Structure of Tetrakis(dimethylammonium) β-Octamolybdate Bis(*N,N*-dimethylformamide), [NH₂(CH₃)₂]₄[Mo₈O₂₆].2C₃H₇NO, with Comments on Relationships among Octamolybdate Anions

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Abstract. $M_r = 1514 \cdot 1$, monoclinic, $C2/c$, $a = 18 \cdot 118$ (4), $b = 14 \cdot 568$ (3), $c = 16 \cdot 288$ (3) Å, $\beta = 101 \cdot 003$ (3)°, $V = 4220 \cdot 1$ (10) Å³, $Z = 4$, $D_m = 2 \cdot 36$, $D_x = 2 \cdot 38$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0 \cdot 71069$ Å, $\mu = 2 \cdot 337$ mm⁻¹, $F(000) = 2928$, room temperature, $R = 0 \cdot 046$ for 2222 reflections. The title compound is the product of the reaction between molybdenum trioxide and dimethylformamide. The octamolybdate anions, $Mo_8O_{26}^{4-}$, are centrosymmetric and possess the previously established β-structure. Mean Mo—O bond lengths are: terminal O, $1 \cdot 698$ (8); single-bridging O, $1 \cdot 909$ (8); triple-bridging O, $2 \cdot 091$ (8); five-bridging O, $2 \cdot 319$ (8) Å. The dimethylformamide solvate molecules are H-bonded [N⋯O = $2 \cdot 73$ (4) Å] to one of the two crystallographically independent cations and the nitrogen atoms of both sets of cations form a number of close contacts with the anion terminal oxygen atoms.

Introduction. Reaction of molybdenum trioxide with electron-donor ligands gives polymeric products, usually of composition MoO₃.*L* (Bernard & Camelot, 1966; Hider & Wilkins, 1984). However, analyses of the only product that could be isolated from the reaction of the trioxide with dimethylformamide (DMF) pointed consistently to a C:H:N ratio of $C_7H_{22-24}N_3$, which is significantly different from the 3:7:1 composition expected for any complex of the kind MoO₃-(DMF)$_x$. The infrared spectrum did show DMF bands, but rather weakly, and in association with probable N—H bands. There were strong Mo—O$_b$—Mo bands at 725, 675 cm⁻¹, and the v(Mo—O$_t$) bands at 943, 905 cm⁻¹ showed evidence of splitting (O$_b$ = bridging O, O$_t$ = terminal O). These features suggested that the product was a salt of a polymolybdate, and the crystal structure determination was made firstly to establish its nature. It proved to be a solvated dimethylammonium β-octamolybdate.

The full course of the reaction leading to the formation of this product has not been established. The reaction occurs even under rigorously anhydrous conditions and in the absence of atmospheric oxygen. It is accompanied by release of carbon monoxide, which suggests dissociation of DMF [to NH(CH₃)₂ and CO] is involved. Subsequent to the present work, it has been found that a polymeric complex, MoO₃.DMF, can be obtained from the reaction of DMF with the complex MoO₃.pyridine.

Experimental. Molybdenum trioxide (7 g) was heated under reflux for 3 h with DMF (40 ml). Resulting yellow-green solution was filtered and crystallization was induced by addition of ethanol or diethyl ether. Colourless tabular crystals separated after 1–2 d in yields up to 25%. The crystals decomposed rapidly in moist air. Colourless crystal coated with Araldite resin, 16 faces, *ca* 0·5 × 0·5 × 0·35 mm, density by flotation (CCl₄ + CHBr₃), space group $C2/c$ consistent with X-ray photographs and distribution of Patterson peaks, Hilger & Watts four-circle diffractometer, Zr-filtered Mo $K\alpha$; refined setting angles of 12 high-angle reflections used to determine lattice parameters; θ–2θ scans, $2\theta_{max} = 52°$ (h −17→19, k 0→15, l 0→17); standard reflections 040, $\bar{4}$04, 402 (no intensity variation); 2351 reflections measured, 2222 with $I > 3\sigma(I)$; no absorption corrections. Coordinates of a group of four Mo atoms obtained from Patterson function and used for initial phasing, remaining non-hydrogen atoms located from subsequent electron density maps, H atoms not located or included in calculations, refinement on 135 parameters with Mo anisotropic but other atoms isotropic, $R = 0 \cdot 046$, $wR = 0 \cdot 052$ with $w = 2 \cdot 55[\sigma^2F + 0 \cdot 00091F^2]^{-1}$, function minimized $\sum w||F_o| - |F_c||^2$, residual electron density in difference Fourier map −0·7 to 1·35 e Å⁻³, max. Δ/σ 0·25. The high apparent thermal parameters of the DMF atoms, combined with large positional uncertainties, strongly suggested that these molecules were disordered. But since knowledge of the total structure made the role of the DMF molecules in the lattice apparent (see below) no attempt was made to model the disorder precisely. Atomic scattering factors from Cromer & Mann (1968), anomalous-dispersion corrections from Cromer & Liberman (1970), structure solution and refinement carried out with *SHELX* (Sheldrick, 1976).

Discussion. The crystal contains the centrosymmetric β-octamolybdate anion Mo$_8$O$_{26}^{4-}$ (*Gmelins Handbuch der Anorganischen Chemie,* 1975) and dimethyl-ammonium cations, which occupy two crystallographically independent sites, centred on N(1) and N(2) (Fig. 1). Atomic coordinates and thermal parameters are given in Table 1.* Bond lengths within the anion are shown in Fig. 2 and selected bond angles are given in Table 2.

In directions away from the methyl groups, N(1) and N(2) show close contacts in the range 2·93–3·12 Å with O$_t$ atoms of the anions.* The N(2)···O(31) distance, 2·73 (4) Å, indicates strong H-bonding to the DMF molecule. A listing of closest contacts to this

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* Lists of structure factors, anisotropic thermal parameters, bond angles around Mo, intermolecular and interionic contacts and a diagram of the Mo$_8$O$_{26}$(OH)$_2^{6-}$ anion (Isobe, Marumo, Yamase & Ikawa, 1978) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39643 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
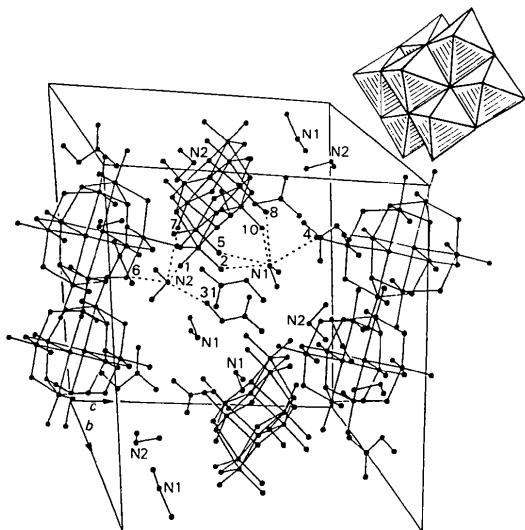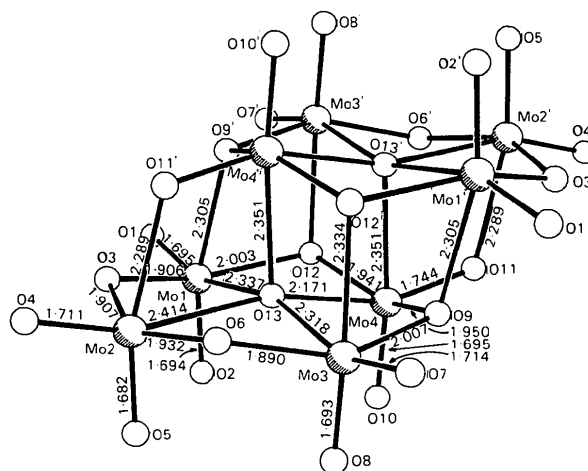

Fig. 1. The unit cell, with close contacts between the cations and numbered oxygen atoms dotted to show cation–anion and cation–DMF relationships. The insert shows the top right-hand anion of the cell retraced in the fused-octahedral representation.

Fig. 2. The β-Mo$_8$O$_{26}^{4-}$ anion, with bond lengths (Å). The e.s.d.'s for all Mo–O bonds are 0·008 Å. Symmetry code: (i) $-x + \frac{1}{2}$, $-y + \frac{1}{2}$, $-z$.

Table 1. *Atomic coordinates and thermal parameters* (Å^2)

	x	y	z	U_{eq}/U_{iso}
Mo(1)	0·4045 (1)	0·2910 (1)	0·0679 (1)	0·040 (1)*
Mo(2)	0·3038 (1)	0·4608 (1)	0·1125 (1)	0·042 (1)*
Mo(3)	0·1778 (1)	0·4198 (1)	−0·0541 (1)	0·039 (1)*
Mo(4)	0·2795 (1)	0·2529 (1)	−0·0983 (1)	0·036 (1)*
O(1)	0·4785 (5)	0·2311 (6)	0·1214 (5)	0·046 (2)
O(2)	0·4439 (4)	0·3647 (6)	0·0083 (5)	0·037 (2)
O(3)	0·3810 (4)	0·3732 (5)	0·1503 (5)	0·033 (2)
O(4)	0·3034 (5)	0·5230 (6)	0·2015 (6)	0·048 (2)
O(5)	0·3486 (5)	0·5268 (6)	0·0528 (5)	0·043 (2)
O(6)	0·2025 (4)	0·4784 (5)	0·0511 (5)	0·033 (2)
O(7)	0·0858 (5)	0·4527 (6)	−0·0847 (5)	0·045 (2)
O(8)	0·2259 (4)	0·4851 (6)	−0·1120 (5)	0·034 (2)
O(9)	0·1779 (4)	0·3033 (5)	−0·1198 (5)	0·027 (2)
O(10)	0·3241 (4)	0·3272 (5)	−0·1524 (5)	0·037 (2)
O(11)	0·2586 (4)	0·1570 (5)	−0·1626 (5)	0·035 (2)
O(12)	0·3636 (4)	0·1997 (5)	−0·0212 (4)	0·025 (2)
O(13)	0·2817 (4)	0·3373 (5)	0·0120 (4)	0·025 (2)
N(1)	0·1166 (6)	−0·0153 (7)	0·1240 (7)	0·042 (3)
C(11)	0·0466 (8)	0·0118 (10)	0·1557 (9)	0·053 (4)
C(12)	0·1281 (8)	−0·1146 (11)	0·1272 (10)	0·061 (4)
N(2)	0·4183 (6)	−0·0625 (8)	0·3667 (7)	0·053 (3)
C(21)	0·3810 (10)	0·1164 (13)	0·2942 (12)	0·084 (5)
C(22)	0·4275 (13)	−0·0354 (15)	0·3456 (15)	0·108 (7)
N(3)	0·3760 (10)	0·2245 (12)	0·6092 (11)	0·094 (5)
O(31)	0·3895 (14)	0·1721 (16)	0·4928 (15)	0·186 (9)
C(31)	0·3336 (21)	0·1866 (26)	0·5350 (26)	0·187 (14)
C(32)	0·3215 (18)	0·2315 (21)	0·6673 (21)	0·160 (11)
C(33)	0·4421 (22)	0·2623 (23)	0·6227 (24)	0·185 (14)

* $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

Table 2. *Selected bond angles* (°) *and bond lengths* (Å)

Octamolybdate anion; e.s.d.'s 0·4°

O(1)–Mo(1)–O(2)	104·0	O(11)–Mo(4)–O(13)	156·7
O(1)–Mo(1)–O(13)	161·8	Mo(1)–O(3)–Mo(2)	116·2
O(2)–Mo(1)–O(9^i)	164·0	Mo(2)–O(6)–Mo(3)	116·5
O(4)–Mo(2)–O(5)	105·5	Mo(2^i)–O(11)–Mo(4)	116·9
O(4)–Mo(2)–O(13)	160·5	Mo(1^i)–O(9)–Mo(3)	104·0
O(5)–Mo(2)–O(11^i)	163·7	Mo(1^i)–O(9)–Mo(4)	111·4
O(7)–Mo(3)–O(8)	104·8	Mo(3)–O(9)–Mo(4)	108·6
O(7)–Mo(3)–O(13)	159·8	Mo(1)–O(12)–Mo(4)	109·9
O(8)–Mo(3)–O(12^i)	164·3	Mo(3^i)–O(12)–Mo(4)	110·3
O(10)–Mo(4)–O(11)	105·7		
O(10)–Mo(4)–O(13^i)	173·6		

Dimethylammonium cations

N(1)–C(11)	1·51 (2)	N(2)–C(21)	1·47 (2)
N(1)–C(12)	1·46 (2)	N(2)–C(22)	1·48 (2)
C(11)–N(1)–C(12)	111·7 (1·1)	C(21)–N(2)–C(22)	112·5 (1·4)

DMF molecule. Values obtained without allowance for disordering: C(31)–O(31) 1·35 (4); N(3)–C(31) 1·42 (4); N(3)–C(32) 1·50 (3); N(3)–C(33) 1·30 (4) Å; O(31)–C(31)–N(3) 99 (3); C(31)–N(3)–C(32) 105 (3); C(31)–N(3)–C(33) 130 (3); C(32)–N(3)–C(33) 124 (3)°.

Table 3. *Types of octamolybdate anions*

Octamolybdate and type, salt	Structural features	Crystallographic identification and reference
Iβ β-Mo$_8$O$_{26}^{4-}$ (NH$_4$)$_4$Mo$_8$O$_{26}$·4H$_2$O	8 condensed octahedra, 14 terminal atoms	Lindquist (1950) Atovmyan & Krasochka (1970)
Iα α-Mo$_8$O$_{26}^{4-}$ [N(C$_4$H$_9$)]$_4$Mo$_8$O$_{26}$	6 condensed octahedra with 2 tetrahedra, 14 terminal atoms	Fuchs & Hartl (1976)
II Mo$_8$O$_{26}$(OH)$_2^{6-}$ (Pr^{i}NH$_3$)$_6$Mo$_8$O$_{26}$(OH$_2$)·2H$_2$O	8 condensed octahedra, 16 terminal positions	Isobe et al. (1978)
III {Mo$_8$O$_{27}^{6-}$}$_n$ (NH$_4$)$_6$Mo$_8$O$_{27}$·4H$_2$O	8 condensed octahedra, as for II, with single-bridge linkage into chains, 14 terminal atoms	Böschen et al. (1974)
IV {Mo$_8$O$_{26}^{4-}$}$_n$ K$_4$Mo$_8$O$_{26}$	8 condensed octahedra as for II, with chain formation through two triple-bridge linkages, 12 terminal atoms	Gatehouse & Leverett (1971)

solvate molecule reveals no others that are unusually short and indeed the number of van der Waals contacts is small. The DMF molecules thus occupy ample cavities and are subject only to the constraint of H-bonding to N(2). It is therefore not surprising that these molecules should be disordered.

The structure of the present anion (type Iβ, in Table 3, where the various octamolybdate anions are listed) matches the structures recently reported for other β-octamolybdates (Vivier, Bernard & Djomaa, 1977; Román, Jaud & Galy, 1981). The Mo—O$_t$ bond lengths from the various determinations generally agree within 0·015 Å and the longer weaker bridging bonds to within 0·04 Å; the differences probably reflect no more than variations in cation fields. The average lengths of the Mo—O bonds to the various types of O atom, with bond orders (Schröder, 1975) in parentheses, are: O$_t$ 1·698 Å (1·9); single bridging 1·909 (0·9); triple-bridging 2·091 (0·4); five-bridging 2·319 (~0·15). Thus the eight bonds of length *ca* 2·3 Å linking the two asymmetric units of the anion (Fig. 2) are weak. The effect of the strongly π-bonded O$_t$ atoms on the bonding within the cluster becomes apparent since these bonds are all subject to the *trans* lengthening effect of the O$_t$ atoms (Cotton & Wing, 1965; Schröder, 1975). Mo(4) is the only Mo atom linked to a single O$_t$ atom, *viz* O(10), but the Mo(4)—O(11)—Mo(2^i) bridge is highly unsymmetrical, with Mo(4)—O(11) = 1·744 (8), Mo(2^i)—O(11) = 2·289 (8) Å, and the O(10)—Mo(4)—O(11) angle of 105·7 (4)° is in line with the other bond angles between O$_t$ pairs. Hence, O(11) in its relationship to Mo(4) might best be described as an O$_t$ atom involved in weak bent bridging. The weakness of the Mo(2^i)—O(11) arm of the bridge can be correlated with the *trans* effect of the O$_t$ atom O(5^i), in conjunction with the well-known preference of Mo^{VI} to form strong bonds with two O$_t$ atoms in *cis* positions. The single-bridging O(3) and O(6), on which there is no such *trans* influence, form fairly symmetrical linkages. The other long inter-unit bonds all involve multiple bridges. In the case of the triple-bridging atoms O(9)

and O(12), the bridging arms linking the different asymmetric units, i.e. Mo(1^i)—O(9) and Mo(3)—O(12^i), are subject to *trans* lengthening and these bonds are some 0·3 Å longer than each of their respective partners. Thus, Mo(1^i)—O(9) *trans* to O(2^i) is 2·305 (8) Å, while Mo(3)—O(9) and Mo(4)—O(9) are 2·007 (8) and 1·950 (8) Å respectively. Bonds to the five-bridging O(13) are all *trans* to O$_t$ atoms and are correspondingly long, but with the qualification that Mo(4)—O(13), which lies *trans* to the bridging O$_t$ atom O(11), remains shorter [2·171 (8) Å] than the other bonds whose average is 2·355 (8) Å. The counterbalancing of longer against shorter bridging bonds across a molybdenum centre is evident. This can be interpreted in terms of a residual π-character in the Mo—O$_b$ bond and a consequential small *trans* lengthening effect exerted by the bond of higher order (Cotton & Wing, 1965; Schröder, 1975).

Of the other octamolybdate anions (Table 3), the isomeric α-anion (Iα) consists of a buckled ring of six octahedra closed on either side by a tetrahedron (Fuchs & Hartl, 1976). As with the β-form, Iα contains a network of weak bridging bonds *trans* to O$_t$ atoms. Collectively, the bonds ensure the stabilities of the anion structures in crystalline salts. But disruption of these weak bonds in solution is considered to open the way for the well-established Iα ⇌ Iβ interconversion (Klemperer & Shum, 1976; Day, Fredrich, Klemperer & Shum, 1977).

The non-isomeric anion Mo$_8$O$_{26}$(OH)$_2^{6-}$ (II) (Table 3) contains the four Mo atoms of the asymmetric unit in a stepped rather than a square pattern (Isobe, Marumo, Yamase & Ikawa, 1978), but with *trans* effects and a highly unsymmetrical bent bridge again in evidence. A discrete non-protonated anion, Mo$_8$O$_{28}^{8-}$, of this same structure would have an unfavourably high charge, but further condensation would reduce the charge and in fact this Isobe-type structure has been known for some time within the chain-polymeric anions {Mo$_8$O$_{27}^{6-}$}$_n$ (III) (Böschen, Buss & Krebs, 1974) and {Mo$_8$O$_{26}^{4-}$}$_n$ (IV) (Gatehouse & Leverett, 1971). From the various

octamolybdate structures it is evident that the bonding within a cluster is controlled in the first place by the dominant influence of the strong bonds in the *cis* Mo(O$_t$)$_2$ groups. The weak internal bonds through oxygen bridges are complementary and can vary in length and direction to meet the needs of a particular structure.

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catena-Poly{μ-(2,2'-bipyrimidine-*N*,*N*':*N''*,*N'''*)-[(nitrato-*O*,*O'*)copper(II)]-di-(μ-nitrato-μ-*O*)-[(nitrato-*O*,*O'*)copper(II)]}, [Cu₂(NO₃)₄(C₈H₆N₄)]

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Abstract. M_r (asymmetric unit) = 266·64, monoclinic, $C2/c$, a = 19·314 (3), b = 7·914 (1), c = 15·060 (2) Å, β = 137·4 (1)°, V = 1558 (3) Å³, Z = 8, D_m (by flotation) = 2·26, D_x = 2·273 g cm⁻³, Mo $K\alpha$, λ = 0·71069 Å, μ = 28·06 cm⁻¹, $F(000)$ = 1056, T = 293 K, final conventional R = 0·039 for 1248 unique observed reflections. The compound is a polymer built up by complex dimeric units formed by two Cu atoms coordinated by a molecule of the organic ligand and four nitrate groups. Both Cu atoms are six-coordinated with a distorted octahedral geometry, being bonded by two N atoms of the organic ligand, acting as doubly-bidentate, by two O atoms of a bidentate nitrate group and by two O atoms of two monodentate nitrate groups bridging two Cu atoms.

Introduction. Binuclear Cu^{II} complexes with ligands containing N atoms have been widely investigated in recent times since they are of great significance in biological systems (De Munno, Denti & Dapporto, 1983; Thompson, 1983; Dapporto, De Munno, Sega & Mealli, 1984). 2,2'-Bipyrimidine is a ligand with four N donor atoms whose Cu^{II} and Fe^{II} mixed complexes have been synthesized because they are possible models for cytochrome oxidase (Petty, Welch, Wilson, Bottomley & Kadish, 1980; McLendon & Smith, 1982). This ligand is potentially interesting for two reasons: it can act either as a doubly-bidentate bridging ligand or simply as a bidentate ligand. Mononuclear and binuclear 2,2'-bipyrimidine Ru^{II} complexes are known (Dose & Wilson, 1978; Hunziker & Ludi, 1977;