

Synthesis and Crystal Structure of $\text{Tl}_{0.8}\text{Sn}_{0.6}\text{Mo}_7\text{O}_{11} \cdot \text{Mo}_{14}\text{O}_{34}$ Clusters Containing Three Condensed Mo_6 Octahedra

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The crystal structure of the new compound $\text{Tl}_{0.8}\text{Sn}_{0.6}\text{Mo}_7\text{O}_{11}$ [$P2_1/a$, $a = 997.2(1)$, $b = 936.2(1)$, $c = 1036.2(1)$ pm, $\beta = 104.14(1)^\circ$, $Z = 4$] contains oligomeric Mo clusters built up from three edge-sharing Mo octahedra in a row. The connectivity scheme of the clusters corresponds to $\text{Mo}_{14}\text{O}_{10}^1\text{O}_{4/2}^2\text{O}_{20/2}^3$. There are pairs of divalent Tl atoms linked by a single bond (284 pm) in the channels of the structure as well as isolated divalent Sn atoms. The average Mo–O and Mo–Mo distances within the clusters lie around 206 and 278 pm and are very similar to those in $\text{In}_{11}\text{Mo}_{40}\text{O}_{62}$, but there also are short inter-cluster distances ($d_{\text{inter}} \geq 299$ pm). The Mo valence electron concentration derived from bond-length–bond-strength calculations is in perfect agreement with the expected value.

Dedicated to Professor Sten Andersson on the occasion of his 60th birthday.

Since the discovery of the compound NaMo_4O_6 ¹ there have been extensive studies in the field of condensed clusters in oxomolybdates. NaMo_4O_6 contains infinite chains built from *trans*-edge-sharing Mo_6 octahedra which are surrounded by O atoms as in the case of the M_6X_{12} cluster.² Electronic band structure calculations³ (EHT-type) proved these chains to be optimally stabilized with 13 electrons per Mo_4 fragment.

In addition to the large number of compounds that only contain infinite Mo chains (see McCarley⁴ and Simon⁵) there are also a few examples of “intermediates” of cluster condensation.⁶ $\text{In}_{11}\text{Mo}_{40}\text{O}_{62}$ was the first compound identified with finite chains of four and five edge-sharing Mo_6 octahedra in a row,⁷ therefore containing oligomers of cluster condensation. Between the alternately packed oligomeric Mo units hitherto unknown metal–metal bonded In chains were found.

From an appropriate fragmentation of an oligomer into Mo_4O_7 , Mo_4O_6 and Mo_2O_5 units one could estimate the optimum valence electron concentrations for clusters of arbitrary length⁵ in order to facilitate the synthesis of other “oligomeric” oxomolybdates. In addition to $\text{In}_{11}\text{Mo}_{40}\text{O}_{62}$, compounds are known with one ($\text{BaMo}_6\text{O}_{10}$,⁸ single octahedron), two (LaMo_5O_8 ,⁹ PbMo_5O_8)^{10,11} and three ($\text{Tl}_{0.8}\text{Sn}_{0.6}\text{Mo}_7\text{O}_{11}$)¹⁰ condensed Mo octahedra. Here we report in detail our investigations (synthesis and single-crystal structure analysis) of the latter compound.

Preparation

Preparations in the system Tl/Sn/Mo/O (molar composition $\approx 1:1:10:14$, $T \approx 1570$ K) lead to hitherto unknown, black shiny crystals with a complicated Guinier diagram. They were brittle and “smeared” upon crushing. Fig. 1 shows a SEM photograph of a typical specimen. All crystals consisted of domains that were intergrown in three orientations differing by 120° (similar to $\text{In}_{11}\text{Mo}_{40}\text{O}_{62}$ ⁷ and PbMo_5O_8),¹¹ and the (010) faces always had a characteristic “maple leaf” shape.

The chemical analysis of selected crystals (7 mg) with AES/ICP yielded a ratio of Tl : Sn : Mo $\approx 0.9:0.7:7$. The

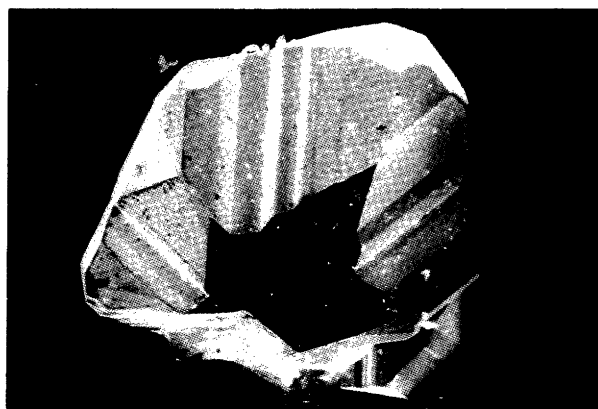


Fig. 1. SEM photograph of a “crystal” of $\text{Tl}_{0.8}\text{Sn}_{0.6}\text{Mo}_7\text{O}_{11}$.

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single-crystal refinement of individual site occupation factors led to the composition $\text{Tl}_{0.8}\text{Sn}_{0.6}\text{Mo}_7\text{O}_{11}$. Crystals up to 1 mm in size could be synthesized in a quantitative yield when choosing the latter metal atom ratio.

Synthesis. 1.535 g MoO_2 (12.0 mmol) (Ventron), 0.314 g Mo (3.3 mmol) (LAB, Merck), 0.357 g Tl (1.7 mmol) (LAB, Merck) and 0.155 g Sn (1.3 mmol) (p.a., Merck) were mixed and pressed to a pellet. The pellet was heated in an evacuated quartz glass ampoule for 7 d at 1573 K. The ampoule was quenched with air (and recrystallized in about 5 min). The product was single-phase.

Structural analysis

Any specimens as large as the one in Fig. 1 were of multiple domain and were therefore crushed under paraffin. Axes photographs of very small fragments proved them to be single-crystalline, showing sharp reflections which suggested an orthorhombic system from metrics but a monoclinic system from intensities.

The extinction rules $h0l$, $h = 2n$ and $0k0$, $k = 2n$ indicated space group $P2_1/a$ (C_{2h}^5 , No. 14). For ease of comparison with the structures of NaMo_4O_6 , $\text{In}_{11}\text{Mo}_{40}\text{O}_{62}$ and PbMo_5O_8 the non-conventional setting was kept. Most of the heavy atom positions were found using direct methods, the rest being added from Fourier syntheses.¹² The localization of some of the O atoms with the help of difference Fourier maps turned out to be difficult, as did the definite assignment of the heavy-atom densities for Tl and Sn, owing to the fact that they are disordered.

The Fourier map phased with the Mo–O partial structure reveals electron densities at the inversion centre in (i) 1/2, 1/2, 0 and near (ii) 0.5, 0.5, 0.6. The elongated peak shapes can be modelled by split positions with atomic positions that are separated by about 40 pm (i_a from i_b) and 60 pm (ii_a from ii_b), respectively. From bond-length–bond-strength and ionic radii considerations it is obvious that Tl has to occupy (i) and (ii_a), whereas Sn has to enter (ii_b).¹³ This assignment is the only one which avoids meaningless site occupation factors (i.e. > 1) in the following refinements.

At first the site occupation factors of Tl and Sn were refined, together with a common free-to-refine displacement factor, and yielded a composition of $\text{Tl}(1) : \text{Tl}(2) : \text{Sn} = 0.383(2) : 0.391(3) : 0.603(5)$, with $U_{\text{eq}} = 204 \text{ pm}^2$. This composition remained constant (within a single standard deviation) in refinements with independent anisotropic displacement parameters. The refined stoichiometry of $\text{Tl}_{0.8}\text{Sn}_{0.6}\text{Mo}_7\text{O}_{11}$ therefore seems reliable.

The two-fold disorder of what looks like a structural unit, Tl–Tl–Sn, in an otherwise centrosymmetric structure raises a question as to the nature of this disorder. It could be a statistic disorder or the result of merohedral twinning (inversion twins). Refinements in the acentric subgroups $P2_1$ and Pa using the twin program SLFS¹⁴ gave a clear answer in favour of the first interpretation. Whereas the conventional refinement of the disorder model yielded $R_{\text{iso}} \approx 0.13$,

Table 1. Crystallographic data for $\text{Tl}_{0.8}\text{Sn}_{0.6}\text{Mo}_7\text{O}_{11}$.

Formula:	$\text{Tl}_{0.8}\text{Sn}_{0.6}\text{Mo}_7\text{O}_{11}$
Molar mass / g mol^{-1}	1082.31
Lattice constants	
a / pm	997.2(1)
b / pm	936.2(1)
c / pm	1036.2(1)
β / °	104.14(1)
	(modified Guinier technique, ²⁰ 21 reflections)
Molar volume / $\text{cm}^3 \text{ mol}^{-1}$	141.25(3)
Space group	$P2_1/a$, C_{2h}^5 (No. 14)
Formula units	4
X-ray density / g cm^{-3}	7.662
Absorption coefficient / mm^{-1}	22.97
Crystal dimensions / mm^3	$0.083 \times 0.071 \times 0.048$
Instrument	Syntex $P\bar{1}$ four-circle diffractometer, Mo- $K\alpha$ radiation, graphite monochromator, scintillation counter
Scan range / °	$3 < 2\theta < 50$
Scan type	Wyckoff scan
Scan speed / ° min^{-1}	variable (1.5–19.5), dependent on prescan
Temperature / K	296
No. of reflections	1882; 1438 symmetry-independent with $F_o \geq 3\sigma(F_o)$
Octants	$-11 \leq h \leq 11$, $0 \leq k \leq 11$, $0 \leq l \leq 12$
Absorption correction	ψ scan with 11 reflections, pseudo-ellipsoid
Minimum, maximum transmission	0.10, 0.18
R_{average}	0.036
Structure solution	direct methods (SHELXS-86) ¹²
Structure refinement	Least-squares method (SHELX-76, XLS), ^{16,17} full matrix
No. of structure factors	1436
No. of variables	193
Weighting scheme	$w = 1 / \sigma^2(F_o)$
Extinction correction	$x = 0.00062$
R_{anisot}, R_w	0.051, 0.046

including all metal atoms, the corresponding twin refinement did not drop below $R_{\text{iso}} \approx 0.18$.

A final control of $F_o - F_c$ differences (DIFABS)¹⁵ did not reveal any remaining absorption errors. After allowing for secondary extinction corrections all atoms could be refined anisotropically.^{16,17} Table 1 shows all relevant data for the structural analysis,¹⁸ while Table 2 contains positional and isotropic displacement parameters.¹⁹ Table 3 lists the reflections from powder diffraction data²⁰ used in the refinement of the lattice constants.²¹ From Table 4 all important interatomic distances²² can be obtained.²³

Description and discussion of the structure

$\text{Tl}_{0.8}\text{Sn}_{0.6}\text{Mo}_7\text{O}_{11}$ is a member of the family composed of oligomeric Mo clusters. A projection of its structural principle is shown in Fig. 2. The cluster anions which are represented by their cores of three Mo_6 octahedra con-

Table 2. Positional parameters, site occupation factors (SOF) and isotropic displacement parameters (pm^2) for $\text{Ti}_{0.8}\text{Sn}_{0.6}\text{Mo}_7\text{O}_{11}$ (standard deviations are given in parentheses).

Atom	x	y	z	SOF	U_{eq}^a
Ti(1)	0.5132(2)	0.5036(2)	0.0182(2)	0.39(1)	274(7)
Ti(2)	0.5612(3)	0.4934(3)	0.2998(3)	0.38(1)	212(9)
Sn	0.4550(3)	0.5006(3)	0.6488(4)	0.61(1)	229(9)
Mo(1)	0.1191(1)	0.3855(1)	0.1391(1)	1	113(4)
Mo(2)	0.9131(1)	0.3809(1)	0.2819(1)	1	141(4)
Mo(3)	0.2261(1)	0.6314(1)	0.2833(1)	1	155(4)
Mo(4)	0.8440(1)	0.3726(2)	0.0010(2)	1	176(5)
Mo(5)	0.1920(1)	0.3843(1)	0.4127(1)	1	112(4)
Mo(6)	0.0503(1)	0.3821(1)	0.8636(1)	1	122(4)
Mo(7)	0.9751(1)	0.3777(2)	0.5841(1)	1	169(5)
O(1)	0.3261(11)	0.7576(11)	0.9984(11)	1	209(40)
O(2)	0.3990(10)	0.7561(11)	0.2846(10)	1	148(37)
O(3)	0.3175(10)	0.2537(10)	0.5705(10)	1	124(35)
O(4)	0.1491(11)	0.5008(11)	0.5712(11)	1	206(36)
O(5)	0.2185(10)	0.5056(11)	0.8588(10)	1	181(34)
O(6)	0.7126(10)	0.4897(12)	0.8547(11)	1	238(39)
O(7)	0.3913(12)	0.2587(12)	0.8600(12)	1	207(38)
O(8)	0.6453(10)	0.4920(11)	0.5749(10)	1	162(34)
O(9)	0.9687(11)	0.7432(10)	0.5682(10)	1	139(35)
O(10)	0.2548(11)	0.7580(10)	0.7116(11)	1	185(39)
O(11)	0.9637(12)	0.2449(12)	0.1482(11)	1	211(38)

^a U_{eq} is a third of the trace of the orthogonalized U_{ij} tensor.

densed in line via edges are arranged in layers parallel to the ac -plane. The resulting short channels in these layers between the clusters are partially occupied by Ti and Sn atoms.

Each Mo_6 octahedron is coordinated by O atoms above

Table 3. Powder reflections used in the lattice constant refinement of $\text{Ti}_{0.8}\text{Sn}_{0.6}\text{Mo}_7\text{O}_{11}$.

h	k	l	I_{rel}	d_0/pm
1	1	0	50	671.7
2	0	0	20	483.5
0	2	0	30	467.9
1	1	3	10	322.4
3	1	0	30	304.7
1	3	0	100	297.0
1	3	1	10	290.7
1	1	3	30	281.4
3	1	1	10	274.5
3	2	1	40	270.5
2	2	3	10	260.5
3	1	2	10	237.4
0	4	0	10	234.1
1	3	3	10	230.9
1	2	4	30	226.6
1	2	4	10	206.3
3	2	4	10	204.2
3	1	3	20	203.2
3	2	3	20	190.3
1	5	0	30	183.9
5	2	1	20	183.3

all free edges (X^i -type positions), i.e. in the manner of an M_6X_{12} -type cluster.² O atoms from adjacent clusters coordinate all octahedral apices (X^a -type). The cluster would have the composition " $\text{Mo}_{14}\text{O}_{34}$ " as a free entity. Confining the analysis to only X^i -bonded O atoms around each Mo_{14}

Table 4. Interatomic distances (in pm) in $\text{Ti}_{0.8}\text{Sn}_{0.6}\text{Mo}_7\text{O}_{11}$ (standard deviations are given in parentheses).^a

Ti(1)–O(7')	262.1(11)	Ti(2)–Mo(3)	354.7(3)	Mo(1)–Mo(2)	281.0(2)	Mo(4)–O(1')	209.2(11)
Ti(1)–O(5')	266.9(9)	Ti(2)–Mo(5')	355.8(3)	Mo(2)–O(5')	201.0(9)	Mo(4)–Mo(6')	276.3(2)
Ti(1)–O(11''')	279.1(12)	Sn–O(8)	224.2(11)	Mo(2)–O(11)	203.4(12)	Mo(4)–Mo(6)	277.4(2)
Ti(1)–O(6')	287.3(12)	Sn–O(9''')	229.3(10)	Mo(2)–O(9')	206.3(10)	Mo(5)–O(10''')	191.7(11)
Ti(1)–O(11'')	288.5(12)	Sn–O(8')	229.9(10)	Mo(2)–O(4')	209.5(12)	Mo(5)–O(8')	197.2(10)
Ti(1)–O(7)	290.7(11)	Sn–O(11'')	287.6(11)	Mo(2)–O(10')	213.4(11)	Mo(5)–O(9')	204.6(11)
Ti(1)–O(6)	291.3(12)	Sn–O(6)	293.6(10)	Mo(2)–Mo(7')	274.3(2)	Mo(5)–O(4)	210.1(11)
Ti(1)–O(1')	294.9(11)	Sn–O(3)	295.2(9)	Mo(2)–Mo(6')	275.7(2)	Mo(5)–O(3)	217.6(9)
Ti(1)–O(1)	299.8(11)	Sn–O(4)	297.2(11)	Mo(2)–Mo(5)	278.1(2)	Mo(5)–Mo(7')	278.7(2)
Ti(1)–O(5)	299.9(9)	Sn–O(2')	305.1(11)	Mo(2)–Mo(4)	282.4(2)	Mo(5)–Mo(7)	311.6(2)
Ti(1)–Ti(2)	284.0(5)	Sn–Sn'	346.3(8)	Mo(2)–Mo(7)	304.0(2)	Mo(6)–O(1'')	202.2(10)
Ti(1)–Sn	373.7(5)	Sn–Mo(5)	340.6(3)	Mo(3)–O(3'')	202.9(11)	Mo(6)–O(5)	204.8(10)
Ti(1)–Mo(4)	356.4(3)	Sn–Mo(3')	343.7(3)	Mo(3)–O(6')	203.3(12)	Mo(6)–O(7''')	205.5(12)
Ti(2)–O(8')	269.3(12)	Sn–Mo(2'')	354.1(3)	Mo(3)–O(7'')	203.6(11)	Mo(6)–O(2'')	209.3(11)
Ti(2)–O(11''')	276.4(11)	Mo(1)–O(1'')	202.8(12)	Mo(3)–O(8')	205.4(9)	Mo(6)–Mo(7)	280.9(2)
Ti(2)–O(9'')	276.5(11)	Mo(1)–O(6')	203.3(11)	Mo(3)–O(2)	208.0(11)	Mo(7)–O(2'')	197.2(10)
Ti(2)–O(8)	276.8(10)	Mo(1)–O(11)	205.3(12)	Mo(3)–Mo(7')	269.6(2)	Mo(7)–O(3''')	197.4(10)
Ti(2)–O(6')	281.2(10)	Mo(1)–O(10'')	210.9(10)	Mo(3)–Mo(5)	273.6(2)	Mo(7)–O(4')	210.8(10)
Ti(2)–O(3')	284.3(9)	Mo(1)–Mo(5)	275.0(2)	Mo(3)–Mo(6')	280.6(2)	Mo(7)–O(4)	211.3(11)
Ti(2)–O(4')	287.3(10)	Mo(1)–Mo(6')	275.0(2)	Mo(3)–Mo(4')	285.6(2)	Mo(7)–O(9')	212.5(11)
Ti(2)–O(2)	292.6(11)	Mo(1)–Mo(4')	276.2(2)	Mo(4)–O(7''')	205.0(12)	Mo(7)–Mo(7')	299.1(3)
Ti(2)–O(7')	295.5(12)	Mo(1)–Mo(6)	276.9(2)	Mo(4)–O(5')	205.9(11)		
Ti(2)–O(10')	300.4(11)	Mo(1)–Mo(4)	277.0(2)	Mo(4)–O(6)	206.0(10)		
Ti(2)–O(5')	304.9(12)	Mo(1)–Mo(3)	280.9(2)	Mo(4)–O(11)	207.2(11)		

^aSymmetry coding: x, y, z: ('); $-x, -y, -z$: (''); $1/2 - x, 1/2 + y, -z$: (''); $-1/2 + x, -1/2 - y, z$: ('').

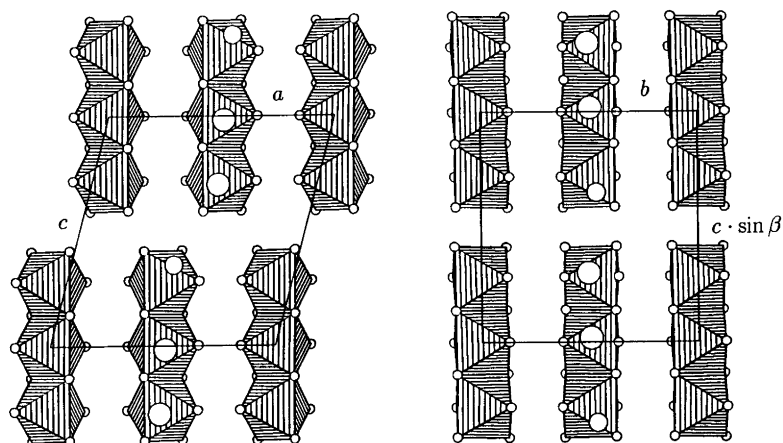


Fig. 2. Polyhedral representation³⁸ of the metal atom substructure of $Tl_{0.8}Sn_{0.6}Mo_7O_{11}$ along [010] (left) and [100] (right); Mo atoms are shown as small circles, Tl atoms as large circles and Sn atoms as medium-sized circles, with both of the possible positions of the structural fragment Tl–Ti–Sn (left \uparrow , right \downarrow), see text. The cluster centres lie at 0, 1/2, 0 and 1/2, 0, 0. For the labelling of the Mo, Tl and Sn atoms, see Figs. 3 and 4, respectively.

core, the connectivity scheme is represented by the formula $Mo_{14}O_{10}O_{4/2}O_{20/2}^{i-a}$ ($= Mo_{14}O_{22} = 2 \times Mo_7O_{11}$). Four O atoms of the inner sphere belong to just one cluster. A view of the new cluster anion is given in Fig. 3.

The range of Mo–O distances is 191–218 pm and is slightly wider than in the compound $PbMo_5O_8$.¹¹ The average Mo–O distance is 206 pm and corresponds to that in $In_{11}Mo_{40}O_{62}$ (207 pm) or $PbMo_5O_8$ (206 pm).

A detailed analysis of the interatomic distances has been performed with the help of bond-length–bond-strength calculations.^{12,24} As can be seen from Table 5 there is an obvious difference in the bond order sums between two groups of Mo atoms. Mo atoms near the centre of the cluster [Mo(1) and Mo(6)] have bond order sums of about 2.4, in contrast to all others, which have bond order sums between 2.9 and 3.2 owing to the greater number of coordinated O atoms. This effect is very similar to the findings in $PbMo_5O_8$.¹¹

Within the cluster the Mo–Mo distances lie between 270 and 286 pm. The average value is 278 pm and shows a small increase of 3 pm with respect to the value in $PbMo_5O_8$, approaching the value in $In_{11}Mo_{40}O_{62}$ (279 pm). Therefore, an increase in cluster length manifests itself in a small but still significant lengthening of the intra-cluster distances.

Compared to the Mo–Mo distances in $In_{11}Mo_{40}O_{62}$ the Mo–Mo distances in $Tl_{0.8}Sn_{0.6}Mo_7O_{11}$ are surprisingly similar.²⁵ The Mo–Mo distances of the shared edges [Mo(1)–Mo(6) and Mo(5)–Mo(7)] are 278 ± 1 pm, and the Mo–Mo distances between the apical Mo atoms [Mo(3)–Mo(4)–Mo(2)] are 284 ± 2 pm. Short (270 pm) and long distances (281 pm) can only be found at Mo(7), which simultaneously has the shortest contacts to the next oligomeric cluster.

These inter-cluster distances are 299 pm (1 \times), 304 pm (2 \times) and 312 pm (2 \times). They are longer than the compara-

ble distances in $PbMo_5O_8$ and much bigger than the average intra-cluster distance. For that reason the clusters prove to be (electronically) more isolated than in $PbMo_5O_8$. The Mo–Mo bond order sum for the five shortest inter-cluster distances reaches a value of 0.9, i.e. there are 0.9 electrons used in inter-cluster metal–metal bonding per formula unit of $Tl_{0.8}Sn_{0.6}Mo_7O_{11}$.

Concerning the coordination of the Tl atoms, a cube-like arrangement of O atoms is found for both independent atoms. The Tl atoms are slightly shifted from the centres of gravity of the coordination polyhedra towards the inversion centre. Bond-length–bond-strength calculations (Table 5) show them to be divalent. This finding is in agreement with the short Tl(1)–Tl(2) distance of 284 pm, representing a Tl–Tl single bond.²⁶

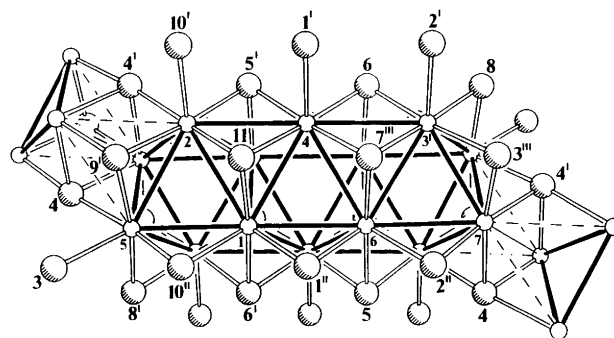


Fig. 3. Perspective view¹⁷ of the Mo–O cluster in $Tl_{0.8}Sn_{0.6}Mo_7O_{11}$, together with fragments of adjacent clusters. Mo atoms are drawn as small circles and O atoms as large circles. The atom labelling refers to Table 5; the inversion centre of the structure and the centre of the cluster coincide. The shortest inter-cluster bond is emphasized as a full, thin line, the others as broken lines. One O(9') atom has been omitted on the right hand side.

Table 5. Bond-order sums [4,12,21,22] of the metal atoms with respect to oxygen in $Tl_{0.8}Sn_{0.6}Mo_7O_{11}$.

Atom	Valence
Tl(1)	1.7
Tl(2)	1.8
Sn	2.2
Mo(1)	2.4
Mo(2)	2.9
Mo(3)	3.0
Mo(4)	2.9
Mo(5)	3.2
Mo(6)	2.4
Mo(7)	3.0

^aParameters: Tl with $R_0 = 2.100 \text{ \AA}$, $N = 6.0$; Sn with $R_0 = 1.860 \text{ \AA}$, $N = 4.5$; Mo with $R_0 = 1.882 \text{ \AA}$, $N = 6.0$.

As in the case of divalent Al,²⁷ Ga²⁸⁻³² or In,^{7,33-35} the remaining valence electron of Tl^{2+} is used for homonuclear bonding. A Tl_2^{4+} species which is isoelectronic and isostructural with Hg_2^{2+} was hitherto unknown.

Of course, the local statistical disorder of the cation allows an alternative occupation of the Tl position to yield a Tl-Tl distance of 320 pm. Such a model is very unlikely owing to the loss of spin-pairing energy, and can be ruled out from magnetic measurements which will be described for the series of oligomeric cluster oxomolybdates in a forthcoming paper. Last, but not least, the convergence of the Tl(1) and Tl(2) site occupation factors to identical values is in agreement with the assumption of Tl_2^{4+} ions. The statistical disorder of the "Tl-Tl-Sn" unit (in contrast to a model of inversion twins) is easily rationalized in terms of an alternative 40 and 60% occupation of the voids between the molybdate clusters by Tl_2^{4+} and Sn^{2+} ions, respectively.

Thus, each channel is occupied by only one of the two ions, Tl_2^{4+} or Sn^{2+} , each in two possible positions, which nicely explains why the refined position of, e.g., Sn^{2+} does not exhibit a split pattern depending on whether the adjacent channel position is empty or occupied by a Sn^{2+} or Tl_2^{4+} ion, respectively. The partial occupation of the available voids again reflects the rigidity of such cluster frameworks, which is well-documented in other systems: $In_2Mo_{15}Se_{19}$ can be modified by "soft chemistry" to yield the empty cluster framework in the compound $Mo_{15}Se_{19}$.³⁶

The coordination of the Sn atom is characterized by three short Sn-O bonds in the range 224-230 pm, and no simple coordination polyhedron exists. The bond order sum shows the Sn atom to be divalent, as expected. The shortest Sn-Sn distance in the averaged structure is found to be 346 pm, but according to the above discussion one would in any case expect the adjacent position to be empty. For that reason the Sn atom (like the Pb atom in $PbMo_5O_8$) simply acts as a two-electron donor for the oxomolybdate cluster.

Fig. 4 presents a perspective view of the coordinations of

the Sn^{2+} and Tl_2^{4+} ions by oxygen atoms. It is remarkable that the cationic disorder is not reflected in the "thermal" ellipsoids for the O atoms. Obviously the Mo-O skeleton is largely a rigid unit, very much as in the oxoniobates, where the "hierarchy of bond strengths" has been discussed in more detail.³⁷

To summarize what has been said about the valence states of the cations and inter-cluster bonding in $Tl_{0.8}Sn_{0.6}Mo_7O_{11}$, one can make up an electron balance to count the number of valence electrons which are left for intra-cluster bonding. According to eqn. (5) one finds 21.9

$$\underbrace{7 \times 6}_{\text{Mo}} + \underbrace{0.4 \times 4}_{\text{Tl}} + \underbrace{0.6 \times 2}_{\text{Sn}} - \underbrace{11 \times 2}_{\text{O}} - \underbrace{0.9}_{\text{inter}} = 21.9 \quad (5)$$

electrons per Mo_7O_{11} unit, which leads to 3.13 electrons per Mo atom, in excellent agreement with the predicted value of 3.1(2).⁵ Obviously the intercluster bonding is necessary to reduce the number of Mo-centred valence electrons which otherwise would enter antibonding cluster states.

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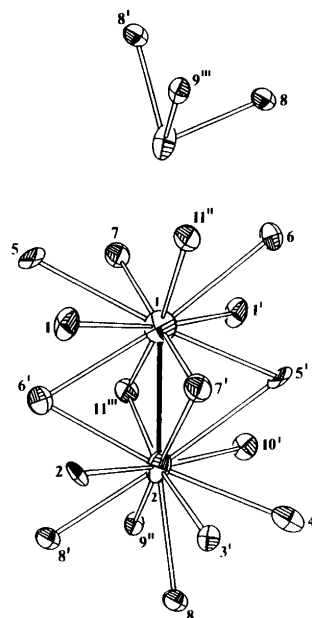


Fig. 4. Perspective view¹⁷ of the Sn (top) and Tl (middle and bottom) coordination spheres in $Tl_{0.8}Sn_{0.6}Mo_7O_{11}$ by O atoms up to 285 and 305 pm, respectively. The labelling of the Tl atoms (small numbers) and the O atoms (bigger numbers) refers to Table 5. The ellipsoids enclose 70% of the electrons' spatial probability. the Tl-Tl single bond is emphasized with a thick line.

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- R* value definitions:

$$R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$$

$$R_w = \frac{\sum [|F_o| - |F_c|] \sigma^{-2}(F_o)}{\sum [|F_o| \sigma^{-2}(F_o)]}$$
- Only for the Tl(1) atom was a strong correlation between site parameters and U_{33} found because of the neighbouring symmetry equivalent position (41 pm). To perform a meaningful anisotropic refinement, site parameters and displacement parameters were allowed to be refined alternatively until a constant *R* value resulted. Therefore the standard deviations for the Tl(1) atom are slightly decreased. For the calculation of the interatomic distances of Tl(1) the same standard deviations as for Tl(2), namely 0.0003 in *x*, *y* and *z*, were used.
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- A list of the observed and calculated structure factors and anisotropic thermal parameters may be obtained from the *Fachinformationszentrum Karlsruhe*, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-53673, the authors' names and the journal citation.
- For the Tl-O and Sn-O bonds we use the relationship and parameters given by Brown [Brown, I. D. In: O'Keefe, M. and Navrotsky, A., Eds., *Structure and Bonding in Crystals*, Academic Press, New York 1981, Vol. II], eqn. (1), for the

$$s = (R/R_0)^{-N} \quad (1)$$

Mo-O bonds the formula of Brown and Wu [Brown, I. D. and Wu, K. K. *Acta Crystallogr., Sect. B* 32 (1976) 1957], eqn. (2),

$$s_{Mo-O} = [d(Mo-O)/1.882 \text{ \AA}]^{-6.10} \quad (2)$$

which McCarley *et al.* [Ref. 4] stated to be well-suited for metal-rich Mo oxides. Mo-Mo bond orders can be obtained with the help of Pauling's formula [Ref. 4], eqn. (3).

$$s_{Mo-Mo} = 10^{[2.614 \text{ \AA} - d(Mo-Mo)/0.6 \text{ \AA}]} \quad (3)$$
- For $In_{11}Mo_{40}O_{62}$ the Mo-Mo distances of the shared edges show a short-long-short pattern while proceeding from the centre of the cluster to its end. All the other Mo-Mo bonds decrease continuously as they approach the cluster's end.
- According to Pauling's covalent radius for the Tl atom (143.7 pm) [Ref. 13], one expects a Tl-Tl single bond distance of about 287 pm.
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