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Reexamination of the structure of $\text{MoO}(\text{O}_2)_2(\text{H}_2\text{O})(\text{hmpa})$, hmpa = hexamethylphosphoramidate by crystallographic and theoretical means

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Abstract

The crystal structure of $\text{MoO}(\text{O}_2)_2(\text{H}_2\text{O})(\text{hmpa})$, hmpa = hexamethylphosphoramidate, has been reassessed and corrected as one of the axial parameters (namely the *c*-axis) was reported incorrectly. This resulted in significant differences in the internal geometry of the molecule, notably an decreased O–O atom distance ($\approx 0.03 \text{ \AA}$) in the metal-bonded peroxo ligands. Crystal packing forces and a flat bending potential of the Mo–O–P angle accounts for discrepancies between theory and experimental structures.

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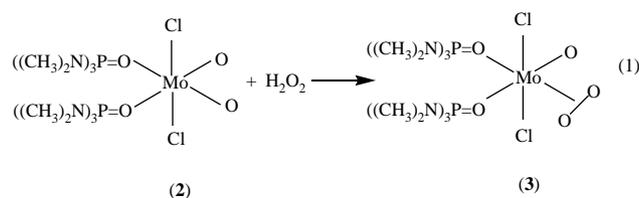
Keywords: Oxo; Peroxide; Hexamethylphosphoramidate; Molybdenum complexes; Crystal structure

1. Introduction

Since the report of its preparation [1] in 1969, the complex $\text{MoO}(\text{O}_2)_2(\text{H}_2\text{O})(\text{hmpa})$, **1**, has been examined for its use in reactions with peroxide [2]; homogeneous bimetallic catalysis [3]; oxidation of 1-alkenes [4], propene [5], cyclohexene [6], primary aromatic amines [7,8], and other oxygen transfer reactions [9]; XPS studies [10]; and Raman studies [11]. The single crystal X-ray determined structure of **1** reported in 1972 [12] has been referenced at least 68 times [13], which in itself is an indication of the general importance of this compound. More recently, the results of the aforementioned crystal structure featured prominently in a paper dealing with theoretical studies of complex **1** [14].

As part of our work on metal oxo/peroxo compounds [15] we had obtained crystals from the reaction displayed as

Eq. (1) of what we had hoped was the molybdenum



oxo/peroxo complex **3**. Complex **3** was reportedly synthesized but not structurally characterized [16]. A search for the unit cell (different from that reported earlier for **1**) on the Cambridge Structural Database [17] did not reveal any sensible matches to the data so we collected the reflections and solved the structure. To our amazement it turned out to be complex **1**. We initially thought that this difference may be due to some variant of bond stretch isomerism [18–22], where O–O atom distances in the peroxo ligand may vary, and thus we explored various theoretical studies to assess the geometry. We also tried to crystallize the compound in different solvents and conditions to produce the cell reported earlier. These results, for which the conclusion is that the unit cell reported earlier is inaccurate, are reported herein.

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Table 1
Crystal data and structure refinement details for **1**

Formula	C ₆ H ₂₀ MoN ₃ O ₇ P, 1	1 ^a	1 ^b
Crystallizing conditions	CH ₂ Cl ₂	CH ₂ Cl ₂	EtOH
<i>M_r</i>	373.16		
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>		
<i>a</i> /Å	10.614(1)	10.615(2)	10.617(1)
<i>b</i> /Å	8.298(2)	8.300(1)	8.295(1)
<i>c</i> /Å	17.007(3)	17.003(3)	17.004(3)
°/deg	103.86(1)	103.81(1)	103.89(1)
<i>V</i> /Å ³	1454.2(4)		
<i>Z</i>	4		
<i>D_x</i> /g cm ⁻³	1.704		
<i>R</i> 1, ^c <i>wR</i> 2 ^d (<i>I</i> > 2σ <i>I</i>)	0.022, 0.060		
<i>R</i> 1, ^c <i>wR</i> 2 ^d (all data)	0.026, 0.062		

^a Prepared from a previously published procedure [1] but crystals grown from concentrating a solution in CH₂Cl₂.

^b Prepared as published but crystals obtained from placing a concentrated solution of **1** in EtOH in the freezer as originally reported [12].

^c $R = \Sigma(F_0 - F_c) / \Sigma(F_0)$.

^d $R_w = \{\Sigma[w(F_0^2 - F_c^2)^2] / \Sigma[w(F_0^2)^2]\}^{1/2}$, where $w = 1/[\sigma^2(F_0^2) + (0.0341 \times P)^2 + 1.03 \times P]$, where $P = (\text{Max}(F_0^2, 0) + 2 \times F_c^2) / 3$.

2. Experimental

2.1. Preparation of MoO(O₂)₂(H₂O)(hmpa), **1**

To a solution consisting of 0.100 g of MoO₂Cl₂(hmpa)₂ was added 50 equiv. of 30% H₂O₂ and this solution was stirred briefly and allowed to stand. Crystals of complex **1** were obtained over a period of weeks. Standard crystallographic techniques [23] were used to determine the structure of **1**. For the final stages of refinement, all non-hydrogen atoms were refined with anisotropic thermal parameters and the H-atoms on the methyl groups were refined with positional (0.96 Å) and isotropic thermal parameters constrained to be 1.5 times the equivalent isotropic thermal parameter for the carbon atoms to which they were attached. The H-atoms on the water molecule were refined freely. Some crystallographic data from the final cycles of refinement plus data from the determination of other crystals of **1** produced under different conditions are summarized in Table 1. We were unable to produce crystals of **1** with the dimensions previously reported [12].

2.2. Theoretical calculations

Theoretical calculations were performed on the MoO(O₂)₂PO[N(CH₃)₂]₃H₂O molecule using the GAUSSIAN 98 program suite [24]. Geometry optimization was carried out at restricted spin level in the framework of Hartree–Fock (HF) and density functional theory (DFT). For the exchange–correlation functional form in DFT, the hybrid functionals, namely, Becke’s 3 parameter exchange functional along with the gradient corrected LYP correlation functional (B3LYP) was employed. For basis Set I (Set-I), a pseudopotential Lanl2DZ basis set was used for molybdenum, whereas all electron 6-31G* basis set was used for rest of the atoms in the molecule. Calculations in

basis Set II (i.e. Set II) were performed using GAMESS-UK. The metal was represented by the modified effective core potential basis set of Lajohn et al. [25,26], the nitrogens, carbons and hydrogens were represented by Dunning’s double-ζ (DZ) basis [27,28], and the phosphorus was represented by the Wadt–Hay ECP DZ basis [29].

3. Results and discussion

A figure of compound **1** based on the single crystal determination of the crystal as discussed in the experimental section is displayed in Fig. 1 together with the numbering scheme. The structure consists of trans oxo and aquo groups in an axial position with the two peroxy ligands and hmpa group forming a distorted pentagon. The P–O–Mo angle at 173.0(2)° is almost linear and the peroxy groups are bonded in an asymmetric fashion with the trans O2 and O5 to Mo1

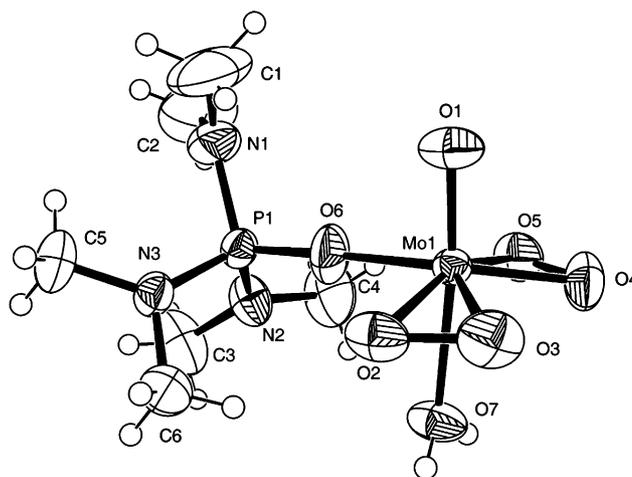


Fig. 1. ORTEP drawing of complex **1** with ellipsoids drawn at the 50% probability level.

Table 2
Bond distances and angles for **1** obtained by various experimental and theoretical calculations

	Exp ^a	Previous [12]	Identical cell refinement ^b	B3LYP/II ^c [14]	B3LYP/III+ [14]	B3LYP/Set I	B3LYP/Set II ^d	B3LYP/Set II ^e	
Mo-oxo	1.664(2)	1.662(5)	1.660(4)	1.689	1.668	1.699	1.689	1.692	1.713
Mo–O1, avg	1.910(3)	1.932(5)	1.927(3)	1.963	1.942	1.956	1.960	1.960	1.988
Mo–O2, avg	1.944(3)	1.952(5)	1.944(3)	1.959	1.943	1.953	1.967	1.966	2.007
Mo–OP	2.021(3)	2.057(5)	2.058(3)	2.145	2.133	2.122	2.071	2.098	2.031
Mo–OH ₂	2.340(3)	2.347(5)	2.336(5)	2.728	2.727	2.592	2.561	2.556	2.322
O1–O2, avg	1.461(3)	1.496(8)	1.483(5)	1.449	1.454	1.446	1.447	1.446	1.521
O–P	1.491(3)	1.522(6)	1.518(3)	1.533	1.534	1.539	1.575	1.595	1.621
P–N avg	1.617(3)	1.620(7)	1.619(3)			1.668	1.717	1.714	1.707
N–C, avg	1.454(6)	1.48(1)	1.463(5)			1.468	1.476	1.477	1.480
Oxo–Mo–O1	101.4(1)	101.0(2)	101.2(1)			105.77	105.0	104.33	100.37
Oxo–Mo–O2	101.9(1)	102.0(2)	101.86(1)			105.88	105.6	105.47	100.79
H ₂ O–Mo–O1	83.2(1)	83.5(2)	83.6(1)			74.38	75.29	75.16	82.77
H ₂ O–Mo–O2	78.2(1)	78.1(2)	78.2(1)			74.11	74.37	74.55	79.21
oxo–Mo–OP	94.0(1)	94.4(2)	94.0(2)			97.17	97.46	97.82	118.77
H ₂ O–Mo–OP	79.6(1)	79.5(2)	79.4(2)			82.61	82.14	82.90	58.93
Mo–O–P	173.0(2)	173.1(2)	174.2(2)	123.6	126.2	131.82	168.44	144.99	158.55

^a Data from crystal structure determination reported herein; O1 corresponds to O3 and O4, O2 corresponds to O2 and O5, oxo is O1, OP is O6, Pis P1, H₂O is O7 as displayed in Fig. 1.

^b These data were obtained by changing the cell parameters to those used previously [12] and refining to convergence.

^c Data for some distances and angles were not available in the publication.

^d Calculations using the results from the crystal structure as the starting point.

^e Calculations using the results from the B3LYP/Set I results as the starting point.

distances of 1.945(3) and 1.942(3) Å and the *cis* O3 and O4 to Mo1 distances significantly shorter at 1.911(2) and 1.910(2) Å, respectively. The O to O atoms distances within the peroxo ligands are 1.462(3) and 1.461(3) Å for O2–O3 and O4–O5, respectively, within the ≈ 1.4–1.5 Å range specified for peroxo ligands. [30] While the overall arrangement of the atoms is similar to that reported previously [12], there are significant differences in certain bond distances and angles as listed in Table 2. To establish the reason for the difference, we repeated this synthesis and determined the unit cell of crystals produced under different solvent conditions to see if the one reported previously could be reproduced. However, despite several attempts as detailed in Table 1, we were unable to get crystals with the previously reported cell dimensions. Those we obtained were identical to the one reported herein, thus they did not include interstitial solvent and we did not collect reflection data for these crystals.

We then decided to refine the data set using the cell reported previously [12] (i.e. $a = 10.648(9)$ Å, $b = 8.299(7)$ Å, $c = 17.288(15)$ Å and $\beta = 104.7(2)^\circ$) in order to see what effect this would have on the bond distances and angles of the molecule. This comparison (i.e. the data in the column entitled ‘Identical cell refinement’) is detailed in Table 2 and a CIF file containing the results of this refinement is available as supplementary material (Section 5). The results here revealed that there are no significant differences in the bond lengths and angles between the data reported previously and the additional refinement using the previous reported cell. This would strongly suggest that the sole problem was that the data for the *c*-axis of the unit cell

was in error in the original determination [12] of this structure.

Geometry optimizations of **1** in Set I gave a structure very similar to that found previously by Deubel et al. [14] The Mo–O–P bond angle is 40° less than that in the crystal structure and the Mo–OH₂ distance is 0.25 Å longer than experiment, but 0.14 Å shorter than the Deubel structure. Calculations in Set II (based on the crystal structure results) give a Mo–O–P angle only 5° less than experiment and a Mo–OH₂ distance slightly shorter than found in Set I. If the Set I optimized geometry is used as a starting geometry for Set II, the calculation converges to a bent conformation (144.99°) slightly lower in energy (1.4 kcal/mol). These large structural differences do not have a significant effect upon the other geometric parameters, which are largely conserved between the bent and linear conformations. Only the small differences (0.01–0.02 Å) in the Mo–OH₂, Mo–OP and O–P distances may indicate slight changes in the donor properties of the phosphine oxide.

The large differences between theory and experiment for the complexation of water partially result from gas phase effects. In the crystal, these protons interact with the oxos of adjacent molecules in the crystal resulting in a partial negative charge on the water oxygen and a stronger and shorter bond to Mo. Sensato et al. incorporated methanol molecules to compensate for a similar long Mo–OH₂ bond in a study of MoO(O₂)₂(OPyr)(OH₂) and obtained a bond length in close agreement with experiment. [31] The long bond lengths in this study and in Deubel et al. results from the absence of an intermolecular hydrogen bonding partner for water which rearranged to interact with the nearby

peroxo ligands. The large variation between our results and Deubel et al. is likely due to differences in basis sets allowing for optimization to different points along the flat potential of the Mo–OH₂ coordinate [32].

4. Conclusions

The dimensions of the *c*-axis for MoO(O₂)₂(H₂O)(hmpa), **1**, at 17.288(15) Å was not measured or reported accurately as crystals of **1** grown under identical and different conditions consisting only of **1** did not contain significant differences in this distance and ranged from 17.003(3) to 17.007(3) Å. The data from the structure reported earlier [12] has been cited frequently in the literature and complex **1** has been the subject of theoretical calculations. The results of our theoretical calculations suggest that a bent conformation for the Mo–O–P angle is slightly lower in energy, but crystal packing forces may favor the linear geometry.

5. Supporting information available

CCDC 273779 and 273780 contains the supplementary crystallographic data for this paper in CIF format for **1** and **1** refined with the longer *c*-axis, respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033).

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