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Bis(piperazinium) Pentakis(trioxomolybdo)-bis(ethylphosphonate) Dihydrate

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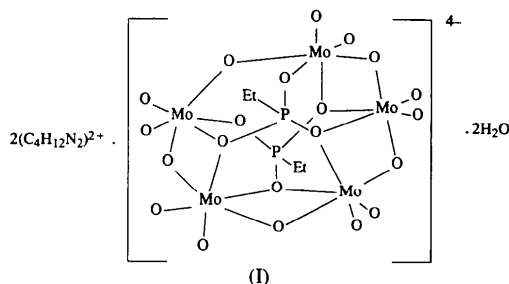
Abstract

The title compound, bis(piperazine-1,4-dylium) bis(ethylphosphonato) - 1κO, 2: 3κ²O', 4: 5κ²O'' ; 1: 2κ²O, - 3: 4κ²O', 5κO'' - penta-μ-oxo-1: 2κ²O; 1: 5κ²O; 2: 3κ²O; 3: 4κ²O; 4: 5κ²O - decaoxo-1κ²O, 2κ²O, 3κ²O, 4κ²O, 5κ²O - penta-molybdenum(4-) dihydrate, (C₄H₁₂N₂)₂[Mo₅O₁₅(C₂H₅-O₃P)₂]₂·2H₂O, crystallizes as isolated five-unit rings of vertex- and edge-sharing distorted-octahedral MoO₆ groups, doubly capped by PC₂H₅ entities [as [(C₂H₅-PO₃)₂]²⁻ ethylphosphonate groups], resulting in [(MoO₃)₅ - {(C₂H₅PO₃)₂}]⁴⁻ {or [Mo₅P₂O₂₁(C₂H₅)₂]⁴⁻} anions.

Doubly protonated piperazinium cations and water molecules complete the structure. This phase shows reversible dehydration/rehydration without loss of structure.

Comment

We have recently reported the hydrothermal syntheses and structures of a family of novel layered alkali metal/ammonium molybdenum methylphosphonates (Harrison, Dussack & Jacobson, 1995), which are based on the hexagonal tungsten oxide (HTO) motif of vertex-sharing octahedra (Gérand, Nowogrocki, Guenot & Figlarz, 1979). We report here the preparation and characterization of (C₄H₁₂N₂)₂[(MoO₃)₅{(C₂H₅)PO₃}₂]₂·2H₂O, (I), a molecular species prepared under similar conditions from closely related starting materials. It is related to similar clusters prepared earlier (Kwak, Pope & Scully, 1975; Stalick & Quicksall, 1976; Kortz & Pope, 1995).



The five crystallographically distinct Mo atoms in the pentamolybdodi(ethylphosphonate) cluster (Fig. 1) are all octahedrally coordinated by O atoms. All the Mo centers show the two short, two intermediate and two long Mo—O bond-distance distribution within the distorted MoO₆ unit which is characteristic of Mo^{VI}. Each MoO₆ center has two short ($d < 1.73$ Å) 'oxo' Mo=O bonds in a *cis* configuration [$\theta_{\text{ave}}(\text{O}=\text{Mo}=\text{O}) = 103.3^\circ$]. These short bonds are both *trans* with respect to a long ($d > 2.18$ Å) Mo—O link, and the two remaining Mo—O bonds are intermediate in length between these two extremes. All the Mo=O links are terminal bonds, not joined to any other atoms in the cluster [three of them (O6, O13 and O14) form hydrogen-bonding links to the piperazinium dications]. These five octahedral MoO₆ units are fused together into an isolated ring. There are four edge-sharing links (Mo1—Mo2, Mo2—Mo3, Mo4—Mo5 and Mo5—Mo1) and one vertex-sharing connection (Mo3—Mo4). Average Mo—O bond lengths and molybdenum bond-valence sum (BVS) values (Brese & O'Keeffe, 1991) are typical for Mo^{VI} (expected BVS = 6.00): $d_{\text{ave}}(\text{Mo1—O}) = 1.985(2)$ Å, BVS(Mo1) = 6.02; $d_{\text{ave}}(\text{Mo2—O}) = 1.983(2)$ Å, BVS(Mo2) = 6.02; $d_{\text{ave}}(\text{Mo3—O}) = 1.977(2)$ Å, BVS(Mo3) = 6.01; $d_{\text{ave}}(\text{Mo4—O}) = 1.979(2)$ Å, BVS(Mo4) = 6.02; $d_{\text{ave}}(\text{Mo5—O}) = 1.972(2)$ Å, BVS(Mo5) = 6.05.

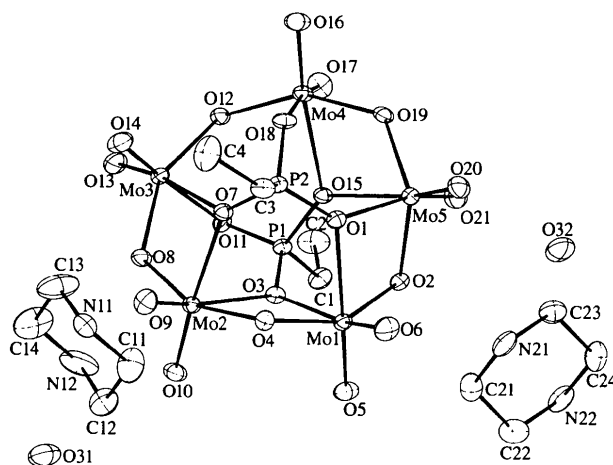


Fig. 1. CAMERON (Watkin, Prout & Pearce, 1996) diagram of the $[(\text{MoO}_3)_5\{(\text{C}_2\text{H}_5)\text{PO}_3\}_2]^{4-}$ cluster and accompanying species (50% probability displacement ellipsoids). H atoms have been omitted for clarity.

Both faces of the Mo_5O_{21} five-unit ring are capped by PC_2H_5 entities, as $[(\text{C}_2\text{H}_5)\text{PO}_3]^{2-}$ ethylphosphonate groups. For both distinct ethylphosphonate groups, one $\text{P}-\text{O}-\text{Mo}$ bond and two $\text{P}-\text{O}-(\text{Mo}, \text{Mo}')$ links are formed, the latter O atoms forming part of the interoctahedral edges. The geometric parameters for the ethylphosphonate group are typical of results obtained from previous studies of the same entity (Stalick & Quicksall, 1976). The O atoms associated with the cluster adopt various bonding geometries: O5, O6, O9, O10, O13, O14, O16, O17, O20 and O21 are terminal O atoms attached only to molybdenum; O2, O4, O8, O12 and O19 form bicoordinate $\text{Mo}-\text{O}-\text{Mo}'$ bridges; O11 and O18 form bicoordinate $\text{Mo}-\text{O}-\text{P}$ bonds; O1, O3, O7 and O21 form tricoordinate $(\text{Mo}, \text{Mo}')-\text{O}-\text{P}$ centers.

The overall formulation of the molybdenum oxide ethylphosphonate cluster is $[(\text{MoO}_3)_5\{(\text{C}_2\text{H}_5)\text{PO}_3\}_2]^{4-}$ {or $[\text{Mo}_5\text{P}_2\text{O}_{21}(\text{C}_2\text{H}_5)_2]^{4-}$ }, assuming the sole presence of Mo^{VI} which is consistent with the crystal color and BVS calculations. Charge compensation for the anionic cluster is provided by a pair of doubly protonated $[\text{N}_2\text{C}_4\text{H}_{12}]^{2+}$ piperazinium cations. Both these species adopt typical chair geometries with normal $\text{N}-\text{C}$ and $\text{C}-\text{C}$ bond lengths and angles. All eight of the $\text{N}-\text{H}$ protons are involved in hydrogen-bonding links, either to O atoms in the $[(\text{MoO}_3)_5\{(\text{C}_2\text{H}_5)\text{PO}_3\}_2]^{4-}$ cluster or to water molecules (non-cluster O atoms). There are two water molecules of crystallization (atoms O31 and O32). The Mo/P/O component of the $[(\text{MoO}_3)_5\{(\text{C}_2\text{H}_5)\text{PO}_3\}_2]^{4-}$ species in this material is essentially identical with similar clusters studied earlier (Stalick & Quicksall, 1976).

The unit-cell packing results in infinite layers of $[(\text{MoO}_3)_5\{(\text{C}_2\text{H}_5)\text{PO}_3\}_2]^{4-}$ anions in the *ab* plane. In the *a* direction, the C_2H_5 segments of the ethyl-

phosphonate groups pack together in a 'herringbone' configuration, interacting only through van der Waals forces. 'Channel-like' voids in the *b* direction are occupied by piperazinium dications and water molecules.

Thermal gravimetric analysis (TGA) for thoroughly ground crystals of (I) (heated to 773 K in a dry O_2 atmosphere) showed weight losses at 368–393 K, a sharp loss at 523 K and a gradual loss from 563–773 K. The post-TGA residue contains orthorhombic MoO_3 . The overall weight loss of 26.3% corresponds well with complete nominal elimination of water, piperazinium cations and the C_2H_5 residues from the ethylphosphonate groups (calc. 26.3%). We assume that a second glassy Mo/P/O component is present in the post-TGA residue. The initial weight loss of 3.2% corresponded well with loss of the water of crystallization from (I) (calc. 3.2%). A new sample was heated to 423 K and then cooled to ambient temperature in a wet O_2 atmosphere. This TGA showed a single-step weight loss (total 3.2%) on heating and a two-step weight gain on cooling to return to the starting weight. This post-TGA residue (powder X-ray diffraction) was essentially identical to the initial sample (some loss of crystallinity observed), indicating that (I) reversibly dehydrates/rehydrates, presumably without loss of structure.

The IR spectrum of (I) shows typical signals for water molecules, protonated secondary amines and pentamolybdo-dialkylphosphonate clusters, as assigned previously (Kwak, Pope & Scully, 1975).

Experimental

The title compound, (I), was hydrothermally prepared from a mixture of 0.1795 g (2.084 mmol) piperazine, 0.6 g (4.168 mmol Mo) MoO_3 and 0.468 g (4.168 mmol P) 98% $\text{CH}_3\text{CH}_2\text{PO}_2\text{H}_2$ in 8 ml deionized H_2O (piperazine:Mo:P ratio 1:2:2). The reactants were sealed in a 23 ml teflon-lined Parr reaction vessel and heated to 408 K for 5 d. After slow cooling to ambient temperature over 24 h, the bomb was opened and the air-stable product recovered by vacuum filtration with water in 92% yield (based on Mo).

Crystal data

$(\text{C}_4\text{H}_{12}\text{N}_2)_2[\text{Mo}_5\text{O}_{15}(\text{C}_2\text{H}_5\text{O}_3\text{P}_2)_2] \cdot 2\text{H}_2\text{O}$
 $M_r = 1148.09$
 Monoclinic
 $P2_1/a$
 $a = 14.935(4) \text{ \AA}$
 $b = 12.158(6) \text{ \AA}$
 $c = 17.499(9) \text{ \AA}$
 $\beta = 96.30(3)^\circ$
 $V = 3158(3) \text{ \AA}^3$
 $Z = 4$
 $D_x = 2.41 \text{ Mg m}^{-3}$
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 25 reflections
 $\theta = 10.5\text{--}17.5^\circ$
 $\mu = 2.13 \text{ mm}^{-1}$
 $T = 298 \text{ K}$
 Irregular lump
 $0.4 \times 0.3 \times 0.3 \text{ mm}$
 Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
 2 θ / ω scans
 Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
 $T_{\min} = 0.493$, $T_{\max} = 0.528$
 4319 measured reflections
 3993 independent reflections

3993 reflections with $F > 0$
 $R_{\text{int}} = 0.019$
 $\theta_{\max} = 22.5^\circ$
 $h = 0 \rightarrow 16$
 $k = 0 \rightarrow 13$
 $l = -18 \rightarrow 18$
 3 standard reflections
 frequency: 167 min
 intensity decay: none

Refinement

Refinement on F
 $R = 0.024$
 $wR = 0.022$
 $S = 2.90$
 3993 reflections
 417 parameters
 H atoms: see below
 Weighting scheme based on measured e.s.d.'s
 $(\Delta/\sigma)_{\max} = 0.034$

$\Delta\rho_{\max} = 0.48 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.43 \text{ e } \text{\AA}^{-3}$
 Extinction correction: Larson (1970)
 Extinction coefficient: 103 (2)
 Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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Table 1. Selected geometric parameters (\AA , $^\circ$)

Mo1—O1	2.352 (3)	Mo4—O16	1.707 (3)
Mo1—O2	1.937 (3)	Mo4—O17	1.708 (3)
Mo1—O3	2.307 (3)	Mo4—O18	2.224 (3)
Mo1—O4	1.905 (3)	Mo4—O19	1.950 (3)
Mo1—O5	1.703 (3)	Mo5—O1	2.347 (3)
Mo1—O6	1.708 (3)	Mo5—O2	1.943 (3)
Mo2—O3	2.405 (3)	Mo5—O15	2.197 (3)
Mo2—O4	1.903 (3)	Mo5—O19	1.937 (3)
Mo2—O7	2.211 (3)	Mo5—O20	1.706 (3)
Mo2—O8	1.973 (3)	Mo5—O21	1.701 (3)
Mo2—O9	1.698 (3)	P1—O3	1.535 (3)
Mo2—O10	1.708 (3)	P1—O11	1.509 (3)
Mo3—O7	2.367 (3)	P1—O15	1.556 (3)
Mo3—O8	1.933 (3)	P1—C1	1.799 (4)
Mo3—O11	2.223 (3)	P2—O1	1.544 (3)
Mo3—O12	1.910 (3)	P2—O7	1.549 (3)
Mo3—O13	1.703 (3)	P2—O18	1.508 (3)
Mo3—O14	1.725 (3)	P2—C3	1.786 (4)
Mo4—O12	1.907 (3)	C1—C2	1.519 (6)
Mo4—O15	2.376 (3)	C3—C4	1.521 (6)

H atoms were located geometrically (N—H and C—H = 0.95 \AA) and from difference maps for the O31 atom. The H atoms of the O32 water molecule were not located.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *RC85* (Baird, 1985). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *CRYSTALS* (Watkin, Prout, Carruthers & Betteridge, 1996). Molecular graphics: *CAMERON* (Watkin, Prout & Pearce, 1996). Software used to prepare material for publication: *CRYSTALS*.

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Lists of structure factors, anisotropic displacement parameters, atomic coordinates and complete geometry have been deposited with the IUCr (Reference: TA1123). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Dichloro(η^5 -cyclopentadienyl)(phenylimido)vanadium(V)

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Abstract

The title compound, [VCl₂(C₅H₅)(C₆H₅N)], contains vanadium in a tetrahedral coordination geometry, with the cyclopentadienyl (Cp) ligand occupying one of the four sites and showing an allyl–ene distortion. The V—N—C angle is 169.1 (4) $^\circ$. The crystal packing involves C—H \cdots Cl interactions, with H \cdots Cl distances in the range 2.87 (5)–2.89 (4) \AA .

Comment

The chemistry of the half-sandwich vanadium imido system has recently been investigated due to the isolobal

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