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Structure of Oxonium Tris(triethylammonium) Octamolybdate(4–) Dihydrate, $(C_6H_{16}N)_3(H_3O)[Mo_8O_{26}].2H_2O$*

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Abstract. $M_r = 1544{\cdot}8$, monoclinic, $P2_1/a$, $a = 21{\cdot}271\ (9)$, $b = 11{\cdot}837\ (1)$, $c = 20{\cdot}189\ (9)$ Å, $\beta = 117{\cdot}92\ (5)°$, $V = 4491\ (3)$ Å^3, $Z = 4$, $D_x = 2{\cdot}29$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 21{\cdot}99$ cm^{-1}, $F(000) = 3008$, $T = 293$ K, $R = 0{\cdot}043$ for 9441 observed data. Two crystallographically independent octamolybdates are situated at the different inversion centers and have approximately the same structure as that of β-$[Mo_8O_{26}]^{4-}$. The H_3O cation connects the two independent anions with complicated hydrogen bonds.

Introduction. Various alkylammonium polymolybdates reveal photochromic properties in the solid state (Yamase & Ikawa, 1977). From the crystal structure and ESR spectra of the three monoalkylammonium salts hexakis(isopropylammonium) dihydrogenoctamolybdate dihydrate (IPAM2), $(C_3H_{10}N)_6[H_2Mo_8O_{28}].2H_2O$ (Isobe, Marumo, Yamase & Ikawa, 1978; Yamase, 1978), hexakis(propylammonium) heptamolybdate trihydrate (PAM), $(C_3H_{10}N)_6[Mo_7O_{24}].3H_2O$, and hexakis(isopropylammonium) heptamolybdate trihydrate (IPAM), $(C_3H_{10}N)_6[Mo_7O_{24}].3H_2O$ (Ohashi, Yanagi, Sasada & Yamase, 1982; Yamase, 1982), it has been elucidated that the Mo atom is photoreduced from VI to V in an MoO_6 octahedral site, accompanying transfer of a hydrogen-bonding proton from the cation to the anion. In order to ascertain the mechanism for the trialkylammonium salts, the crystal structure of the title compound (TEAM) has been analyzed.

Experimental. Colorless prismatic crystals obtained by a similar method to that reported previously (Yamase & Ikawa, 1977); composition: C 13·94, H 3·76, N 3·57%; calculated for $(C_6H_{16}N)_3(H_3O)[Mo_8O_{26}].2H_2O$: C 13·99, H 3·11, N 2·72%; systematic absences: $h0l$ for $h = 2n + 1$, $0k0$ for $k = 2n + 1$; approximate dimensions of crystal $0{\cdot}2 \times 0{\cdot}2 \times 0{\cdot}3$ mm; Rigaku AFC-4 diffractometer, graphite monochromator, cell parameters refined by least squares on basis of 24 independent 2θ values, $20 < 2\theta < 30°$; intensity measurement up to $2\theta = 55°$ ($\pm h+k+l$ set; h 0–25, k 0–15, l 0–26), θ–2θ scan, speed 2° min^{-1}(θ); 3 standard reflections showed intensity variation <5%; 10 834 reflections measured, 9441 intensities with $|F_o| > 3\sigma(|F_o|)$ considered observed and used for the structure determination; correction for Lorentz and polarization, absorption ignored; direct methods (*MULTAN*78, Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and subsequent difference-Fourier calculation, block-diagonal least squares (*HBLS*, Ohashi, 1975), anisotropic thermal parameters for all non-H atoms; H atoms bonded to N atoms located on difference map and 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 so that constant values of $\langle w(|F_o|-|F_c|)^2\rangle$ obtained in different $|F_o|$ and $\sin\theta$ intervals, $C = 0{\cdot}015$; $R = 0{\cdot}043$, $R_w = 0{\cdot}056$ for 9441 observed reflections; atomic scattering factors including the anomalous

* Crystal Structure and Photochemistry of Isopolymolybdates. II.

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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.*

* Lists of structure factors, anisotropic thermal parameters for non-H atoms, positional and thermal parameters for H atoms and bond angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38835 (39 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates with equivalent isotropic thermal parameters for non-*H *atoms (coordinates* $\times 10^5$ *for* Mo, $\times 10^4$ *for other atoms)*

$$B_{eq} = \tfrac{1}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$$

	x	y	z	B_{eq}(Å^2)
Mo(1*A*)	61838 (2)	8990 (4)	63083 (2)	2·2
Mo(2*A*)	54093 (2)	20774 (4)	45601 (3)	2·3
Mo(3*A*)	44853 (2)	6478 (4)	53783 (2)	1·9
Mo(4*A*)	63141 (3)	−18476 (4)	63874 (3)	2·5
Mo(1*B*)	38619 (2)	3585 (4)	85194 (3)	2·3
Mo(2*B*)	37078 (2)	−6192 (4)	100335 (3)	2·3
Mo(3*B*)	51097 (2)	−13015 (4)	96129 (2)	2·0
Mo(4*B*)	50530 (3)	23475 (4)	88806 (3)	2·6
O(1*A*)	6072 (2)	920 (4)	7093 (2)	2·8
O(2*A*)	6797 (2)	1929 (4)	6457 (2)	2·8
O(3*A*)	6762 (2)	−397 (3)	6489 (2)	2·3
O(4*A*)	5280 (2)	1681 (3)	5624 (2)	1·8
O(5*A*)	6020 (2)	752 (3)	5084 (2)	1·7
O(6*A*)	5351 (2)	−512 (3)	5697 (2)	1·7
O(7*A*)	5957 (2)	3173 (4)	5016 (2)	3·0
O(8*A*)	5443 (2)	1960 (4)	3736 (2)	2·8
O(9*A*)	4503 (2)	2770 (3)	4229 (2)	2·2
O(10*A*)	4424 (2)	645 (3)	6187 (2)	2·4
O(11*A*)	3806 (2)	1576 (3)	4780 (2)	2·3
O(12*A*)	6996 (2)	−2753 (4)	6611 (3)	3·5
O(13*A*)	6192 (2)	−1781 (4)	7169 (2)	2·9
O(1*B*)	4018 (2)	−164 (4)	7825 (2)	3·1
O(2*B*)	2959 (2)	401 (4)	8147 (2)	3·0
O(3*B*)	4067 (2)	1921 (3)	8503 (2)	2·3
O(4*B*)	4081 (2)	−1033 (3)	9137 (2)	1·9
O(5*B*)	3933 (2)	836 (3)	9692 (2)	1·8
O(6*B*)	5046 (2)	483 (3)	9400 (2)	1·6
O(7*B*)	2846 (2)	−760 (4)	9380 (3)	3·0
O(8*B*)	3683 (2)	−124 (4)	10812 (2)	2·9
O(9*B*)	3996 (2)	−2125 (3)	10319 (2)	2·3
O(10*B*)	5216 (2)	−1745 (3)	8875 (2)	2·5
O(11*B*)	5095 (2)	−2530 (3)	10078 (2)	2·1
O(12*B*)	5003 (3)	3773 (4)	8765 (3)	3·5
O(13*B*)	5179 (2)	1836 (4)	8166 (2)	3·2
O(*W*1)	4732 (3)	456 (4)	2371 (3)	4·2
O(*W*2)	4249 (3)	4356 (5)	5247 (4)	5·1
O(*W*3)	3037 (3)	3501 (5)	7857 (3)	5·8
N(1)	1552 (3)	433 (4)	7974 (3)	2·6
N(2)	3039 (3)	3948 (6)	5453 (4)	4·2
N(3)	1745 (4)	368 (5)	1254 (4)	4·4
C(11)	1258 (4)	−723 (6)	7949 (4)	3·7
C(12)	494 (6)	−756 (9)	7699 (8)	8·1
C(13)	1205 (5)	1047 (7)	7249 (5)	5·3
C(14)	1220 (7)	442 (9)	6599 (6)	7·4
C(15)	1553 (4)	1129 (7)	8599 (4)	3·9
C(16)	2032 (5)	2133 (7)	8798 (5)	5·0
C(21)	3216 (6)	2894 (8)	5904 (6)	6·4
C(22)	3893 (10)	3005 (12)	6619 (7)	11·9
C(23)	2833 (5)	4868 (7)	5848 (6)	5·1
C(24)	3345 (6)	5810 (9)	6073 (7)	7·0
C(25)	2459 (5)	3724 (10)	4668 (6)	6·5
C(26)	2296 (6)	4617 (13)	4159 (7)	8·8
C(31)	1221 (4)	107 (8)	480 (5)	5·6
C(32)	1406 (5)	−913 (8)	125 (5)	5·8
C(33)	2504 (4)	527 (6)	1357 (5)	4·4
C(34)	2574 (5)	1570 (8)	982 (5)	5·6
C(35)	1607 (7)	1387 (9)	1624 (8)	8·1
C(36)	1070 (9)	1160 (12)	1848 (9)	10·0

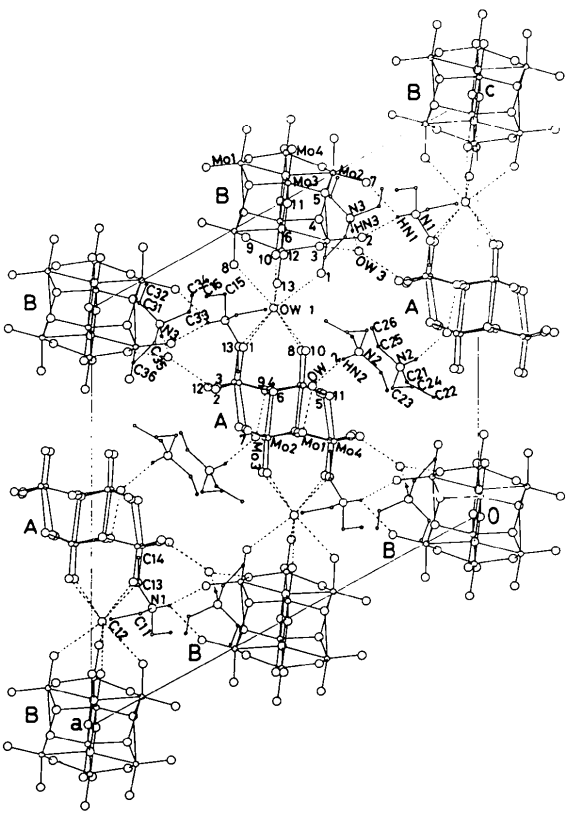

Fig. 1. Crystal structure viewed along the *b* axis. The hydrogen bonds are indicated by the broken lines.

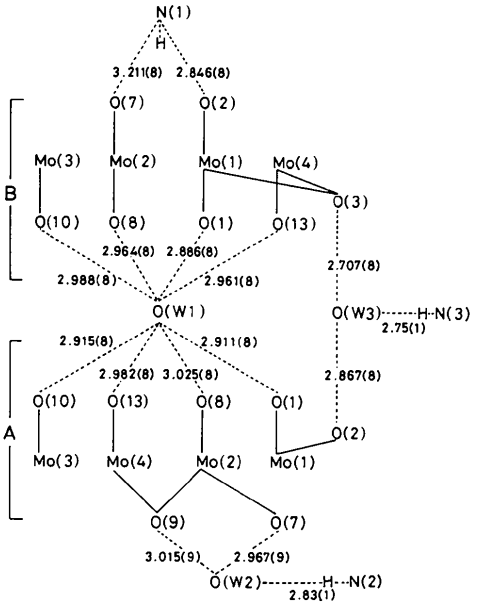

Fig. 2. Schematic drawing of the hydrogen bonds in the TEAM crystal. (Distances in Å.)

Discussion. The crystal structure viewed along the *b* axis is shown in Fig. 1. Two crystallographically independent octamolybdate anions, *A* and *B*, are situated at the two different inversion centers and are stacked alternately along the *c* axis. All the triethylammonium cations and water molecules participate in the hydrogen bonding, which is schematically drawn in Fig. 2. The solvent molecule, O(*W*1), makes hydrogen bonds with the terminal oxygen atoms of *A* and *B* in a complicated manner and connects the two anions along the *c* axis. The geometries of the two octamolybdates are approximately the same and essentially equal to that of the β-$[Mo_8O_{26}]^{4-}$ anion (Atovmyan & Krasochka, 1972; Lindqvist, 1950). Fig. 3 shows the stereoscopic drawing of the *A* anion. Eight MoO_6 octahedra are joined together by edges. Bond distances of the two octamolybdates are given in Table 2. To keep the crystal electrically neutral, two protons must be attached to the two Mo_8O_{26} anions. In the $[H_2Mo_8O_{28}]^{6-}$ anion (Isobe, Marumo, Yamase & Ikawa, 1978), two protons are bonded to the terminal oxygen atoms. The Mo—OH distance [1·972 (7) Å] is significantly longer than the other terminal Mo=O distances [1·708–1·722 Å].

In the two Mo_8O_{26} anions of the present crystal, the terminal Mo=O distances range from 1·692–1·717 Å. The corresponding distances between the two anions are in fair agreement with each other. On the other hand, the water molecule, O(*W*1), is surrounded by the negative oxygen atoms and forms complicated hydrogen bonds with these atoms. The above results strongly suggest that the protons are not attached to the terminal oxygen atoms but to the water molecule connecting the two anions. The proton would be easily transferred to the terminal oxygen atoms around O(*W*1) through the hydrogen bonds. This may cause the characteristic photochromism, different from the monoalkylammonium polymolybdates.

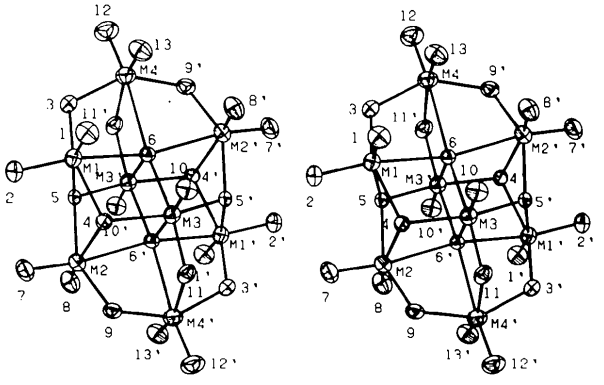

Fig. 3. Stereoscopic drawing (*ORTEP*; Johnson, 1965) of the *A* anion with the numbering of atoms.

Table 2. *Bond distances* (Å)

	Anion *A*	Anion *B*		
Mo(1)–O(1)	1·709 (5)	1·701 (5)	N(1)–C(11)	1·50 (1)
–O(2)	1·707 (5)	1·704 (5)	C(11)–C(12)	1·46 (2)
–O(3)	1·891 (4)	1·904 (4)	N(1)–C(13)	1·48 (1)
–O(4)	1·994 (4)	1·986 (4)	C(13)–C(14)	1·51 (2)
–O(5)	2·335 (4)	2·368 (4)	N(1)–C(15)	1·51 (1)
–O(6)	2·325 (4)	2·309 (4)	C(15)–C(16)	1·49 (1)
Mo(2)–O(4)	2·337 (4)	2·343 (4)	N(1)–H(N1)	0·87 (7)
–O(5)	1·995 (4)	1·995 (4)	N(2)–C(21)	1·49 (2)
–O(6)*	2·352 (4)	2·350 (4)	C(21)–C(22)	1·49 (3)
–O(7)	1·698 (5)	1·692 (5)	N(2)–C(23)	1·53 (1)
–O(8)	1·703 (5)	1·700 (5)	C(23)–C(24)	1·47 (2)
–O(9)	1·904 (4)	1·885 (4)	N(2)–C(25)	1·51 (1)
Mo(3)–O(4)	1·953 (4)	1·961 (4)	C(25)–C(26)	1·40 (2)
–O(5)*	1·957 (4)	1·935 (4)	N(2)–H(N2)	0·85 (7)
–O(6)	2·140 (4)	2·147 (4)	N(3)–C(31)	1·47 (1)
–O(6)*	2·359 (4)	2·374 (4)	C(31)–C(32)	1·55 (2)
–O(10)	1·697 (5)	1·692 (5)	N(2)–C(33)	1·54 (1)
–O(11)	1·767 (4)	1·739 (4)	C(33)–C(34)	1·49 (1)
Mo(4)–O(3)	1·927 (4)	1·933 (4)	N(3)–C(35)	1·52 (2)
–O(6)	2·442 (4)	2·446 (4)	C(35)–C(36)	1·44 (3)
–O(24)	1·686 (5)	1·701 (5)	N(3)–H(N3)	0·90 (7)
–O(13)	1·717 (5)	1·697 (5)		
–O(9)*	1·934 (4)	1·927 (4)		
–O(11)*	2·273 (4)	2·277 (4)		

* Symmetry code: *A* anion 1–*x*, –*y*, 1–*z*; *B* anion 1–*x*, –*y*, 2–*z*.

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