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An Oxomolybdenum(V) Cluster, [Mo₈O₁₆(OCH₃)₈(C₅H₅N)₄]

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Abstract

The structure of octa-μ-methoxo-octa-μ-oxo-octaoxo-tetrapyridineoctamolybdenum(V), [Mo₈O₁₆(CH₃O)₈(C₅H₅N)₄], consists of discrete puckered cyclic molecules, made up of eight Mo atoms which are linked together by pairs of oxo bridges and pairs of bridging methoxo groups. It may also be regarded as a linkage of four [Mo₂O₄]²⁺ units, whose two Mo centres differ in that one is coordinated by a pyridine ligand. Short Mo—Mo distances [2.570 (1) Å] alternate with longer Mo···Mo contacts [3.435 (1) Å].

Comment

The title compound belongs to the family of poly-oxoalkoxymolybdate(V) complexes with various organic ligands. The O-donor groups can serve as terminal, μ- or μ_3-bridging ligands, thereby providing a means for the structure to expand (Khan & Zubieta, 1995). The [Mo₂O₄]²⁺ structural unit, which is common to all polynuclear oxomolybdenum(V) compounds and which dominates the chemistry of Mo^V, is known to occur in a well known geometry and is usually not affected by the metal environment (Chae *et al.*, 1993). The Mo(μ-O)₂Mo ring is severely puckered, thus making possible the close approach (2.5–2.7 Å) of two Mo atoms and the formation of a localized single metal–metal bond, which accounts for the experimentally observed diamagnetism (Cotton & Ilsley, 1982).

Diverse geometries are adopted among oxomolybdenum(V) complexes with pyridine. A single, almost linear, oxo bridge connects two octahedrally coordinated Mo centres in [Mo₂O₃Cl₄py₄].CH₂Cl₂ (py = C₅H₅N,

pyridine) (El-Essawi *et al.*, 1986). The [Mo₂O₄]²⁺ core was found in the binuclear complex [Mo₂O₄-(SN₂C₄H₃)₂py₂].py (SN₂C₄H₃⁻ is a thiopyrimidinato anion) (Cotton & Ilsley, 1982). In [Mo₄O₈(O^{i}Pr)₄py₄].-2py (O^{i}Pr = C₃H₇O⁻, isopropoxide), four octahedra are connected in an edge-sharing manner to form a tetranuclear fragment (Chisholm *et al.*, 1981). In the recently determined structure of a pentanuclear mixed-valence complex, [Mo₅O₁₁(OCH₃)₄py₄].CH₃OH, two [Mo₂O₄]²⁺ moieties are fused with a six-valent Mo centre (Modec *et al.*, 1998). We report here on the structure of a related octanuclear complex, [Mo₈O₁₆-(OCH₃)₈py₄], (I). It was obtained as a product in the reaction of mononuclear [MoOCl₅]²⁻ with pyridine and methanol. The labile chloride ligands undergo a facile substitution reaction, then the formation of larger less soluble aggregates takes place. Factors such as concentration and reaction temperature have a substantial influence on the course of the reaction.

(I)
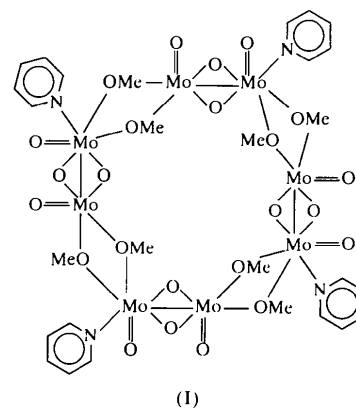
The title compound, illustrated in Fig. 1, is seen to consist of discrete molecules with the [Mo₈O₁₆(OCH₃)₈-py₄] stoichiometry. An octanuclear ring is produced by the action of the crystallographic S_4 axis on an [Mo₂O₄]²⁺ binuclear asymmetric unit, whose two Mo centres are in different coordination environments. Both Mo atoms are ligated by a terminal O atom, a pair of bridging O atoms and a pair of methoxo groups. While Mo2 exhibits a five-coordinate square-pyramidal geometry, Mo1 attains a distorted octahedral coordination by bonding to pyridine. The short bonds between Mo and the terminal multiply-bonded O atom [Mo1—O1 1.682 (4) and Mo2—O2 1.664 (4) Å] are in a *syn* disposition with respect to the Mo1—O3—Mo2—O4 rhombus. The *trans* influence of the terminal O atom is demonstrated by the square-pyramidal geometry of Mo2, with the vacant site in a *trans* position to the molybdenyl group. The position of Mo2, 0.622 (2) Å above the approximate basal plane defined by O3, O4, O5^i and O6^i [symmetry code: (i) $\frac{1}{4}+y, \frac{7}{4}-x, \frac{3}{4}-z$], is a characteristic feature of Mo^V in a square-pyramidal

environment, with the multiply-bonded O atom in the apical position (Stiefel, 1977). Important distances and angles are given in Table 1. The short distance between the metal centres [Mo1—Mo2 = 2.570 (1) Å] indicates a localized Mo—Mo single bond. The bonding interactions are afforded by the geometry of the bis(μ-O) bridge, with the distances between the metal atoms and the bridging O atoms (Mo1—O3, Mo1—O4, Mo2—O3 and Mo2—O4) in the range 1.916 (4)–1.936 (4) Å, the Mo—O—Mo angles (Mo1—O3—Mo2 and Mo1—O4—Mo2) 83.7 (1) and 83.6 (2)°, respectively, and the O—Mo—O angles (O3—Mo1—O4 and O3—Mo2—O4) 93.1 (2) and 92.3 (2)°, respectively. The substantial deviation of the bridge from planarity is shown by the fold angle of 150.1 (2)° between two MoO₂ planes, one being defined by Mo1, O3 and O4, the other by Mo2, O3 and O4. The dimensions of the [Mo₂O₄]²⁺ unit in the title compound agree with the literature values (Spivack & Dori, 1975). The bis(μ-OCH₃) bridged unit, i.e. the Mo1—O5—Mo2ⁱⁱ—O6 rhombus [symmetry code: (ii) $\frac{7}{4} - y$, $x - \frac{1}{4}$, $\frac{3}{4} - z$] shows only a slight deviation from planarity, the dihedral angle between the two MoO₂ planes being 175.8 (1)°. A distance of 3.435 (1) Å is spanned by the methoxo bridges between two neighbouring Mo atoms. The distances between Mo atoms and the bridging methoxo groups are longer and range from 2.017 (4) to 2.220 (4) Å, with the longest [Mo1—O6 = 2.220 (4) Å] in a *trans* position to the terminal Mo1—O1 bond. The methoxo Mo—O—Mo angles (Mo1—O5—Mo2ⁱⁱ and Mo1—O6—Mo2ⁱⁱ) are 110.6 (2) and 108.2 (2)°, respectively, while the methoxo O—

Mo—O angles (O5—Mo1—O6 and O5—Mo2ⁱⁱ—O6) are 67.6 (1) and 73.4 (1)°, respectively.

Pyridine coordinates to Mo1 at a distance of 2.255 (5) Å, which is essentially the same as the distances reported for [Mo₄O₈(OⁱPr)₄py₄].2py [2.229 (3)– 2.269 (3) Å; Chisholm *et al.*, 1981] and [Mo₅O₁₁-(OCH₃)₄py₄].CH₃OH [2.215 (8)–2.264 (9) Å; Modec *et al.*, 1998], and longer than in [Mo₂O₃Cl₄py₄].CH₂Cl₂ [2.169 (5)–2.209 (5) Å; El-Essawi *et al.*, 1986]. The pyridine ligands project outwards from the ring centre, while one half of the oxo (O4) and methoxo (O6) bridges point into the central cavity, whose perimeter may be defined by the O4···O4ⁱ [4.345 (4) Å] and O4···O4ⁱⁱⁱ [5.082 (4) Å] distances [symmetry code: (iii) $2 - x$, $\frac{3}{2} - y$, z]. The rings are stacked along the *c* axis. The short intermolecular O2···O2ⁱᵛ contact [2.942 (6) Å; symmetry code: (iv) $1 - x$, $\frac{3}{2} - y$, z] is slightly shorter than the sum of the van der Waals radii (3.04 Å; Douglas *et al.*, 1994).

The structure of [Mo₈O₁₆(OCH₃)₈{P(CH₃)₃}₄] is almost identical to that of (I) (Darensbourg *et al.*, 1985). A comparison of the appropriate bond lengths and angles shows that the ring geometry remains virtually unaltered on the introduction of pyridine instead of P(CH₃)₃. Although no crystallographic symmetry is imposed, the molecules of [Mo₈O₁₆(OCH₃)₈{P(CH₃)₃}₄] approximate S₄ symmetry.

A similar cyclic octagonal framework was also found in [(n-C₄H₉)₄N]₂[Mo₈O₁₆(OCH₃)₈(C₂O₄)] (Chen *et al.*, 1988) and [(n-C₄H₉)₄N]₂[Mo₈O₁₆(OC₂H₅)₈(C₂O₄)] (Chen *et al.*, 1989), where the central cavity is occupied by an oxalate ligand whose O atoms bridge pairs of neighbouring non-bonded Mo centres. The geometry of the ring is markedly changed on oxalate coordination, in that the eight Mo atoms, the eight terminal oxo groups and the oxalate moiety all lie in a plane.

Experimental

Fig. 1. *ORTEP*II (Johnson, 1976) view of [Mo₈O₁₆(OCH₃)₈py₄], with the atom labels. The rest of the molecule is related to the asymmetric unit by the S₄ axis. Displacement ellipsoids are plotted at the 30% probability level. H atoms have been omitted for clarity.

Crystal data

[Mo₈O₁₆(CH₃O)₈(C₅H₅N)₄]	Mo *K*α radiation
$M_r = 1588.19$	$\lambda = 0.71069$ Å
Tetragonal	Cell parameters from 25
$I4_1/a$	reflections
$a = 12.243 (2)$ Å	$\theta = 8.19$–$14.22°$
$c = 32.923 (4)$ Å	$\mu = 2.04$ mm⁻¹
$V = 4934.9 (17)$ Å³	$T = 293$ K
$Z = 4$	Square bipyramid
$D_x = 2.138$ Mg m⁻³	0.33 × 0.14 × 0.13 mm
D_m not measured	Light orange

Data collection

Enraf–Nonius CAD-4 diffractometer	1582 reflections with $I > 3\sigma(I)$
$\omega/2\theta$ scans	$R_{int} = 0.041$
Absorption correction: Gaussian ($Xtal3.4$; Hall et al., 1995)	$\theta_{max} = 28.02°$ $h = 0 \rightarrow 16$ $k = 0 \rightarrow 16$
$T_{min} = 0.779$, $T_{max} = 0.836$	$l = -43 \rightarrow 43$
6562 measured reflections	3 standard reflections
2990 independent reflections	every 100 reflections intensity decay: 0.40%

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.009$
$R = 0.027$	$\Delta\rho_{max} = 1.33$ e Å^{-3}
$wR = 0.028$	$\Delta\rho_{min} = -2.23$ e Å^{-3}
$S = 0.976$	Extinction correction: none
1582 reflections	Scattering factors from *Inter-*
145 parameters	*national Tables for X-ray*
H atoms not refined	*Crystallography* (Vol. IV)
Weighting scheme: see below	

Table 1. *Selected geometric parameters (Å, °)*

Mo1—Mo2	2.570 (1)	Mo2—O2	1.664 (4)
Mo1—O1	1.682 (4)	Mo2—O3	1.936 (4)
Mo1—O3	1.916 (4)	Mo2—O4	1.929 (4)
Mo1—O4	1.926 (4)	Mo2—O5^i	2.040 (4)
Mo1—O5	2.138 (4)	Mo2—O6^i	2.017 (4)
Mo1—O6	2.220 (4)	O5—C5o	1.423 (8)
Mo1—N	2.255 (5)	O6—C6o	1.414 (9)
O1—Mo1—O3	109.8 (2)	O2—Mo2—O3	111.5 (2)
O1—Mo1—O4	108.7 (2)	O2—Mo2—O4	109.5 (2)
O1—Mo1—O5	93.4 (2)	O2—Mo2—O5^i	106.1 (2)
O1—Mo1—O6	156.1 (2)	O2—Mo2—O6^i	106.0 (2)
O1—Mo1—N	89.2 (2)	O3—Mo2—O4	92.3 (2)
O3—Mo1—O4	93.1 (2)	O3—Mo2—O6^i	140.9 (2)
O3—Mo1—O5	155.7 (2)	O3—Mo2—O5^i	85.8 (2)
O3—Mo1—O6	88.1 (2)	O4—Mo2—O6^i	85.3 (2)
O3—Mo1—N	86.4 (2)	O4—Mo2—O5^i	142.4 (2)
O4—Mo1—O5	86.0 (2)	O6^i—Mo2—O5^i	73.4 (1)
O4—Mo1—O6	85.1 (1)	Mo1—O3—Mo2	83.7 (1)
O4—Mo1—N	161.0 (2)	Mo1—O4—Mo2	83.6 (2)
O5—Mo1—O6	67.6 (1)	Mo1—O5—Mo2^{ii}	110.6 (2)
O5—Mo1—N	86.8 (2)	Mo1—O6—Mo2^{ii}	108.2 (2)
O6—Mo1—N	75.9 (2)		

Symmetry codes: (i) $\frac{1}{4} + y, \frac{7}{4} - x, \frac{3}{4} - z$; (ii) $\frac{7}{4} - y, x - \frac{1}{4}, \frac{3}{4} - z$.

The weighting scheme used was $w = W_F.W_S$, where $W_F(F_o < 90) = (F_o/90)^2$, $W_F(F_o > 160) = (160/F_o)^{1.5}$ and $W_F(90 < F_o < 160) = 1$, and $W_S(\sin\theta < 0.42) = (\sin\theta/0.42)^2$, $W_S(\sin\theta > 0.55) = (0.55/\sin\theta)^4$ and $W_S(0.42 < \sin\theta < 0.55) = 1$. Of the four peaks exceeding 1.0 e Å^{-3} in the final difference Fourier map, one (1.194 e Å^{-3}) is located on an S_4 special position in the middle of the octanuclear ring. The other three peaks (1.33, 1.091 and 1.035 e Å^{-3}) lie closest to O6 [$1.385(3)$ Å], O4 [$1.296(4)$ Å] and O2 [$0.561(5)$ Å], respectively. The two deepest holes, with values of -2.232 and -2.191 e Å^{-3}, are found on the Mo1 and Mo2 positions. The remaining 11 holes, with values ranging from -1.466 to -1.014 e Å^{-3}, lie close to Mo1 and Mo2. The relatively high number of peaks and holes results from the high symmetry of the space group.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *Xtal3.4* (Hall et al., 1995). Program(s) used to solve structure: *SIR92* (Altomare et al., 1994). Program(s) used to refine

structure: *Xtal3.4*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *Xtal3.4*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1365). Services for accessing these data are described at the back of the journal.

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Ferrocenium Tetrachloroferrate Revisited, and Ferrocenium Tetrachloroaluminate

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Abstract

The structure of the title compound, [Fe(Cp)$_2$][FeCl$_4$] (Cp = cyclopentadienyl, C$_5$H$_5$), was reported in 1978 in the non-centrosymmetric space group *Pna2$_1$* at room