

# The Scope of the Applicability of Non-relativistic DFT Calculations of NMR Chemical Shifts in Pyridine-Metal Complexes for Applied Applications

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Heavy metals are toxic, but it is impossible to stop using them. Considering the variety of molecular systems in which they can be present, the multicomponent nature and disorder of the structure of such systems, one of the most effective methods for studying them is NMR spectroscopy. This determines the need to calculate NMR chemical shifts for expected model systems. For elements beyond the third row of the periodic table, corrections for relativistic effects are necessary when calculating NMR parameters. Such corrections may be necessary even for light atoms due to the shielding effect of a

neighboring heavy atom. This work examines the extent to which non-relativistic DFT calculations are able to reproduce experimental  $^{15}\text{N}$  and  $^{113}\text{Cd}$  NMR chemical shift tensors in pyridine-metal coordination complexes. It is shown that while for the calculation of  $^{15}\text{N}$  NMR chemical shift tensors there is no real need to consider relativistic corrections, for  $^{113}\text{Cd}$ , on the contrary, none of the tested calculation methods could reproduce the experimentally obtained tensor to any extent correctly.

## Introduction

Heavy metals are vital to our very existence and critical to our industrial development. Heavy metals are toxic for all living things.<sup>[1]</sup> Both statements are equally true. For example, zinc is necessary for the growth of living beings in general and the function of carbonic anhydrase in particular.<sup>[2]</sup> It can be used to reduce cadmium toxicity.<sup>[3]</sup> On the other hand, zinc is involved in the pathogenesis of Alzheimer's disease.<sup>[4]</sup> In any case, heavy metals are and will be actively used in industry.<sup>[5]</sup> As a result, they are present in wastewater from where they must be removed in one way or another. The most used method is their adsorption onto amorphous sorbents.<sup>[6]</sup> Regardless of whether the goal is to optimize the sorption properties of the host or to understand the mechanisms of chemical and biological activity of a heavy metal, success depends on the ability to model the complex molecular system being studied.<sup>[7]</sup> The most obvious way to check the realism of simulation results is to compare some selected experimental parameters measured for the system under study and calculated for the model used. Considering the diversity of the systems under study, their multi-component nature, and the disorder of their structure,

one of the most acceptable methods for such verification is NMR spectroscopy. The experimental part of such testing can often be carried out using standard methods. The nuclei of some heavy metals are NMR-active in themselves.<sup>[8]</sup> In addition, one can find NMR-active nuclei of ligands whose NMR parameters depend on the properties of the metal-ligand interactions.<sup>[9]</sup> Such studies are very numerous.

In contrast, the theoretical part is generally less straightforward. For elements beyond the third row of Mendeleev's periodic table, it is necessary to introduce corrections for relativistic effects when calculating NMR parameters.<sup>[10]</sup> Moreover, such corrections may be necessary to consider the shielding effects of a neighboring heavy atom on light atoms, the spin-orbit heavy-atom effect on the light-atom (SO\_HALA effect).<sup>[11]</sup> In recent years, great progress has been made in the accuracy of accounting for these relativistic corrections.<sup>[12]</sup> However, not all software packages allow such calculations, the number of corresponding basis sets remains limited, and the discrepancies between calculated and experimental values are sometimes too large to use such calculations for applied purposes.<sup>[13]</sup> At the same time, some studies have shown that the chemical shifts of heavy atoms can be correctly reproduced using non-relativistic calculations.<sup>[14]</sup> In other studies, relativistic corrections on the SO\_HALA effect were either very small or even worsened the results.<sup>[15]</sup> Summarizing the data available in the literature, it can be said that for elements beyond the third row of the periodic table, the proximity between experimental chemical shifts and their non-relativistic calculations occurs only in the case of accidental cancellation of calculation errors. In contrast,  $^{31}\text{P}$  NMR chemical shift calculations do not require relativistic corrections for molecules in which phosphorus is coordinated to lighter atoms.<sup>[16]</sup> These corrections are small for phosphine sulfides but become significant for selenides and tellurides.<sup>[17]</sup> It also appears that in coordination compounds,

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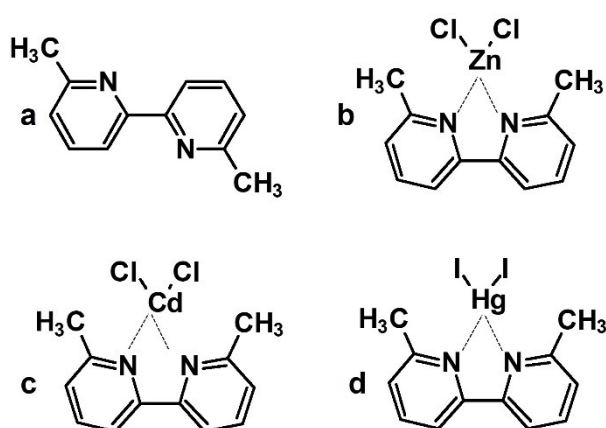
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$^{31}\text{P}$  NMR chemical shift calculations rarely require relativistic corrections.<sup>[18]</sup> On the other hand, most of the studies cited above refer to isotropic chemical shifts and not to the corresponding chemical shift tensors. It seems important to find out the importance of considering the SO\_HALA effect on the chemical shift tensors of the atoms of the ligands in coordination complexes.

Figure 1 shows model systems studied in this work. Bipyridine was selected as the ligand because the activity of many sorbents used for the removal of heavy metals is based precisely on the presence of a nitrogen atom in the active sites. The zinc-cadmium-mercury series should make it possible to follow the amplification of the SO\_HALA effect on the  $^{15}\text{N}$  NMR chemical shift tensor as the atomic number of the metal increases. The single-crystal structures of these model systems are known. These structures will be used for non-relativistic calculations of their  $^{15}\text{N}$  NMR chemical shift tensors. The same tensors will be measured for these systems experimentally. Accordingly, the reliability of the theoretical calculations will be verified experimentally. This is the main goal of this work, which should answer the question whether non-relativistic calculations of the  $^{15}\text{N}$  NMR chemical shifts in such coordination complexes can be used to define the most probable structure of these complexes in composite amorphous systems.

Besides that, the  $^{113}\text{Cd}$  chemical shift tensor of MeBiPy\_Cd will be measured experimentally and calculated using different non-relativistic Density Function Theory (DFT) functionals. This secondary goal is to answer the question of whether an accidental cancellation of calculation errors makes a particular functional/basis set combination useful for at least a qualitative analysis of limited confidence.



**Figure 1.** Model systems studied in this work. a) 6,6'-dimethyl-2,2'-bipyridine (MeBiPy), b) dichloro-(6,6'-dimethyl-2,2'-bipyridine- $\kappa^2\text{N,N}'$ )-zinc(II) (MeBiPy\_Zn), c) dichloro-(6,6'-dimethyl-2,2'-bipyridine- $\kappa^2\text{N,N}'$ )-cadmium(II) (MeBiPy\_Cd), d) diiodido-(6,6'-dimethyl-2,2'-bipyridine- $\kappa^2\text{N,N}'$ )-mercury(II) (MeBiPy\_Hg).

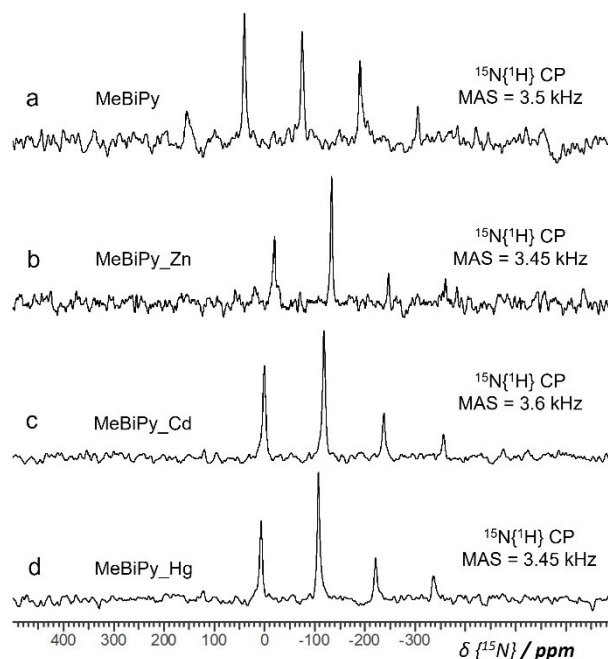
## Results and Discussion

### $^{15}\text{N}$ NMR

Whether bipyridine adopts the *cis* or *trans* conformation in a given molecular system depends on the nature of non-covalent interactions in which its nitrogens participate.<sup>[19]</sup> In the absence of specific interactions or upon adsorption on silica, the *cis* conformer has the lowest energy, whereas after protonation the *trans* conformer has the lowest energy.<sup>[20]</sup> Therefore, although the  $^{15}\text{N}$  chemical shift of pyridines very characteristically depends on the geometric parameters of a non-covalent interaction involving nitrogen,<sup>[21]</sup> the *cis/trans* isomerism of bipyridine violates this dependence.

Due to the low sensitivity of  $^{15}\text{N}$  NMR, the  $^{15}\text{N}$  NMR chemical shift tensors of the studied model systems were obtained from MAS spectra at slow rotation rates. Typical spectra are shown in Figure 2. Table 1 presents these tensors in the Herzfeld-Berger convention using the isotropic value,  $\delta_{\text{iso}}$ , the span,  $\Omega$ , and the skew,  $k$ .<sup>[16a]</sup> Note that the numerical values of  $\delta_{\text{iso}}$  can be measured with high accuracy within an error of about 0.3 ppm, the values of  $\Omega$  and  $k$  can only be estimated.

Three structures of MeBiPy were used for  $^{15}\text{N}$  NMR calculations. In the structures referred as to NOFZUD and NOFZUD01 the nitrogen and carbon positions were taken from the experimental XRD structures NOFZUD and NOFZUD01 while the hydrogen positions were optimized using the  $\omega\text{B97XD/def2tzvp}$  approximation.<sup>[22]</sup> Here and below, these designations correspond to the refcodes of the systems in the Cambridge Crystallographic Data Centre (CCDC) database. The structure referred as to MeBiPy\_DFT was fully optimized using the same approximation. These structures are reported in Tables S1–S3,



**Figure 2.** MAS  $^{15}\text{N}\{^1\text{H}\}$  CP NMR spectra of a) MeBiPy, b) MeBiPy\_Zn, c) MeBiPy\_Cd, d) MeBiPy\_Hg.

**Table 1.** Experimental and calculated at the  $\omega$ B97XD/def2tzvp approximation  $^{15}\text{N}$  NMR chemical shift tensors of the model systems.

Structure	Method	$\delta_{\text{iso}}(^{15}\text{N})$ [ppm]	$\Omega$ [ppm]	$\kappa$
MeBiPy	NMR	$-76.3 \pm 0.3$	$610 \pm 20$	$0.35 \pm 0.05$
NOFZUD <sup>[b]</sup>	DFT	$-67^{\text{[a]}}$	616	0.386
NOFZUD01 <sup>[b]</sup>	DFT	$-70^{\text{[a]}}$	612	0.389
MeBiPy_DFT	DFT	$-75^{\text{[a]}}$	613	0.380
MeBiPy_Zn	NMR	$-135.0 \pm 0.3$	$400 \pm 20$	$0.7 \pm 0.1$
BUDCAF <sup>[c]</sup>	DFT	$-127^{\text{[a]}}$	439	0.713
BUDCAF01 <sup>[b]</sup>	DFT	$-128^{\text{[a]}}$	434	0.728
		$-128^{\text{[a]}}$	431	0.731
MeBiPy_Cd	NMR	$-120.0 \pm 0.3$	$470 \pm 10$	$0.70 \pm 0.05$
DURYIZ <sup>[d]</sup>	DFT	$-121^{\text{[a]}}$	464	0.632
		$-121^{\text{[a]}}$	459	0.651
MeBiPy_Hg	NMR	$-108.6 \pm 0.3$	$450 \pm 10$	$0.50 \pm 0.05$
ULAXIP <sup>[e]</sup>	DFT	$-108^{\text{[a]}}$	508	0.483
		$-101^{\text{[a]}}$	515	0.489

[a]  $\delta_{\text{iso}} = \sigma^{\text{ref}} - \sigma_{\text{iso}}$ ,  $\sigma^{\text{ref}}(^{15}\text{N}) = -143 \pm 3$  ppm.<sup>[23]</sup> [b] The standard deviation (SD(CN)) for N–C bonds in this structure is 0.002 Å. [c] SD(CN) = 0.003 Å. [d] SD(CN) = 0.004 Å. [e] SD(CN) = 0.009 Å.

Supporting Information. Their  $^{15}\text{N}$  NMR chemical shielding tensors were calculated using the  $\omega$ B97XD/def2tzvp approximation. The isotropic chemical shift values of these tensors,  $\delta_{\text{iso}}$ , reported in Table 1, were obtained from the original isotropic absolute shielding values,  $\sigma_{\text{iso}}$ , as  $\delta_{\text{iso}} = \sigma^{\text{ref}} - \sigma_{\text{iso}}$ . The value of the absolute shielding of the reference compound  $^{15}\text{NO}_2\text{CH}_3$  in the  $\omega$ B97XD/def2tzvp approximation is  $\sigma^{\text{ref}}(^{15}\text{N}) = -143 \pm 3$  ppm.<sup>[23]</sup> It is expected that the error in estimating the  $\delta_{\text{iso}}$  in this approximation should not exceed 3 ppm and does not change when using a larger basis set.<sup>[23]</sup> The value calculated for MeBiPy\_DFT falls within this range. For NOFZUD and NOFZUD01 the error is larger regardless of the basis set for the  $\omega$ B97XD functional but falls within the expected range for the TPSSh and B3LYP functionals, Table S4. However, the 3 ppm error range is only achievable if the atomic coordinates are determined with high precision, which requires the use of complex refinement methods and is rare for structures deposited at the CCDC.<sup>[24]</sup> Therefore, the deviation of the  $\delta_{\text{iso}}$  calculated for NOFZUD and NOFZUD01 from the experimental value should more likely be attributed to the insufficient accuracy of these structures themselves, and not to the shortcomings of the calculation methods.

Two structures of MeBiPy\_Zn were used for  $^{15}\text{N}$  NMR calculations. In these structures referred as to BUDCAF and BUDCAF01 the nitrogen and carbon positions were taken from the experimental XRD structures BUDCAF and BUDCAF01 while the hydrogen positions were optimized using the  $\omega$ B97XD/def2tzvp approximation.<sup>[25]</sup> These structures are reported in Tables S5, S6. The BUDCAF and BUDCAF01 structures exhibit different space groups,  $P2_1/m$  and  $P2_1/n$ , respectively. Thus, in BUDCAF01, the nitrogen atoms of bipyridine are crystallographically different. However, despite this difference, the calculated  $\delta_{\text{iso}}$  values of these nitrogens differ by less than 1 ppm. For both structures, the calculated  $\delta_{\text{iso}}$  values deviate from the experimental one by 7–8 ppm, which exceeds the

expected range of 3 ppm. The use of other functionals does not solve the problem, Table S4. The  $\Omega$  of the calculated tensors also differ from the experimental value. The reason for all these differences may be either, again, the inaccuracy of the atomic coordinates, or the SO\_HALA effect. In the latter case, an increase in the deviations of the calculated values from the experimental ones should be expected for complexes with Cd and Hg.

One structure of MeBiPy\_Cd was used for  $^{15}\text{N}$  NMR calculations. In this structure referred as to DURYIZ the nitrogen and carbon positions were taken from the experimental XRD structure DURYIZ while the hydrogen positions were optimized using the  $\omega$ B97XD/def2tzvp approximation.<sup>[26]</sup> This structure is reported in Table S7. In DURYIZ, the nitrogen atoms of bipyridine are crystallographically different, but their  $\delta_{\text{iso}}$  differ by less than 1 ppm and are within the error range of the experimental value for all studied functionals, Tables 1 and S4. The calculated values of  $\Omega$  and  $\kappa$  also agree well with the experimental ones.

One structure of MeBiPy\_Hg was used for  $^{15}\text{N}$  NMR calculations. In this structure referred as to ULAXIP the nitrogen and carbon positions were taken from the experimental XRD structure ULAXIP while the hydrogen positions were optimized using the  $\omega$ B97XD/def2tzvp approximation.<sup>[27]</sup> This structure is reported in Table S8. In ULAXIP, the nitrogen atoms of bipyridine are crystallographically different and their  $\delta_{\text{iso}}$  differ greatly. This result clearly contradicts the experimental spectrum and cannot be explained by the SO\_HALA effect, Figure 2d. The inaccuracy of the atomic coordinates appears to be a much more credible explanation. Note that the standard deviation for N–C bonds in this structure is the largest among the structures studied, Table 1. Therefore, there is no reason to attribute the moderate differences between the calculated and experimental tensors to the shortcomings of the calculation method. The full optimization of the studied pyridine-metal

complexes was intentionally refrained from because the geometric parameters of these systems in the solid state and the isolated state are expected to differ, even without corrections for relativistic effects. In contrast, the influence of the environment on the geometry of bipyridine itself should be significantly less. Therefore, optimizing it in the isolated molecule approximation is justified.

Based on the foregoing, it seems reliable to assert that for coordination complexes of the type under consideration, the calculation of their  $^{15}\text{N}$  chemical shift tensors can be carried out using the non-relativistic methods described here. One of the reasons for this is that the tensor parameters are very sensitive to atomic coordinates, which are known with sufficient accuracy only in special cases. The errors caused by this imprecision seems to obscure the  $\text{SO\_HALA}$  effect.

### $^{113}\text{Cd}$ NMR

A crystalline MeBiPy\_Cd sample was prepared from an amorphous MeBiPy\_Cd sample following the original procedure.<sup>[26]</sup> When a methanol solution of MeBiPy is mixed with a methanol solution of  $\text{CdCl}_2$  at room temperature, amorphous MeBiPy\_Cd precipitates from the solution. This amorphous MeBiPy\_Cd was dissolved in dimethyl sulfoxide. Crystalline MeBiPy\_Cd was obtained by methanol diffusion into this solution after several days.

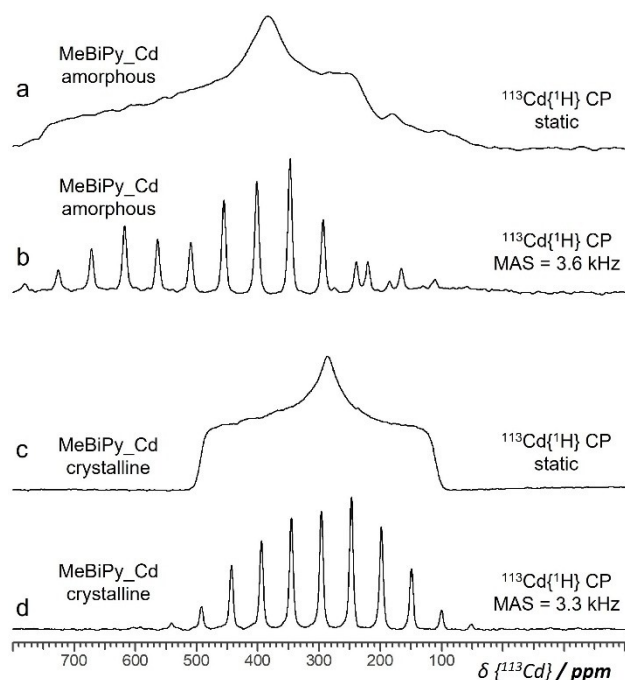
Figure 3 shows the  $^{113}\text{Cd}$  NMR spectra of the amorphous and crystalline samples of MeBiPy\_Cd. The significant difference between these spectra clearly indicates different molecular packing in these two samples. The parameters of the  $^{113}\text{Cd}$  NMR

chemical shift tensor of the dominated structure of the amorphous MeBiPy\_Cd are:  $\delta_{\text{iso}} = 455$  ppm,  $\Omega = 500$  ppm, and  $\kappa = -0.425$ . For the crystalline MeBiPy\_Cd these parameters are:  $\delta_{\text{iso}} = 295.5 \pm 0.3$  ppm,  $\Omega = 390 \pm 10$  ppm, and  $\kappa = -0.09 \pm 0.01$ . The difference between these two structures is also visible in the  $^{15}\text{N}$  NMR spectra, where  $\delta_{\text{iso}}$  is  $-129.3$  ppm and  $-120.0$  for the amorphous and the crystalline sample, respectively. The structure of the amorphous MeBiPy\_Cd is not known. But the observed differences, firstly, once again emphasize the sensitivity of NMR parameters to molecular packing, and secondly, demonstrate how much stronger this effect is manifested in the spectra of heavy atoms.

Table 2 reports the  $^{113}\text{Cd}$  NMR chemical shielding tensor of DURYIZ calculated using selected non-relativistic approximations. Tensors calculated in other approximations are listed in Table S9. This structure corresponds to the crystalline MeBiPy\_Cd.

The Gaussian 09.D.01 program package does not have a basis set that is optimized for  $^{113}\text{Cd}$  NMR calculations.<sup>[28]</sup> For this reason, all-electron basis sets available at the Basis Set Exchange were used for these calculations.<sup>[29]</sup>

Note that when comparing the experimental chemical shift tensor and the calculated absolute shielding tensors, the following must be taken into account. Their  $\Omega$  should be equal. The calculated value of  $k$  has the opposite sign to the corresponding experimental value. The calculated value of the isotropic absolute shielding,  $\sigma_{\text{iso}}$ , differs from the experimental  $\delta_{\text{iso}}$  on the  $\sigma^{\text{ref}}$ , the numerical value of which depends on the approximation used for the calculations and is unknown in the



**Figure 3.**  $^{113}\text{Cd}\{^1\text{H}\}$  CP NMR spectra of the amorphous MeBiPy\_Cd sample a) static and b) MAS spectrum and the crystalline MeBiPy\_Cd (DURYIZ) sample c) static and d) MAS spectrum.

Method	Basis set	$\Omega$ [ppm]	$\kappa$	$\sigma_{\text{iso}}$ [ppm]
NMR	NMR	$390 \pm 10$	$0.09 \pm 0.01$ <sup>[a]</sup>	–
$\omega$ B97XD	UGBS	531	0.497	3366
B3LYP	UGBS	538	0.487	3348
TPSSh	UGBS	533	0.508	3400
SVWN5	UGBS	574	0.450	3154
LC-wPBE	UGBS	512	0.560	3392
$\omega$ B97XD	ANO-R1	272	0.454	3881
B3LYP	ANO-R1	274	0.417	3868
TPSSh	ANO-R1	277	0.482	3875
SVWN5	ANO-R1	283	0.289	3671
LC-wPBE	ANO-R1	254	0.630	3909
B3LYP	ANO-R2	481	0.374	3373
SVWN5	ANO-R2	514	0.303	3127
LC-wPBE	ANO-R2	431	0.509	3462
MP2	jorge-DZP	304	0.456	3783
SVWN5	jorge-DZP	384	0.477	3363
SVWN5	jorge-TZP	484	0.383	3252
SVWN5	jorge-QZP	598	0.346	3116

[a] The skew,  $k$ , of an absolute shielding tensor has the opposite sign to the corresponding chemical shift tensor.

cases under consideration. Therefore, the  $\sigma_{\text{iso}}$  given in Tables 2 and S9 cannot be used in this study in any way and are reported only for the sake of unambiguity in defining the tensors.

None of the tested calculation methods was able to reproduce the  $\Omega$  and  $k$  of the experimentally obtained tensor to any extent correctly. It is noteworthy that most methods give approximately the same estimates for the anisotropy and asymmetry of the tensor,  $\Omega \approx 500$  ppm and  $k \approx 0.5$ . However, both values are significantly above the experimentally obtained values.

At the same time most of the tested method provide acceptable estimates of the  $^{15}\text{N}$  NMR chemical shielding tensor of DURYIZ. The use of all-electron basis sets for such calculations is difficult to justify, since the calculations take longer and their accuracy is lower than when using the def2tzvp basis. But if for some reason this is necessary, then, with a few exceptions, the results of the calculations will remain satisfactory, Table S10.

## Conclusions

The main goal of this work was to determine whether non-relativistic calculations of the  $^{15}\text{N}$  NMR chemical shifts in pyridine-metal coordination complexes are consistent with observed experimental values, or the spin-orbit heavy-atom effect on the light-atom renders such calculations meaningless. The results obtained clearly demonstrate that the  $^{15}\text{N}$  chemical shift tensors in such compounds can be reliably reproduced using non-relativistic DFT methods. The heavy-atom effect is small, and the main contribution to the calculation error arises from inaccuracies in the geometry of the molecular structure under consideration.

The secondary aim of this work was to find a combination of a non-relativistic DFT functional and an all-electron basis set, which, due to an accidental cancellation of calculation errors, can be used for a qualitative analysis of the NMR chemical shift tensors of elements beyond the third row of the periodic table. This search was carried out using the  $^{113}\text{Cd}$  NMR tensor as an example. None of the tested calculation methods was able to reproduce the experimentally obtained tensor to any extent correctly.

This study was not extended to the  $^{199}\text{Hg}$  NMR chemical shift tensor for two reasons. Firstly, in this case the influence of relativistic corrections is even more significant. Secondly, for the studied MeBiPy\_Hg complex, the shape of the signal in its  $^{199}\text{Hg}$  NMR spectrum is mainly determined not by the chemical shift tensor, but by the strong dipole-dipole interaction with two iodine nuclei.<sup>[30]</sup> The signal is located at  $-2300$  ppm, Figure S1.

It cannot be ruled out that for a small set of structurally similar complexes it is possible to accidentally find a non-relativistic method that will give acceptable approximations of the isotropic chemical shift for a selected heavy atom. However, this would not be a reason to expect either that this method is able to reliably describe the corresponding chemical shift

tensor, nor that this agreement will be preserved when expanding the set of complexes studied, nor that this method will give good results for other heavy atoms.

## Experimental Section

The MeBiPy sample was obtained by recrystallization from ethanol.<sup>[22a]</sup> The MeBiPy\_Zn sample was obtained as follows.<sup>[25a]</sup> A methanol solution of MeBiPy was mixed with an acetonitrile solution of  $\text{ZnCl}_2$  and heated under stirring at  $80^\circ\text{C}$  until complete dissolution. Polycrystalline MeBiPy\_Zn was isolated after several days. The MeBiPy\_Hg sample was obtained as follows.<sup>[27]</sup> An acetonitrile solution of MeBiPy was mixed with a methanol solution of  $\text{HgI}_2$  and heated under stirring at  $80^\circ\text{C}$  until complete dissolution. Polycrystalline MeBiPy\_Hg was isolated after several days.

Solid-state  $^{15}\text{N}$  NMR measurements were performed on an Infinity<sub>plus</sub> spectrometer system (Agilent) operated at 7 T, equipped with a variable-temperature Chemagnetics-Varian 6 mm pencil CPMAS probe.  $^{15}\text{N}\{^1\text{H}\}$  static and MAS CP NMR spectra were recorded using a  $90^\circ$  pulse length of  $5.0 \mu\text{s}$ . The cross-polarization contact times and relaxation delays were 10 ms and 5 s, respectively. The spectra were indirectly referenced to  $\text{CH}_3\text{NO}_2$  using solid  $^{15}\text{NH}_4\text{Cl}$  ( $\delta_{\text{iso}} = -341.3$  ppm).<sup>[31]</sup> To convert these values to the liquid ammonia scale, 380.6 ppm must be added to them.  $^{113}\text{Cd}\{^1\text{H}\}$  static and MAS CP NMR spectra were recorded using a  $90^\circ$  pulse length of  $5.0 \mu\text{s}$ . The cross-polarization contact times and relaxation delays were 10 ms and 5 s, respectively. The spectra were indirectly referenced to solid  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  ( $\delta_{\text{iso}} = -100$  ppm).<sup>[31]</sup>  $^{199}\text{Hg}\{^1\text{H}\}$  static and MAS CP NMR spectra were recorded using a  $90^\circ$  pulse length of  $5.0 \mu\text{s}$ . The cross-polarization contact times and relaxation delays were 15 ms and 5 s, respectively. The spectra were indirectly referenced to solid hexakis (dimethyl sulphoxide) mercury(II) trifluoromethane sulphate  $[\text{Hg}(\text{DMSO})_6](\text{O}_3\text{SCF}_3)_2$  ( $\delta_{\text{iso}} = -2313$  ppm).<sup>[33]</sup> The numerical NMR parameters have been extracted from the experimentally obtained spectra using the WSolids1 program package.<sup>[34]</sup>

The Gaussian 09. D.01 program package was used for geometry optimizations and NMR calculations.<sup>[28]</sup> Geometry optimization was done at the very tight convergence criteria. NMR calculations were carried out using the GIAO approach. All calculations were done using the polarizable continuum model (PCM) with DMSO as the solvent.<sup>[35]</sup> This choice is arbitrary. The outcomes of the PCM approximation are not very sensitive to the value of the dielectric constant.<sup>[36]</sup> However, this correction is necessary in order to at least approximately consider the effect of the crystal field. Note that local electrostatic fields not only impact the geometric parameters of non-covalent interactions but also influence the catalytic activity of enzymes.<sup>[37]</sup>

## Supporting Information

The atomic coordinates of NOFZUD, Table S1. The atomic coordinates of NOFZUD01, Table S2. The atomic coordinates of MeBiPy\_DFT, Table S3. Calculated  $^{15}\text{N}$  NMR chemical shift tensors, Table S4. The atomic coordinates of BUDCAF, Table S5. The atomic coordinates of BUDCAF01, Table S6. The atomic coordinates of DURYIZ, Table S7. The atomic coordinates of ULAXIP, Table S8. Experimental and calculated  $^{113}\text{Cd}$  NMR chemical shift tensors of DURYIZ, Table S9. Experimental and

calculated  $^{15}\text{N}$  NMR chemical shift tensors of DURYIZ, Table S10.  $^{199}\text{Hg}\{^1\text{H}\}$  MAS CP NMR spectra of MeBiPy\_Hg, Figure S1.

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## Conflict of Interests

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

**Keywords:** NMR spectroscopy · Density functional calculations · Transition metals · Solid-state structures · Noncovalent interactions

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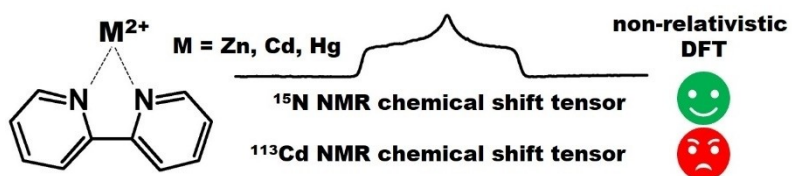
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The Scope of the Applicability of Non-relativistic DFT Calculations of NMR Chemical Shifts in Pyridine-Metal Complexes for Applied Applications

Is there a royal road to NMR chemical shift calculations? Specifically, can relativistic effects be neglected when estimating NMR parameters with an accuracy sufficient for applied

purposes? This question is answered based on the study of the  $^{15}\text{N}$  and  $^{113}\text{Cd}$  NMR chemical shift tensors of pyridine-metal coordination complexes.

