

Structure of Octakis(methylammonium) Decamolybdate(8–) Dihydrate

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Abstract. $[\text{NH}_3(\text{CH}_3)]_8[\text{Mo}_{10}\text{O}_{34}]\cdot 2\text{H}_2\text{O}$, $M_r = 1795.9$, monoclinic, $P2_1/n$, $a = 12.596(2)$, $b = 17.175(2)$, $c = 10.653(2)$ Å, $\beta = 91.04(2)^\circ$, $V = 2304.2(6)$ Å³, $Z = 2$, $D_m = 2.56$ g cm⁻³ (floatation), $D_x = 2.58$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 11.38$ cm⁻¹, $F(000) = 1728$, $T = 293$ K, $R = 0.041$ for 4838 observed data. The discrete $[\text{Mo}_{10}\text{O}_{34}]^{8-}$ anion has a center of symmetry and is built up of one Mo_8O_{28} unit and two MoO_4 tetrahedra joined to the unit at the corners. The Mo_8O_{28} unit is composed of eight MoO_6 octahedra joined together by edges. The Mo–O distances in MoO_6 can be separated into three classes: 1.695 (4)–1.768 (4), 1.869(3)–2.011 (4) and 2.142 (4)–2.433 (3) Å, which is also observed in the related isopolymolybdate anions.

Introduction. Colorless crystals of various alkylammonium polymolybdates turn reddish brown or violet when they are irradiated with UV light and return to colorless in the dark (Yamase & Ikawa, 1977). In order to ascertain this mechanism, several crystal structures have been analysed (Isobe, Marumo, Yamase & Ikawa, 1978; Ohashi, Yanagi, Sasada & Yamase, 1982; Bharadwaj, Ohashi, Sasada, Sasaki & Yamase, 1984) and their ESR spectra have been examined (Yamase, 1978, 1982). Although the title crystals (abbreviated as MAM) also turned red on exposure to UV light, they were not decolorized in the dark at room temperature. The present work was undertaken to elucidate their characteristic behavior.

Experimental. Colorless prismatic crystals obtained by the method reported previously (Yamase & Ikawa, 1977); preliminary unit-cell dimensions and space group (systematic absences: $h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$) obtained from oscillation and Weissenberg photographs; dimensions of crystal $0.2 \times 0.15 \times 0.1$ mm; Rigaku AFC-4 diffractometer; graphite mono-

chromator; cell parameters refined by least squares on the basis of 23 independent 2θ values; Mo $K\alpha$ radiation ($22 < 2\theta < 31^\circ$); intensity measurement performed up to $2\theta = 55^\circ$, $\pm h$ (–16 to 16), $\pm k$ (0 to 22), $\pm l$ (0 to 13); ω – 2θ scan technique, scan speed 2° (θ) min⁻¹; three standard reflections (083, 600, 305) measured at 50-reflection intervals showed less than 2% variation in intensity; 5285 reflections measured, 4838 with $|F_o| > 3\sigma(|F_o|)$ considered observed and used for structure determination; corrections for Lorentz and polarization, absorption ignored; direct methods (*MULTAN78*, Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); difference Fourier calculation and block-diagonal least squares (*HBLS*; Ohashi, 1975) with anisotropic thermal parameters for all non-H atoms; H atoms bonded to N atoms located on difference map, other H-atom positions obtained geometrically, $\sum w(|F_o| - |F_c|)^2$ minimized, $w = [\sigma^2(|F_o|) + (C|F_o|)^2]^{-1}$, C adjusted to give constant values of $\langle w(|F_o| - |F_c|)^2 \rangle$ in different ranges of $|F_o|$ and $\sin\theta$, $C = 0.030$; final $R = 0.041$ and $wR = 0.050$ for 4838 observed reflections; max. Δ/σ 0.25 (non-H) and 0.92 (H); max. and min. heights in final difference map 1.50 and -1.42 e Å⁻³ around Mo atom (less than 1 Å); atomic scattering factors including anomalous terms from *International Tables for X-ray Crystallography* (1974); calculation carried out on FACOM-HITAC system M-180 computer at this Institute; final atomic parameters for non-H atoms in Table 1.†

Discussion. Fig. 1 shows the stereoscopic drawing of the decamolybdate anion, $[\text{Mo}_{10}\text{O}_{34}]^{8-}$. Bond distances and Mo...Mo distances in the anion are given in Table 2.

† Lists of structure factors, anisotropic thermal parameters for non-hydrogen atoms, positional and thermal parameters for hydrogen atoms, bond distances of the CH_3NH_3^+ cations, bond angles and a figure of the hydrogen-bonding scheme have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42702 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. Atomic coordinates with the equivalent isotropic thermal parameters (\AA^2) for non-H atoms, coordinates $\times 10^5$ for Mo and $\times 10^4$ for O, N and C atoms

$$B_{\text{eq}} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	B_{eq}
Mo(1)	55075 (3)	52578 (2)	35529 (4)	1.3
Mo(2)	71701 (3)	60096 (3)	58892 (4)	1.7
Mo(3)	79716 (3)	45636 (3)	41366 (4)	1.8
Mo(4)	52926 (3)	34068 (2)	41998 (4)	1.5
Mo(5)	76678 (4)	47975 (3)	7327 (4)	1.9
O(1)	7718 (3)	4965 (2)	5789 (3)	1.5
O(2)	6324 (3)	4220 (2)	4131 (3)	1.3
O(3)	5568 (3)	5450 (2)	5816 (3)	1.2
O(4)	6891 (3)	5611 (2)	3862 (3)	1.2
O(5)	5469 (3)	5081 (2)	1979 (3)	1.7
O(6)	7701 (3)	4371 (3)	2296 (4)	2.1
O(7)	8258 (3)	6522 (2)	5419 (4)	2.1
O(8)	6146 (3)	6815 (2)	5422 (3)	1.4
O(9)	5231 (3)	3174 (2)	2623 (3)	1.9
O(10)	4780 (3)	6130 (2)	3727 (3)	1.4
O(11)	7182 (3)	6083 (3)	7502 (4)	2.3
O(12)	8885 (3)	4621 (3)	24 (4)	2.8
O(13)	7483 (3)	5808 (2)	762 (4)	2.4
O(14)	6000 (3)	2641 (2)	4848 (4)	2.2
O(15)	8415 (3)	3664 (2)	4539 (4)	2.3
O(16)	6683 (4)	4373 (3)	-211 (4)	2.8
O(17)	9092 (3)	5111 (3)	3809 (4)	2.9
N(1)	5829 (4)	1229 (3)	6104 (5)	2.6
N(2)	4593 (4)	3811 (3)	304 (5)	2.6
N(3)	7308 (5)	3757 (3)	7430 (5)	3.3
N(4)	6730 (4)	1834 (3)	2293 (5)	2.6
C(1)	5132 (6)	1483 (6)	7113 (8)	4.8
C(2)	4722 (8)	3083 (5)	-397 (8)	4.5
C(3)	7609 (8)	2951 (5)	7499 (10)	5.3
C(4)	7537 (6)	2428 (4)	2107 (7)	3.5
O(W1)	4750 (6)	999 (4)	2846 (7)	6.0

The anion is built up of the Mo_8O_{28} unit and two MoO_4 tetrahedra, the latter being connected to the former at its corners. The Mo_8O_{28} unit is composed of eight MoO_6 octahedra joined together by edges. Such a framework is common to those in the crystals of $(\text{NH}_4)_8\text{Mo}_{10}\text{O}_{34}$ (Fuchs, Hartl, Hunnius & Mahjour, 1975) and $\text{Tl}_8\text{Mo}_{10}\text{O}_{34}$ (Touboul, Idoura & Toledano, 1984). However, the linkage mode of MoO_4 to the octamolybdate unit is different among the three

Table 2. Bond distances (\AA) in $[\text{Mo}_{10}\text{O}_{34}]^{8-}$ and $\text{Mo}\cdots\text{Mo}$ distances (\AA)

Mo(1)—O(2)	2.142 (4)	Mo(3)—O(1)	1.922 (4)
—O(3)	2.433 (3)	—O(2)	2.158 (4)
—O(3')	1.949 (3)	—O(4)	2.271 (3)
—O(4)	1.869 (3)	—O(6)	2.011 (4)
—O(5)	1.704 (4)	—O(15)	1.695 (4)
—O(10)	1.768 (4)	—O(17)	1.737 (5)
Mo(2)—O(1)	1.926 (4)	Mo(4)—O(2)	1.910 (4)
—O(3)	2.235 (3)	—O(3')	2.243 (3)
—O(4)	2.286 (3)	—O(8')	1.902 (4)
—O(7)	1.711 (4)	—O(9)	1.728 (4)
—O(8)	1.950 (4)	—O(10')	2.350 (4)
—O(11)	1.722 (4)	—O(14)	1.726 (4)
		Mo(5)—O(6)	1.819 (4)
		—O(12)	1.748 (5)
		—O(13)	1.752 (4)
		—O(16)	1.743 (5)
Mo(1)—Mo(1')	3.474 (1)	Mo(2)—Mo(3)	3.277 (1)
—Mo(2)	3.472 (1)	—Mo(4')	3.260 (1)
—Mo(2')	4.067 (1)	Mo(3)—Mo(4)	3.918 (1)
—Mo(3)	3.372 (1)	—Mo(5)	3.661 (1)
—Mo(4)	3.265 (1)		
—Mo(4')	3.478 (1)		

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

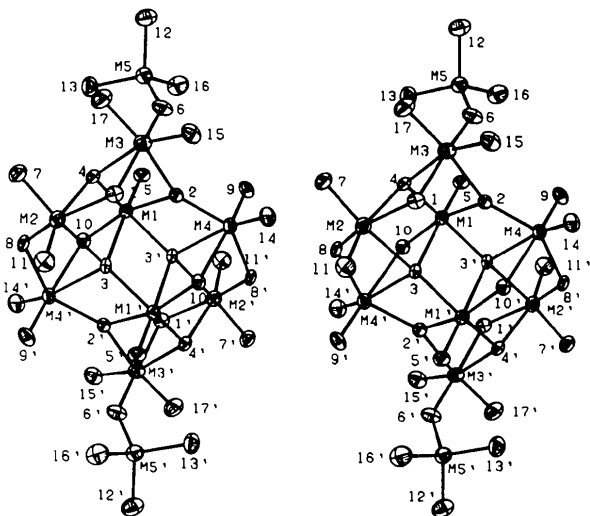


Fig. 1. Stereoscopic drawing (ORTEP; Johnson, 1965) of the decamolybdate anion with the numbering of atoms.

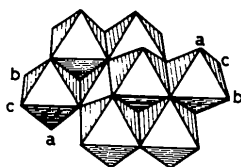


Fig. 2. Schematic drawing of Mo_8O_{28} unit. Each octahedron corresponds to an MoO_6 unit.

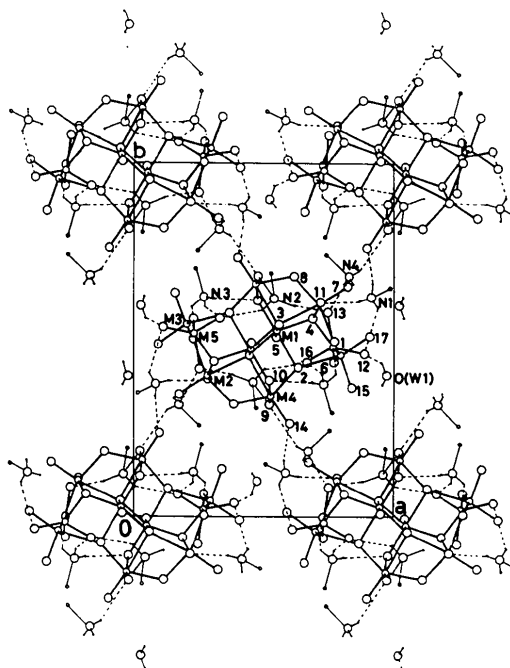


Fig. 3. Crystal structure viewed along the c axis. The hydrogen bonds are indicated by broken lines.

decamolybdate anions. In the ammonium and thallium salts, the MoO_4 units occupy the linking sites b in Fig. 2, whereas they are situated at the a sites in MAM. The distance $\text{Mo}(3)\cdots\text{Mo}(5)$, 3.661 (1) Å, in MAM is significantly shorter than those in the NH_4^+ [3.700 (1) Å] and Tl^+ salts [3.741 (3) Å].

Such linkage isomers have been found in the octamolybdate anions represented by $[(X)_2\text{Mo}_8\text{O}_{26}]^{2n-4}$, where n is the formal charge of the coordinated base, X (McCarron, Whitney & Chase, 1984). MAM has the same linkage mode as those of $[\text{H}_2\text{Mo}_8\text{O}_{28}]^{6-} \equiv [(\text{HO})_2\text{Mo}_8\text{O}_{26}]^{6-}$, $[(\text{HCO})_2\text{Mo}_8\text{O}_{28}]^{6-} \equiv [(\text{HCOO})_2\text{Mo}_8\text{O}_{26}]^{6-}$, $[\text{Mo}_8\text{O}_{27}]_n^{6-} \equiv [\text{O}_{2/2} \text{Mo}_8\text{O}_{26}]_n^{6-}$ and $[(\text{C}_5\text{H}_5\text{N})_2\text{Mo}_8\text{O}_{26}]^{4-}$ (Isobe, Marumo, Yamase & Ikawa, 1978; Adams, Klemperer & Liu, 1979; Boschen, Buss & Krebs, 1974; McCarron, Whitney & Chase, 1984).

The crystal structure viewed along the c axis is shown in Fig. 3. The decamolybdate anions are connected by $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds. All the $\text{N}-\text{H}$ groups of the methylammonium cations and the terminal O atoms of the MoO_4 units participate in the three-dimensional hydrogen-bonding scheme.

The crystals of MAM turn red on exposure to UV light but the color does not fade away in the dark. On the other hand, photochromism was observed in crystals of $(\text{C}_5\text{H}_5\text{N})_6[\text{H}_2\text{Mo}_8\text{O}_{28}]$ (Yamase & Ikawa, 1977). The coloration of these crystals is due to the formation of the photoreduced Mo^{V} site in the lattice (Yamase, 1978). Based on the fact that the structure of the octamolybdate unit in MAM is the same as that in $[\text{H}_2\text{Mo}_8\text{O}_{28}]^{6-}$, the reason the red color of the

photoreduced MAM is conserved in the dark may be the stabilization of the Mo^{V} site due to the linkage of the MoO_4 tetrahedra at the corners of the Mo_8O_{28} unit.

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Structure of Dichloro({(1*R*)-[(2*S*)-2-(diphenylphosphino)-1-ferrocenyl]ethyl}-dimethylamine-*N,P*)palladium(II) Deuteriochloroform Solvate

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Abstract. $[\text{PdCl}_2(\text{C}_{26}\text{H}_{28}\text{FeNP})].2\text{CDCl}_3$, $M_r = 859.39$, monoclinic, $P2_1$, $a = 9.9811$ (12), $b = 19.329$ (2), $c = 10.013$ (2) Å, $\beta = 114.78$ (1)°, $V = 1753.9$ (6) Å³, $Z = 2$, $D_x = 1.627$ g cm⁻³, $\lambda(\text{Cu K}\alpha) = 1.54184$ Å, $\mu = 133.29$ cm⁻¹, $F(000) = 856$, $T = 294$ K, $R = 0.079$ for 2258 observed reflections. The chelating ligand is bonded to PdCl_2 by N and P, resulting in a slightly distorted square-planar Pd^{II}

complex. The absolute configuration of the disubstituted ferrocene is *S* and that of the α -C atom is *R*. The $\text{Cl}-\text{Pd}-\text{Cl}$ angle is small [86.4 (3)°], a feature that is considered advantageous in stereoselective cross-coupling of organometallic reagents.

Introduction. In recent years there has been considerable interest in stereoselective catalysts for a variety of