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$Sn_{4.4}Mo_{24}O_{38}$

N. Barrier, J. Tortelier and P. Gougeon*

Laboratoire de Chimie du Solide et Inorganique Moléculaire, URA CNRS No. 6511, Université de Rennes I, Avenue du Général Leclerc, 35042 Rennes CEDEX, France
Correspondence e-mail: patrick.gougeon@univ-rennes1.fr

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The single-crystal structure of tetratin tetracosamolybdenum octatriacontaoxide, $Sn_{4.4}Mo_{24}O_{38}$, contains infinite chains of centrosymmetric dioctahedral Mo_{10} and centrosymmetric trioctahedral Mo_{14} clusters. These clusters, as well as the O atoms, the arrangement of which derives from a closest-packing with the layer sequence ...*ABAC*..., form sheets parallel to the *ac* plane of the monoclinic unit cell. The Mo—Mo distances range from 2.6225 (7) to 2.8212 (9) Å and from 2.6270 (7) to 2.8365 (7) Å in the Mo_{10} and Mo_{14} clusters, respectively. The Mo—O distances vary between 1.949 (4) and 2.151 (4) Å in the Mo_{10} cluster and between 1.938 (4) and 2.140 (4) Å in the Mo_{14} cluster. The three crystallographically independent Sn^{2+} ions are off the centre of distorted oxygen octahedra.

Comment

Finite cluster chains built up from *trans*-edge-shared Mo_6 octahedra were first discovered in $In_{11}Mo_{40}O_{62}$ (Mattausch *et al.*, 1986), where tetraoctahedral Mo_{18} and pentaoctahedral Mo_{22} clusters co-exist in equal proportion. Subsequently, several reduced molybdenum oxides of the form $M_{n-x}Mo_{4n+2}O_{6n+4}$ containing finite Mo_{4n+2} clusters (*n* denotes the number of *trans*-edge-shared Mo octahedra) with $n = 1$ (Lii *et al.*, 1988), $n = 2$ (Hibble *et al.*, 1988), $n = 3$ (Dronskowski & Simon, 1991; Schimek *et al.*, 1995), $n = 4$ (Schimek *et al.*, 1994; Fais *et al.*, 1995) and $n = 5$ (Dronskowski *et al.*, 1993; Schimek & McCarley, 1994) were synthesized by either solid-state reaction or fused-salt electrolysis. The final member of the series corresponds to $NaMo_4O_6$ (Torardi & McCarley, 1979), in which infinite chains of *trans*-edge-shared Mo_6 octahedra occur. While in the first members of the $M_{n-x}Mo_{4n+2}O_{6n+4}$ series, the Mo_{4n+2} clusters form either zigzag ($n = 1$) or stair-step ($n = 2$ or 3) infinite chains in which the shortest Mo—Mo distances between Mo_{4n+2} clusters vary from 2.67 to 2.80 Å, in the compounds containing larger clusters ($n = 4$ or 5), intercluster distances are greater than 3 Å, leading to only weak metal–metal interaction between the Mo clusters. In the early nineties, investigation of the Sn—Mo—O system led us to the synthesis of $Sn_2Mo_{10}O_{16}$ (Gougeon *et al.*, 1990) containing infinite stair-step chains of dioctahedral Mo_{10} clusters ($n = 2$).

Recent high-resolution electron microscopy (HREM) investigations on reduced tin oxomolybdates in the $Sn_xMo_{10}O_{16}$–$Sn_yMo_{14}O_{22}$ system revealed random and ordered intergrowth of di- and trioctahedral cluster structures (Ramlau *et al.*, 1996). In particular, ordered regions consisting of alternating layers of di- and trioctahedral clusters were observed. The resulting structure was found to be orthorhombic, with approximate cell parameters $a = 10$, $b = 9.3$ and $c = 34$ Å, and the composition $Sn_{4.4}Mo_{24}O_{38}$. We present here the crystal structure of a new compound having the same composition, $Sn_{4.4}Mo_{24}O_{38}$, but crystallizing in the monoclinic system. This new compound is characterized by infinite chains based on dioctahedral Mo_{10} and trioctahedral Mo_{14} clusters.

The metal–oxygen framework of the title compound consists of infinite cluster chains built up from alternating $Mo_{10}O_{26}$ and $Mo_{14}O_{30}$ cluster units (Fig. 1) which are arranged in layers parallel to the *ac* plane. The oxygen network can be derived from a stacking of close-packed layers with the sequence ...*ABAC*... along the *b* direction. While the *B* ($y \simeq 0.25$) and *C* ($y \simeq 0.75$) layers are occupied entirely by O atoms and have the composition O_{24}, in the *A* layers ($y \simeq 0.0$ and $\simeq 0.5$), ten of the 24 O atoms are missing. The Sn atoms partially occupy sites close to those of some of the missing O atoms. Within the oxygen network, half of the octahedral interstices are occupied by the atoms which form di- and trioctahedral Mo_{10} and Mo_{14} clusters (Fig. 2). The interconnection between both types of cluster units within the chains is identical to that observed between the $Mo_{10}O_{26}$ units in the series of compounds $M_2Mo_{10}O_{16}$ (Hibble *et al.*, 1988). The shortest intercluster Mo—Mo distances in the title compound are 2.7704 (6) Å for Mo1—Mo6, 2.9854 (7) Å for Mo2—Mo6, 3.0244 (7) Å for Mo1—Mo7, 3.0614 (7) Å for Mo1—Mo9 and 3.0856 (7) Å for Mo4—Mo6, while the Mo—Mo distances between adjacent Mo chains are greater than 4 Å. The Mo—Mo distances within the dioctahedral Mo_{10} cluster range from 2.6225 (7) to 2.8212 (9) Å, with an average distance of 2.747 Å. The Mo—O distances vary from 1.949 (4) to 2.151 (4) Å (average value 2.065 Å). In the trioctahedral cluster, the Mo—Mo distances lie in about the same range [2.6270 (7)–2.8365 (7) Å], if we preclude the non-bonding apical Mo8—Mo12 distance of 2.9972 Å. The average Mo—Mo bond distance is 2.763 Å and the Mo—O distances vary from 1.938 (4) to 2.140(4) Å (average value 2.058 Å).

The infinite chains which run parallel to the [101] direction are then interlinked through O atoms to form layers parallel to the *ac* plane which are shifted by *c*/2 with respect to each other. This leads to one-dimensional channels delimited by the Mo—O chains, where the Sn^{2+} cations are distributed statistically over three crystallographically independent distorted octahedral sites. The existence of compounds with $n = 2$, $M_2Mo_{10}O_{16}$ (M = Ca, Sr, Sn, Pb, La, Ce, Pr, Nd, Sm, Eu or Gd; Gall, 1993) and $n = 3$, $K_{3-x}M_xMo_{14}O_{22}$ ($x = 0$, $x = 1.34$ for M = Pb and $x = 1.71$ for M = Sn; Schimek *et al.*, 1995) and $Tl_{1.6}Sn_{1.2}Mo_{14}O_{22}$ (Dronskowski & Simon, 1991), containing, respectively, only Mo_{10} and Mo_{14} clusters with different electron

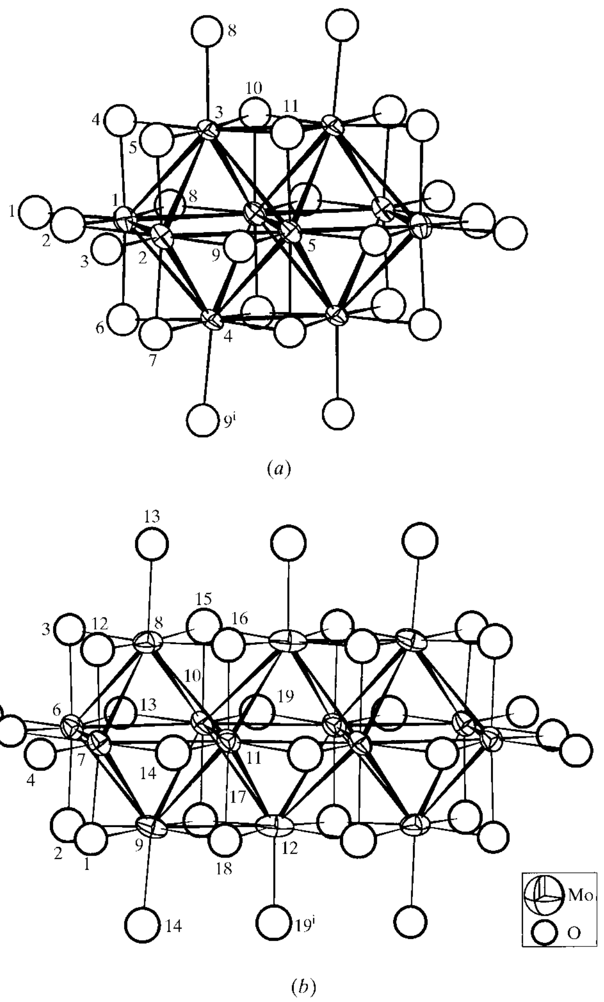

Figure 1
View of (*a*) the Mo_{10} and (*b*) the Mo_{14} clusters with their oxygen environment. Displacement ellipsoids are drawn at the 97% probability level [symmetry code: (i) $-x, \frac{1}{2}+y, \frac{1}{2}-z$].

counts, leads us to a comparative study of the Mo—Mo distances in the last two series of compounds with those in $Sn_{4.4}Mo_{24}O_{38}$ for each cluster-type. This study clearly revealed that the different Mo—Mo distances within the Mo_{10} and Mo_{14} clusters present in $Sn_{4.4}Mo_{24}O_{38}$ compare well with those observed in $M_2Mo_{10}O_{16}$ (M is a divalent cation) for the dioctahedral cluster and with those in $K_{1.66}Pb_{1.34}Mo_{14}O_{22}$ for the trioctahedron. Consequently, we can roughly estimate 32 and 44.3 electrons per Mo_{10} and Mo_{14} cluster, respectively. These values lead to a total of 76.3 electrons and to the hypothetical formula $Sn_2Mo_{10}O_{16}$–$Sn_{2.15}Mo_{14}O_{22}$. The excess of electrons brought by the supplementary 0.25 Sn in the investigated compound are accommodated in the intercluster bonds, as confirmed by the shorter intercluster bonds observed in the title compound compared with those in $Sn_2Mo_{10}O_{16}$ and $K_{1.66}Pb_{1.34}Mo_{14}O_{22}$. By using the Pauling bond order (Pauling, 1960), we could estimate the excess to be about 0.7 electron, leading to 77 electrons on the Mo network. This value is close to that of 76.8 electrons based on the stoichiometry, given Sn^{2+} and O^{2-}. In addition, the valences of the 12 crystallographically independent Mo atoms were calculated from the Mo—O bond lengths using the relationship of Brown & Wu (1976). This yields an average value of 2.785 and thus a total of 77 electrons on the Mo network, which is in good agreement with the previous two values.

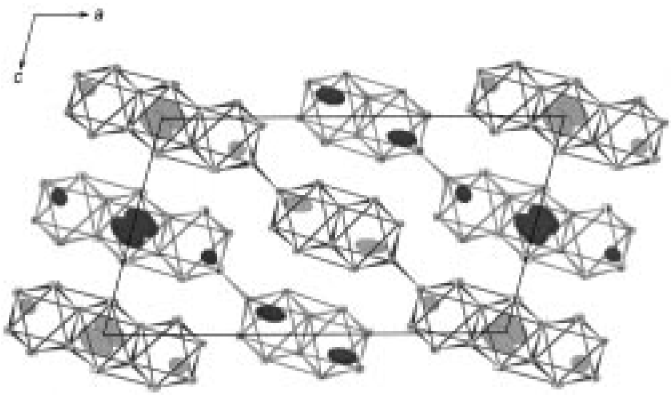

Figure 2
A projection of the Mo network and Sn atoms (unconnected ellipsoids) on the *ac* plane (O atoms omitted for clarity). Clusters whose centre lies in the plane $y = 0$ are represented by black lines, those whose centre is at $y = 0.5$ by a light grey line. Only Mo—Mo bonds of less than 2.9 Å are drawn. Sn atoms at $y \sim 0$ and ~ 0.5 are represented as black and grey ellipsoids, respectively (97% probability level).

In summary, the combination of di- and trioctahedral clusters forming infinite chains is unprecedented in reduced molybdenum oxide chemistry. This discovery suggests the synthesis of new compounds with zigzag or stair-step chains based on different types of multioctahedral Mo_{4n+2} clusters. Another interesting perspective would be to modify the number of electrons on the Mo_{10} and Mo_{14} clusters in this new compound. Indeed, this could lead to various electrical resistivity behaviours, as in the series $M_2Mo_{10}O_{16}$ (McCarroll *et al.*, 1998).

Experimental

Single crystals of $Sn_{4.4}Mo_{24}O_{38}$ were obtained from a mixture of SnO_2, MoO_3 and Mo, all in powder form, in the ratio 4:1:3. Before use, the Mo powder was reduced under H_2 flux at 1273 K for 10 h in order to eliminate any trace of oxygen. Starting reagents were mixed, ground together in a mortar and then cold-pressed using a hand press. The pellet was then loaded into an Mo crucible which was sealed under a low argon pressure using an arc welding system. The crucible was heated at a rate of 300 K h^{-1} to 2073 K and held there for 6 h, then cooled at 100 K h^{-1} to 1300 K and finally furnace-cooled to room temperature.

Crystal data

$Sn_{4.4}Mo_{24}O_{38}$
$M_r = 3433.04$
Monoclinic, $P2_1/c$
$a = 17.806$ (2) Å
$b = 9.2562$ (6) Å
$c = 9.9337$ (13) Å
$\beta = 105.955$ (6)°
$V = 1574.2$ (3) Å^3
$Z = 2$

$D_x = 7.243$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10$–27°
$\mu = 12.722$ mm^{-1}
$T = 293$ (2) K
Irregular, black
0.14 × 0.12 × 0.08 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
θ–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.260$, $T_{\max} = 0.361$
5726 measured reflections
5446 independent reflections

$R_{\rm int} = 0.021$
$\theta_{\max} = 31.96°$
$h = -26 \rightarrow 25$
$k = -13 \rightarrow 0$
$l = 0 \rightarrow 14$
3 standard reflections
frequency: 60 min
intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.077$
$S = 1.252$
5446 reflections
216 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0169P)^2 + 28.2165P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 2.90$ e Å^{-3}
$\Delta\rho_{\min} = -2.08$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.00116 (3)

Table 1
Selected geometric parameters (Å).

Sn1—O5$^{\rm i}$	2.217 (4)	Sn2—O12$^{\rm iii}$	2.545 (4)
Sn1—O12$^{\rm ii}$	2.231 (4)	Sn2—O11$^{\rm vi}$	2.551 (4)
Sn1—O1$^{\rm iii}$	2.313 (4)	Sn3—Sn3$^{\rm vii}$	0.759 (3)
Sn2—O5$^{\rm iv}$	2.286 (4)	Sn3—O17$^{\rm viii}$	2.384 (4)
Sn2—O7$^{\rm v}$	2.444 (4)	Sn3—O15$^{\rm iv}$	2.514 (5)

Symmetry codes: (i) $1-x, y-\frac{3}{2}, \frac{3}{2}-z$; (ii) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (iii) $x, y-1, z$; (iv) $1-x, 1-y, 1-z$; (v) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$; (vi) $x, \frac{1}{2}-y, z-\frac{1}{2}$; (vii) $2-x, 2-y, 1-z$; (viii) $x, 1+y, z$.

Refinement of the anisotropic displacement parameters of the O atoms did not significantly improve the reliability indices on the basis of Hamilton's test (Hamilton, 1965) at the 0.005 level. In addition, non-physical values were obtained for one O atom. For the Sn atoms, site-occupancy factors were refined to 0.915 (3), 0.866 (3) and 0.420 (3) for Sn1, Sn2 and Sn3, respectively. The possibility of O atoms on the latter three sites was excluded from geometric considerations due to incompatible O—O distances. In addition, the distance of 0.759 (3) Å between Sn3 sites precludes both sites being occupied simultaneously, in agreement with the site occupancy, which is less than 0.5.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1252). Services for accessing these data are described at the back of the journal.

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