METAL-ORGANIC COMPOUNDS

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Tris(piperazinium) Octamolybdate, $(C_4H_{12}N_2)_3[Mo_8O_{27}]$

WILLIAM T. A. HARRISON, LAURIE L. DUSSACK AND ALLAN J. JACOBSON

Department of Chemistry, University of Houston, Houston, TX 77204-5641, USA. E-mail: harrison@madmax.chem.uh.edu

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Abstract

The hydrothermal synthesis and single-crystal structure of tris(piperazinediium) octamolybdate are reported. $(C_4H_{12}N_2)_3[Mo_8O_{27}]$ contains infinite chains of $[Mo_8O_{27}]^{6-}$ anions, fused together by linear Mo—O—Mo bonds. A network of N—H···O hydrogen bonds link the doubly protonated piperazinium dications to the anionic octamolybdate chains.

Comment

$(C_4H_{12}N_2)_3[Mo_8O_{27}]$ is another example of a phase built up from infinite chains of linked anionic octamolybdate clusters, $[Mo_8O_{27}]^{6-}$, fused together by Mo—O—Mo bonds, as was previously observed for the phase $(NH_4)_6[Mo_8O_{27}].4H_2O$ (Böschen, Buss & Krebs, 1974). The structural building unit in $(C_4H_{12}N_2)_3[Mo_8O_{27}]$ is a zigzag double chain of edge-sharing MoO_6 octahedra (Fig. 1). Mo—Mo separations for the various edge-sharing octahedra in the cluster range from 3.2379 (3) to 3.5176 (3) Å. The only vertex-sharing octahedral link is between adjacent clusters, *via* O(1). The anionic chains propagate in the *b* unit-cell direction.

The $[Mo_8O_{27}]$ unit in $(C_4H_{12}N_2)_3[Mo_8O_{27}]$ has inversion symmetry about its center (Fig. 1) and about the O(1) atom linking clusters together; it comprises four crystallographically distinct Mo atoms and 14 distinct O atoms. All four of the Mo centers display typical distorted octahedral coordination to their O-atom neighbors, with two short (d < 1.76 Å) 'molybdyl' Mo═O bonds in *cis* configuration, each of which is *trans* to a long (d > 2.11 Å) Mo—O link. Two intermediate-length Mo—O bonds complete the two short + two intermediate + two long MoO_6 coordination environment, which is typical for molybdenum(VI) (Kunz & Brown, 1995). Bond-valence sum (BVS) calculations (Brese & O'Keeffe, 1991) support this valence assignment: values of BVS[Mo(1)] = 6.03, BVS[Mo(2)] = 5.98, BVS[Mo(3)] = 5.95 and BVS[Mo(4)] = 6.02 are obtained, compared with the expected value of 6.00 for Mo^{VI}.

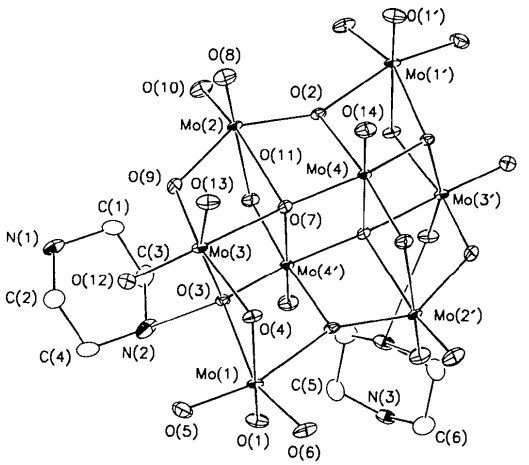

Fig. 1. View of the $[Mo_8O_{27}]$ cluster unit in $(N_2C_4H_{12})_3[Mo_8O_{27}]$ showing the atom-labelling scheme (50% probability ellipsoids). N···O hydrogen-bonding contacts are indicated by thin lines.

The O atoms in the cluster divide into the following groups: O(1) occupies a special position (site symmetry 1) and forms a linear Mo(1)—O(1)—Mo(1) bond as the inter-cluster linking atom; O(5), O(6), O(8), O(10), O(12), O(13) and O(14) are bonded only to their Mo-atom neighbor; O(11) makes a short molybdyl bond to Mo(4), but also makes a long link to a second Mo atom [Mo(2)]; O(4) and O(9) participate in Mo—O—Mo bridges; O(2) and O(3) make bonds to three Mo-atom neighbors in approximate T-shaped geometry; O(7) bonds to four Mo atoms, in distorted pyramidal coordination.

The two distinct piperazinium centers (1.5 molecules in the asymmetric unit) in $(C_4H_{12}N_2)_3[Mo_8O_{27}]$ adopt typical chair geometries, and the N—C and C—C bond lengths are unexceptional. The three distinct N atoms are all doubly protonated, and all six N—H bonds are involved in hydrogen-bonding links [d(O···H) < 1.9 Å] to six of the 14 O atoms belonging to the $[Mo_8O_{27}]$ cluster. Four of these O atoms are Mo═O species, one is a Mo—O—Mo bridging atom, and one is a triply bridging atom (Table 2).

The $[Mo_8O_{27}]^{6-}$ cluster in $(C_4H_{12}N_2)_3[Mo_8O_{27}]$ is essentially isostructural with the similar unit in $(NH_4)_6[Mo_8O_{27}].4H_2O$ (Böschen *et al.*, 1974). In both phases, the $[Mo_8O_{27}]$ clusters have inversion symmetry, and are fused by a linear Mo—O—Mo bridge (Fig. 2). The hydrogen-bonding scheme in $(NH_4)_6[Mo_8O_{27}].4H_2O$ is complex, and probably involves interactions between ammonium cations and wa-

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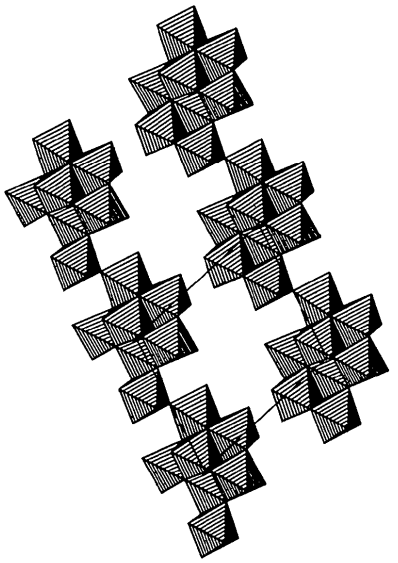

Fig. 2. Polyhedral view down [100] of the octamolybdate chains in $(C_4H_{12}N_2)_3[Mo_8O_{27}]$. The chains propagate in the [010] direction.

ter molecules, as well as ammonium–cluster links. The relationship between the $[Mo_8O_{27}]_n^{6-}$ chain and other polymolybdate clusters and chain anions has been discussed previously (Böschen *et al.*, 1974).

Thermogravimetric analysis (TGA) of $(C_4H_{12}N_2)_3[Mo_8O_{27}]$ (DuPont 9900 system; ramp at 10 K min^{-1} to 873 K under oxygen) showed a two-step 21.7% weight loss over the temperature range 623–673 K. X-ray powder diffraction on the post-TGA residue gave a clean orthorhombic MoO_3 pattern [predicted weight decrease for nominal loss of three piperazine molecules and three water molecules from $(C_4H_{12}N_2)_3[Mo_8O_{27}]$ = 21.3%].

The IR spectrum (Galaxy FTIR 5000 series spectrometer; KBr pellet method) of $(C_4H_{12}N_2)_3[Mo_8O_{27}]$ shows a broad multi-band feature at 3000–2400 cm^{-1}, which may be correlated with C—H and N—H stretches. H—N—H (1605 and 1454 cm^{-1}) and H—C—H (1423 and 1317 cm^{-1}) bending modes are visible, and characteristic MoO_6 modes occur at 941, 856, and 690 cm^{-1}.

Experimental

Purple to pink crystals (0.1–0.2 mm) of $(C_4H_{12}N_2)_3[Mo_8O_{27}]$ were prepared from a mixture of 0.241 g (2.8 mmol) of piperazine and 0.6 g (4.2 mmol) of MoO_3 in 8 ml of H_2O (*i.e.* 2:3 piperazine:MoO_3). The reactants were sealed in a 23 ml capacity Parr hydrothermal bomb and heated to 453 K for 3 d. Slow cooling over 24 h and product recovery by vacuum filtration (filtrate pH 6.8) resulted in a 62% yield (based on Mo) of $(C_4H_{12}N_2)_3[Mo_8O_{27}]$. Similar reactions carried out at the product stoichiometric ratio (3:8 piperazine:MoO_3) resulted in a mixture of $(C_4H_{12}N_2)_3[Mo_8O_{27}]$, MoO_3 and unidentified white fibrous phase(s) (filtrate pH 5.4).

Crystal data

$(C_4H_{12}N_2)_3[Mo_8O_{27}]$	Mo $K\alpha$ radiation
M_r = 1463.96	λ = 0.71073 Å
Triclinic	Cell parameters from 25 reflections
$P\bar{1}$	θ = 6–14°
a = 8.802 (6) Å	μ = 2.98 mm^{-1}
b = 9.517 (5) Å	T = 298 K
c = 10.989 (8) Å	Irregular lump
α = 100.15 (5)°	0.40 × 0.35 × 0.30 mm
β = 106.51 (6)°	Slight purple tint
γ = 101.75 (5)°	
V = 837 (1) Å^3	
Z = 1	
D_x = 2.952 Mg m^{-3}	

Data collection

Enraf–Nonius CAD-4 automated diffractometer	R_{int} = 0.018
ω–2θ scans	θ_{max} = 30°
Absorption correction: ψ scans (Enraf–Nonius, 1989)	h = −12 → 11
T_{min} = 0.456, T_{max} = 0.562	k = −13 → 13
7313 measured reflections	l = 0 → 15
4812 independent reflections	3 standard reflections frequency: 10000 s intensity decay: none
4812 observed reflections [$I > 0$]	

Refinement

Refinement on F	$(\Delta/\sigma)_{max}$ = 0.005
R = 0.033	$\Delta\rho_{max}$ = 0.8 e Å^{-3}
wR = 0.026	$\Delta\rho_{min}$ = −1.2 e Å^{-3}
S = 1.03	Extinction correction: Larson (1970)
4812 reflections	Extinction coefficient: 7.3 (3)
243 parameters	Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)
H atoms: see below	
Tukey–Prince weighting scheme, fitted using a 3-term Chebychev polynomial (Carruthers & Watkin, 1979)	

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Mo(1)	−0.05994 (3)	0.62675 (2)	0.12183 (2)	0.0082
Mo(2)	0.28198 (3)	1.22728 (2)	0.18752 (2)	0.0080
Mo(3)	0.12764 (3)	0.96196 (2)	0.30920 (2)	0.0086
Mo(4)	−0.10703 (3)	1.12728 (2)	0.02054 (2)	0.0072
O(1)	0	1/2	0	0.0156
O(2)	0.1281 (2)	1.2558 (2)	0.0360 (2)	0.0096
O(3)	0.1524 (2)	0.8022 (2)	0.1375 (2)	0.0094
O(4)	−0.0755 (3)	0.8121 (2)	0.2344 (2)	0.0110
O(5)	0.0428 (3)	0.5750 (2)	0.2566 (2)	0.0174
O(6)	−0.2639 (3)	0.5415 (2)	0.0855 (2)	0.0160
O(7)	0.0410 (2)	1.0465 (2)	0.1319 (2)	0.0100
O(8)	0.2570 (3)	1.3570 (2)	0.3048 (2)	0.0182
O(9)	0.3212 (3)	1.0884 (2)	0.2944 (2)	0.0128
O(10)	0.4714 (3)	1.3035 (3)	0.1817 (2)	0.0180
O(11)	0.2812 (3)	1.0248 (2)	0.0352 (2)	0.0127
O(12)	0.2348 (3)	0.8866 (2)	0.4258 (2)	0.0161
O(13)	0.0601 (3)	1.0900 (2)	0.3980 (2)	0.0156

O(14)	−0.1538 (3)	1.2489 (2)	0.1274 (2)	0.0162
N(1)	0.6914 (3)	0.9012 (3)	0.3365 (3)	0.0172
N(2)	0.4179 (3)	0.6941 (3)	0.1357 (3)	0.0203
N(3)	0.0171 (4)	0.3785 (3)	0.4132 (3)	0.0167
C(1)	0.6052 (4)	0.9448 (3)	0.2181 (3)	0.0182
C(2)	0.5747 (4)	0.7898 (4)	0.3699 (3)	0.0200
C(3)	0.5329 (4)	0.8089 (4)	0.1042 (3)	0.0204
C(4)	0.4974 (4)	0.6536 (4)	0.2567 (4)	0.0209
C(5)	0.1503 (4)	0.4563 (4)	0.5383 (3)	0.0208
C(6)	−0.1484 (4)	0.3838 (4)	0.4212 (4)	0.0228

Table 2. *Selected interatomic distances (Å)*

Mo(1)—O(1)	1.9022 (2)	Mo(3)—O(13)	1.731 (2)
Mo(1)—O(2^{i})	2.232 (2)	Mo(4)—O(2)	2.122 (2)
Mo(1)—O(3)	2.181 (2)	Mo(4)—O(3^{i})	1.938 (2)
Mo(1)—O(4)	2.022 (2)	Mo(4)—O(7)	1.903 (2)
Mo(1)—O(5)	1.712 (2)	Mo(4)—O(7^{i})	2.419 (2)
Mo(1)—O(6)	1.711 (2)	Mo(4)—O(11^{i})	1.753 (2)
Mo(2)—O(2)	1.926 (2)	Mo(4)—O(14)	1.696 (2)
Mo(2)—O(7)	2.289 (2)	N(1)—C(1)	1.483 (4)
Mo(2)—O(8)	1.716 (2)	N(1)—C(2)	1.490 (4)
Mo(2)—O(9)	1.936 (2)	N(2)—C(3)	1.490 (5)
Mo(2)—O(10)	1.702 (2)	N(2)—C(4)	1.473 (5)
Mo(2)—O(11)	2.317 (2)	N(3)—C(5)	1.478 (4)
Mo(3)—O(3)	2.298 (2)	N(3)—C(6)	1.494 (4)
Mo(3)—O(4)	1.903 (2)	C(1)—C(3)	1.512 (5)
Mo(3)—O(7)	2.233 (2)	C(2)—C(4)	1.510 (5)
Mo(3)—O(9)	1.941 (2)	C(5)—C(6^{ii})	1.514 (5)
Mo(3)—O(12)	1.720 (2)		

Symmetry codes: (i) $-x, 2-y, -z$; (ii) $-x, 1-y, 1-z$.

Table 3. *Hydrogen-bonding geometry (Å)*

N(2)···O(3)	2.741 (3)	N(2)···O(6^{ii})	2.783 (4)
N(1)···O(4^{i})	2.805 (3)	N(1)···O(12^{iii})	2.823 (3)
N(3)···O(5)	2.775 (3)	N(3)···O(13^{iv})	2.829 (3)

Symmetry codes: (i) $x-1, y, z$; (ii) $-x, 1-y, -z$; (iii) $1-x, 2-y, 1-z$; (iv) $x, 1+y, z$.

H atoms were geometrically placed and their positions refined riding on appropriate N or C atoms with d(N—H) = 1.00 or d(C—H) = 1.00 Å. Carrier-atom-type isotropic displacement parameters were refined for H atoms.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *RC*85 (Baird, 1985). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *CRYSTALS* (Watkin, Carruthers & Betteridge, 1990). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: local routines.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, including contact distances, have been deposited with the IUCr (Reference: TA1054). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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$[N(CH_3)_4]_2[Co_2Mo_6O_{12}(OH)_4(PO_4)(HPO_4)_2(H_2PO_4)].5H_2O$, a New One-Dimensional Molybdenum Phosphate

PHILIP LIGHTFOOT AND DIANE MASSON

School of Chemistry, University of St Andrews, St Andrews, Fife, KY16 9ST, Scotland. E-mail: pl@st-and.ac.uk

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Abstract

The title compound, bis(tetramethylammonium) dicobaltio-μ-dihydrogenphosphato-μ-bis(hydrogenphosphato)-μ_6-phosphato-tetrahydroxycyclohexamolybdate-(*Mo—Mo*) pentahydrate, was synthesized hydrothermally and crystallizes as a polymeric ionic complex with anionic chains, composed of $[Mo_6O_{12}(OH)_3(H_xPO_4)_4]^{n-}$ clusters held together by Co^{2+} cations running parallel to the *b* axis. Neighbouring chains are linked by hydrogen bonds only *via* intervening $[N(CH_3)_4]^+$ cations and water molecules.

Comment

The title compound was prepared as part of an exploratory project aimed at synthesizing molybdenum phosphates of varying dimensions. Previous work (Haushalter & Mundi, 1992) suggested that related compounds contain the complex anion $[Mo_6O_{15}(HPO_4)(H_2PO_4)_3]^{5-}$ ('Mo_6P_4') as a primary building unit. This anion is composed of a ring of edge-sharing MoO_6 octahedra, with Mo in the +5 oxidation state complexed with PO_4 tetrahedra both internal and external to the ring. We have shown recently (Light-

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