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## The polyoxometallate $[(\text{CH}_3)_4\text{N}]_2\text{[Mo}_4\text{O}_{10}(\text{OCH}_3)_4\text{Cl}_2]$

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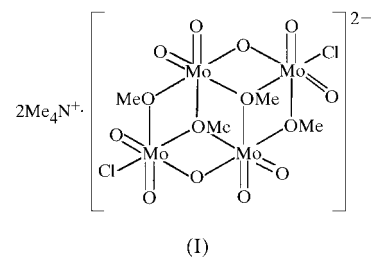
The crystal and molecular structure of bis(tetramethylammonium) dichlorotetra- $\mu_2$ -methoxo-di- $\mu_2$ -oxo-octooxo-tetramolybdate(VI),  $(\text{C}_4\text{H}_{12}\text{N})_2[\text{Mo}_4\text{O}_{10}(\text{OCH}_3)_4\text{Cl}_2]$ , has been determined from X-ray diffraction data. The crystallographically centrosymmetric anion is built up of four edge-sharing octahedra, two  $\text{MoO}_6$  and two  $\text{MoO}_5\text{Cl}$ .

### Comment

During a continuing investigation of the structure–mechanism–function relationship regarding the role of molybdenum as a catalyst in the esterification reactions of 2-mercaptopyridonic acid (Cindrić *et al.*, 1998), we obtained the tetramethylammonium salt of dichlorotetra- $\mu_2$ -methoxo-di- $\mu_2$ -oxo-octaoxotetramolybdate(VI),  $[(\text{CH}_3)_4\text{N}]_2[\text{Mo}_4\text{O}_{10}(\text{OCH}_3)_4\text{Cl}_2]$ . The same anion has already been observed in the complex  $(\text{Bu}_4\text{N})[\text{Mo}_4\text{O}_{10}(\text{OCH}_3)_4\text{Cl}_2]$  (Liu *et al.*, 1987; Kang *et al.*, 1989). The tetranuclear unit is by far the most common compositional motif in the coordination chemistry of polyoxomolybdates, as adopted by  $[\text{Mo}_4\text{O}_{10}(\text{OMe})_6]^{2-}$  (Liu *et al.*, 1987; Kang *et al.*, 1989), with four edge-sharing octahedra in the compact cluster. Such structures illustrate a common feature of the chemistry of polymolybdates in alcoholic solvents, *i.e.* the incorporation of alkoxy groups into the cluster. Formation of the underivatized polyoxomolybdate parent structure,  $[\text{Mo}_4\text{O}_{16}]^{8-}$ , is most likely precluded by the high negative charge. Replacement of bridging oxo groups by alkoxy ligands serves to reduce the overall cluster charge and hence to stabilize the unit in alcoholic solvents. Thus, the same core structure with replacement of peripheral and/or bridging alkoxy groups is common to the structures of  $[\text{Mo}_4\text{O}_{10}(\text{OCH}_3)_4\text{Cl}_2]^{2-}$ ,  $[\text{Mo}_4\text{O}_{10}(\text{OCH}_3)_2(\text{OC}_6\text{H}_4\text{O})_2]^{2-}$  (Kang *et al.*, 1989) and  $[\text{Mo}_4\text{O}_8(\text{OC}_2\text{H}_5)_2\{\text{RC}(\text{CH}_2\text{O})_3\}_2]$  (Wilson *et al.*, 1983).

The crystal structure of the title complex, (I), is built up of tetranuclear  $[\text{Mo}_4\text{O}_{10}(\text{OCH}_3)_4\text{Cl}_2]^{2-}$  anions and tetramethyl-

ammonium cations. The centrosymmetric anion consists of four edge-sharing octahedra, two  $\text{MoO}_6$  and two  $\text{MoO}_5\text{Cl}$ . As a result of displacement of metal ions towards the polyanion surface, all four octahedra are distorted. The Mo2 site displays an  $[\text{MoO}_6]$  geometry through ligation by two terminal and one bridging oxo groups, and two triply bridging and one doubly bridging methoxo group, while the Mo1 centre displays  $[\text{MoO}_5\text{Cl}]$  coordination by one doubly bridging and one triply bridging methoxy group, one bridging and two terminal oxo groups, and the terminal chloride ligand. All bond lengths and angles are comparable with those observed in previously mentioned complexes (Table 1).



### Experimental

In an attempt to prepare a molybdenum(VI) complex with the methyl ester of 2-hydroxynicotinic acid, a mixture of  $\text{MoO}_2\text{Cl}_2$  (0.4 g),  $[(\text{CH}_3)_4\text{N}]\text{Cl}$  (0.22 g) and a methanol suspension of 2-hydroxynicotinic acid (0.31 g in 10 ml MeOH) was dissolved in methanol (20 ml) and heated under reflux for 4 h. The resulting colourless solution was left to stand at room temperature. After 2 d, transparent colourless crystals (0.17 g; 38.6% yield) were isolated. Elemental analysis (%) found (calculated) for  $[(\text{CH}_3)_4\text{N}]_2[\text{Mo}_4\text{O}_{10}(\text{OCH}_3)_4\text{Cl}_2]$ : Mo 43.6 (43.3), C 16.6 (16.3), H 4.2% (4.1%).

#### Crystal data

$(\text{C}_4\text{H}_{12}\text{N})_2[\text{Mo}_4\text{O}_{10}(\text{OCH}_3)_4\text{Cl}_2]$   
 $M_r = 887.09$   
 Monoclinic,  $P2_1/c$   
 $a = 8.810$  (2) Å  
 $b = 11.047$  (2) Å  
 $c = 15.085$  (3) Å  
 $\beta = 98.67$  (3)°  
 $V = 1451.4$  (5) Å<sup>3</sup>  
 $Z = 2$

$D_x = 2.030$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 6079 reflections  
 $\theta = 2.73$ – $28.23$ °  
 $\mu = 1.931$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 Prism, colourless  
 $0.38 \times 0.36 \times 0.35$  mm

#### Data collection

Nonius KappaCCD diffractometer  
 $2^\circ \varphi$  and  $\omega$  scans  
 6079 measured reflections  
 3568 independent reflections  
 3048 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.016$   
 $\theta_{\text{max}} = 28.23$ °  
 $h = -11 \rightarrow 11$   
 $k = -13 \rightarrow 14$   
 $l = -20 \rightarrow 20$

#### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.031$   
 $wR(F^2) = 0.079$   
 $S = 1.044$   
 3568 reflections  
 161 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0358P)^2 + 0.9758P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.034$   
 $\Delta\rho_{\text{max}} = 0.43$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.68$  e Å<sup>-3</sup>  
 Extinction correction: *SHELXL97*  
 Extinction coefficient: 0.0035 (4)

**Table 1**

Selected geometric parameters (Å, °).

Mo1—O11	1.692 (2)	Mo2—O21	1.689 (2)
Mo1—O12	1.694 (2)	Mo2—O22	1.694 (2)
Mo1—O1	1.913 (2)	Mo2—O1	1.904 (2)
Mo1—O3	2.221 (2)	Mo2—O3 <sup>i</sup>	2.027 (2)
Mo1—O2	2.272 (2)	Mo2—O2 <sup>i</sup>	2.217 (2)
Mo1—Cl	2.4395 (12)	Mo2—O2	2.384 (2)
O11—Mo1—O12	105.62 (12)	O21—Mo2—O3 <sup>i</sup>	101.17 (11)
O11—Mo1—O1	99.99 (11)	O22—Mo2—O3 <sup>i</sup>	91.65 (11)
O12—Mo1—O1	100.07 (11)	O1—Mo2—O3 <sup>i</sup>	150.91 (9)
O11—Mo1—O3	93.94 (10)	O21—Mo2—O2 <sup>i</sup>	94.90 (11)
O12—Mo1—O3	159.31 (11)	O22—Mo2—O2 <sup>i</sup>	156.30 (11)
O1—Mo1—O3	82.72 (9)	O1—Mo2—O2 <sup>i</sup>	85.73 (8)
O11—Mo1—O2	161.34 (10)	O3 <sup>i</sup> —Mo2—O2 <sup>i</sup>	72.13 (8)
O12—Mo1—O2	93.00 (10)	O21—Mo2—O2	164.68 (11)
O1—Mo1—O2	75.17 (8)	O22—Mo2—O2	89.30 (10)
O3—Mo1—O2	67.72 (7)	O1—Mo2—O2	72.60 (8)
O11—Mo1—Cl	94.70 (9)	O3 <sup>i</sup> —Mo2—O2	82.53 (8)
O12—Mo1—Cl	90.62 (9)	O2 <sup>i</sup> —Mo2—O2	71.91 (8)
O1—Mo1—Cl	158.71 (7)	Mo2—O1—Mo1	117.98 (11)
O3—Mo1—Cl	80.96 (6)	Mo2 <sup>i</sup> —O2—Mo1	105.27 (8)
O2—Mo1—Cl	86.01 (5)	Mo2 <sup>i</sup> —O2—Mo2	108.10 (8)
O21—Mo2—O22	105.35 (13)	Mo1—O2—Mo2	89.22 (7)
O21—Mo2—O1	99.27 (11)	Mo2 <sup>i</sup> —O3—Mo1	114.16 (9)
O22—Mo2—O1	102.65 (11)		

Symmetry code: (i) 2 - x, 1 - y, -z.

All H atoms were fixed geometrically.

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); software used to prepare material for publication: *SHELXL97*.

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