

Communication

Pyridinium Pentachloridooxomolybdate(V), $(\text{PyH})_2[\text{MoOCl}_5]$, Revisited: Single-Crystal X-ray Structure Determination

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Abstract: $(\text{PyH})_2[\text{MoOCl}_5]$ was obtained in the form of emerald green crystals unintentionally from $(\text{PyH})_5[\text{MoOCl}_4(\text{H}_2\text{O})]_3\text{Cl}_2$ in acetonitrile. $(\text{PyH})_2[\text{MoOCl}_5]$ has been used as a starting material in molybdenum(V) coordination chemistry for decades, yet its true identity has not been known until now. The X-ray structure analysis has undoubtedly confirmed the existence of this compound. The $[\text{MoOCl}_5]^{2-}$ ion displays the usual structural characteristics of the mononuclear MoO^{3+} -containing compounds.

Keywords: pentachloridooxomolybdate(V); molybdenum; coordination chemistry; crystal structure



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1. Introduction

The main motivation for pursuing research on the coordination chemistry of molybdenum has been its biological importance. As of today, molybdenum has been found in over 50 enzymes [1]. Two groups may be recognised: nitrogenases with an iron–molybdenum cluster as a cofactor and a larger group of enzymes with a pterin-based cofactor [1]. These enzymes catalyse oxidation-reduction reactions that form part of nitrogen, sulphur, and carbon metabolism [2]. Versatile redox behaviour and oxophilic nature make molybdenum suitable for this role. Molybdenum has a strong tendency to bind oxygen and, at the same time, the capacity to lose it. In the course of catalysis, molybdenum shuttles between oxidation states +6, +5, and +4 with some reactions involving oxygen atom transfer (OAT) processes.

We have been interested in the coordination chemistry of the intermediate oxidation state, +5 [3,4]. The MoO^{3+} structural entity pervades this oxidation state. Owing to its multiple bond character, it lies at the origin of the geometric distortions of molybdenum(V) complex species which are eventually manifested also in their reactivity. Herein, a crystal structure of $(\text{PyH})_2[\text{MoOCl}_5]$, another MoO^{3+} -containing species, will be presented. The compounds containing $[\text{MoOCl}_5]^{2-}$ ions were prepared as early as 1927 [5]. $(\text{PyH})_2[\text{MoOCl}_5]$ formed upon the molybdate(VI) reduction with hydrazine in 11 M hydrochloric acid. After the addition of pyridine, needle-shaped crystals of emerald green colour formed [6]. The compound was of interest as it provided, in spite of its inherent air sensitivity, a suitable entry into the molybdenum(V) coordination chemistry. A drawback of using this compound was that its true identity was not known until 2005 [7]. Its composition was proposed on the basis of the elemental analyses on Cl and Mo. On the other hand, a comparison of the reflectance spectrum of the solid ammonium pentachloridooxomolybdate(V) with the spectrum of its HCl solution has suggested the presence of either the $[\text{MoOCl}_5]^{2-}$ or the $[\text{MoOCl}_4(\text{H}_2\text{O})]^-$ ions [8]. The X-ray structure analysis of crystals obtained by a modified procedure, a reduction of MoO_3 with hydroiodic acid in concentrated HCl(aq), followed by the addition of pyridine, has disclosed the $[\text{MoOCl}_4(\text{H}_2\text{O})]^-$ ions as the only molybdenum(V) species in the product. The correct composition of the emerald green crystals, unequivocally established by the X-ray structure analysis, turned out to be more complex than initially assumed. The $[\text{MoOCl}_4(\text{H}_2\text{O})]^-$ ions co-crystallised with chloride and pyridinium

cations resulting in the $(\text{PyH})_5[\text{MoOCl}_4(\text{H}_2\text{O})]_3\text{Cl}_2$ formula [7]. It is of interest to note that $(\text{PyH})_5[\text{MoOCl}_4(\text{H}_2\text{O})]_3\text{Cl}_2$ and the at-first-proposed $(\text{PyH})_2[\text{MoOCl}_5]$ share similar Cl and Mo contents. The chlorine and the molybdenum contents in $(\text{PyH})_5[\text{MoOCl}_4(\text{H}_2\text{O})]_3\text{Cl}_2$ are 38.57% and 22.37%, whereas for $(\text{PyH})_2[\text{MoOCl}_5]$, the values amount to 39.44% and 21.35%, respectively. The “missing” compound, $(\text{PyH})_2[\text{MoOCl}_5]$, has been obtained just recently in our laboratory. It was isolated in the course of the $(\text{PyH})_5[\text{MoOCl}_4(\text{H}_2\text{O})]_3\text{Cl}_2$ reactions with pyrazinecarboxylic acid in acetonitrile. With this reaction aiming towards the coordination of pyrazinecarboxylic acid to molybdenum(V), the formation of $(\text{PyH})_2[\text{MoOCl}_5]$ was surprising. Although the reaction was found to be reproducible, no rational explanation can be provided for the transformation of $[\text{MoOCl}_4(\text{H}_2\text{O})]^-$ into $[\text{MoOCl}_5]^{2-}$. The starting material, $(\text{PyH})_5[\text{MoOCl}_4(\text{H}_2\text{O})]_3\text{Cl}_2$, which is the source of chloride, provides only two-thirds of the amount necessary for a quantitative transformation. Even more puzzling is the role of pyrazinecarboxylic acid. In its absence, no $(\text{PyH})_2[\text{MoOCl}_5]$ could be isolated. Although the synthetic conditions necessary for the formation of $(\text{PyH})_2[\text{MoOCl}_5]$ remain as elusive as ever, our study undoubtedly confirms its existence. We may also conclude that with the available literature data, it remains unclear whether the early reports were on $(\text{PyH})_5[\text{MoOCl}_4(\text{H}_2\text{O})]_3\text{Cl}_2$ or $(\text{PyH})_2[\text{MoOCl}_5]$.

2. Results

The solid-state structure of pyridinium pentachloridooxomolybdate(V) consists of the mononuclear $[\text{MoOCl}_5]^{2-}$ anions and protonated pyridine molecules as counteranions. Although part of the $[\text{MoOCl}_5]^{2-}$ ion resides on the twofold rotation axis, its symmetry is that of the C_{4v} point group. The drawing of the formula unit is shown in Figure 1, and relevant geometric parameters of the $[\text{MoOCl}_5]^{2-}$ ion are listed in Table 1.

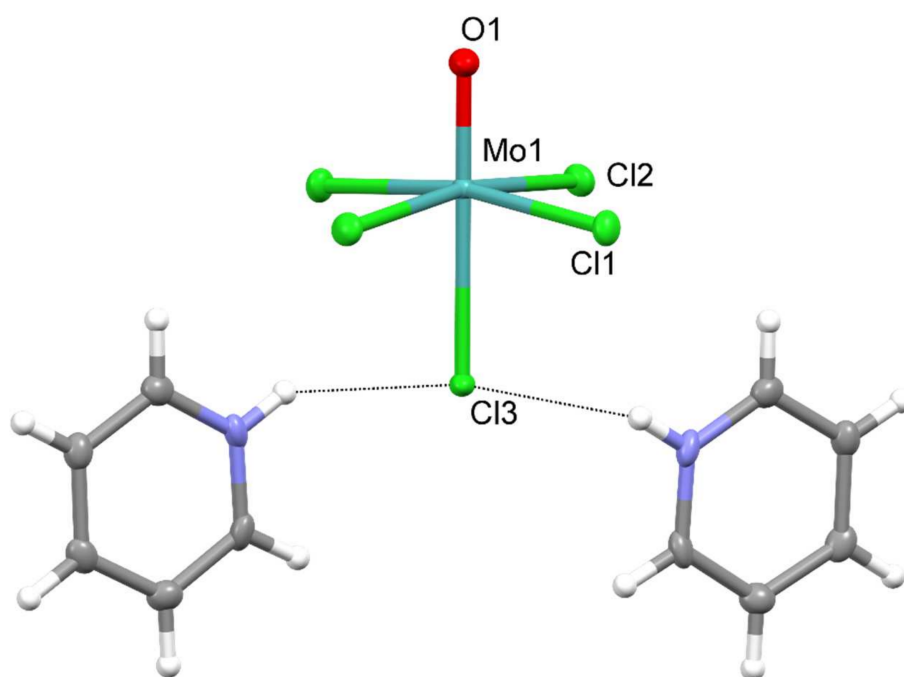


Figure 1. Displacement ellipsoids plot of formula unit in $(\text{PyH})_2[\text{MoOCl}_5]$. The ellipsoids are drawn at a 50% probability level, whereas hydrogen atoms are drawn as spheres of arbitrary radii. Dotted lines are the N–H···Cl interactions.

Table 1. Relevant geometric parameters [\AA , $^\circ$] for the $[\text{MoOCl}_5]^{2-}$ ion of $(\text{PyH})_2[\text{MoOCl}_5]$.

Parameter	
Mo(1)–O(1)	1.665(3)
Mo(1)–Cl(1)	2.4072(8)
Mo(1)–Cl(2)	2.3845(8)
Mo(1)–Cl(3)	2.6038(10)
O(1)–Mo(1)–Cl(1)	95.88(2)
O(1)–Mo(1)–Cl(2)	95.295(19)
O(1)–Mo(1)–Cl(3)	180.0
Cl(1)–Mo(1)–Cl(2)	90.44(3)
Cl(2)–Mo(1)–Cl(1) ¹	88.47(3)
Cl(3)–Mo(1)–Cl(1)	84.12(2)
Cl(3)–Mo(1)–Cl(2)	84.705(19)

¹ Related through symmetry: $5/2-x, y, 2-z$.

The most prominent feature of the complex ion is the Mo=O structural fragment with the Mo–O length of 1.665(3) \AA . The six-coordinate metal environment consists of the oxide and five chlorides. The equatorial chlorides, Cl(1), Cl(2), and their symmetry counterparts, are at 2.3845(8)–2.4072(8) \AA , whilst Cl(3), which occupies the position *trans* to the multiply bonded oxide, is at a significantly longer distance, 2.6038(10) \AA . The highly distorted octahedral environment of molybdenum(V) is a result of an operating *trans* influence of the multiply bonded oxide [9]. With the metal ion being located 0.2333(7) \AA above the best plane of four equatorial chlorides, the shape of the $[\text{MoOCl}_5]^{2-}$ ion may be described as umbrella-like.

It should be noted that the lengthening of the Mo(1)–Cl(3) bond is a joint result of the operating *trans* influence of the molybdenyl moiety and the engagement of the Cl(3) chloride in hydrogen bonding with pyridinium cations. Cl(3) forms two hydrogen bonds with two pyridinium cations, with the N(1)···Cl(3) contacts being 3.092(3) \AA , a significantly shorter distance than the sum of the N and Cl van der Waals radii, 3.3 \AA [10]. Such connectivity is known as a bifurcated hydrogen bond. The pattern, the $[\text{MoOCl}_5]^{2-}$ ion with two hydrogen-bonded pyridinium cations, is shown in Figure 1. These hydrogen-bonded clusters interact with adjacent ones via $\pi\cdots\pi$ stacking interactions occurring between pairs of pyridinium cations (Table 2, Figures 2 and 3).

Table 2. Intermolecular interactions [\AA , $^\circ$] in $(\text{PyH})_2[\text{MoOCl}_5]$.

Hydrogen Bond	
Type	Parameters
N–H···Cl	N(1)···Cl(3)[$2-x, -1-y, 2-z$] = 3.092(3)
	N(1)–H(1) = 0.83(3)
	H(1)···Cl(3)[$2-x, -1-y, 2-z$] = 2.51(3)
	N(1)–H(1)···Cl(3)[$2-x, -1-y, 2-z$] = 129(2)
$\pi\cdots\pi$ Stacking	
Type	Parameters ¹
PyH ⁺ ···PyH ⁺	Cg···Cg = 3.5058(2)
	α = 0.0
	slippage = 0.944

¹ Parameters, as defined in [11].

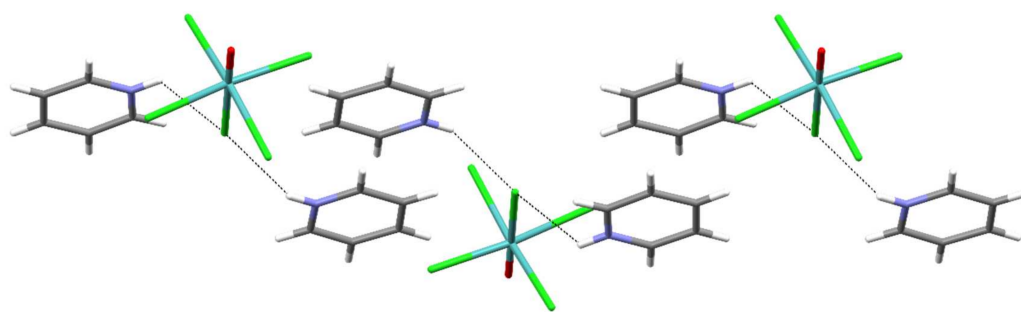


Figure 2. $\pi \cdots \pi$ stacking of pyridinium cations in $(\text{PyH})_2[\text{MoOCl}_5]$. Dotted lines are the $\text{N-H} \cdots \text{Cl}$ hydrogen bonds.

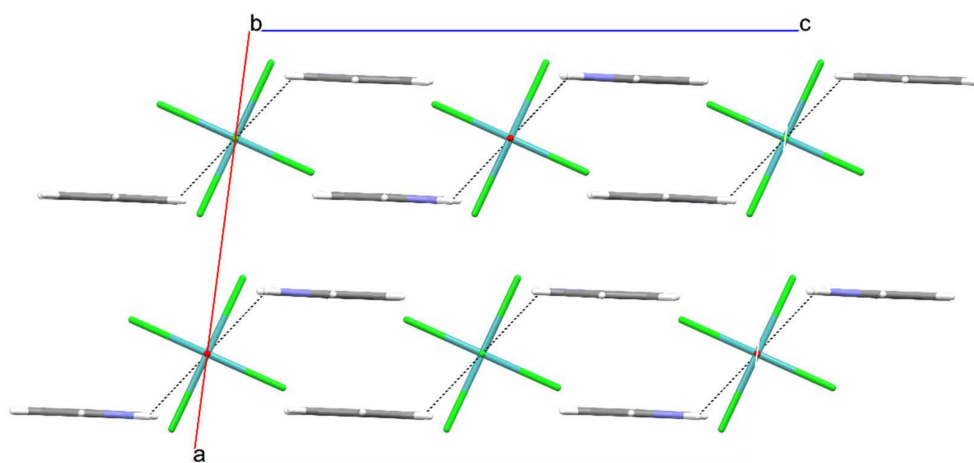


Figure 3. Packing of ions in $(\text{PyH})_2[\text{MoOCl}_5]$: a view along b -axis.

There are only six structurally characterised compounds with pentachloridooxomolybdate(V) ions: $\{\text{HP}(\text{Ph})_3\}_2[\text{MoOCl}_5]$ [12], $(\text{Me}_4\text{N})_2[\text{MoOCl}_5] \cdot \text{CH}_3\text{CN}$ [13], $(\text{C}_5\text{H}_{10}\text{NO})_2[\text{MoOCl}_5]$ ($\text{C}_5\text{H}_{10}\text{NO}^+ = \text{O-protonated valerolactam}$) [14], $(\text{PyH})_{10}[(\text{Mo}_2\text{O}_4\text{Cl}_4)_2(\mu_4\text{-hda})][\text{MoOCl}_5]\text{Cl}_2$ (where hda^{2-} stands for a dianion of heptanedioic acid) [15], $(\text{PyH})_2[\text{MoOCl}_5] \cdot \text{CH}_2\text{Cl}_2$ [16], and $\{\text{P}(\text{Ph})_4\}_2[\text{MoOCl}_5] \cdot 2\text{CH}_2\text{Cl}_2$ [17]. The listed compounds were products of very diverse reactions, and therefore, no synthetic guidelines concerning the formation of the $[\text{MoOCl}_5]^{2-}$ ion can be elucidated. The geometry of the $[\text{MoOCl}_5]^{2-}$ ion in the title compound is very similar to those in the cited examples. A solvate with dichloromethane, $(\text{PyH})_2[\text{MoOCl}_5] \cdot \text{CH}_2\text{Cl}_2$ [16], features a slightly longer bond between molybdenum and chloride that is *trans* to the terminal oxide, 2.6910(6) Å. An even larger discrepancy in the molybdenum-to-the-chloride bonding pattern was observed for $(\text{C}_5\text{H}_{10}\text{NO})_2[\text{MoOCl}_5]$ in which the bonds to equatorial chlorides are in the 2.3741(7)–2.3820(7) Å range, whereas the bond to the apical chloride is as long as 2.7582(7) Å [14]. The elongation of this bond was explained with the engagement of the *trans*-positioned chloride in hydrogen-bonding interactions with the counteranions.

3. Materials and Methods

3.1. General

All reagents but $(\text{PyH})_5[\text{MoOCl}_4(\text{H}_2\text{O})]_3\text{Cl}_2$ were purchased from commercial sources and used without further purification. Molybdenum(V) starting material was prepared following the published procedure [7]. IR spectrum of the Nujol suspension was recorded in the 4000–600 cm^{-1} spectral region using an FTIR instrument PerkinElmer Spectrum 100 (PerkinElmer, Shelton, CT, USA). Owing to the decomposition of crystalline $(\text{PyH})_2[\text{MoOCl}_5]$ when exposed to the air atmosphere, no elemental CHN analysis was performed. Single crystal X-ray diffraction data were collected on an Agilent SuperNova diffractometer (Agilent Technologies XRD Products, Oxfordshire, UK) with copper ($\text{Cu-K}\alpha$, $\lambda = 1.54184$ Å) X-ray

source at 150 K. CrysAlis PRO [18] was used for data processing and Olex² software [19] for data analysis. The structure was solved by ShelXT [20] and refined by the least-squares method in ShelXL [21]. Anisotropic displacement parameters were determined for all nonhydrogen atoms. Platon [22] and Mercury [23] were used for the analysis of the crystal structure and the preparation of figures. The crystal structure was deposited to the CCDC and assigned the deposition number 2088930. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk). The crystallographic data are summarised in Table 3.

Table 3. Crystallographic data for (PyH)₂[MoOCl₅].

Data	(PyH) ₂ [MoOCl ₅]
Empirical formula	C ₁₀ H ₁₂ Cl ₅ MoN ₂ O
Formula weight	449.41
Crystal system	monoclinic
Space group	<i>I</i> 2/ <i>a</i>
<i>T</i> [K]	150.00(10)
<i>λ</i> [Å]	1.54184
<i>a</i> [Å]	12.4835(5)
<i>b</i> [Å]	8.0098(3)
<i>c</i> [Å]	15.7823(8)
<i>α</i> [°]	90
<i>β</i> [°]	97.459(4)
<i>γ</i> [°]	90
<i>V</i> [Å ³]	1564.72(12)
<i>Z</i>	4
<i>D</i> _{calc} [g/cm ³]	1.908
<i>μ</i> [mm ^{−1}]	14.662
Size [mm]	0.08 × 0.09 × 0.10
Collected reflections	3368
Unique reflections	1518
Observed reflections	1367
<i>R</i> _{int}	0.0369
<i>R</i> ₁ (<i>I</i> > 2σ(<i>I</i>))	0.0330
<i>wR</i> ₂ (all data)	0.0847
Goodness of fit	1.09
Largest diff. peak/hole [e [−] / Å ³]	1.2 / −1.0

3.2. Synthesis

(PyH)₅[MoOCl₄(H₂O)]₃Cl₂ (428 mg, 1.00 mmol of molybdenum(V) complex) was dissolved in acetonitrile (20 mL). To thus obtained emerald green solution, pyrazinecarboxylic acid (80 mg, 0.65 mmol) was added. No colour change ensued. The solution was left to stand at ambient conditions in a closed Erlenmeyer flask for an hour. Afterwards, diethyl ether (25 mL) was added dropwise. On the following day, a copious amount of emerald green crystals of (PyH)₂[MoOCl₅] was obtained. Notes. The crystals decompose almost instantaneously when taken out from the mother liquor. On exposure to the air, the solution acquires a deep violet colour. IR (Nujol, cm^{−1}): 1632, 1601, 1527, 1321, 1236, 1189, 1161, 1080, 1049, 1030, 979, 960 [*ν*(Mo=O)], 851, 729, 672, 607. The Nujol signature bands are not listed. The IR spectrum may be found in Supplementary Materials.

Supplementary Materials: The following are available online, Figure S1: IR spectrum of (PyH)₂[MoOCl₅].

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Informed Consent Statement: Not applicable.

Data Availability Statement: Crystal structure data can be found at CCDC (Deposition Number 2088930).

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