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Structure of $SnMo_5O_8$ Containing Bioctahedral Mo_{10} Clusters

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Abstract. Tin pentamolybdate, $SnMo_5O_8$, $M_r = 726{\cdot}4$, monoclinic, $P2_1/c$, $a = 7{\cdot}533\ (4)$, $b = 9{\cdot}268\ (4)$, $c = 9{\cdot}970\ (4)$ Å, $\beta = 109{\cdot}73\ (2)°$, $V = 655{\cdot}2\ (5)$ Å^3, $Z = 4$, $D_x = 7{\cdot}363$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 128{\cdot}6$ cm^{-1}, $F(000) = 1296$, $T = 298$ K, $R = 0{\cdot}033$ for 1690 observed reflections. The title compound is isostructural with $LaMo_5O_8$ and therefore contains infinite chains built up from bioctahedral cluster units $Mo_{10}O_{18}$, cross-linked to form channels where the Sn atoms are located.

Introduction. Compounds containing condensed clusters built up from Mo_6 octahedra may be divided in two different types on the basis of their elementary building blocks, namely the Mo_6X_8-type cluster unit which typically occurs in the ternary molybdenum sulfides and selenides and the Mo_6X_{12}-type found in the oxides. In the former group, the Mo_6 clusters condense *via* face sharing as observed in the homologous series $M_{2n-2}Mo_{6n}X_{6n+2}$ (M = Rb, Cs; X = S, Se; n = 2, 3, 4 and 5) in which the number of condensed octahedra is 3, 5, 7 and 9 respectively (Gougeon, 1984; Gougeon, Potel, Padiou & Sergent, 1987, 1988). The end member ($n = \infty$) corresponds to the one-dimensional compounds $M_2Mo_6X_6$ (Potel, Chevrel & Sergent, 1980) comprising infinite chains of face-shared Mo_6 clusters. In the second group, the Mo_6 clusters condense *via* edge sharing as observed for the first time in $NaMo_4O_6$ (Torardi & McCarley, 1979) which contains infinite chains of *trans* edge-shared Mo_6 octahedra. The intermediate clusters of four and five edge-shared Mo_6 octahedra were later isolated in $In_{11}Mo_{40}O_{62}$ (Mattausch, Simon & Peters, 1986).

More recently, the Mo_6 and the Mo_{10} (two edge-shared Mo_6) clusters were obtained in $BaMo_6O_{10}$ (Lii, Wang & Wang, 1988) and $LaMo_5O_8$ (Hibble, Cheetham, Bogle, Wakerley & Cox, 1988) respectively. The structure of these was later determined from X-ray and neutron powder-diffraction data with rather high R factors ($R \sim 11\%$) due to some impurities.

We report here the single-crystal X-ray determination of the structure of $SnMo_5O_8$ which is isostructural with the La phase.

Experimental. Single crystals were obtained by heating a mixture of SnO_2, 2 MoO_3 and 3 Mo in a sealed molybdenum crucible at about 2030 K for 1 h, then cooling to 1673 K at the rate of 25 K h^{-1} and finally to 1273 K at 120 K h^{-1}.

Intensities were measured from a crystal fragment with dimensions $0{\cdot}03 \times 0{\cdot}06 \times 0{\cdot}08$ mm on an Enraf–Nonius CAD-4 diffractometer equipped with graphite-monochromated Mo $K\alpha$ radiation. Accurate cell parameters were obtained by a least-squares refinement of the setting angles of 25 reflections with $7 \le \theta \le 14°$. Systematic absences: $h0l$ ($l = 2n$), $0k0$ ($k = 2n$). 2119 unique reflections were recorded over the range $1 \le \theta \le 32°$ with h: $0 \rightarrow 28$, k: $0 \rightarrow 13$, l: $-14 \rightarrow 14$; ω–2θ scan method was used with scan width $\Delta\omega = (0{\cdot}9 + 0{\cdot}35\tan\theta)°$ and counter aperture $\Delta l = (2 + 0{\cdot}6\tan\theta)$ mm. Three orientation and three intensity control reflections were checked every 250 reflections and every hour respectively and showed no significant variation. Data were corrected for Lorentz–polarization and an empirical absorption correction following the *DIFABS* procedure (Walker & Stuart,

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Table 1. *Positional parameters and equivalent isotropic thermal parameters*

$B_{eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{eq}(Å^2)
Sn	0·26701 (9)	0·51884 (8)	0·52159 (7)	1·16 (1)
Mo(1)	0·61071 (8)	−0·11470 (7)	0·48243 (6)	0·227 (9)
Mo(2)	0·38293 (8)	−0·11723 (7)	0·68149 (6)	0·221 (9)
Mo(3)	0·17715 (8)	−0·12160 (7)	0·38412 (6)	0·204 (9)
Mo(4)	0·80961 (8)	−0·13067 (7)	0·29737 (6)	0·191 (9)
Mo(5)	−0·00029 (8)	−0·12236 (7)	0·58542 (6)	0·201 (9)
O(1)	0·4018 (7)	0·0051 (7)	0·8498 (6)	0·37 (9)
O(2)	0·0047 (8)	−0·2317 (7)	0·9306 (6)	0·38 (9)
O(3)	−0·0152 (8)	0·0036 (7)	0·2358 (6)	0·48 (9)
O(4)	0·3977 (7)	−0·2563 (7)	0·0186 (6)	0·37 (9)
O(5)	0·7999 (8)	−0·2503 (7)	0·1197 (6)	0·52 (9)
O(6)	0·2032 (7)	−0·2520 (7)	0·2201 (6)	0·43 (9)
O(7)	0·5994 (8)	−0·2435 (7)	0·8247 (6)	0·43 (9)
O(8)	0·3874 (7)	−0·0003 (7)	0·3340 (6)	0·46 (9)

Table 2. *Selected interatomic distances* (Å)

Mo(1)—Mo(2)	2·711 (1)	Mo(1)—O(7)	2·030 (6)
Mo(3)	2·772 (1)	O(5)	2·038 (6)
Mo(4)	2·746 (1)	O(8)	2·112 (6)
Mo(5)	2·759 (1)	O(8)	2·114 (6)
Mo(1)*	2·796 (1)	O(4)	2·127 (6)
Mo(2)*	3·030 (1)		
Mo(3)*	3·077 (1)	Mo(2)—O(6)	1·950 (6)
		O(1)	1·990 (6)
Mo(2)—Mo(3)	2·844 (1)	O(4)	2·036 (6)
Mo(4)	2·763 (1)	O(8)	2·094 (6)
Mo(5)	2·718 (1)	O(7)	2·120 (6)
Mo(3)—Mo(4)	2·608 (1)	Mo(3)—O(2)	2·039 (6)
Mo(5)	2·693 (1)	O(3)	2·046 (6)
Mo(5)	2·762 (1)	O(4)	2·082 (6)
		O(6)	2·095 (6)
Mo(4)—Mo(5)	2·743 (1)	O(8)	2·134 (6)
Mo(5)	2·792 (1)		
		Mo(4)—O(3)	2·053 (6)
Mo(5)—Mo(5)	2·837 (1)	O(2)	2·058 (6)
		O(7)	2·058 (6)
Sn—O(1)	2·278 (6)	O(5)	2·070 (6)
O(1)	2·392 (5)	O(1)	2·113 (6)
O(4)	2·415 (6)		
O(3)	2·630 (6)	Mo(5)—O(6)	2·029 (6)
O(2)	2·722 (6)	O(5)	2·031 (6)
O(5)	2·825 (7)	O(2)	2·062 (6)
O(7)	2·869 (6)	O(3)	2·064 (6)
O(8)	2·941 (6)		
O(6)	3·076 (6)		
O(2)	3·236 (6)		

* Intercluster distance.

1983) was applied to isotropically refined data. Min. and max. correction factors were 0·847 and 1·182.

The structure was solved using the *MULTAN*11/82 series of programs (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and subsequent difference Fourier synthesis. The refinement on F of all atoms anisotropically and extinction coefficient (128 variables) converged to $R = 0{\cdot}033$, $wR = 0{\cdot}044$ where $w = 1/[\sigma^2(F_o) + 0{\cdot}0004F^2 + 1]$ (Killean & Lawrence, 1969), $S = 1{\cdot}013$ for 1690 reflections with $F_o^2 \geq 3\sigma(F_o^2)$. In the final cycle of refinement, the largest shift/e.s.d. was $< 0{\cdot}01$ and the largest residuals on final difference map were $+2{\cdot}99$ and $-3{\cdot}06$ e Å^{-3} (near the Sn atom); final value of g was $6{\cdot}38 \times 10^{-7}$ (Stout & Jensen, 1968). Atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). All the calculations were performed on a PDP 11/60 using the *SDP* programs (B. A. Frenz & Associates Inc., 1985). Final atomic coordinates and equivalent isotropic thermal parameters with their e.s.d.'s are given in Table 1 and selected interatomic distances in Table 2.*

Discussion. The main structural building block of $SnMo_5O_8$ is the centrosymmetric double-cluster unit $Mo_{10}O_{18}$ which results from the metal-edge condensation of two Mo_6O_{12}-type clusters (Fig. 1). The condensation process is identical to that described previously for the $Mo_{18}O_{30}$ and $Mo_{22}O_{36}$ units (Mattausch *et al.* 1986) as well as for the infinite chains $|Mo_2Mo_{4/2}O_2O_{8/2}|^1_\infty$ (Torardi *et al.* 1979) which are formed by condensing four, five and an infinity of Mo_6O_{12}-type clusters respectively. The $Mo_{10}O_{18}$ dimers are next linked on opposite edges *via* common O atoms [O(4) and O(8)] to form infinite chains in which the Mo_{10} clusters are strongly linked through Mo(1)—Mo(1) bonds (Fig. 2*a*). This interunit linking is quite similar to that encountered in $Gd_{10}I_{16}(C_2)_2$ comprising $Gd_{10}I_{18}$ double-cluster units centered by dicarbon units (Simon, 1985). The infinite chains which run parallel to the *a* axis are then interlinked through O atoms [O(5), O(6) and

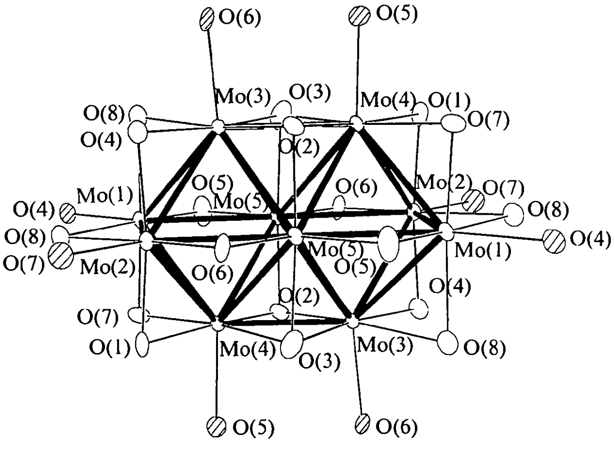

Fig. 1. The $Mo_{10}O_{16}$ cluster unit shown with its eight additional corner-linked O atoms (cross hatched). Inversion center at the middle of the Mo(5)—Mo(5) bonds.

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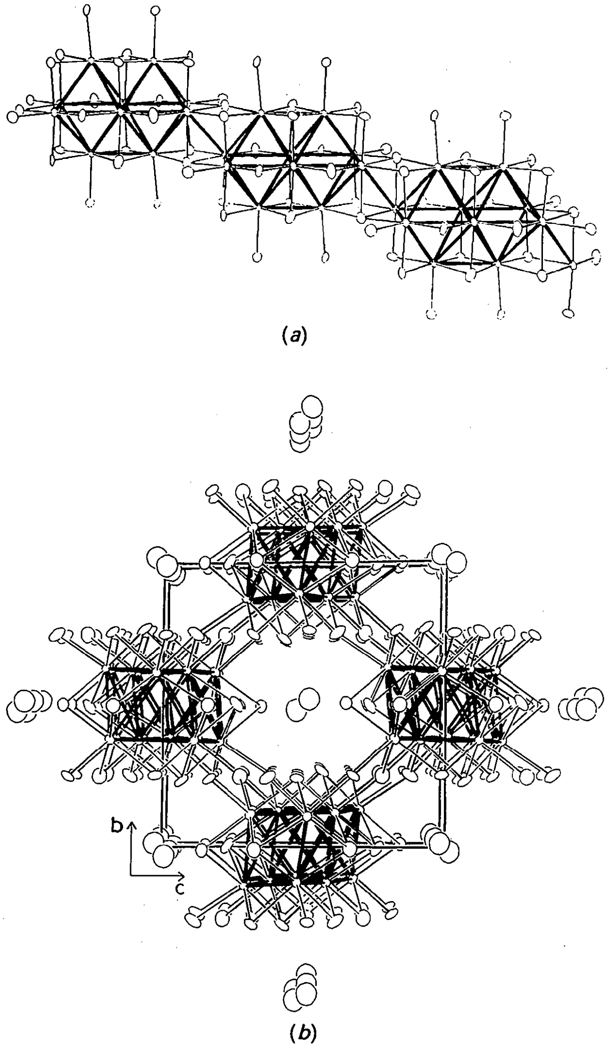
* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52668 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

O(7)] to create one-dimensional channels where the Sn atoms are located (Fig. 2*b*).

From this arrangement, it results that the O atoms are bonded to the Mo atoms in different ways as reflected by the connective formula $|Mo_{10}O^{i}_{6}O^{i\text{-}i}_{4/2}\text{-}O^{i\text{-}a}_{8/2}|O^{a\text{-}i}_{8/2}$: oxygens of *i*-type are O(1) which are only connected to two Mo atoms and O(2) as well as O(3) which are linked to three Mo atoms of one cluster; the oxygen O(8) is of *i-i* type and bridges simultaneously two edges of adjacent Mo_{10} clusters in a chain. The remaining oxygens are of *i-a* or *a-i* type and lie above edges but also coordinate in corner positions neighbouring clusters of the same chain [O(4)] or of an adjacent one [O(5), O(6) and O(7)]. Moreover all the O atoms contribute to the tin environment.


(*a*)

(*b*)

Fig. 2. (*a*) A section of a bioctahedral cluster chain of $SnMo_5O_8$. (*b*) View of the structure down the *a* axis. The unconnected open ellipsoids represent the Sn atoms.

The Mo atoms are found to have different coordination numbers: Mo(1): 5 O + 7 Mo; Mo(2): 5 O + 5 Mo; Mo(3): 5 O + 6 Mo; Mo(4): 5 O + 5 Mo and Mo(5): 4 O + 7 Mo. The Mo—Mo distances within the Mo_{10} cluster range from 2·608 to 2·844 Å while the shortest intercluster distance Mo(1)—Mo(1) is only 2·796 Å. The Mo(1) atom also forms weaker intercluster bonds with Mo(2), 3·030 Å and Mo(3), 3·077 Å. With the exception of the Mo(5) atom, which is shared by both octahedra, the Mo atoms are in an approximately square-pyramidal environment of oxygens with Mo—O distances ranging from 1·950 to 2·134 Å.

The Sn site has no crystallographically imposed symmetry and is surrounded by ten O atoms at distances ranging from 2·278 to 3·236 Å.

By using the bond length–bond strength formula for the Mo–O and Sn–O bonds [$S = (d\text{Mo—O}/1{\cdot}882)^{-6{\cdot}0}$ and $S = (d\text{Sn—O}/1{\cdot}860)^{-4{\cdot}5}$] (Brown & Wu, 1976), the valence of each independent Mo and Sn atom was determined as follows: Mo(1) +3·16, Mo(2) +2·73, Mo(3) +2·77, Mo(4) +2·83, Mo(5) +2·42 and Sn +2·03. From these values, we can deduce an average valence of +2·78 for the molybdenum which is in good agreement with that based on the stoichiometry (+2·8).

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