3)	α (°)	90	β (°)	90
γ (°)	90	Volume (Å ³)	810.62(5)	Wavelength (Å)	0.71073
μ (mm ⁻¹)	7.425	GoF	1.0011	Z	4
Z'	0.5	R1	0.0231	R_int	0.0249791
R $_{\sigma}$	0.021087	wR2	0.0583464	RMS residual (e·Å ⁻³)	0.191549
Max peak (e·Å ⁻³)	1.64606	Max hole (e·Å ⁻³)	-1.16953	Completeness	0.945205
Total reflections	8353	Unique reflections	2001	Friedel merged	1
Friedel pairs	1343	Datacount	2001	F000	510.334
Filemaxindices	(17, 17, 10)	Fileminindices	(-18, -18, -10)	Filteredoff	0
Inconsistentequivalents	1	Intensitytransformed	0	Limdmax	100
Limdmin	0.355365	Maxd	8.02551	Maxindices	(18, 18, 10)
Meanoversigma	32.7914	Mind	0.593558	Minindices	(0, 0, 0)
Nr. Npd	0	Omittedbyuser	0	Omittedreflections	0
R1 All	0.0290456	R1 Gt	0.0230673	R All	0.029
Redundancy	(5680, 1335, 1)	Reflectionapotmax	9	Systematicabsencesremoved	532
Weight	True	Exact Formula	{'W': 0.2730060166099097, 'O': 3.0, 'C': 3.0, 'Cr': 0.22699398339009025}	Last Shift	-0.0006
Max Shift Over Esd	-0.00057569	Tot Reflins	7821		

Table S38: Crystallographic information of ACK001_Kristmeth_evap_03_auto_fin

Parameter	Value	Parameter	Value	Parameter	Value
Dataset	ACK001_Kristmeth_evap_03_auto_fin	a (Å)	11.6067(3)	b (Å)	11.0596(2)
c (Å)	6.2755(3)	α (°)	90	β (°)	90
γ (°)	90	Volume (Å ³)	805.56(5)	Wavelength (Å)	0.71073
μ (mm ⁻¹)	7.472	GoF	1.0354	Z	4
Z'	0.5	R1	0.0697	R_int	0.101213
R $_{\sigma}$	0.0855416	wR2	0.190482	RMS residual (e·Å ⁻³)	0.684952
Max peak (e·Å ⁻³)	4.53851	Max hole (e·Å ⁻³)	-6.7946	Completeness	0.920208
Total reflections	8132	Unique reflections	1949	Friedel merged	1
Friedel pairs	1267	Datacount	1949	F000	510.334
Filemaxindices	(18, 16, 10)	Fileminindices	(-18, -17, -9)	Filteredoff	0
Inconsistentequivalents	1	Intensitytransformed	0	Limdmax	100
Limdmin	0.355365	Maxd	8.00673	Maxindices	(18, 17, 10)
Meanoversigma	9.28808	Mind	0.59197	Minindices	(0, 0, 0)
Nr. Npd	0	Omittedbyuser	0	Omittedreflections	0
R1 All	0.101084	R1 Gt	0.0696621	R All	0.1011
Redundancy	(5532, 1300)	Reflectionapotmax	10	Systematicabsencesremoved	449
Weight	True	Exact Formula	{'W': 0.27604503233381034, 'O': 3.0, 'C': 3.0, 'Cr': 0.2239549676661897}	Last Shift	-0.0005
Max Shift Over Esd	-0.000458973	Tot Reflins	7683		

Table S39: Crystallographic information of ACK001_Kristmeth_evap_02_fin

Parameter	Value	Parameter	Value	Parameter	Value
Dataset	ACK001_Kristmeth_evap_02_fin	a (Å)	11.6239(3)	b (Å)	11.0900 (2)
c (Å)	6.2829(3)	α (°)	90	β (°)	90
γ (°)	90	Volume (Å ³)	809.92(5)	Wavelength (Å)	0.71073
μ (mm ⁻¹)	7.432	GoF	1.0528	Z	4
Z'	0.5	R1	0.0128	R_int	0.01488 81
R $_{\sigma}$	0.0137749	wR2	0.0260739	RMS residual (e·Å ⁻³)	0.11820 2
Max peak (e·Å ⁻³)	0.938666	Max hole (e·Å ⁻³)	-0.66507	Completeness	0.94379 4
Total reflections	8492	Unique reflections	2015	Friedel merged	1
Friedel pairs	1393	Datacount	2015	F000	510.334
Filemaxindices	(17, 18, 10)	Fileminindices	(-19, -18, -10)	Filteredoff	0
Inconsistentequivalents	0	Intensitytransformed	0	Limdmax	100
Limdmin	0.355365	Maxd	8.0239	Maxindices	(19, 18, 10)
Meanoversigma	51.548	Mind	0.591441	Minindices	(0, 0, 0)
Nr. Npd	0	Omittedbyuser	0	Omittedreflections	0
R1 All	0.0167202	R1 Gt	0.0127606	R All	0.0167
Redundancy	(5694, 1399)	Reflectionapotmax	11	Systematicabsencesremoved	591
Weight	True	Exact Formula	{'W': 0.2640351109854 3186, 'O': 3.0, 'C': 3.0, 'Cr': 0.2359648890145 681}	Last Shift	-0.0007
Max Shift Over Esd	-0.000681463	Tot Reflins	7901		

Table S40: Crystallographic information of ACK001_Kristmeth_evap_02

Parameter	Value	Parameter	Value	Parameter	Value
Dataset	ACK001_Kristmeth_evap_02	a (Å)	11.6239(3)	b (Å)	11.0900(2)
c (Å)	6.2829(3)	α (°)	90	β (°)	90
γ (°)	90	Volume (Å ³)	809.92(5)	Wavelength (Å)	0.71073
μ (mm ⁻¹)	7.432	GoF	1.0555	Z	4
Z'	0.5	R1	0.0127	R_int	0.0146126
R $_{\sigma}$	0.0136014	wR2	0.025921	RMS residual (e·Å ⁻³)	0.118844
Max peak (e·Å ⁻³)	0.9199	Max hole (e·Å ⁻³)	-0.650735	Completeness	0.943794
Total reflections	8484	Unique reflections	2015	Friedel merged	1
Friedel pairs	1392	Datacount	2015	F000	510.334
Filemaxindices	(17, 18, 10)	Fileminindices	(-19, -18, -10)	Filteredoff	0
Inconsistentequivalents	0	Intensitytransformed	0	Limdmax	100
Limdmin	0.355365	Maxd	8.0239	Maxindices	(19, 18, 10)
Meanoversigma	52.3227	Mind	0.591441	Minindices	(0, 0, 0)
Nr. Npd	0	Omittedbyuser	0	Omittedreflections	0
R1 All	0.0166941	R1 Gt	0.0127204	R All	0.0167
Redundancy	(5700, 1392)	Reflectionapotmax	11	Systematicabsencesremoved	592
Weight	True	Exact Formula	{'W': 0.2640014807031015, 'O': 3.0, 'C': 3.0, 'Cr': 0.23599851929689847}	Last Shift	0.0001
Max Shift Over Esd	0.000111056	Tot Reflins	7892		

Table S41: Crystallographic information of ACK001_Kristmeth_evap_01_fin

Parameter	Value	Parameter	Value	Parameter	Value
Dataset	ACK001_Kristmeth_evap_01_fin	a (Å)	11.6198(3)	b (Å)	11.0843 (2)
c (Å)	6.2811(3)	α (°)	90	β (°)	90
γ (°)	90	Volume (Å ³)	808.99(5)	Wavelength (Å)	0.71073
μ (mm ⁻¹)	7.44	GoF	0.9958	Z	4
Z'	0.5	R1	0.0161	R_int	0.02227 12
R $_{\sigma}$	0.0198157	wR2	0.0342919	RMS residual (e·Å ⁻³)	0.15616 4
Max peak (e·Å ⁻³)	0.658942	Max hole (e·Å ⁻³)	-0.760222	Completeness	0.94905 7
Total reflections	8492	Unique reflections	2012	Friedel merged	1
Friedel pairs	1391	Datacount	2012	F000	510.334
Filemaxindices	(19, 18, 10)	Fileminindices	(-19, -17, -9)	Filteredoff	0
Inconsistentequivalents	0	Intensitytransformed	0	Limdmax	100
Limdmin	0.355365	Maxd	8.02042	Maxindices	(19, 18, 10)
Meanoversigma	35.4217	Mind	0.592623	Minindices	(0, 0, 0)
Nr. Npd	0	Omittedbyuser	0	Omittedreflections	0
R1 All	0.0233196	R1 Gt	0.0161208	R All	0.0233
Redundancy	(5711, 1389, 1)	Reflectionapotmax	10	Systematicabsencesremoved	573
Weight	True	Exact Formula	{'W': 0.2480391321831716, 'O': 3.0, 'C': 3.0, 'Cr': 0.25196086781688287}	Last Shift	0
Max Shift Over Esd	-3.88e-05	Tot Reflins	7919		

Table S42: Crystallographic information of ACK001_Kristmeth_evap_01

Parameter	Value	Parameter	Value	Parameter	Value
Dataset	ACK001_Kristmeth_evap_01	a (Å)	11.6198(3)	b (Å)	11.0843 (2)
c (Å)	6.2811(3)	α (°)	90	β (°)	90
γ (°)	90	Volume (Å ³)	808.99(5)	Wavelength (Å)	0.71073
μ (mm ⁻¹)	7.441	GoF	0.9904	Z	4
Z'	0.5	R1	0.0166	R_int	0.02510 08
R $_{\sigma}$	0.0214542	wR2	0.0359331	RMS residual (e·Å ⁻³)	0.16557 1
Max peak (e·Å ⁻³)	0.695541	Max hole (e·Å ⁻³)	-0.791667	Completeness	0.94905 7
Total reflections	8477	Unique reflections	2012	Friedel merged	1
Friedel pairs	1383	Datacount	2012	F000	510.334
Filemaxindices	(19, 18, 9)	Fileminindices	(-19, -17, -10)	Filteredoff	0
Inconsistentequivalents	0	Intensitytransformed	0	Limdmax	100
Limdmin	0.355365	Maxd	8.02042	Maxindices	(19, 18, 10)
Meanoversigma	34.0591	Mind	0.592624	Minindices	(0, 0, 0)
Nr. Npd	0	Omittedbyuser	0	Omittedreflections	0
R1 All	0.0238137	R1 Gt	0.0165932	R All	0.0238
Redundancy	(5712, 1381, 1)	Reflectionapotmax	10	Systematicabsencesremoved	572
Weight	True	Exact Formula	{'W': 0.2479769224638 2244, 'O': 3.0, 'C': 3.0, 'Cr': 0.2520230775361 776}	Last Shift	-0.0001
Max Shift Over Esd	-9.97e-05	Tot Reflins	7905		

10 Conclusion

This dissertation examined how modern single-crystal X-ray diffraction can progress from rapid structure determination towards reliable and chemically informative modelling of electron density. The individual studies addressed different stages of the crystallographic process, ranging from the statistical quality of deposited structures and the reproducibility of serial refinement to heavy-element specific effects, radiation dose induced changes, and direct analyses of chemical bonding. Taken together, these studies demonstrate that the current limitations of crystallography are no longer dominated solely by the quality of measured data. They arise increasingly from the relationship between the data and the model. Whether the physical experiment has been described correctly, whether systematic changes have been recognised, whether the chosen electron-density model is appropriate, and whether the chemical interpretation is supported by independent methods.

10.1 Structural quality in crystal structures

The analysis of the Cambridge Structural Database (Figure 10.1) provided a broad perspective on the development of small-molecule crystallography. The conventional agreement factor $R1$ improved strongly during the early decades but reached an approximately constant level around 1980. In contrast, $wR2$ showed a small but statistically significant increase over time, and the magnitudes of the minimum and maximum residual electron-density peaks did not show a corresponding general decrease. These observations do not imply that modern crystallography has become less capable. When unit-cell volume was included as a coarse measure of structural complexity, both normalised $R1$ and normalised $wR2$ indicated improvement. Modern experiments therefore solve and refine increasingly complex structures without a proportional deterioration of the principal agreement indicators.

The database analysis also exposed two complementary limitations of routine structural models. Relative agreement factors tend to improve with increasing atomic number because heavy atoms dominate the total scattering and define positions and displacement parameters strongly. Absolute residual electron densities, however, increased with atomic number, reflecting the greater sensitivity of heavy-element structures to absorption, anomalous dispersion, relativistic density changes, and other systematic effects. At the light-element end of the periodic table, bonding density represents a larger fraction of the total scattering which is not described by the independent atom model. Consequently, the same statistical trends that document the success of modern crystallography also identify where improved physical corrections and non-spherical atomic models are most urgently required.

10.2 Serial refinement

The SISYPHOS program addresses the practical consequences of the growing abundance of data. By refining a common model against multiple data sets, or multiple models against a common data set, the program establishes a consistent basis for comparison and records model parameters and quality indicators in machine-readable form. Its applications to crystal screening, temperature series, anomalous dispersion, quantum-

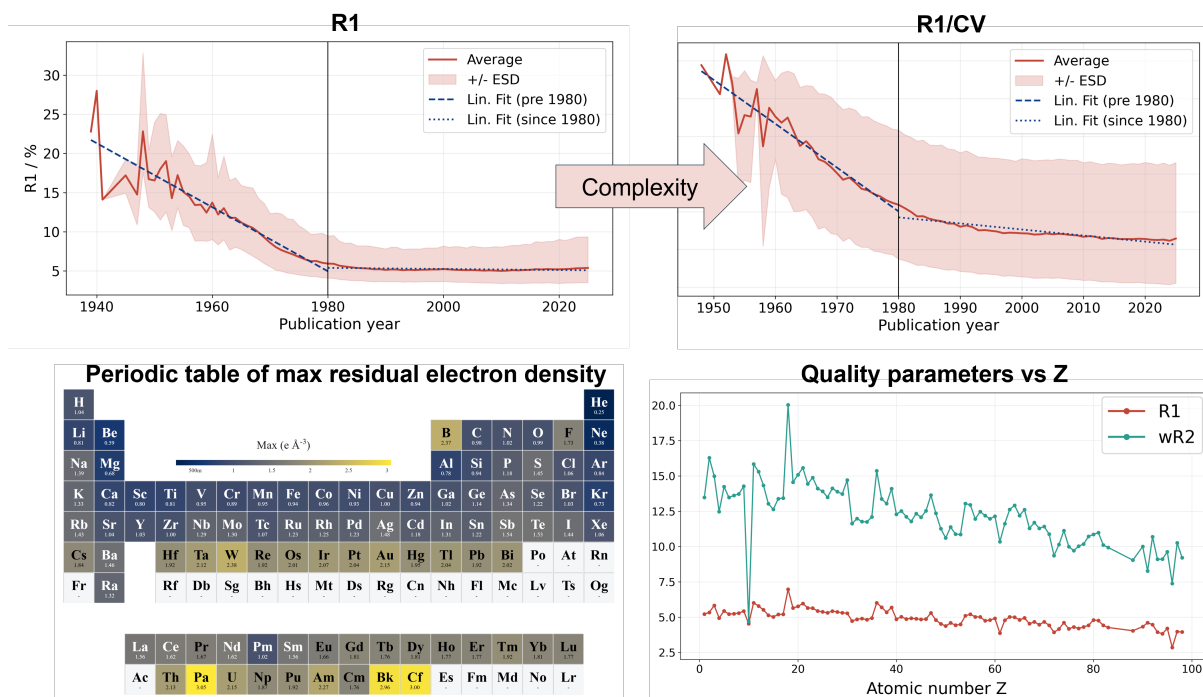


Figure 10.1: Key results from the CSD study in Chapter 3. The top figures show the temporal progression of the agreement factor $R1$ (left) and the cell volume normalized $R1$ (right). The bottom figures show the periodic table of the elements highlighting the maximum residual density (left) and $R1$ as a function of atomic number Z (right).

crystallographic benchmarking, electron diffraction, and mixed occupancies demonstrate that many repetitive refinement tasks can be automated without restricting the underlying functionality of Olex2, olex2.refine, or NoSpherA2. This reduces manual transcription, inconsistent refinement decisions, and the risk that apparent trends originate from differences in model setup rather than from the experiment.

Automation, however, does not make a model correct. SISYPHOS is most useful when the scientific question and the relevant comparison criteria have been defined in advance. The serial output can reveal outliers, parameter correlations, or systematic trends, but these observations still require chemical and crystallographic interpretation. The broader methodological conclusion is therefore that high-throughput crystallography should combine automation with explicit model validation rather than treating refinement as an unsupervised optimisation of a single residual factor.

10.3 Anomalous dispersion refinement

The uranium study demonstrated that anomalous dispersion parameters can be refined robustly even in the pronounced and rapidly varying region of heavy-element L absorption edges. The refined f'' values followed the independently measured X-ray absorption spectra, while f' followed their Kramers–Kronig transforms. Agreement was obtained not only at the intense L_3 edge but also at the weaker L_2 and L_1 edges. Chemically equivalent uranium sites produced closely similar parameters, whereas the comparison among different compounds showed the expected sensitivity to the chemical environment.

These results demonstrate that anomalous dispersion is not merely a tabulated correction.

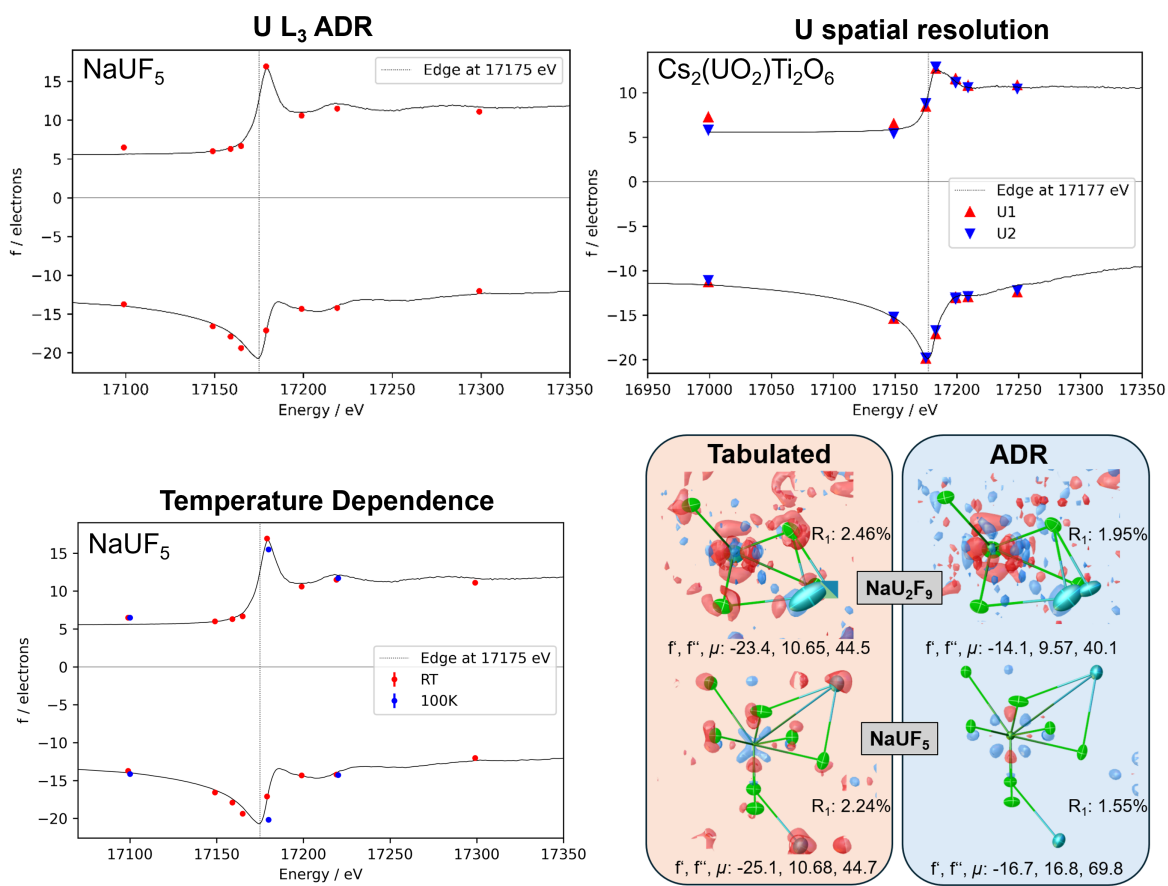


Figure 10.2: Key results from the uranium ADR study in Chapter 7. The top figures show results obtained from anomalous dispersion refinement of the compounds NaUF_5 (left) and $\text{Cs}_2(\text{UO}_2)\text{Ti}_2\text{O}_6$ (right). The bottom figures show the the temperature independence of ADR for NaUF_5 (left) and the residual electron density around the asymmetric unit of NaUF_5 and NaU_2F_9 at the $1.0 \text{ e} \cdot \text{\AA}^{-3}$ (top) and the $0.9 \text{ e} \cdot \text{\AA}^{-3}$ iso-level between for using tabulated and refined values for anomalous dispersion paramters (right).

It is rather a compound-specific contribution to the crystallographic scattering model and contains spatially resolved spectroscopic information. Tabulated values may differ substantially from the values appropriate to a particular chemical environment, especially where the absorption spectrum contains sharp near-edge structure. Inaccurate values can influence atomic positions, displacement parameters, occupancies, disorder models, or weighting parameters and can therefore propagate beyond the immediate environment of the resonating atom.

Application of anomalous dispersion refinement to previously published $\text{Mo K}\alpha$ data improved the four uranium structures, despite the laboratory wavelength being fixed and the original models already being of high quality. The reductions in residual electron density and refinement weights show that the benefit is not restricted to synchrotron experiments. This is especially relevant for uranium because $\text{Mo K}\alpha$ radiation lies just above the uranium L_3 edge. At the same time, the study established an important limitation: refinement of additional dispersion parameters should not be used to absorb unresolved disorder, twinning, anharmonic motion, or inadequate absorption correction. The method is most defensible for high-quality data and when changes in f' and f'' can

be evaluated against physical expectations or independent spectroscopy.

10.4 Radiation damage

The systematic study of BiPh₃, summarised in Figure 10.3, established radiation damage as a significant limitation not only for macromolecular crystallography but also for small-molecule and quantum-crystallographic experiments. Across 24 crystals and 330 diffraction data sets, the decay of diffraction intensity could be described as a dose-dependent process, but the fitted rates varied substantially among experimental arrangements. This variation shows why a universal exposure-time limit is not meaningful: photon energy, flux, beam profile, detector strategy, temperature, crystal mounting, and dose calculation all affect the measured progression.

The structural evolution of BiPh₃ indicated that the decrease of diffraction power with radiation dose primarily resulted from a gradual loss of long-range periodicity. Unit-cell dimensions and atomic displacement parameters increased, bond-length precision deteriorated, and the residual density around bismuth became progressively larger. The covalent molecular framework, however, remained largely intact while the crystal was still structurally refinable. Stable bond distances also indicate that chemical bonding is not influenced in the process. X-ray absorption spectra of diffractionless crystals retained a local bismuth environment similar to that of fresh material. These observations support an X-ray-induced transition towards an amorphous or highly disordered state before extensive cleavage of the Bi–C bonds. Only exceptionally prolonged exposure produced clear spectroscopic evidence for substantial oxidation.

When the damage progression was considered as a function of absorbed dose, no statistically significant change in decay mechanism was found on crossing the Bi L_3 edge. The edge nevertheless remains experimentally important because absorption, fluorescence, and dose accumulation increase above it, while anomalous dispersion and absorption corrections become more uncertain. The apparent interaction between photon energy and temperature further indicates that cooling cannot be assumed to affect all experiments in an energy-independent manner. This observation requires confirmation with a larger, deliberately balanced data set before it can be generalised.

The main conclusion from the radiation-damage study is therefore not a single universal correction or safe dose. Instead, radiation damage must be treated as an experiment-specific and dose-dependent source of model error. Serial measurements, continuous monitoring of intensity statistics and displacement parameters, and dose-aware data-collection strategies are essential, especially when minute electron-density features are the target of the experiment. The study also shows the value of simultaneous or sequential diffraction and spectroscopy: diffraction reports the loss of periodic order, whereas X-ray absorption spectroscopy tests whether the local chemical environment has changed.

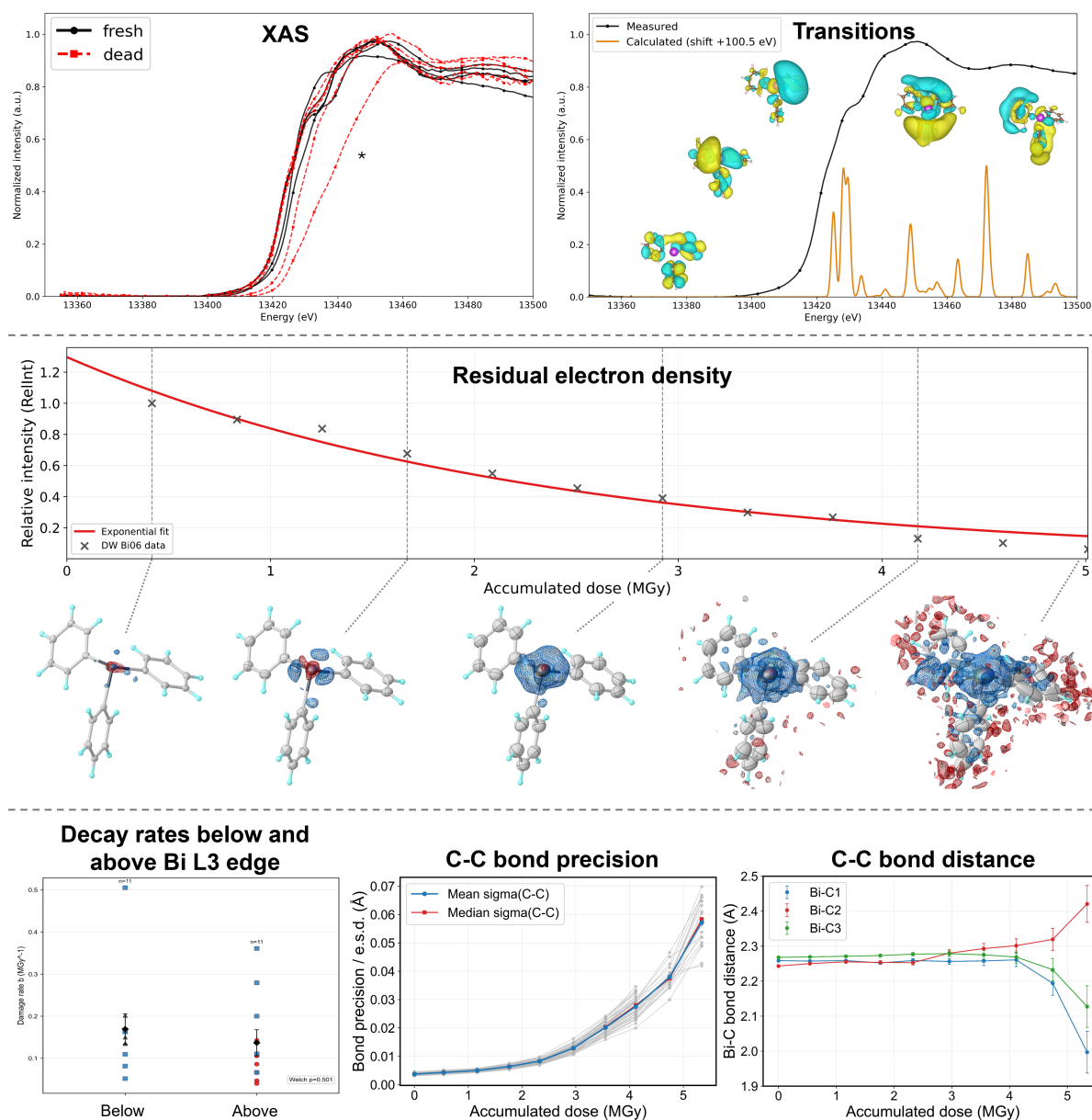


Figure 10.3: Key results from the radiation damage study in Chapter 8. The top figures show X-ray absorption spectra of fresh and diffractionless single-crystals of BiPh₃ (left) and the comparison with the calculated transitions obtained from ROCIS-DFT (right). The middle figure shows the residual electron density around the asymmetric unit in BiPh₃ at the $0.7 \text{ e} \cdot \text{\AA}^{-3}$ iso-level as a function of radiation decay, given by the decrease of signal-to-noise-ratio as a function of dose. The bottom pictures show the decay rates for the ESRF (blue) and APS (red) datasets which are recorded below and above the Bi L₃ absorption edge at 13.42 keV (left), as well as C-C bond precision (middle) and C-C bond distance (right) as a function of dose in MGy.

10.5 Quantum crystallography

The analysis of $\text{Cp}^{\text{III}}\text{NiP}_3$ demonstrated how complementary quantum-crystallographic methods can convert a crystal structure into a chemically interpretable electronic structure. Multipolar modelling and X-ray restrained wavefunction fitting gave consistent descriptions of the Ni–P and P–P interactions and supported the isolobal relationship between the $\text{Cp}^{\text{III}}\text{Ni}$ fragment and a phosphorus vertex of P_4 . The Ni–P bonds are polarised and covalent in origin. Together with the topology and orbital interactions, this supports the description of the NiP_3 unit as a metallatetrahedrane rather than π -coordination by a planar cyclo- P_3 ligand.

The P–P bonds in $\text{Cp}^{\text{III}}\text{NiP}_3$ are shorter and have comparable or somewhat higher bond orders than those in white phosphorus, although the electronic delocalisation between phosphorus atoms is lower. This distinction reconciles geometric strength with electronic localisation and helps explain why the nickel complex is markedly more air-stable than pyrophoric P_4 while retaining useful reactivity. The experimentally restrained frontier orbitals also identify chemically accessible regions consistent with both nucleophilic attack and electrophilic insertion into P–P bonds. Solid-state ^{31}P NMR spectroscopy and calculations further showed that the cyclo- P_3 unit undergoes dynamic exchange, with a calculated rotational barrier of only 8.9 kJ mol^{-1} . The work also established the first Cu $\text{K}\beta$ multipolar model and X-ray restrained wavefunction fitted model. Anomalous dispersion refinement in these models significantly improved the model quality and realistic charges were only obtained after ADR was applied. This shows that even for laboratory data, ADR can have a significant effect on the derived electron density and bonding analysis. Chemically similar conclusions were obtained from Mo $\text{K}\alpha$ and lower-resolution Cu $\text{K}\beta$ data, despite the strong absorption associated with nickel at the latter energy. High-resolution data remain preferable for freely parameterised charge-density models, but the comparison indicates that meaningful wavefunction-based and topological information is not necessarily restricted to a single ideal experimental configuration. More important than any individual bonding index was the agreement among geometry, QTAIM, orbital analyses, localisation measures, NMR spectroscopy, and the known reactivity of the compound.

The WYLID study extended the complementary approach to a highly delocalised organic system with competing Lewis and resonance descriptions. WYLID was identified as the red condensation product associated with conventional YLID synthesis and was obtained selectively from Bindandione. The combination of multi-wavelength diffraction, HAR, multipolar modelling, X-ray restrained wavefunction fitting, and conventional quantum-chemical calculations consistently favoured an ylide-type S–C interaction over an ylene description.

For the C–O groups, the analyses favoured carbonyl bonding over the enolate alternative. The C–O group adjacent to the SMe_2 fragment did not differ from the two more remote carbonyl groups, and comparison with Bindandione showed that introduction of a SMe_2 group did not significantly shift the local carbonyl/enolate equilibrium. Reference profiles of the Laplacian along the C–O bond path and the agreement of multiple bond indices provided a practical way to distinguish the two limiting descriptions. The natural resonance analysis nevertheless found a large number of contributing structures, with no individual Lewis structure carrying a dominant weight. The appropriate conclusion is therefore not that delocalisation is absent, but that the dominant local bonding characteristics are ylidic and carbonyl-like within a strongly delocalised π system.

The WYLID and $\text{Cp}^{\text{III}}\text{NiP}_3$ studies illustrate why a chemically meaningful reference is essential. Electron-density values or bond critical points have limited interpretative power in isolation. Their significance becomes clearer when equivalent quantities are compared among related bonds, alternative models, known reference compounds, and independently observed reactivity. This comparative principle was also decisive in the most demanding study of the dissertation.

The trithorium clusters provided an extreme test of whether experimentally informed electron-density analysis can resolve a weak interaction between several very heavy atoms. HAR models based on routine Mo $K\alpha$ and Cu $K\alpha$ diffraction data reproduced the main features of independent relativistic quantum-chemical calculations. Both the three-centre two-electron and three-centre one-electron clusters exhibited three Th–Th bond paths, a central ring critical point, valence-shell charge concentration in the Th_3 region, and corresponding ELI-D and deformation-density features. The two-electron species consistently showed stronger and more concentrated interaction density than the one-electron analogue, in agreement with its shorter Th–Th distances and electronic formulation.

The combined evidence experimentally visualised cooperative Th_3 σ bonding arising from constructive contributions of the three thorium centres. The result validates earlier quantum-chemical descriptions while also demonstrating that HAR can be extended from conventional light-element applications to systems containing three adjacent $Z = 90$ atoms. Importantly, the decisive advantage was not an attempt to derive a completely theory-free density. HAR used the experimentally determined geometry and diffraction data to constrain a quantum-chemical description, and this experiment–theory combination produced substantially better agreement than calculations based solely on an optimised geometry.

The actinide study does not eliminate the intrinsic challenges of heavy-atom charge-density work. Residual features remain near thorium, and the derived density depends on the quantum-chemical method, relativistic treatment, partitioning scheme, and quality of the diffraction data. Nevertheless, the close agreement of independent experimental wavelengths, HAR and purely quantum-mechanical topologies, deformation densities, localisation indicators, and prior spectroscopic evidence makes the bonding assignment substantially more robust than any single method alone. The study therefore expands the realistic scope of routine quantum crystallography and suggests that chemically relevant bonding information can be obtained for fragile, radioactive, and synthetically scarce compounds without requiring an idealised high-resolution synchrotron experiment in every case.

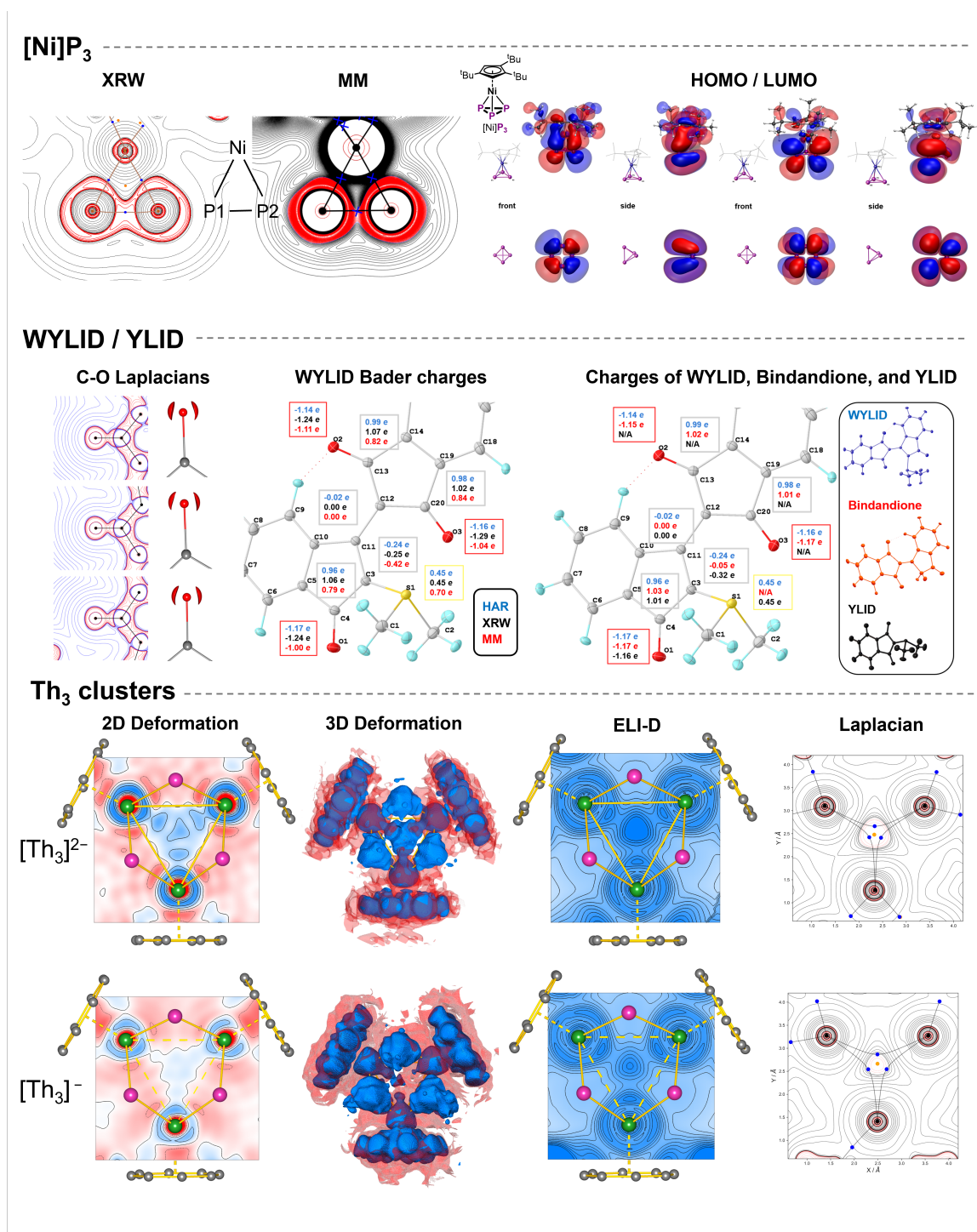


Figure 10.4: Key results from the quantum crystallographic studies in Chapters 4, 5, and 6. The top figures show the comparison of the Ni–P bond 2D Laplacian profiles obtained from XRD and MM (left), and the obtained HOMO/LUMO orbital plots of the Cp^{'''}NiP₃ XRW model and the DFT P₄ orbitals. The middle figures show C–O Laplacian profiles in WYLID (left), Bader charges between the HAR, MM, and XRW models of WYLID (middle), and the comparison HAR bader charges of WYLID, Bindandione, and YLID (right). The bottom figures show the 2D (left) and 3D (center-left) dynamic deformation electron density, the ELI-D (center-right), and the Laplacian (right) of the [Th₃]^{2−} (top) and [Th₃][−] clusters.

10.6 General conclusions

Several general conclusions emerge from the combined work.

First, a small crystallographic residual is necessary but not sufficient for a reliable chemical model. Agreement factors can remain acceptable while anomalous dispersion, absorption, radiation damage, disorder, or an inadequate spherical density is compensated by other parameters. Residual-density distributions, parameter stability, independent wavelengths, serial measurements, spectroscopy, and chemically reasonable trends are therefore indispensable parts of validation.

Second, the independent atom model remains highly effective for routine connectivity and geometry, but it is not neutral with respect to advanced chemical questions. Its neglect of bonding density is most evident in light-element structures, whereas heavy-element structures are dominated by imperfect descriptions of core scattering and experimental effects. The appropriate advance is not to replace the independent atom model indiscriminately, but to use aspherical and wavefunction-based models when the scientific question requires them and when the data support the additional information.

Third, experimental and theoretical methods are most powerful when they are combined rather than placed in competition. Multipolar modelling offers a flexible experimental density, HAR provides an accessible experiment-based geometry and aspherical scattering model, and X-ray restrained wavefunction fitting tests how the measured data modify a wavefunction. Quantum-chemical calculations, spectroscopy, and reference compounds then provide independent constraints on interpretation. The strongest conclusions in this dissertation arose where these descriptions converged.

Fourth, reproducibility becomes increasingly important as crystallography moves towards serial and high-throughput experiments. Tools such as SISYPHOS make it possible to apply identical refinement logic to hundreds or thousands of models and to preserve the resulting parameters for statistical analysis. This is essential for resonant diffraction, radiation-damage series, model benchmarking, and database-scale studies, but it must be accompanied by transparent settings, physically motivated constraints, and inspection of outliers.

Finally, the work demonstrates that diffraction can provide substantially more than atomic coordinates. It can measure the consequences of resonant electronic transitions, follow the loss of crystalline order under irradiation, distinguish competing local bonding descriptions, connect an isolobal analogy to reactivity, and visualise one- and two-electron metal-metal bonding between actinides. Achieving this level of chemical information requires the experiment, correction procedure, structural model, and bonding analysis to be designed as a single workflow.

10.7 Outlook

The immediate methodological priority is a more coherent approach of experimental corrections and electron-density models. For resonant heavy-element diffraction, anomalous dispersion and absorption should be refined or iterated self-consistently and validated against X-ray absorption spectra where possible. Radiation-dose calculations should become a standard part of high-flux small-molecule experiments, and diffraction metadata should record flux, beam size, exposure, crystal dimensions, and temperature sufficiently well for later dose reconstruction. Systematic studies across chemically diverse compounds

are required before transferable small-molecule dose limits or damage classifications can be proposed.

Serial refinement should be extended from model execution to automated diagnostics. Future versions of SISYPHOS will detect parameter correlations, detector saturation, abrupt changes in unit-cell or intensity statistics, and physically implausible dispersion parameters.

For quantum crystallography, the next step is to define practical uncertainty estimates for derived bonding descriptors. Crystallographic standard uncertainties do not directly represent the sensitivity of QTAIM, NBO, ELI-D, or deformation-density properties to the choice of functional, basis set, relativistic Hamiltonian, cluster environment, resolution cutoff, weighting scheme, or treatment of thermal motion. Ensembles of serial refinements in which these choices are varied systematically will provide confidence intervals for chemically important conclusions.

The results for the trithorium clusters indicate that HAR can be applied to other f-element systems in which covalency, oxidation state, or metal-metal interactions remain controversial. Combining HAR with energy-dependent diffraction, XANES, EPR, vibrational spectroscopy, and magnetic measurements should allow geometric, electronic, and oxidation-state effects to be separated more rigorously. Likewise, the comparative protocols developed for $\text{Cp}^{\text{III}}\text{NiP}_3$ and WYLID can be transferred to reactive main-group compounds, transition-metal clusters, and delocalised organic systems in which conventional Lewis structures provide incomplete or conflicting descriptions.

At the database level, future quality assessment should move beyond global averages and incorporate resolution, completeness, disorder, diffraction technique, radiation source, temperature, structural complexity, refinement model, and data availability. The long-term objective should be a fit-for-purpose assessment of a crystal structure rather than a universal ranking by one residual factor. Such developments would connect the central themes of this dissertation: reliable experiments, physically correct models, reproducible computation, and the extraction of chemical information from electron density.

Appendices

Abbreviations

AD	anomalous dispersion
ADP	atomic displacement parameter
ADR	anomalous dispersion refinement
AI	artificial intelligence
ANL	Argonne National Laboratory
API	application programming interface
APS	Advanced Photon Source
B3LYP	Becke three-parameter Lee–Yang–Parr density functional
BCP	bond critical point
BM20-CRG	BM20 Collaborative Research Group beamline at the European Synchrotron Radiation Facility; the Rossendorf Beamline
BP86	Becke 1988 exchange and Perdew 1986 correlation density functional
CCD	charge-coupled device
CCDC	Cambridge Crystallographic Data Centre
COD	1,5-cyclooctadiene
CPCM	conductor-like polarizable continuum model
Cp'''	1,2,4-tri- <i>tert</i> -butylcyclopentadienyl
CPU	central processing unit
CSD	Cambridge Structural Database
CSV	comma-separated values
DFT	density functional theory
DI	delocalization index
DKH2	second-order Douglas–Kroll–Hess Hamiltonian
DME	1,2-dimethoxyethane
DMSO	dimethyl sulfoxide
DOI	digital object identifier
ELI-D	electron localizability indicator in the ELI-D representation
EPR	electron paramagnetic resonance
ESD	estimated standard deviation
ESP	electrostatic potential
ESRF	European Synchrotron Radiation Facility
GGA	generalized gradient approximation
GUI	graphical user interface

HAR	Hirshfeld atom refinement
HF	Hartree–Fock
HOMO	highest occupied molecular orbital
HZDR	Helmholtz-Zentrum Dresden-Rossendorf
IAM	independent atom model
KKT	Kramers–Kronig transformation
LUMO	lowest unoccupied molecular orbital
M06-2X	Minnesota 2006 hybrid meta-GGA density functional with a high fraction of exact exchange
meta-GGA	meta-generalized gradient approximation
MM	multipolar model or multipolar modelling
MO	molecular orbital
NBO	natural bond orbital
NIR	near-infrared
NLMO	natural localized molecular orbital
NMR	nuclear magnetic resonance
NPA	natural population analysis
NPD	non-positive definite
NRT	natural resonance theory
PBE	Perdew–Burke–Ernzerhof density functional
PBE0	hybrid Perdew–Burke–Ernzerhof density functional
Ph	phenyl
PNO	pair natural orbital
QM	quantum mechanics or quantum-mechanical
QTAIM	quantum theory of atoms in molecules
QZVP	quadruple-zeta valence polarized
r^2SCAN	revised regularized strongly constrained and appropriately normed density functional
RCP	ring critical point
RI	resolution of the identity
RIJCOSX	resolution-of-the-identity treatment of Coulomb integrals combined with the chain-of-spheres exchange approximation
ROBL	Rossendorf Beamline
ROCIS	restricted open-shell configuration interaction singles
RT	room temperature
SARC	segmented all-electron relativistically contracted basis-set family
SCF	self-consistent field
SC-XRD	single-crystal X-ray diffraction
SEM	standard error of the mean

SI	Supporting Information
SOC	spin-orbit coupling
SVP	split-valence polarized
THF	tetrahydrofuran
TZVP	triple-zeta valence polarized
UV	ultraviolet
UV-Vis-NIR	ultraviolet-visible-near-infrared
VSCC	valence-shell charge concentration
VSCD	valence-shell charge depletion
WBI	Wiberg bond index
WYLID	red condensation product formed from YLID and 1,3-indandione; compound name introduced in the corresponding study
XANES	X-ray absorption near-edge structure
XAS	X-ray absorption spectroscopy or X-ray absorption spectrum
XRD	X-ray diffraction
XRW	X-ray restrained wavefunction
YLID	2-dimethylsulfuranylidene-1,3-indanedione
ZORA	zeroth-order regular approximation
ω B97X-D	range-separated hybrid density functional including an empirical dispersion correction
ω B97X-V	range-separated hybrid density functional including nonlocal VV10 correlation

Selected Crystallographic Symbols and Data Descriptors

F_{obs}	observed structure-factor amplitude
F_{calc}	calculated structure-factor amplitude
f'	dispersive part of the anomalous scattering correction
f''	absorptive part of the anomalous scattering correction
$I/\sigma(I)$	intensity-to-standard-uncertainty ratio; a measure of signal-to-noise
R_1	conventional crystallographic residual factor based on structure-factor amplitudes
R_{int}	internal agreement factor of symmetry-equivalent reflections
U_{eq}	equivalent isotropic displacement parameter
wR_2	weighted crystallographic residual factor based on squared structure-factor amplitudes

Statement for the use of generative artificial intelligence

In different sections of this thesis, generative artificial intelligence (AI) tools were used to assist in the writing process, data analysis, and programming. The following statement provides an overview of the extent and nature of AI usage in this thesis.

Generative AI tools were employed to assist in the writing process, particularly for improving the clarity, coherence, and overall readability of the text. AI was used to suggest alternative phrasings, correct grammatical errors, and enhance the flow of sentences. However, all scientific content, interpretations, and conclusions presented in this thesis are the original work of the author and were not generated by AI. The use of AI in writing was limited to language enhancement and did not contribute to the scientific substance of the thesis.

In particular, generative AI was used in chapters 1, 2, 3, 7, 8 and 10. Generative AI helped to generate the code for the data analysis and visualisation in chapters 2, and 8. All text, code, plots, and results the AI generated were critically evaluated and edited by the author to ensure accuracy and relevance to the research presented in this thesis. The author takes full responsibility for the content of this thesis, including any sections where AI tools were used for writing assistance or data analysis.

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