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Trinuclear polyoxomolybdates, the crystal and molecular structure of $[(n\text{-}C_4H_9)_4N][Mo_3O_6(OCH_2CH_2Cl)\{(OCH_2)_3CCH_3\}_2]$

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Abstract

The reaction of $[(n\text{-}C_4H_9)_4N]_4[Mo_8O_{26}]$ with 2-(hydroxymethyl)-2-methyl-1,3-propanediol (H_3hmmp) in acetonitrile yields $(TBA)_2[Mo_3O_7(hmmp)_2]$ (**1**). Complex **1** reacts with chloroacetic acid and alkylating agents to yield the derivatives $(TBA)[Mo_3O_6(OH)(hmmp)_2]$ (**2**) and $(TBA)[Mo_3O_6(OR)(hmmp)_2]$ (**3**), respectively. The direct reaction of $(TBA)_4[Mo_8O_{26}]$ with H_3hmmp in chloroethanol yields $(TBA)[Mo_3O_6(OCH_2CH_2Cl)(hmmp)_2$ (**4**). The structure of **4** consists of discrete trinuclear anions $[Mo_3O_6(OCH_2CH_2Cl)(hmmp)_2]^-$ and TBA^+ cations. Two of the molybdenum centers exhibit similar coordination environments, each bonding to two terminal oxo groups, one terminal hmmp alkoxy donor and three bridging alkoxy oxygens from the hmmp ligands. The third molybdenum center coordinates to two terminal oxo groups, a terminal chloroethanolate ligand, and three bridging alkoxy oxygens of the hmmp ligands. Crystal data: monoclinic space group $P2_1/n$, $a=12.224(2)$, $b=23.178(3)$, $c=13.562(3)$ Å, $\beta=97.05(1)°$, $V=3813.1(11)$ Å^3, $Z=4$. Structure solution and refinement based on 4794 reflections (Mo Kα, $\lambda=0.71073$ Å, $2\theta\leqslant 45°$) converged at a conventional discrepancy value of 0.052.

Introduction

Investigations of the coordination chemistry of polyoxomolybdates with alkoxy and carbonyl oxygen donor ligands [1–7] derive their impetus from the analogies of these systems to surface-bound intermediates in heterogeneous catalysis employing molybdenum oxides [8–13]. Structurally characterized examples of polyoxomolybdate complexes incorporating simple organic substrates with oxygen donors include $[Mo_8O_{26}(HCO_2)_2]^{6-}$ [14], $[Mo_8O_{24}(OCH_3)_4]^{4-}$ [15], $[Mo_4O_{14}(OH)CH_2]^{3-}$ [16] and the related $[RMo_4O_{15}X]^{3-}$ class of clusters [6], $[Mo_4O_8(OC_2H_5)_2\{(OCH_2)_3CCH_3\}_2]$ [17], and the recently described $[Mo_3O_7\{(OCH_2)_3CCH_3\}_2]^{2-}$ [7]. The latter complex is unusual as a rare example of a polyoxomolybdate with a molybdenum center coordinated to three terminal oxo groups $[MoO_3]$. When present in the polynuclear species $[Mo_{10}O_{34}]^{8-}$ [18] and $[Mo_8O_{24}(OCH_3)_2]^{4-}$ [19], the $[MoO_3]$ unit is weakly associated with the cluster as a corner-sharing $[MoO_4]^{2-}$ tetrahedron which is readily displaced in solution. Lipscomb has rationalized the absence of stable polyanion species containing addenda MO_6 octahedra with more than two terminal oxo groups in terms of the strong *trans* influence of the M–O (terminal) bonds which would dissociate the *fac* $[MO_3]$ groups attached to the structure by weak bonds [20]. The presence of ligating groups such as $[(OCH_2]_3CCH_3]^{3-}$ (hmmp), capable of adopting terminal and a variety of bridging coordination modes, appears to stabilize the $[MoO_3]$ unit in complexes such as $[Mo_3O_7(hmmp)_2]^{2-}$ (**1**), suggesting that 'Lipscomb's principle' does not extend to coordination complexes of polyoxomolybdates. However, the $[MoO_6]$ moiety with the facial trioxomolybdate(VI) core should be relatively unstable and reactive toward substitution or protonation of terminal oxo groups so as to adopt the more favorable *cis* dioxo geometry.

In this paper, we present details for the synthesis of the previously reported $(TBA)_2[Mo_3O_7(hmmp)_2]$ (**1**) and its reactions with protonating and alkylating reagents to give complexes of the class $(TBA)[Mo_3O_6(OR)(hmmp)_2]$ (R = H, **2**; R = –CH$_3$, **3a**; R = –CH$_2$CH$_3$, **3b**). Direct reactions of $(TBA)_4[Mo_8O_{26}]$ with H_3hmmp in the appropriate alcohol may also be employed to give complexes of this class. The reaction is general as indicated by the isolation of $(TBA)[Mo_3O_6(OCH_2CH_2Cl)(hmmp)_2]$ (**4**) from reactions in chloroethanol.

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Experimental

Materials

All reagents and solvents were obtained from common commercial sources unless otherwise noted. $(TBA)_2[Mo_2O_7]$ was prepared according to the published method [21].

Preparation of complexes

$(TBA)_2[Mo_3O_7(hmmp)_2] \cdot 0.5(C_2H_5)_2O$ (1)

A solution of H_3hmmp (1.2 g, 10 mmol) in CH_2Cl_2 (10 ml) was added to a solution of $(TBA)_2[Mo_2O_7]$ (0.97 g, 2.5 mmol) in CH_2Cl_2 (20 ml). The colorless solution was stirred for 9 h at room temperature and then refluxed for 24 h. The solvent was then stripped on a rotary evaporator to yield a colorless oil, which was dissolved in 20 ml of methanol. After carefully layering with 30 ml of diethylether, the solution was allowed to stand at room temperature for 2 weeks, whereupon colorless crystals of **1** were deposited and collected in 20% yield. *Anal.* Calc. for $C_{44}H_{95}N_2O_{13.5}Mo_3$: C, 45.7; H, 8.22, N, 2.42. Found: C, 45.6; H, 8.03; N, 2.45%. IR (KBr pellet, cm^{-1}): 2912(vs), 1460(s), 1397(m), 1119(m), 1040(vs),

TABLE 1. Crystallographic data for $(TBA)[Mo_3O_6(OCH_2CH_2Cl)(hmmp)_2]$ (4)

Crystal data[a]	
Temperature (K)	293
a (Å)	12.244(2)
b (Å)	23.178(3)
c (Å)	13.562(3)
α (°)	90.00
β (°)	97.05(1)
γ (°)	90.00
V (Å^3)	3813.1(11)
Space group	$P2_1/n$
Z	4
D_{calc} (g cm^{-3})	1.64
Measurement of intensity data	
Crystal shape and color	
Crystal dimensions (mm)	0.25 × 0.31 × 0.22
Instrument	Nicolet R3m diffractometer
Radiation	Mo Kα ($\lambda = 0.71073$ Å)
Scan mode	coupled θ(crystal)–2θ(counter)
Scan rate (°/min)	2.0–10.0
Scan range (°)	$0° < 2\theta \leqslant 45°$
Scan length	from $[2\theta(K\alpha_1) - 1.0]°$ to $[2\theta(K\alpha_2) + 1.0]°$
Background measurement	stationary crystal, stationary counter, at the beginning and at end of each 2θ scan, each for half the time taken for the scan
Standards	3 collected every 300
No reflections collected	7068
No. reflections used in solution $F_o \geqslant 6\sigma(F_o)$	4794
Reduction of intensity data and summary of structure solution and refinement[b]	
Data corrected to background, attenuators, Lorentz and polarization effects in the usual fashion	
Absorption coefficient (cm^{-1})	10.7
Absorption corrections	(not applied)
Structure solution	Patterson synthesis yielded the heavy atom positions; all remaining non-hydrogen atoms were located via standard Fourier techniques
Atom scattering factors[c]	neutral atomic scattering factors were used throughout the analysis
Anomalous dispersion[d]	applied to all non-hydrogen atoms
Final discrepancy factor[e]	
R	0.052
R_w	0.063
Goodness of fit[f]	1.92

[a] From at least-squares fitting of the setting angle of 25 reflections. [b] All calculations were performed on a Micro-Vax II computer using local versions of the Nicolet SHELXTL interactive crystallographic software package as described in ref. 22. [c] Ref. 23. [d] Ref. 24. [e] $R = \Sigma[|F_o| - |F_c|/\Sigma|F_o|]$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1-2}$, $w = 1/\delta^2(F_o) + g^*(F_o)^2$, $g = 0.005$. [f] $GOF = [\Sigma w(|F_o| - F_c|)^2/(NO - NV)]^{1/2}$ where NO is the number of observations and NV is the number of variables.

988(m), 932(vs), 917(vs), 901(vs), 640(s), 600(m), 530(m), 490(m), 332(m).

(TBA)[Mo_3O_6(OH)(hmmp)$_2$] (**2**)

A solution of chloroacetic acid (0.215 g, 2.28 mmol) in 2 ml of tetrahydrofuran was added dropwise to a stirred slurry of $(TBA)_2[Mo_3O_7(hmmp)_2]\cdot 0.5 (C_2H_5)_2O$ (0.58 g, 0.5 mmol) in 20 ml of tetrahydrofuran. After stirring the white slurry for 20 min, the mixture was added to 40 ml of THF/ether (1:1. vol./vol.). The white solid was filtered and washed with THF (yield 87%) Anal. *Calc.* for $C_{26}H_{55}NO_{13}Mo_3$: C, 35.6; H, 6.27; N, 1.60. Found: C, 35.3; H, 6.11; N, 1.43%.

(TBA)[Mo_3O_6(OCH_3)(hmmp)$_2$] (**3a**)

A solution of trimethyloxonium tetrafluoroborate (1.48 g, 10 mmol) in 10 ml of dichloroethane was added to a solution of **1** (2.89 g, 2.5 mmol) in 20 ml of dichloroethane. After stirring for 2 h, the solution was concentrated to 15 ml and diethylether carefully layered. Upon standing for 5 d, colorless crystals of **3a** were isolated in 22% yield. *Anal.* Calc. for $C_{27}H_{52}NO_{13}Mo_3$: C, 36.4; H, 6.40; N, 1.57. Found: C, 36.2; H, 6.29; N, 1.50.

(TBA)[Mo_3O_6(OC_2H_5)(hmmp)$_2$] (**3b**)

$(C_2H_5O)_2SO_2$ (160 μL, 1.0 mmol) was added to a solution of **1** (0.29 g, 0.25 mmol) in 10 ml of dichloroethane. After stirring for 5 min, the solution was evaporated to dryness and the resultant white solid dissolved in 20 ml of dichloroethane. Upon addition of 20 ml of ether, white microcrystals of **3b** were collected in 30% yield. *Anal.* Calc. for $C_{28}H_{59}NO_{13}Mo_3$: C, 37.1; H, 6.52; N, 1.55. Found: C, 37.5; H, 6.66; N, 1.43%.

(TBA)[Mo_3O_6(OCH_2CH_2Cl)(hmmp)$_2$] (**4**)

A solution of $(TBA)_4[Mo_8O_{26}]$ (3.1 g, 1.4 mmol) in 50 ml of 2-chloroethanol was refluxed for 45 min, whereupon H_3hmmp (1.21 g, 10 mmol) was added. After refluxing for 48 h, the solution was layered with ether and allowed to stand for 2 days whereupon colorless crystals were collected in 25% yield. *Anal.* Calc. for $C_{28}H_{58}NO_{13}ClMo_3$: C, 35.8; H, 6.17; N, 1.49. Found: C, 36.0; H, 6.26; N, 1.39%. IR (KBr pellet, cm^{-1}): 2890(vs), 1460(s), 1390(m), 1035(vs), 910(vs), 800(w), 760(m), 740(m), 630(s), 600(s), 540(s).

X-ray crystallographic study

The crystal data and experimental details for the X-ray diffraction study of **4** are summarized in Table 1. Atomic positional parameters and isotropic temperature factors are listed in Table 2. Full details of the crystallographic methods used may be found in ref. 25.

Results and discussion

A number of studies of the coordination chemistry of molybdates with polyhydroxylic ligands have been reported [17, 26, 27]. The chemistry exploits the tendency of Mo(VI) to develop distorted octahedral coordination with oxygen ligands through the use of different combinations of bridging and terminal oxo groups and ligand alkoxy groups. However, the core structure adopted by the complexes isolated from these reactions is clearly dependent on reaction conditions. Thus, the reactions of MoO_3 with H_3hmmp in aqueous media, followed by addition of alcohol, yield $[Mo_2O_2(OC_2H_5)_2(hmmp)_2]$ [26] and $[Mo_4O_8(OC_2H_5)_2(hmmp)_2$ [17], while the reaction of $(TBA)[Mo_2O_7]$ with H_3hmmp in methanol yields $(TBA)_2[Mo_8O_{20}(OCH_3)_4(hmmp)_2]$ [27].

By appropriate modification of the reaction conditions, the trinuclear species $(TBA)_2[Mo_3O_7(hmmp)_2]$ (**1**) was isolated and structurally characterized [7]. Complex **1**, shown schematically in Fig. 1, reacts with chloroacetic acid and alkylating agents according to eqn. (1) to yield derivatives of the general class $[Mo_3O_6(OR)(hmmp)_2]^{1-}$.

$$[Mo_3O_7(hmmp)_2]^{2-} \xrightarrow[-X^-]{+RX} [Mo_3O_6(OR)(hmmp)_2]^{1-}$$

2: $R=H$; $X=ClCH_2CO_2^-$
3a: $R=CH_3$; $X=(CH_3)_2OBF_4^-$
3b: $R=C_2H_5$; $X=CH_3CH_2OSO_3^-$

The molybdenum–oxo groups of polyoxomolybdate anions are generally inert toward protonation and alkylation. The relatively facile protonation and alkylation of **1** at the trioxomolybdate site indicates the relative lability of the oxo groups of this unit. Since a facial arrangement of three terminal oxo groups in a $[MoO_6]$ moiety of a polymolybdate is expected to be unfavorable for reasons previously discussed, the reactivity of the trioxomolybdate moiety of **1** is not altogether unexpected.

Complex **3a** may also be synthesized directly from the reaction of $(TBA)_4$ $[Mo_8O_{26}]$ with H_3hmmp in methanol [28]. To test the general application of these reaction conditions, $(TBA)_4[Mo_8O_{26}]$ was reacted with H_3hmmp in 2-chloroethanol. The analogous complex $(TBA)[Mo_3O_6(OCH_2CH_2Cl)(hmmp)_2]$ (**4**) was readily isolated as colorless block shaped crystals.

Crystal structure analysis of **4** revealed the discrete trinuclear anion illustrated in Fig. 2. The structure is analogous to those of **1** and **3a** which were previously

TABLE 2. Atomic positional parameters ($\times 10^4$) and isotropic temperature factors ($\AA^2 \times 10^3$) for $(TBA)[Mo_3O_6(OCH_2CH_2Cl)(hmmp)_2]$

	x	y	z	U_{eq}[a]
MO(1)	6307(1)	1169(1)	1856(1)	52(1)
Mo(2)	8365(1)	1914(1)	3503(1)	40(1)
Mo(3)	8672(1)	452(1)	2888(1)	45(1)
O(1)	6653(4)	1631(3)	3233(4)	51(2)
O(2)	8481(4)	1085(2)	4067(3)	37(2)
O(3)	6972(4)	507(2)	2830(4)	50(2)
O(4)	4964(5)	1053(3)	2048(6)	81(3)
O(5)	6555(6)	752(3)	865(5)	74(3)
O(6)	7914(4)	2492(2)	2542(4)	50(2)
O(7)	6285(5)	1892(3)	1212(5)	62(2)
O(8)	8154(4)	1320(2)	2173(3)	39(2)
O(9)	8141(5)	2231(2)	4603(4)	57(2)
O(10)	9742(5)	1954(2)	3426(5)	58(2)
O(12)	8644(5)	171(3)	1733(4)	62(2)
O(13)	8704(6)	−114(3)	3684(5)	36(2)
C(1)	6125(7)	1431(4)	4065(6)	60(3)
C(2)	7837(7)	934(3)	4841(6)	49(3)
C(3)	6445(7)	406(4)	3719(7)	63(3)
C(4)	6619(7)	871(4)	4482(6)	53(3)
C(5)	6040(8)	708(5)	5404(7)	73(4)
C(6)	8397(8)	2574(4)	1662(6)	62(3)
C(7)	6996(8)	2027(4)	475(6)	61(3)
C(8)	8673(7)	1523(4)	1322(6)	52(3)
C(9)	8205(7)	2088(4)	901(6)	52(3)
C(10)	8835(9)	2226(5)	22(7)	80(4)
O(11)	10153(4)	691(3)	3067(4)	54(2)
Cl(1)	12903(4)	1079(2)	4762(4)	151(2)
C(11)	10838(7)	733(4)	3990(7)	61(2)
C(12)	11751(13)	1012(7)	3849(13)	132(5)
N(1)	2358(5)	1190(2)	9839(4)	38(2)
C(13)	2875(6)	1560(3)	10701(5)	43(2)
C(14)	2099(7)	1894(4)	11223(6)	55(3)
C(15)	2745(8)	2288(4)	12017(6)	64(3)
C(16)	2042(10)	2724(5)	12441(8)	98(5)
C(17)	1682(6)	1578(3)	9117(5)	41(2)
C(18)	1323(6)	1326(3)	8052(5)	45(2)
C(19)	554(7)	1759(4)	7471(6)	49(3)
C(20)	300(9)	1565(5)	6408(7)	76(4)
C(21)	3305(6)	896(4)	9371(7)	53(3)
C(22)	4077(7)	1311(4)	8910(7)	65(3)
C(23)	4752(18)	993(7)	8234(18)	171(12)
C(24)	4938(20)	612(11)	8020(20)	309(23)
C(25)	1627(6)	715(3)	10168(5)	42(2)
C(26)	2187(7)	263(4)	10855(7)	57(3)
C(27)	1331(8)	−160(4)	11144(8)	69(4)
C(28)	1761(10)	−606(5)	11831(10)	100(5)

[a]Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

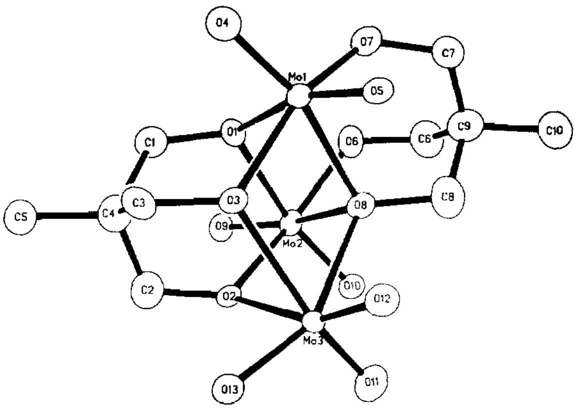

Fig. 1. Perspective view of the structure of $[Mo_3O_7(hmmp)_2]^{2-}$ (**1**).

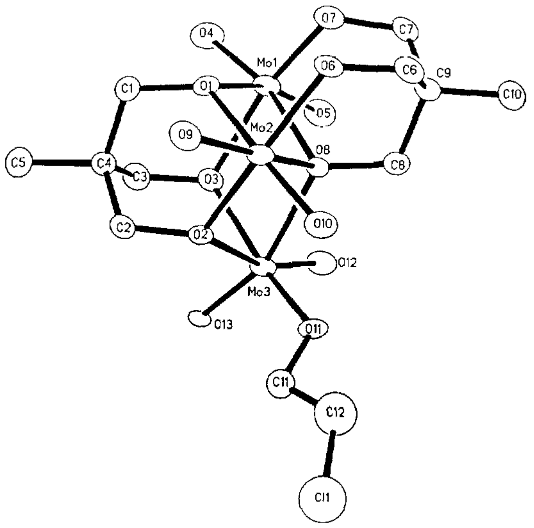

Fig. 2. ORTEP view of the structure of $[Mo_3O_6(OCH_2CH_2Cl)(hmmp)_2]^{1-}$ (**4**) showing the atom-labelling scheme.

reported [7]. The overall structure may be described as three $[MoO_6]$ octahedra in an edge-sharing arrangement. Two of the Mo centers display grossly similar geometries; Mol and Mo2 are each coordinated to two terminal oxo groups in the *cis* configuration, with bridging and terminal alkoxy donors from the hmmp ligands completing the coordination. In contrast, the Mo3 coordination geometry consists of the *cis* dioxo unit, three bridging alkoxy donors from the hmmp ligands, and the alkoxy donor of the terminal chloroethanolate. The two hmmp ligands are inequivalent. Thus, one ligand unit provides three doubly bridging alkoxy ligands O1, O2 and O3, while the second provides the triply bridging O8 and the terminal alkoxy groups O6 and O7. The metrical parameters summarized in Table 3 illustrate the influence of ligand oxygen donors in distorting the 2 long–2 intermediate–2 short bond parameter pattern generally associated with $[MoO_6]$ sites in polyoxomolybdates.

TABLE 3. Selected bond lengths (Å) and angles (°) for (TBA)[$Mo_3O_6(OCH_2CH_2Cl)(hmmp)_2$]

Lengths (Å)			
Mo1–O1	2.150(5)	Mo2–O10	1.702(6)
Mo1–O3	2.120(5)	Mo2–O6	1.903(5)
Mo1–O4	1.715(6)	Mo2–O8	2.257(5)
Mo1–O5	1.713(7)	Mo3–O2	2.203(5)
Mo1–O(7)	1.888(6)	Mo3–O3	2.067(5)
Mo1–O(8)	2.273(5)	Mo3–O12	1.693(6)
Mo2–O1	2.180(5)	Mo3–O13	1.696(7)
Mo2–O2	2.067(5)	Mo3–O11	1.880(5)
Mo2–O9	1.715(6)	Mo3–O8	2.289(5)
Angles (°)			
O1–Mo1–O3	78.4(2)	O2–Mo2–O10	92.9(2)
O1–Mo1–O4	92.1(3)	O6–Mo2–O8	83.5(2)
O1–Mo1–O5	158.2(3)	O6–Mo2–O9	103.3(2)
O1–Mo1–O7	87.1(2)	O6–Mo2–O10	97.1(3)
O1–Mo1–O8	71.0(2)	O8–Mo2–O9	160.3(2)
O3–Mo1–O4	95.3(3)	O8–Mo2–O10	90.1(2)
O3–Mo1–O5	89.4(3)	O9–Mo2–O10	107.1(3)
O3–Mo1–O7	155.9(2)	O2–Mo3–O3	78.0(2)
O3–Mo1–O8	72.4(2)	O2–Mo3–O8	71.0(2)
O4–Mo1–O5	107.2(3)	O2–Mo3–O11	84.0(2)
O4–Mo1–O7	104.5(3)	O2–Mo3–O12	159.4(2)
O4–Mo1–O8	160.5(3)	O2–Mo3–O13	92.8(3)
O5–Mo1–O7	97.6(3)	O3–Mo3–O8	72.9(2)
O5–Mo1–O8	88.2(3)	O3–Mo3–O11	158.6(2)
O7–Mo1–O8	84.7(2)	O3–Mo3–O12	94.8(3)
O1–Mo2–O2	78.7(2)	O3–Mo3–O13	91.0(3)
O1–Mo2–O6	84.6(2)	O8–Mo3–O11	90.4(2)
O1–Mo2–O8	70.7(2)	O8–Mo3–O12	88.5(2)
O1–Mo2–O9	91.3(3)	O8–Mo3–O13	158.9(3)
O1–Mo2–O10	160.5(2)	O11–Mo3–O12	98.2(3)
O2–Mo2–O6	155.4(2)	O11–Mo3–O13	101.5(3)
O2–Mo2–O8	74.1(2)	O12–Mo3–O13	106.7(3)
O2–Mo2–O9	95.0(2)		

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