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The X-Ray Structural Characterization of a Tetrameric Binuclear Bis(μ-oxo) Molybdenum(V) Compound Bridged by Methoxide Ligands

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The literature is replete with structural characterizations of diamagnetic binuclear Mo(V) compounds with the $Mo_2O_4^{+2}$ unit accompanied by O, N, and S-donor ligands [1, 2]. A Mo–Mo bond distance in the range 2.53–2.58 Å, characteristic of a single bond, is observed in these species. We report herein an additional X-ray structural characterization of a compound possessing the $Mo_2O_4^{+2}$ moiety which concomitantly contains two unique structural features. The crystallographically unrelated $Mo_2O_4^{+2}$ units form a tetrameric derivative by way of bis-μ_2-methoxy bridges, and these binuclear moieties are composed of five- and six-coordinate Mo(V) centers which differ in their coordination spheres by a PMe_3 ligand.

Experimental

A pure sample of *fac*-$Mo(CO)_3(PMe_3)_3$ was sealed in a glass vial with a rubber septum, degassed, and dissolved in a minimum of dry methanol. In the presence of sunlight, the colorless solution slowly turned orange, yielding dark orange crystals after approximately 3 weeks. The reaction was shown to be reproducible under the same conditions as indicated by the formation of crystals with identical unit cell parameters. A parallel experiment carried out in a completely oxygen-free, moisture-free dry box resulted in no reaction.

X-ray Experimental

An orange prismatic crystal of the title compound measuring 0.3 mm × 0.2 mm × 0.1 mm was sealed in epoxy inside a glass capillary tube to prevent solvent loss. Room temperature intensity data were measured on an Enraf-Nonius CAD-4 diffractometer with Mo-Kα radiation by the θ–2θ scan method. Lattice parameters were determined by least squares fit of 25 well-centered reflections ($3° < \theta < 13°$). Data were corrected for Lorentz and polarization effects to yield observed structure factors. An empirical absorption correction based on psi-scan information was also applied to the reflection data. Periodic checks of standard reflection intensities demonstrated no significant decay due to X-ray exposure. Table I contains a summary of crystal data and intensity collection.

TABLE I. Summary of Crystal Data and Intensity Collection.

Empirical Formula	$Mo_8P_4O_{24}C_{20}H_{80}$
Formula Weight	1596.3
Space Group	$P2_1/c$
a (Å)	25.30(2)
b (Å)	13.024(9)
c (Å)	15.36(1)
β (deg)	91.79(7)
V (Å^3)	5064(2)
Z	4
Density (calcd.)	2.093
Radiation	Mo-K$_\alpha$ (λ = 0.71073 A)
μ (cm^{-1})	20.7
Range of Data Collection	$0° < \theta < 22.5°$
Total No. Measured Data	6981
No. Unique Data ($I > 3\sigma(I)$)	2083
No. of Variables Refined	350
Largest Shift/esd, Final Cycle	0.01

The structure was solved by direct methods** which yielded the positions of the eight Mo atoms. Subsequent difference Fourier synthesis revealed the locations of the remaining non-hydrogen atoms. Table II contains the final atomic positional and thermal parameters. Due to the scarcity of sufficiently intense data, only those atoms expected to demonstrate considerable thermal motion were allowed to refine anisotropically. All other non-hydrogen atoms were refined isotropically. Hydrogen atoms were included in fixed, calculated positions with fixed temperature factors. The structure was refined by full-matrix weighted least squares ($w = 1/\sigma(F_o)^2$ minimizing the function $\Sigma w(|F_o| - |F_c|)^2$. Convergence was achieved at $R = 0.072$ and $R_w = 0.082$ with

$$R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$$

and

$$R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$$

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**All crystallographic computing and plotting was carried out using the Enraf-Nonius SDP system of programs. Enraf-Nonius, Delft, Holland.

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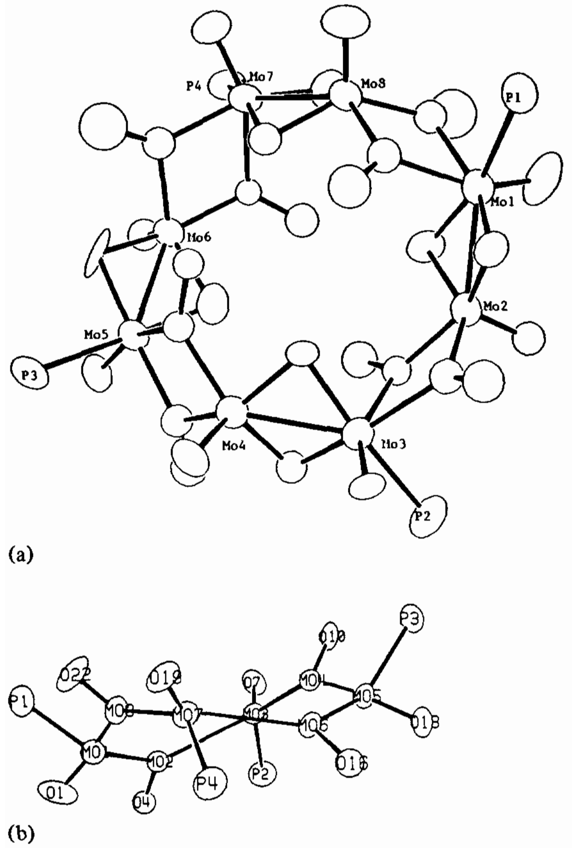
TABLE II. Table of Positional Parameters and Their e.s.d.s.

Atom	*x*	*y*	*z*
Mo1	0.3618(1)	0.2031(3)	0.8640(2)
Mo2	0.3868(1)	0.0202(3)	0.8150(2)
Mo3	0.3635(1)	−0.2347(3)	0.8685(2)
Mo4	0.2720(1)	−0.2891(3)	0.9185(2)
Mo5	0.1396(1)	−0.2398(3)	0.8784(2)
Mo6	0.1106(1)	−0.0534(3)	0.8543(2)
Mo7	0.1404(1)	0.1941(3)	0.9170(2)
Mo8	0.2373(1)	0.2470(3)	0.9418(2)
P1	0.3944(4)	0.3228(10)	0.9877(8)
P2	0.4134(5)	−0.2909(11)	0.7339(8)
P3	0.1219(5)	−0.3708(9)	1.0004(8)
P4	0.0673(4)	0.2475(10)	0.8051(7)
O1	0.3940(10)	0.278(2)	0.799(2)
O2	0.3239(9)	0.099(2)	0.800(2)
O3	0.4107(9)	0.098(2)	0.914(2)
O7	0.4059(9)	−0.304(2)	0.928(2)
O8	0.3108(9)	−0.167(2)	0.940(1)
O10	0.2841(9)	−0.379(2)	0.995(2)
O13	0.0988(9)	−0.316(2)	0.814(2)
O14	0.0989(8)	−0.151(2)	0.949(1)
O15	0.1700(9)	−0.131(2)	0.816(2)
O19	0.1056(10)	0.264(2)	0.988(2)
O20	0.1849(9)	0.284(2)	0.853(2)
O21	0.2005(9)	0.120(2)	0.973(1)
O22	0.2350(10)	0.331(2)	1.020(2)
O4	0.4277(10)	0.034(2)	0.732(2)
O5	0.3440(9)	−0.107(2)	0.779(1)
O6	0.4146(9)	−0.104(2)	0.884(2)
O9	0.3078(9)	−0.318(2)	0.817(1)
O11	0.2094(9)	−0.209(2)	0.966(1)
O12	0.2031(9)	−0.331(2)	0.844(1)
O16	0.0577(10)	−0.060(2)	0.783(2)
O17	0.0950(10)	0.061(2)	0.941(2)
O18	0.1489(9)	0.072(2)	0.819(1)
O23	0.2898(10)	0.294(2)	0.856(2)
O24	0.3038(9)	0.165(2)	0.964(2)
C1	0.393(3)	0.274(5)	1.092(4)
C2	0.366(3)	0.443(6)	0.991(5)
C3	0.462(2)	0.366(5)	0.978(4)
C5	0.294(2)	−0.106(3)	0.729(3)
C6	0.459(2)	−0.102(3)	0.945(3)
C7	0.375(3)	−0.266(5)	0.632(4)
C8	0.429(3)	−0.428(5)	0.740(4)
C9	0.472(3)	−0.231(7)	0.719(5)
C11	0.213(1)	−0.124(3)	1.024(2)
C12	0.204(2)	−0.384(3)	0.763(3)
C13	0.138(2)	−0.312(3)	1.110(3)
C14	0.154(2)	−0.485(4)	1.002(3)
C15	0.052(2)	−0.402(4)	0.997(3)
C17	0.075(2)	0.030(4)	1.023(3)
C18	0.187(2)	0.077(3)	0.754(3)
C19	0.004(2)	0.201(4)	0.834(3)
C20	0.073(2)	0.213(4)	0.691(3)
C21	0.061(2)	0.383(5)	0.800(4)
C23	0.282(2)	0.345(5)	0.775(4)
C24	0.308(2)	0.080(4)	1.019(3)
H1	0.4081(0)	0.2076(0)	1.0932(0)
H2	0.4124(0)	0.3184(0)	1.1303(0)
H3	0.3574(0)	0.2706(0)	1.1095(0)
H4	0.3292(0)	0.4367(0)	0.9956(0)
H5	0.3806(0)	0.4801(0)	1.0390(0)
H6	0.3737(0)	0.4790(0)	0.9385(0)
H7	0.4660(0)	0.3946(0)	0.9220(0)
H8	0.4691(0)	0.4175(0)	1.0210(0)
H9	0.4850(0)	0.3100(0)	0.9868(0)
H10	0.2814(0)	−0.1742(0)	0.7202(0)
H11	0.2682(0)	−0.0680(0)	0.7600(0)
H12	0.2984(0)	−0.0739(0)	0.6741(0)
H13	0.4764(0)	−0.0370(0)	0.9409(0)
H14	0.4470(0)	−0.1112(0)	1.0019(0)
H15	0.4830(0)	−0.1550(0)	0.9311(0)
H16	0.3666(0)	−0.1951(0)	0.6280(0)
H17	0.3951(0)	−0.2858(0)	0.5837(0)
H18	0.3431(0)	−0.3052(0)	0.6320(0)
H19	0.3973(0)	−0.4661(0)	0.7485(0)
H20	0.4442(0)	−0.4495(0)	0.6873(0)
H21	0.4530(0)	−0.4404(0)	0.7873(0)
H22	0.4945(0)	−0.2403(0)	0.7689(0)
H23	0.4885(0)	−0.2599(0)	0.6696(0)
H24	0.4664(0)	−0.1597(0)	0.7093(0)
H25	0.1787(0)	−0.1004(0)	1.0363(0)
H26	0.2311(0)	−0.1440(0)	1.0761(0)
H27	0.2322(0)	−0.0700(0)	0.9971(0)
H28	0.2366(0)	−0.4215(0)	0.7601(0)
H29	0.1755(0)	−0.4304(0)	0.7585(0)
H30	0.2021(0)	−0.3357(0)	0.7170(0)
H31	0.1207(0)	−0.2467(0)	1.1140(0)
H32	0.1254(0)	−0.3557(0)	1.1546(0)
H33	0.1748(0)	−0.3029(0)	1.1173(0)
H34	0.1910(0)	−0.4731(0)	1.0036(0)
H35	0.1445(0)	−0.5229(0)	1.0516(0)
H36	0.1445(0)	−0.5226(0)	0.9507(0)
H37	0.0425(0)	−0.4324(0)	0.9422(0)
H38	0.0446(0)	−0.4496(0)	1.0421(0)
H39	0.0318(0)	−0.3414(0)	1.0045(0)
H40	0.0693(0)	0.0891(0)	1.0573(0)
H41	0.0426(0)	−0.0056(0)	1.0132(0)
H42	0.0999(0)	−0.0139(0)	1.0514(0)
H43	0.1849(0)	0.0178(0)	0.7184(0)
H44	0.1816(0)	0.1370(0)	0.7198(0)
H45	0.2216(0)	0.0803(0)	0.7814(0)
H46	−0.0016(0)	0.2171(0)	0.8937(0)
H47	−0.0225(0)	0.2335(0)	0.7989(0)
H48	0.0025(0)	0.1291(0)	0.8262(0)
H49	0.0770(0)	0.1405(0)	0.6858(0)
H50	0.0425(0)	0.2346(0)	0.6589(0)
H51	0.1034(0)	0.2458(0)	0.6682(0)
H52	0.0936(0)	0.4130(0)	0.7846(0)
H53	0.0344(0)	0.4012(0)	0.7576(0)
H54	0.0512(0)	0.4089(0)	0.8552(0)
H55	0.3151(0)	0.3574(0)	0.4797(0)
H56	0.2608(0)	0.3031(0)	0.7370(0)
H57	0.2644(0)	0.4089(0)	0.7836(0)
H58	0.2786(0)	0.0790(0)	1.0566(0)
H59	0.3079(0)	0.0185(0)	0.9858(0)
H60	0.3397(0)	0.0841(0)	1.0534(0)



(a)

(b)

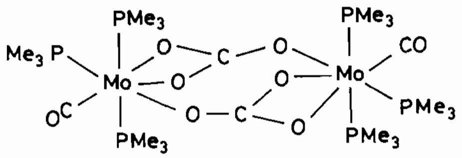
Fig. 1. (a) Computer-generated perspective diagram of (1) with atom-labelling scheme. The hydrogen atoms and methyl groups of PMe_3 have been omitted for clarity. (b) Computer-generated conformation of the eight molybdenum atoms in (1) stripped of the methoxy bridging ligands, hydrogen atoms, and methyl groups of PMe_3 for simplicity.

The maximum peak in the final difference Fourier map measured 1.6 $e^-/Å^3$, not associated with any particular chemical features of the model. A table of observed and calculated structure factors is provided as supplementary material.

Results and Discussion

Synthesis

While performing a routine crystal growing exercise on the *fac*-$Mo(CO)_3(PMe_3)_3$ compound (prepared from *fac*-$Mo(CO)_3(pyridine)_3$ and excess PMe_3) in a methanol solution in a septum-sealed glass vial on a laboratory bench with plenty of southern exposure (intense sunlight), the slow aventious introduction of oxygen resulted in the production of large orange crystals of the title compound (**1**). We have thus far been unable to identify any reaction intermediates during the formation of (**1**). However, the unascertained reaction process was quite reproducible, with no reaction occurring in the absence of sunlight and oxygen. A recently reported, equally perplexing, formation of a $Mo_2O_4^{+2}$ moiety has appeared where it is suggested to result from the intermediate depicted below (2) [3].



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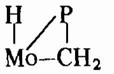
Alternatively, the intermediacy of a molybdenum hydride species of the form



$$\overset{\mathrm{H}}{\mathrm{Mo}}\!-\!\overset{\mathrm{P}}{\mathrm{C}}\mathrm{H_2}$$

resulting from oxidative addition of a C–H unit to the metal center following photochemical loss of CO may be of importance [4]. This is particularly true since we have demonstrated the formation of metal alkoxides from the reaction of metal alkyls or metal hydrides and methanol [5]. Because of the lack of supportive experimental evidence, further speculative discussion on the mode of formation of (**1**) is unwarranted.

Description of Crystal Structure

The molecular structure and pertinent atom labelling scheme for the tetrameric derivative, $[Mo_2O_4(OMe)_2PMe_3]_4$ (**1**), are presented in Fig. 1a. The conformation of the ring comprised of the eight molybdenum atoms, stripped of the methoxy bridging ligands for simplicity, is depicted in Fig. 1b. The individual binuclear Mo(V) units display bonding features common to those of the other $Mo_2O_4^{+2}$ moieties that have been structurally characterized [1, 2, 6]. The Mo–Mo distances in (**1**) span the range of 2.557–2.578 Å, and have an average value of 2.567 Å which is representative of a Mo–Mo single bond. The central $\mathrm{Mo}\overset{\mathrm{O}}{\underset{\mathrm{O}}{\diamond}}\mathrm{Mo}$ ring (ave. $\mathrm{Mo}\overset{\mathrm{O}}{\wedge}\mathrm{Mo}$ angle being 83.5°) is puckered as is seen in Fig. 1b, with the terminal Mo=O groups being *cis* with respect to one another.

The coordination geometry about one of the Mo(V) atom, that which possesses the PMe_3 ligand, is a distorted octahedron; whereas, the other Mo(V) atom's coordination is that of a distorted square pyramid. The averages of selected interatomic distances and angles in a repeating entity of the tetramer are provided in Fig. 2, whereas a complete listing of bond distances and angles are supplied in supple-

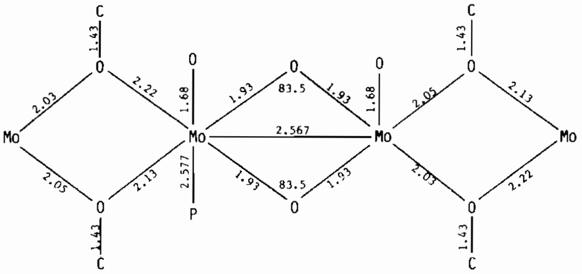


Fig. 2. Skeletal representations of the averages of selected bond distances and angles in (**1**).

mentary materials*. The presence of the very basic PMe_3 donor ligand does not have a significant *trans* influence on the bridging Mo–O bond of the binuclear unit.

Acknowledgement

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Supplementary Material Available

Listings of observed and calculated structure factor amplitudes, bond distances and bond angles, torsional angles, and thermal parameters of (**1**) (18 pages). Ordering information is given on any current masthead page.

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*The reported structure is not particularly good owing to lack of observable data.

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