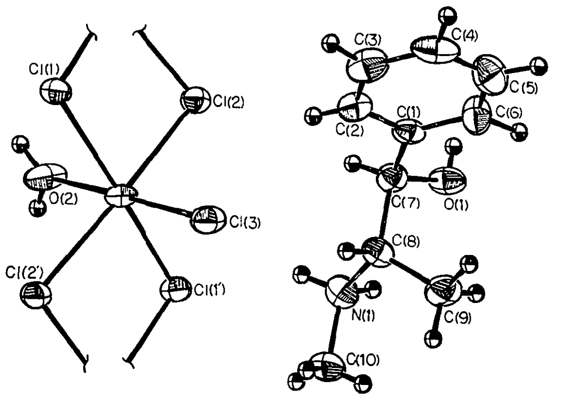

Fig. 2. An *ORTEP* drawing showing the chain structure of $[CdCl_3(H_2O)]_n^{n-}$ and the isolated ephedrinium ions. The thermal ellipsoids are drawn at the 50% probability level and the H atoms are drawn with an arbitrary radius of 0·1 Å.

al., 1983) and in bis(α,α'-bipyridyl)$Cd(H_2O)NO_3^+$ (Rodesiler, Turner, Charles, Griffith & Amma, 1984). It is even longer than that found in $CdCl_2.2\frac{1}{2}H_2O$, ~2·33 Å (Leligny & Monier, 1974). The distances and angles in the ephedrinium ion (see Fig. 2 for atom numbering) are the expected values.

The solid-state cross-polarization magic-angle spinning (CP/MAS) ^{113}Cd NMR signal for this compound is observed at +200 (5) p.p.m., deshielded from the 0·1 mol dm^{-3} $Cd(ClO_4)_2$ in D_2O standard, half width at half peak height in parentheses. This number is to be compared with the CP/MAS ^{113}Cd of +213 p.p.m. (5 chlorine, 1 oxygen, octahedral coordination sphere) in $CdCl_2.\frac{5}{2}$ H_2O (Mennitt *et al.*, 1981), +187 p.p.m. (4 chlorine, 2 oxygen, octahedral coordination sphere) in the same compound and +215 p.p.m. (6 chlorine, octahedral) in $H_3NC_2H_4NH_3^{2+}.CdCl_4^-$ (Honkonen, Griffith, Charles & Amma, 1984).

Although the chemical-shift differences are small, one should be able to compare directly the 5 chlorine, 1 oxygen coordination-sphere signal with other results. The trends make sense in that the stronger the donor–acceptor interaction, the greater should be the deshielding of the ^{113}Cd nucleus. The strongest covalent chemical bonding (octahedral) should be with 6 Cl (+215 p.p.m.); followed by 5 Cl, 1 water oxygen lone pair (+213 p.p.m.); 5 Cl, 1 water oxygen perhaps with a different water orientation (+200 p.p.m.), present case; 4 Cl, 2 water oxygen lone pairs (+187 p.p.m.).

We wish to thank the PHS for research support *via* grant GM-27721 and the NSF-supported regional NMR centers at the University of South Carolina (CHE 78-18723) and Colorado State University (CHE 78-18581) for their help, discussions and assistance with the ^{113}Cd NMR data.

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Structure of a Second Crystalline Form of a Molybdenum Trioxide–Dimethyl Sulphoxide Polymer, $Mo_3O_9.4(CH_3)_2SO$

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Abstract. $M_r = 744\cdot3$, orthorhombic, $P2_12_12$, $a = 10\cdot4455$ (16), $b = 13\cdot5653$ (20), $c = 7\cdot8997$ (10) Å, $V = 1119\cdot36$ (28) Å^3, $D_m = 2\cdot20$, $D_x = 2\cdot21$ Mg m^{-3}, $Z = 2$, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 2\cdot029$ mm^{-1}, $F(000) = 732$, $T = 298$ K, $R = 0\cdot0338$, $R_w = 0\cdot0358$, 1508 observed reflections. The form of this dimorphous

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polymer $Mo_3O_9.4dmso$ (dmso = dimethyl sulphoxide) resembles the previously characterized form [McCarron & Harlow (1983). *J. Chem. Soc. Chem. Commun.* pp. 90–91] in containing a chain in which there is the same sequence $Mo_{tet}Mo_{oct}Mo_{oct}$ of tetrahedrally and octahedrally coordinated centres. However, the asymmetric unit is smaller and the bridging O bond angles are lower [Mo_{tet}—O—Mo_{oct} = 134·6 (2), Mo_{oct}—O—Mo_{oct} = 145·1 (4)° in the present structure]. The differing chain-packing arrangements in the two forms are discussed.

Introduction. The crystal structure of a phase of composition $Mo_3O_9.4dmso$ which is readily obtainable from solutions of molybdenum trioxide or molybdic acid in dimethyl sulphoxide has recently been determined (McCarron & Harlow, 1983). They showed this crystalline form, (i), to contain polymer chains with a relatively large asymmetric unit extending over six Mo atoms. In the course of our own work on the MoO_3–dmso system (Hider & Wilkins, 1984) we found that slow cooling of an almost saturated solution of the trioxide in dmso within the temperature range 393–373 K often produced small needles of a second crystalline phase, (ii), having the same composition $Mo_3O_9.4dmso$. The infrared spectra of the two forms differed chiefly in the 760–650 cm^{-1} region containing the O bridge vibrations and in view of the unusual association of tetrahedral and octahedral Mo^{VI} centres in the polymer chain of form (i), it was of interest to determine the crystal structure of (ii).

Experimental. Data from a stubby needle 0·31 × 0·13 × 0·10 mm. D_m by flotation ($CCl_4 + CHBr_3$). Nicolet *R3M* four-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation. Space group from systematic absences $P2_12_12$; cell parameters determined using least-squares refinement on 25 accurately centred reflections ($26° < 2\theta < 34°$). 1749 unique reflections recorded, θ–2θ scan technique, $2\theta_{max} = 58°$ (h 0→15, k 0→19, l 0→11), 1508 [$I > 3\sigma(I)$] used in analysis. Crystal stability monitored but no significant variation in 600, 060, 005 intensities. Lorentz–polarization and absorption corrections (transmission range 0·585–0·671). One Mo atom located from a Patterson map and the remaining non-hydrogen atoms from difference Fourier syntheses. H atoms not located, but introduced at calculated positions. Least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms; thermal parameters for H held at 1·2 U for their carrier atoms. $\sum w||F_o|-|F_c||^2$ minimized, 127 parameters, $R = 0·0338$, $R_w = 0·0358$; $w = [\sigma^2(F_o) + 0·00094F_o^2]^{-1}$. $(\Delta/\sigma)_{max} = 0·007$. Final difference Fourier maps showed no significant residual features ($\Delta\rho$ within −1·4 and +0·5 e Å^{-3}) so that there is no evidence of ligand disorder, as exists in form (i). The *SHELXTL* (version 3) package used included atomic scattering factors and all programs required for data reduction and structure determination (Sheldrick, 1981).

Discussion. Atomic parameters are listed in Table 1* and interatomic distances and bond angles in Table 2, with the atom numbering as in Fig. 1. The tetrahedrally coordinated Mo(1) and the O(2) atom bridging the two octahedrally coordinated centres, Mo(2) and Mo(2′), lie on special positions. O(2) and O(2′) provide chain linking at either end of a stoichiometric unit, which itself comprises two asymmetric units sharing Mo(1). The two dmso ligands coordinated through O(6) lie alternately on opposite sides of the chain, while the ligands coordinated through O(7) lie in the same direction (*i.e.* upwards from the plane of the paper). Within the cell (Fig. 2)* the chains extend along the *a* axis with their positions related through twofold screw axes. The O(6) ligands extend into recesses bounded mainly by O atoms. Disposition of the O(7) ligands, on the other hand, is largely in the direction of the *c* axis, with all ligands on a given chain extending in either the positive or negative direction, so that they straddle the equivalent adjacent chain. The view along the *c* axis (Fig. 2) shows further that (moving along the *b* axis) there is an alternation of chains with positive and negative dispositions of these O(7) ligands, in accordance with the screw-axis relationship. Table 3 (deposited) lists distances (up to 4 Å) from the C(1), C(2), C(3) and C(4) atoms of the ligand methyl groups to their surrounding non-bonded atoms. There are close O contacts in the range 3·16–3·41 Å and other enclosing O atoms lie at 3·62–3·69 Å. Four C···C distances fall in the range 3·47–3·93 Å.

Bond lengths in the present structure are closely similar to the average values of the comparable bonds in form (i) and fall within the usual ranges for the various bond types. However, O bridge angles along the chains are quite different in the two forms, since in form (i) $Mo_{tet}O_bMo_{oct}$ values are 137·7, 155·2, 169·2, 165·5° [*cf.* form (ii) 134·6 (2)°] and $Mo_{oct}O_bMo_{oct}$ angles are 165·8, 180° [*cf.* form (ii) 145·1 (4)°]. The chain packing in the crystals is also entirely different since form (i) contains subparallel flexed chains (Fig. 3) with the reversal of orientation in alternate chains producing relatively small effects on the disposition of the dmso ligands. The dimorphism of the polymer can thus be related to variability in O bond angles in conjunction with the availability of completely different packing arrangements, which nevertheless permit

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* Lists of structure amplitudes, anisotropic thermal parameters, calculated H-atom coordinates, interatomic contacts <4 Å, and stereoscopic versions of Figs. 2 and 3 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39514 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($Å^2 \times 10^3$)

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	U_{eq}
Mo(1)	5000	5000	8047	28 (1)
Mo(2)	8925 (1)	4742 (1)	7017 (1)	20 (1)
S(1)	8262 (2)	5466 (1)	11141 (2)	33 (1)
S(2)	8906 (2)	7169 (1)	7138 (3)	30 (1)
O(1)	6420 (4)	5053 (4)	6690 (5)	29 (1)
O(2)	10000	5000	7739 (8)	25 (2)
O(3)	5146 (6)	4004 (6)	9306 (9)	77 (3)
O(4)	8042 (4)	3676 (4)	8077 (8)	43 (2)
O(5)	8564 (4)	4373 (4)	4983 (7)	38 (1)
O(6)	8399 (5)	6314 (3)	6092 (6)	32 (1)
O(7)	7801 (4)	5653 (4)	9333 (5)	28 (1)
C(1)	6938 (7)	5850 (9)	12377 (9)	59 (3)
C(2)	9305 (8)	6424 (7)	11616 (12)	55 (3)
C(3)	9406 (8)	8010 (6)	5574 (12)	49 (3)
C(4)	7557 (9)	7819 (6)	7885 (12)	54 (3)

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

Mo(1)–O(1)	1·832 (4)	Mo(2)–O(7)	2·268 (4)
Mo(1)–O(3)	1·685 (8)	S(1)–O(7)	1·528 (5)
Mo(2)–O(1)	2·020 (4)	S(1)–C(1)	1·771 (8)
Mo(2)–O(2)	1·903 (2)	S(1)–C(2)	1·736 (9)
Mo(2)–O(4)	1·691 (5)	S(2)–O(6)	1·519 (5)
Mo(2)–O(5)	1·706 (5)	S(2)–C(3)	1·762 (9)
Mo(2)–O(6)	2·257 (4)	S(2)–C(4)	1·764 (9)
Mo(1)–O(1)–Mo(2)	134·6 (2)	O(2)–Mo(2)–O(7)	82·6 (2)
Mo(2)–O(2)–Mo(2′)	145·1 (4)	O(4)–Mo(2)–O(5)	104·0 (3)
O(1)–Mo(1)–O(1′)	108·4 (3)	O(4)–Mo(2)–O(6)	167·2 (2)
O(1)–Mo(1)–O(3)	107·7 (3)	O(4)–Mo(2)–O(7)	91·8 (2)
O(1)–Mo(1)–O(3′)	112·8 (3)	O(5)–Mo(2)–O(6)	88·0 (2)
O(1′)–Mo(1)–O(3)	112·8 (3)	O(5)–Mo(2)–O(7)	163·2 (2)
O(1′)–Mo(1)–O(3′)	107·7 (3)	O(6)–Mo(2)–O(7)	75·9 (2)
O(3)–Mo(1)–O(3′)	107·7 (5)	O(6)–S(2)–C(3)	102·5 (3)
O(1)–Mo(2)–O(2)	155·1 (2)	O(6)–S(2)–C(4)	106·5 (3)
O(1)–Mo(2)–O(4)	95·2 (2)	C(3)–S(2)–C(4)	98·4 (4)
O(1)–Mo(2)–O(5)	95·8 (2)	O(7)–S(1)–C(1)	102·7 (3)
O(1)–Mo(2)–O(6)	78·9 (2)	O(7)–S(1)–C(2)	106·0 (4)
O(1)–Mo(2)–O(7)	76·6 (2)	C(1)–S(1)–C(2)	98·7 (5)
O(2)–Mo(2)–O(4)	98·9 (2)	Mo(2)–O(6)–S(2)	124·2 (3)
O(2)–Mo(2)–O(5)	100·5 (2)	Mo(2)–O(7)–S(1)	126·3 (3)
O(2)–Mo(2)–O(6)	83·0 (1)		

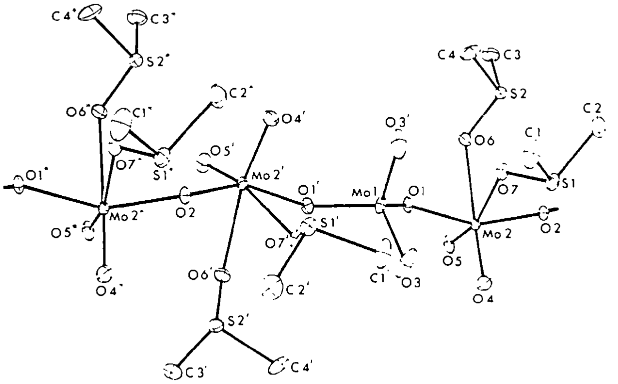

Fig. 1. The chain structure of the polymer, plotted with 20% thermal ellipsoids. The stoichiometric unit extends between the O(2′) and O(2) bridging atoms and is divided into two asymmetric units at Mo(1).

attainment of closely similar densities, *viz* (i) 2·18, (ii) 2·21 Mg m^{-3}. The appearance of the otherwise unexpected stoichiometry Mo_3O_9.4dmso may itself be a consequence of these factors.

O bond angles between Mo^{VI} centres are characteristically variable, but without imposed constraints single core-O bridges tend towards 180°, as in anion complexes containing the Mo_2O_5 core (Cotton, Morehouse & Wood, 1964; Knobler, Penfold, Robinson, Wilkins & Yong, 1980). Angles as low as 125–130° are well known, but only when there is bending brought about by an additional ligand-O bridge, as for example with coordinated malate (Porai-Koshits, Aslanov, Ivanova & Polynova, 1968). A bridging angle of 162° in association with two weakly constraining H bonds has been reported (Matheson & Penfold, 1979). The low O_b angles in the present dimorphs, especially form (ii), apparently develop in response to the 'lock and key' effect arising from packing of the laterally extended ligands. These low angles afford evidence of the response of the angle to relatively small crystal forces.

The association of tetrahedral and octahedral Mo as in these neutral structures is not common, although it is

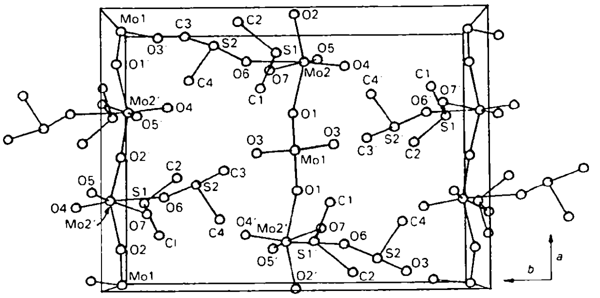

Fig. 2. Chain packing and ligand orientation in the present form, (ii), of the polymer, as viewed along **c**.

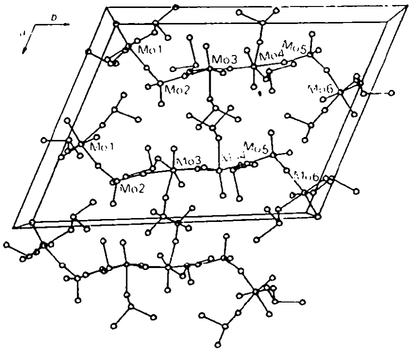

Fig. 3. The packing of the polymer chains in form (i) viewed along **c**, as plotted from the coordinates given in McCarron & Harlow (1983).

known in molybdates (Magarill & Klevtsova, 1972; Day, Fredrich, Klemperer & Shum, 1977). It does imply, however, that Mo may not have a particularly strong preference for octahedral over tetrahedral coordination, as was originally remarked upon by Kihlborg (1963) in his interpretation of the molybdenum trioxide structure. It may be noted that solutions of molybdenum trioxide in dmso show significant conductivity, Λ_m (for an Mo_3O_9 unit) = 9·6 Ω^{-1} cm^{2}mol^{-1} at 298 K, and 34·1 Ω^{-1} cm^{2}mol^{-1} at 388 K. This raises the possibility that crystallization of the chain polymer may occur by way of ionic species, *viz* $Mo_2O_5(dmso)_n^{2+}$ and MoO_4^{2-}.

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Coordination Chemistry of Alkali and Alkaline-Earth Cations: X-ray Structural Redetermination of Tetraaquabis(1,10-phenanthroline)barium(II) Perchlorate–Bis(1,10-phenanthroline), $[Ba(C_{12}H_8N_2)_2(H_2O)_4](ClO_4)_2.2C_{12}H_8N_2$

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Abstract. $M_r = 1129{\cdot}1$, triclinic, $P\bar{1}$, $a = 7{\cdot}026\ (2)$, $b = 13{\cdot}003\ (3)$, $c = 13{\cdot}361\ (2)$ Å, $\alpha = 75{\cdot}51\ (2)$, $\beta = 84{\cdot}84\ (2)$, $\gamma = 80{\cdot}00\ (2)^\circ$, $V = 1162{\cdot}5\ (4)$ Å^3, $Z = 1$, $D_m = 1{\cdot}610$, $D_x = 1{\cdot}613$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}5418$ Å, $\mu = 8{\cdot}347$ mm^{-1}, $F(000) = 570$, $T = 293$ K, $R = 0{\cdot}055$ for 3955 unique reflections. Four N atoms from two *o*-phenanthrolines and four O atoms from four water molecules are coordinated to Ba in a distorted cubic arrangement. Two other phenanthrolines are stacked parallel to the coordinated phenanthrolines, slightly offset with one above and one below the plane formed by the coordinated phenanthrolines. The previously reported structure [Smith, O'Reilly, Kennard & White (1977). *J. Chem. Soc. Dalton Trans.* (12), pp. 1184–1190] is confirmed.

Introduction. The structure of $[Ba(phen)_2(H_2O)_4](ClO_4)_2.2phen$ (phen is 1,10-phenanthroline) was previously determined (Smith, O'Reilly, Kennard & White, 1977) and refined to $R = 0{\cdot}13$. Our structure, refined to $R = 0{\cdot}055$, confirms the original determination but has resulted in additional insight concerning the chemistry involved.

In an attempt to understand the biological functions of Na, K, Ca, and Mg (Poonia & Bajaj, 1979; Poonia, 1981), one of the authors (NSP) has been interested in complexation and structural studies of M^{2+}.phen complexes (Vijaywargia, 1983). The complex $[Ba(phen)_2(H_2O)_4](ClO_4)_2.2phen$ which was encountered during these studies had been reported earlier (Pfeiffer & Christeleit, 1938; Schilt & Taylor, 1959) and had been examined crystallographically (Smith, O'Reilly, Kennard & White, 1977). The compound was

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