

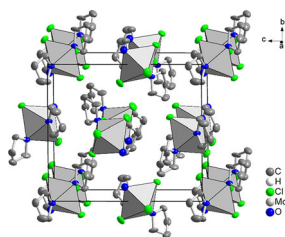
Structural characterization of $\text{MoOCl}_3(\text{THF})_2$, the pre-reagent for Kauffmann olefination reactions

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Abstract Single crystals of molybdenum-oxy-di-tetrahydrofuran-trichloride were obtained by the reaction of $\text{Mo}_2\text{Cl}_{10}$, tetrahydrofuran, sulfur, and P_4S_3 in carbon disulfide after layering the solution with *n*-hexane. Single crystal structure determination at $T = 123$ K reveals that $\text{MoOCl}_3(\text{THF})_2$ crystallizes in the orthorhombic space group $P2_12_12_1$ with the lattice constants $a = 7.8620(9)$ Å, $b = 12.302(1)$ Å, $c = 14.043(2)$ Å, $V = 1304.10(3)$ Å³, and $Z = 4$. EPR experiments on the solid compound showed a g value of 1.94 at 347.46 mT, which accords to a Mo(V) species. The electronic structure of the title compound was investigated with DFT methods.

Graphical abstract



Keywords X-ray structure determination · Kauffmann olefination · EPR spectroscopy · Quantum chemical calculations

Introduction

Molybdenum-oxy-di-tetrahydrofuran-trichloride $\text{MoOCl}_3(\text{THF})_2$ is known as a pre-reagent for Kauffmann olefination [1–3], and has been reported some time before this interesting application was found [4]. However, there are no precise data on the molecular and crystal structure of this compound available in the literature. Only EPR, UV–Vis, and vibrational spectroscopy data for $\text{MoOCl}_3(\text{THF})_2$ in solution have been reported [1, 5].

Tetrahydrofuran (THF) is well known as a ligand for the early transition metals. One typical adduct compound is $\text{NbCl}_4(\text{THF})_2$ which is commercially available [6]. Further known THF adducts are, for example, $\text{WOCl}_3(\text{THF})_2$, $\text{WOBBr}_3(\text{THF})_2$, $\text{MoBr}_3(\text{THF})_2$ [7], $\text{Re}_2\text{Br}_2(\text{CO})_6(\text{THF})_2$ [8], $\text{TiCl}_3(\text{THF})_3$, $\text{TiCl}_4(\text{THF})_2$, $\text{VCl}_3(\text{THF})_3$, $\text{VOCl}_3(\text{THF})_2$, $\text{CrCl}_2(\text{THF})_2$, $\text{CrCl}_3(\text{THF})_3$, $\text{NiCl}_2(\text{THF})_2$, and $\text{ZnCl}_2(\text{THF})_2$ [9].

Herein, the crystal structure, an X-ray powder pattern, and ESR data of the solid compound are reported. In addition, DFT calculations have been performed to get some insight into the reactivity of $\text{MoOCl}_3(\text{THF})_2$ as a pre-reagent in the Kauffmann olefination.

The Kauffmann olefination is a less known alternative to the Wittig or the Tebbe reaction. All three reactions convert ketones into alkenes. To yield the reactive molecule for the Kauffmann olefination, $\text{MoOCl}_3(\text{THF})_2$ has to be reacted with methyllithium. Scheme 1 gives a short overview of the Kauffmann olefination.

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Scheme 1

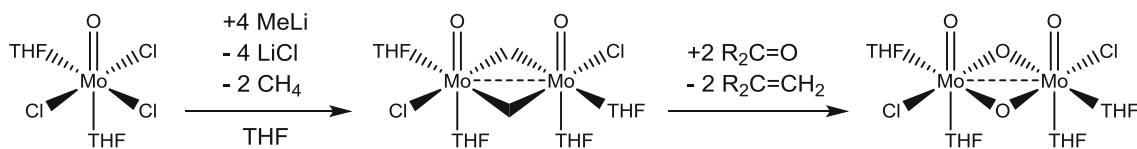


Table 1 Crystallographic data

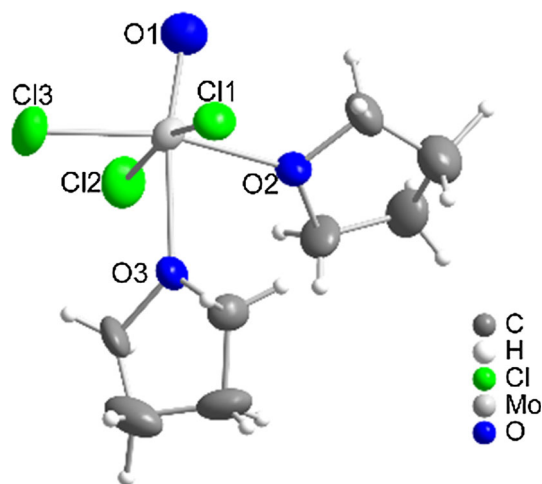
Compound	MoOCl ₃ (C ₄ H ₈ O) ₂
Molar mass	362.5 g mol ⁻¹
Crystal colour	Ochre
Crystal system	Orthorhombic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁ (no. 19)
<i>a</i>	7.7835(1) Å
<i>b</i>	12.2296(2) Å
<i>c</i>	13.7001(2) Å
<i>V</i> , <i>Z</i>	1304.10(3) Å ³ , 4
Absorption coefficient $\mu(\text{Mo-K}\alpha)$	1.605 mm ⁻¹
ρ_{calc}	1.8464 g cm ⁻³
Radiation	Mo-K α , $\lambda = 0.71073$ Å
Temperature	123 K
θ (range)	2.97°–25.05°
<i>hkl</i> (range)	−9 ≤ <i>h</i> ≤ 9 −14 ≤ <i>k</i> ≤ 14 −16 ≤ <i>l</i> ≤ 16
Number of reflections	41,472
Independent reflections	2314
<i>R</i> _σ , <i>R</i> _{int}	0.0098, 0.0343
Completeness to $\theta = 25.05^\circ$	99.9%
Parameters	137
Number of constraints	64
Flack X parameter	−0.02(5)
Goof	1.69
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 3 σ (<i>I</i>)]	0.0215, 0.0745
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0218, 0.0750
Residual electron density	0.96, −0.49 eÅ ⁻³

Results and discussion

MoOCl₃(THF)₂ forms yellow, moisture sensitive crystals. It crystallizes in the orthorhombic space group *P*2₁2₁2₁ (no. 19) with *a* = 7.7835(1) Å, *b* = 12.2296(2) Å, *c* = 13.7001(2) Å, *V* = 1304.1(3) Å³ (*T* = 123 K, single crystal data), and *Z* = 4; *a* = 7.8620(9) Å, *b* = 12.302(1) Å, *c* = 14.043(2) Å, and *V* = 1358.3(4) Å³ (*T* = 293 K, powder data). The refinement of the crystal structure converged at *R*₁ = 0.0215 and *wR*₂ = 0.0745 for *I* > 3 σ , and *R*₁ = 0.0218 and

Table 2 Selected distances within the MoOCl₃(THF)₂ molecules

Ligand atom	<i>d</i> (Mo—ligand)/Å
Cl1	2.3646(8)
Cl2	2.3513(9)
Cl3	2.3191(9)
O1 (oxide)	1.682(2)
O2 (THF)	2.146(2)
O3 (THF)	2.277(2)

Fig. 1 Molecular structure of MoOCl₃(THF)₂

*wR*₂ = 0.0750 for all data. Crystallographic data are given in Table 1. Figure 1 displays the molecular structure of MoOCl₃(THF)₂ and the labelling scheme.

The ligand atoms are forming a *mer*-arranged octahedral coordination around the central molybdenum atom. Table 2 lists selected distances and angles within the MoOCl₃(THF)₂ molecule. One THF molecule (bound by O2) is in a *trans* position to Cl3, and one THF (bound by O3) is located *trans* to O1, which forms a very short bond to Mo. The third couple of *trans* ligands is formed by Cl1 and Cl2. Cl3 forms a slightly shorter bond to Mo than Cl1 and Cl2 (*d*(Mo-Cl1) = 2.3646(8) Å, *d*(Mo-Cl2) = 2.3513(9) Å, and *d*(Mo-Cl3) = 2.3191(9) Å). The THF molecule opposite to Cl3 exhibits a distance of *d*(Mo-

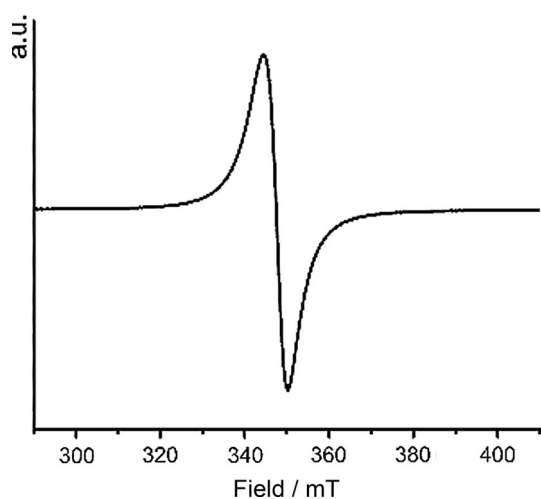
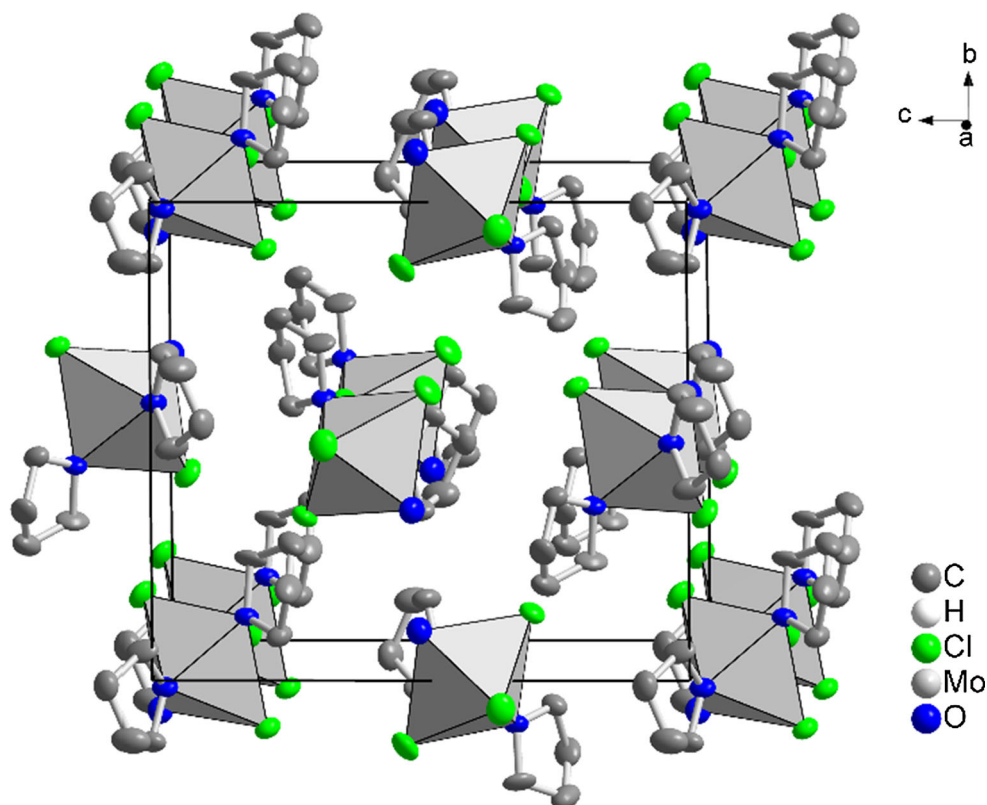


Fig. 2 Continuous wave EPR spectrum of solid $\text{MoOCl}_3(\text{THF})_2$

$d(\text{O}2) = 2.146(2) \text{ \AA}$, which is significantly shorter than $d(\text{Mo}-\text{O}3) = 2.277(2) \text{ \AA}$. This is due to the very short bond $d(\text{Mo}-\text{O}1) = 1.682(2) \text{ \AA}$ in *trans* position.

We could not determine the source of O1, but hydrolysis is the only plausible explanation for this oxygen atom. The chemical nature of O1 has some impact on the oxidation state of Mo, i.e., Mo is tetravalent when O1 is the oxygen atom of a hydroxy ligand. On the other hand, Mo is pentavalent when O1 is an oxido ligand. The bond distance $d(\text{Mo}-\text{O}1)$ gives a clear hint for a terminal oxygen atom, but

Fig. 3 Section of the crystal structure of $\text{MoOCl}_3(\text{THF})_2$ showing the $\text{Mo}-\text{O}_3-\text{Cl}_3$ octahedra arranged in the motif of a hexagonal close packing. Hydrogen atoms are omitted for clarity



seems to be much too short for a coordinating OH group. However, the question for the oxidation state of Mo(IV) and Mo(V) can be answered much better by EPR spectroscopy.

A g value of 1.94 at 347.46 mT was determined at ambient temperature, which is exactly the value reported for the molecule dissolved in CH_2Cl_2 [5]. Typical g values for molecular Mo(V) compounds are around 1.95 [10]. This indicates one unpaired electron, which fits our structure model containing a terminal oxygen atom O1. The EPR spectrum is shown in Fig. 2.

The $\text{MoOCl}_3(\text{THF})_2$ moieties are arranged in the motif of a hexagonal closest packing with $[0\ 1\ 0]$ as the hexagonal axis when the molecules are regarded as spheric units, see Fig. 3.

An X-ray powder diffraction pattern was recorded to prove the purity of the sample and to check for the lattice constants at ambient temperature, see Fig. 4. All reflections could be indexed and refined taking the extinctions for the space group $P2_12_12_1$ into account. A significant thermal expansion of the unit cell along $[0\ 0\ 1]$ with increasing temperature becomes obvious, whereas the expansion is much smaller along $[1\ 0\ 0]$ and $[0\ 1\ 0]$. The orientation of the dipole of $\text{MoOCl}_3(\text{THF})_2$ might be regarded as a reason for this anisotropic thermal expansion during temperature changes. Thus, these dipoles are oriented more or less parallel to $[0\ 0\ 1]$, but more or less perpendicular and anti-parallel to $[1\ 0\ 0]$ and $[0\ 1\ 0]$.

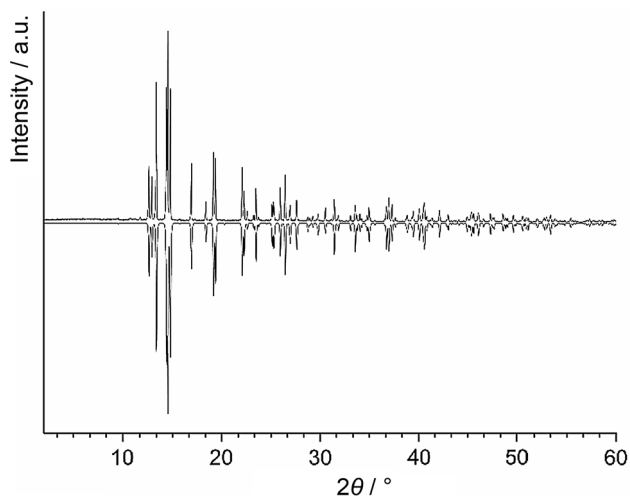


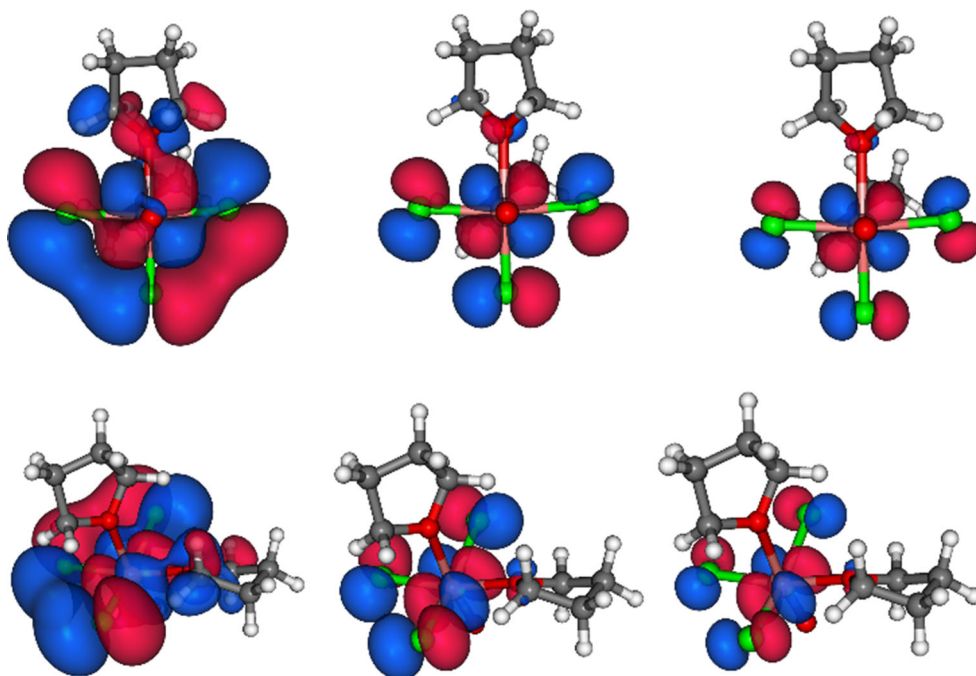
Fig. 4 Comparison of the measured X-ray powder pattern (Cu- $K_{\alpha 1}$ radiation in Debye-Scherrer geometry) with a diffractogram calculated from the single crystal data. The calculated pattern is shown with negative intensity

The most reactive orbital is the SOMO, which is predominantly located around the chlorine atoms, see Fig. 5. Two of these chlorine atoms have to be leaving groups in the case of the initial reaction steps [1–3].

Conclusion

$\text{MoOCl}_3(\text{THF})_2$ forms molecules with an octahedral, *mer*-configured surrounding of molybdenum. EPR spectra clearly indicate +V as the oxidation state of molybdenum,

Fig. 5 SOMO ($E = -6.2628$ eV) with different probability levels in two viewing directions



which is in agreement with the presence of an oxido ligand O1. X-ray powder diffraction has been used to verify the single crystal data. A pronounced thermal expansion along [0 0 1] becomes obvious from these data and can be explained by the mutual orientation of the molecules in the solid state. DFT calculations help to identify the chlorine atoms as most reactive sites, since the SOMO is mostly located on these atoms.

Experimental

Single crystals of $\text{MoOCl}_3(\text{THF})_2$ were obtained during our explorative investigations of the reactivity of phosphorus chalcogenide cage molecules towards transition metal halides [11–26]. We stirred 0.1 g $\text{Mo}_2\text{Cl}_{10}$ (0.4 mmol, 1 equiv.), 0.087 g P_4S_3 (0.4 mmol, 1 equiv.), and 0.013 g sulfur (0.4 mmol, 1 equiv.) in a mixture of 2.5 cm³ THF and 5 cm³ carbondisulfide for 1 day, covered with *n*-hexane and subsequently kept at room temperature for 7 weeks. The stopcock was not airtight, and therefore, moist air took part in the reaction. Single crystals of the title compound had formed after the reaction period and could be isolated for some basic characterization.

One of these single crystals was measured at 123 K on a Rigaku Super Nova with monochromatic Mo- $K\alpha$ radiation ($\lambda = 0.71073$ Å). Diffraction data were processed by the CrysAlis Pro software, followed by an empirical absorption correction with the included Scale3 Abspack program [27]. The crystal structure was solved by charge flipping methods in Superflip [28], followed by structure refinement with

JANA2006 [29]. All heavy atoms were located by the structure solution routine, and the carbon atoms were found by subsequent refinement and Fourier/Difference Fourier syntheses. Anisotropic displacement parameters were applied for all non-hydrogen atoms. Hydrogen atoms were added with a riding model using fixed geometrical sites for each hydrogen atom to the according carbon atoms in the THF ligand. Three reflections, probably originating from some adhesions on the crystal, had to be excluded from the refinement. The absolute structure was refined according to a flack parameter of $-0.02(5)$.

Some single crystals were ground for X-ray powder diffraction and ESR experiments in inert atmosphere. Powder diffraction was performed on a STOE STADI-P diffractometer equipped with a Dectris Mythen 1 K detector and using monochromatic Cu-K α_1 radiation. The X-ray powder diffraction data were analyzed with the WinX^{POW} software [30]. ESR data have been collected on a Miniscope MS 400.

DFT calculations were done with ORCA [31], using B3LYP exchange correlation functional [32] and def2-TZVP [33, 34] as basis set. The graphical representation files were generated using orca plot (included in ORCA).

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