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Structure of SrMo_5O_8 Containing Chains of Bioctahedral Mo_{10} Clusters

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Abstract

The title compound, strontium pentamolybdate, is isostructural with LaMo_5O_8 and therefore contains bioctahedral $\text{Mo}_{10}\text{O}_{18}$ cluster units strongly linked by $\text{Mo}(1)\text{—Mo}(1)$ intercluster bonds of 2.7651 (9) Å to form infinite molybdenum oxide chains. These are interconnected through Mo—O—Mo bonds to create four-sided channels, in which the Sr^{2+} cations are located. The Mo—Mo distances within the Mo_{10} cluster lie between 2.6034 (6) and 2.8324 (9) Å (average 2.740 Å). The Mo—O distances range between 1.902 (4) and 2.148 (4) Å (average 2.062 Å). The Sr^{2+} cation is surrounded by ten O atoms at distances ranging from 2.529 (4) to 2.935 (4) Å, with an eleventh O atom at 3.219 (4) Å.

Comment

The present work constitutes part of our program on the study of the structural and physical properties of the compounds MMo_5O_8 ($M = \text{Ca}, \text{Sr}, \text{Ba}, \text{Sn}, \text{Pb}, \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}$ and Gd), containing chains of bioctahedral Mo_{10} clusters. The prototype compound LaMo_5O_8 was synthesized by Hibble, Cheetham, Bogle, Wakerley & Cox (1988). Later isostructural compounds were obtained with other

light rare earths (RE) such as Ce, Pr, Nd, Sm, Eu and Gd (Gougeon, Gall & Sergent, 1991; Gall, 1990, 1993), as well as with elements of Group IVB (Sn: Gougeon, Potel & Sergent, 1990; and Pb: Dronskowski & Simon, 1989; Dronskowski, Simon & Mertin, 1991) and alkaline-earth metals (Ca: Torardi & McCarley, 1981; Sr: Gougeon, Gall & Sergent, 1991; and Ba: McCarley, Schimek, Chen & Nagaki, 1992). We present here the crystal structure of SrMo_5O_8 .

The structure type MMo_5O_8 has been described previously in detail by many authors (Hibble, Cheetham, Bogle, Wakerley & Cox, 1988; Dronskowski & Simon, 1989; Gougeon, Potel & Sergent, 1990). Its basic structural building block is the bioctahedral cluster unit $\text{Mo}_{10}\text{O}_{18}$, which results from the metal-edge condensation of two Mo_6O_{12} -type cluster units (Fig. 1). The $\text{Mo}_{10}\text{O}_{18}$ cluster units are linked on opposite edges *via* common O atoms to form infinite chains in which the Mo_{10} clusters are strongly linked through intercluster Mo—Mo bonds (Fig. 2a). These chains, which run parallel to the *a* axis, then interlink through O atoms to create one-dimensional four-sided channels where the cations reside (Fig. 2b).

The Mo—Mo distances within the double-octahedron range between 2.6034 (6) and 2.8324 (9) Å, with the shortest of these occurring between the apical atoms $\text{Mo}(3)$ and $\text{Mo}(4)$ and the largest between the $\text{Mo}(5)$ atoms of the shared edge. The average value is 2.740 Å and does not change significantly from those observed in the other compounds with divalent (SnMo_5O_8 2.746 Å and PbMo_5O_8 2.745 Å) or trivalent cations ($\text{RE}^{3+}\text{Mo}_5\text{O}_8$ 2.746–2.750 Å). The intercluster distances are 2.7651 (9), 3.0380 (6) ($\times 2$) and 3.0869 (6) Å ($\times 2$) and are close to the corresponding distances in SnMo_5O_8 [2.796 (1), 3.037 (1) ($\times 2$) and 3.089 (1) Å ($\times 2$)] and PbMo_5O_8 [2.784 (5), 3.034 (4) ($\times 2$) and 3.083 (3) Å ($\times 2$)]. On the other hand, the two short-

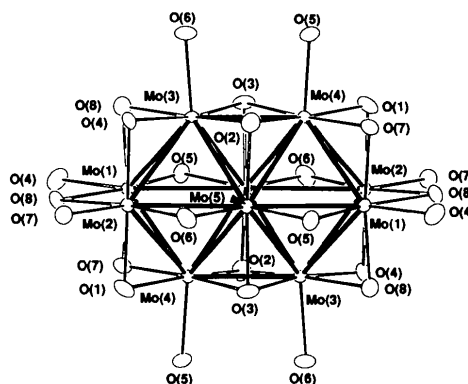


Fig. 1. The $\text{Mo}_{10}\text{O}_{18}$ cluster unit and its eight additional corner-linked O atoms. The inversion centre occurs at the middle of the $\text{Mo}(5)\text{—Mo}(5)$ bond.

est Mo(1)—Mo(1) and Mo(1)—Mo(2) intercluster distances are much larger than those observed in the RE³⁺Mo₅O₈ compounds, which are almost equal to 2.68 and 2.90 Å, respectively (Gall, 1990, 1993). The range of the Mo—O distances is 1.902 (4)–2.148 (4) Å. The average Mo—O distance is 2.062 Å and corresponds to that in SnMo₅O₈ (2.064 Å) or PbMo₅O₈ (2.061 Å). In the RE³⁺Mo₅O₈ compounds, the average values are a little larger, as expected, and range from 2.074 to 2.078 Å.

The Sr²⁺ site has no crystallographically imposed symmetry and is formed from ten O atoms at distances ranging from 2.529 (4) to 2.935 (4) Å, with an eleventh O atom at 3.219 (4) Å.

By using the bond-length–bond-strength formula (Brown & Wu, 1976) for the Mo—O bonds [$s = (d_{\text{Mo—O}}/1.882)^{-6.0}$], the valence of each independent Mo atom was determined as follows: Mo(1) +2.76, Mo(2) +3.31, Mo(3) +2.76, Mo(4) +2.82 and Mo(5) +2.42. From these values, we can deduce an average Mo oxidation state of +2.81 in SrMo₅O₈, which agrees very well with that based on the stoichiometry, +2.80. A similar calculation for the Sr ions [$s = (d_{\text{Sr—O}}/2.143)^{-7.0}$] leads to the value of +2.02, which is also close to the expected value of +2.

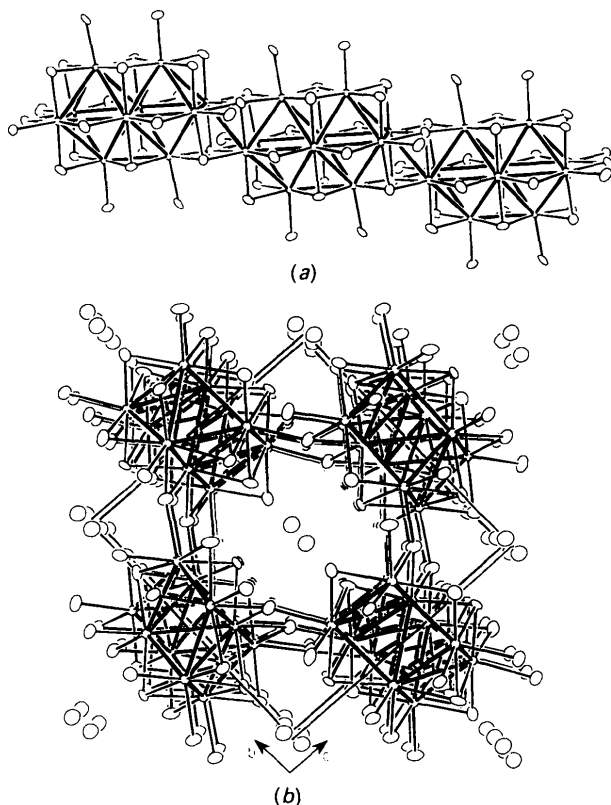


Fig. 2. (a) A section of a bioctahedral cluster chain of SrMo₅O₈; (b) view of the structure down the *a* axis. The unconnected open ellipsoids represent the Sr²⁺ cations.

Experimental

Crystal data

SrMo₅O₈
 $M_r = 695.32$
 Monoclinic
 $P2_1/c$
 $a = 7.553 (2) \text{ \AA}$
 $b = 9.1556 (8) \text{ \AA}$
 $c = 9.966 (2) \text{ \AA}$
 $\beta = 109.301 (8)^\circ$
 $V = 650.4 (2) \text{ \AA}^3$
 $Z = 4$

$D_x = 7.101 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 25 reflections
 $\theta = 13.2\text{--}29.6^\circ$
 $\mu = 17.01 \text{ mm}^{-1}$
 $T = 295 \text{ K}$
 Irregular
 $0.11 \times 0.09 \times 0.08 \text{ mm}$
 Black

Data collection

Enraf-Nonius CAD-4 diffractometer
 ω - 2θ scans
 Absorption correction: empirical (DIFABS; Walker & Stuart, 1983)
 $T_{\text{min}} = 0.875$, $T_{\text{max}} = 1.082$
 3179 measured reflections
 2550 independent reflections

1958 observed reflections [$I > 2\sigma(I)$]
 $R_{\text{int}} = 0.029$
 $\theta_{\text{max}} = 35^\circ$
 $h = 0 \rightarrow 12$
 $k = 0 \rightarrow 14$
 $l = -16 \rightarrow 16$
 3 standard reflections
 frequency: 90 min
 intensity variation: -0.1%

Refinement

Refinement on F
 $R = 0.029$
 $wR = 0.034$
 $S = 1.065$
 1958 reflections
 128 parameters
 $w = 4F_o^2 / [\sigma^2(F_o^2) + (0.04F_o^2)^2]$
 $(\Delta/\sigma)_{\text{max}} < 0.01$

$\Delta\rho_{\text{max}} = 1.79 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.86 \text{ e \AA}^{-3}$
 Extinction correction: Stout & Jensen (1968)
 Extinction coefficient: $1.078 (7) \times 10^{-6}$
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

The structure was solved using MULTAN11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and subsequent difference Fourier syntheses. Refinement of the occupancy factor for the Sr site confirmed that it is fully occupied. All calculations were performed using the MolEN (Fair, 1990) programs on a Digital MicroVAX 3100.

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2)

$$B_{\text{eq}} = \left(\frac{4}{3}\right) \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
Sr	0.25329 (7)	0.50438 (6)	0.53902 (5)	0.565 (8)
Mo(1)	0.61055 (6)	-0.11419 (5)	0.48310 (4)	0.197 (6)
Mo(2)	0.37999 (6)	-0.11642 (5)	0.68173 (4)	0.218 (6)
Mo(3)	0.17811 (6)	-0.12613 (5)	0.38723 (4)	0.202 (6)
Mo(4)	0.81300 (6)	-0.13202 (5)	0.29940 (4)	0.199 (6)
Mo(5)	-0.00147 (6)	-0.12251 (5)	0.58638 (4)	0.201 (6)
O(1)	0.3950 (5)	0.0057 (4)	0.8395 (4)	0.38 (6)
O(2)	0.0045 (5)	-0.2248 (4)	0.9357 (4)	0.32 (6)
O(3)	-0.0078 (5)	0.0006 (4)	0.2371 (4)	0.37 (6)
O(4)	0.4010 (5)	-0.2563 (4)	0.0196 (4)	0.38 (6)
O(5)	0.7983 (5)	-0.2486 (5)	0.1179 (4)	0.43 (6)
O(6)	0.2018 (5)	-0.2462 (4)	0.2160 (4)	0.43 (6)
O(7)	0.6029 (5)	-0.2401 (5)	0.8270 (4)	0.50 (6)
O(8)	0.3864 (5)	-0.0017 (5)	0.3335 (4)	0.36 (6)

Table 2. Selected geometric parameters (Å)

Mo(1)—Mo(2)	2.6905 (6)	Sr—O(3)	3.219 (4)
Mo(1)—Mo(4)	2.7507 (6)	Mo(1)—O(5)	2.034 (4)
Mo(1)—Mo(5)	2.7672 (6)	Mo(1)—O(7)	2.036 (4)
Mo(1)—Mo(3)	2.7740 (7)	Mo(1)—O(4)	2.104 (4)
Mo(1)—Mo(1)*	2.7651 (9)	Mo(1)—O(8)	2.106 (4)
Mo(1)—Mo(2)*	3.0380 (6)	Mo(1)—O(8)	2.117 (4)
Mo(1)—Mo(3)*	3.0869 (6)	Mo(2)—O(1)	1.902 (4)
Mo(2)—Mo(5)	2.7196 (6)	Mo(2)—O(6)	1.953 (4)
Mo(2)—Mo(4)	2.7413 (7)	Mo(2)—O(4)	2.040 (4)
Mo(2)—Mo(3)	2.8263 (6)	Mo(2)—O(8)	2.117 (4)
Mo(3)—Mo(4)	2.6034 (6)	Mo(2)—O(7)	2.145 (4)
Mo(3)—Mo(5)	2.6950 (6)	Mo(3)—O(3)	2.042 (4)
Mo(3)—Mo(5)	2.7494 (6)	Mo(3)—O(2)	2.058 (4)
Mo(4)—Mo(5)	2.7389 (6)	Mo(3)—O(4)	2.065 (4)
Mo(4)—Mo(5)	2.7715 (7)	Mo(3)—O(6)	2.087 (4)
Mo(5)—Mo(5)	2.8324 (9)	Mo(3)—O(8)	2.148 (4)
Sr—O(1)	2.529 (4)	Mo(4)—O(3)	2.061 (4)
Sr—O(1)	2.552 (4)	Mo(4)—O(7)	2.062 (4)
Sr—O(4)	2.597 (4)	Mo(4)—O(1)	2.070 (4)
Sr—O(7)	2.648 (4)	Mo(4)—O(5)	2.071 (4)
Sr—O(2)	2.718 (4)	Mo(4)—O(2)	2.087 (4)
Sr—O(5)	2.750 (4)	Mo(5)—O(5)	2.023 (4)
Sr—O(3)	2.764 (4)	Mo(5)—O(6)	2.039 (4)
Sr—O(8)	2.770 (4)	Mo(5)—O(2)	2.063 (4)
Sr—O(2)	2.930 (4)	Mo(5)—O(3)	2.065 (4)
Sr—O(6)	2.935 (4)		

* Intercluster distance.

Single crystals were obtained by heating a stoichiometric mixture (starting materials SrMoO₄, MoO₃ and Mo) in a sealed molybdenum crucible at ca 2220 K for 15 min. The crucible was then cooled at the rate of 100 K h⁻¹ to 1300 K and finally furnace-cooled to room temperature.

Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71430 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: DU1050]

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Sn_{8.7}(Ni_{0.5}Zn_{0.4}Cu_{0.1})_{10.4}, a New Tin-Based Alloy from a Complex Metallic Mixture

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Abstract

The title alloy has a complicated composition, Sn_{8.7}(Ni_{0.5}Zn_{0.4}Cu_{0.1})_{10.4}, and was synthesized from the elements. It is a new structure type consisting of primitive cubic (p.c.), body-centred cubic (b.c.c.) and face-centred cubic (f.c.c.) blocks. It is related to γ -brass and to BaHg₁₁. The compound undergoes a phase transition to a CsCl-type structure when subjected to the electron beam of a high-resolution electron microscope.

Comment

Tin-based alloys are of vast technological importance and include materials such as soft solder, type metal, fusible metal, pewter, bronze, bell metal, Babbitt's metal, white metal, die-casting alloy and phosphor-bronze. As tin can act as both metal and non-metal, the compounds of tin exhibit a rich and varied structural chemistry of great theoretical interest.

In search of new tin-based alloys, equal amounts of Al, Zn, Cu, Ni, Co, Fe, Mn, Cr, V, Mg and Ti were mixed together with a large excess of Sn. The mixture was heated under Ar in a sealed stainless-steel ampoule to 1073 K for 5 h and then cooled to room temperature at a rate of approximately 100 K h⁻¹. After leaching the ingot in hydrochloric acid (6 M) for 3 days, the residue consisted of crystals of mainly three different habits, one being dull-greyish thin hexagonal rods and needles, the other two silvery metallic cuboctahedra or fat rods. The thin hexagonal rods were of the CoSn type and are discussed elsewhere (Larsson & Lidin, 1994). The latter two habits proved to come from the same cubic phase.