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Ag$_{2.54}$Tl$_2$Mo$_{12}$Se$_{15}$: a new structure type containing Mo$_6$ and Mo$_9$ clusters

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The novel structure-type Ag$_{2.54}$Tl$_2$Mo$_{12}$Se$_{15}$ (silver thallium molybdenum selenide) is built up of Mo$_6$Se$_i$Se$_{6/2}$ and Mo$_9$Se$_i$Se$_{6/2}$ cluster units in a 1:2 ratio, which are threedimensionally connected to form the Mo–Se network. The Ag and Tl cations are distributed in several voids within the cluster network. Three of the seven independent Se atoms and one Tl atom lie on sites with 3.. symmetry (Wyckoff sites 2e or 2c).

Comment

In solid-state chemistry, the crystal structures of reduced molybdenum chalcogenides are characterized by molybdenum clusters of various sizes and geometries. Although most Mo cluster compounds contain just one type of cluster, some of them can present up to four different types, as observed in Pr$_2$Mo$_6$O$_{15}$ (Tortelier & Gougeon, 1998). In most reduced Mo chalcogenides, we have observed only one type of cluster, as exemplified by the series $M_{n-2}$Mo$_n$X$_{3n+2}$ $(M =$ Rb or Cs; $X =$ S, Se or Te; $n = 3, 4, 5, 6, 7, 8, 10$ or $12$) containing Mo$_9$, Mo$_{12}$, Mo$_{15}$, Mo$_{18}$, Mo$_{21}$, Mo$_{24}$, Mo$_{30}$ and Mo$_{36}$ clusters (Gautier et al., 1998; Gougeon, 1984; Gougeon et al., 1984, 1987, 1988, 1989a,b, 1990; Thomas et al., 1997; Picard, Gougeon & Potel, 1999; Picard, Halet et al., 1999). On the other hand, in the series Rb$_{2n}$Mo$_n$X$_{11}$Mo$_{2n}$X$_{2n+2}$ $(n = 1, 2, 3, 4$ and $5$; Picard et al., 2000), we found clusters of odd and even nuclearity which co-exist in equal proportions. Subsequently, we presented a new structural type, Rb$_2$Mo$_{12}$Se$_{24}$ (Picard et al., 2001), also containing odd and even nuclearity clusters, i.e. Mo$_{12}$ and Mo$_{16}$, but in the ratio 1:2. We report here a new structural type, Ag$_{2.54}$Tl$_2$Mo$_{12}$Se$_{15}$, containing Mo$_6$ and Mo$_9$ clusters in the ratio 1:2.

A view of the crystal structure of Ag$_{2.54}$Tl$_2$Mo$_{12}$Se$_{15}$ is shown in Fig. 1. It is based on octahedral Mo$_6$ and biocathedral Mo$_9$ clusters surrounded by 14 and 17 Se atoms, respectively (Fig. 2), to form Mo$_6$Se$_i$Se$_{6/2}$ and Mo$_9$Se$_i$Se$_{6/2}$ cluster units. The latter units share some of their Se ligands according to the connective formulae Mo$_6$Se$_i$Se$_{6/2}$ and Mo$_9$Se$_i$Se$_{6/2}$ to form the three-dimensional Mo–Se framework [for details of the i- and a-type (inner and ausser) ligand notation, see Schäfer & von Schnering (1964)]. This arrangement results in each Mo$_9$Se$_6$Se$_6$ unit being surrounded by six Mo$_6$Se$_{11}$Se$_6$ units centred at the apices of a trigonal prism, while each Mo$_9$Se$_{11}$Se$_6$ unit is surrounded by three Mo$_6$Se$_6$Se$_6$ and three Mo$_6$Se$_{11}$Se$_6$ units, also forming a trigonal prism.

The Mo$_9$ cluster exhibits 3.. symmetry, as in the rhombohedral Chevrel phase $M'_2$Mo$_6$Se$_6$. The Mo$_9$ cluster is slightly distorted, with Mo–Mo distances of 2.6879 (10) Å for the intra-triangle distances (distances between the Mo atoms related through the threefold axis) and 2.7007 (7) Å for the inter-triangle distances. This clearly indicates that the number of electrons per Mo$_9$, also called the metallic electron count (MEC), should be close to 23. Indeed, previous work on the
Chevrel phases (Yvon et al., 1977) has shown that when the MEC increases from 20 to 24, the Mo9 cluster becomes more regular. Thus, in Mo8Se6 in which the MEC is 20, the intra- and inter-triangle Mo—Mo distances are 2.683 and 2.836 (8) Å, respectively (Bars et al., 1973), while in Pt0.5Mo0Se6 (Le Berre et al., 2000), with an MEC of 22.58, the intra- and inter-triangle Mo—Mo distances are 2.6812 (6) and 2.7268 (7) Å, respectively, and in Li32Mo8Se6, with an MEC of 23.2, they are 2.6727 and 2.6733 Å, respectively (Cava et al., 1984).

The Mo9 cluster exhibits 3s symmetry. The Mo—Mo distances within the Mo9 clusters are very similar, 2.6163 (9) Å within the triangles made by atoms Mo2, Mo3 and Mo4, respectively, 2.6896 (8) and 2.7757 (7) Å for the inter-triangle distances between the two triangles formed by atoms Mo2 and Mo3, respectively, and 2.6628 (8) and 2.7475 (8) Å for the the inter-triangle distances between the two triangles formed by atoms Mo3 and Mo4, respectively.

In the Mo9 cluster, the MEC, which can vary from 32 to 36 (Hughbanks & Hoffmann, 1983; Gautier et al., 1997), predominantly affects the Mo—Mo bonds within the median triangle (Mo3—Mo36 bonds in the title compound; symmetry codes are as in Table 1) (Potel et al., 1984). A comparison of the Mo—Mo bonds within the median triangle in different compounds containing only Mo9 clusters shows they are similar in the title compound [2.7346 (7) Å] and in Ag41Cl8Mo8Se11 [2.7362 (5) Å], in which the MEC is 35.1 (Gougeon et al., 2004). Consequently, the approximately nine electrons contributed by the five Ag and four Tl atoms are distributed uniformly over the Mo9 and the two Mo6 clusters contained in the unit cell (about three electrons on each cluster). The average Mo—Mo distances in the two clusters are very similar, 2.693 Å in the Mo9 cluster and 2.694 Å in the Mo6 cluster. The shortest inter-cluster Mo—Mo distances are 3.6041 (11) Å between the Mo9 and Mo6 clusters, and 3.6725 (9) Å between the Mo6 clusters. The Se atoms bridge either one or two Mo triangular faces of the clusters. Moreover, atoms Se1 and Se2 are linked to an Mo atom of a neighbouring cluster. The Mo—Se bond distances range from 2.5492 (9) to 2.6457 (11) Å within the Mo9Se6Se6 unit and from 2.5319 (9) to 2.7085 (10) Å within the Mo6Se12Se6 unit.

The Ag and Tl atoms reside in cavities between the cluster units. Atom Ag1 partially occupies [0.845 (3)] triangular groups of distorted tetrahedral sites of Se atoms having the apex atom Se7 in common around the threefold axis (Fig. 3). The maximum of the Ag1 probability density function is very close to the triangular face opposite the common apex atom Se7, with Ag1—Se distances of 2.577 (2), 2.6675 (17) and 2.6834 (16) Å, the Ag1—Se7 distance being 3.0215 (17) Å. The Tl1 and Tl2 cations are in penta- and tetracapped trigonal prismatic environments of Se atoms (Fig. 4); the former is similar to that observed for the M element in the ternary compounds M2Mo15Se19 (M = In and Ba), in which Mo9 and Mo6 clusters co-exist in equal proportions (Potel et al., 1981; Gougeon et al., 1989c). The Tl—Se distances range from 3.0677 (14) to 4.2039 (9) Å for the Tl1 site.

It is interesting to note that, while in Ba2Mo15Se19 the Ba atom is nearly equidistant from the axial atoms Se6 and Se7 [3.4689 (5) and 3.4761 (5) Å, respectively], in Ag2.53Mo15Se19, atom Tl1 is displaced towards the axial atom Se6, with a Tl1—Se6 distance of 3.0677 (14) Å compared with 3.8863 (14) Å for Tl1—Se7. This effect, which may result from the lone pair, is also observed to a lesser extent in In2Mo15Se19, with In—Se distances of 3.468 (6) and 3.593 (6) Å. The environment of atom Tl2 has been observed previously in Tl2Mo6S11 (Potel et al., 1980), in which Mo9 and Mo12 clusters are found, as well as in Cs14.5Tl1.85Mo15Se19, containing an equal mixture of Mo6 and Mo9 clusters (Gougeon et al., 2009). In the latter compound, the Tl—Se distances range from 3.1152 (11) to 4.2214 (9) Å, compared with 2.9991 (15) to 4.0667 (9) Å in the title compound. The average Tl—Se values of 3.67 and 3.68 Å for the Tl1 and Tl2 sites, respectively, are in very good agreement with the distance of 3.68 Å expected from the sum of the ionic radii of

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**Figure 3**
The Se coordination polyhedron for Ag1. The symmetry codes are as in Table 1.

**Figure 4**
The environments of atoms Tl1 and Tl2. The symmetry codes are as in Table 1.
Because there are twice as many Mo whole molybdenum cluster in the title compound is 46.5. oxidation state for the Ag and Tl cations, the MEC of the assumption, based on distance analysis, that electrons

TB calculations have been carried out in order to check the
level of the three-dimensional maps is 0.05 Å.

Nonharmonic probability density isosurfaces, viewed along the c axis, for (a) Tl1, (b) Tl2 and (c) Ag1. Se atoms are drawn at an arbitrary size. The level of the three-dimensional maps is 0.05 Å⁻³.

Se²⁻ and Tl⁺ with coordination number 12, according to Shannon (1976).

In Rb₂₆(Mo₆S₁₁)(Mo₆O₆S₁₁) compounds, extended Hückel tight-binding (EH-TB) calculations have shown that the clusters are hypoelectronic (Picard et al., 2000). Assuming a +1 oxidation state for the Ag and Tl cations, the MEC of the whole molybdenum cluster in the title compound is 46.5. Because there are twice as many Mo₉ as Mo₆ in this compound, the MEC of one Mo₆ and two Mo₉ units is 93. EH-TB calculations have been carried out in order to check the assumption, based on distance analysis, that electrons

provided by Ag and Tl cations are uniformly distributed over both clusters. The electronic structure of the title compound is approximated by (Mo₉Se₁₁)⁶. The molybdenum and selenium extended Hückel parameters used by Gautier et al. (1998) have been considered. The total and Mo projected density of states (DOS) curves obtained from 32 irreducible k points are sketched in Fig. 5. The Fermi level cuts a narrow peak of DOS centred on the Mo₉ cluster. This peak is derived mainly from the doubly degenerate e level of the molecular orbital diagram of an isolated Mo₉Se₁₁ cluster (Hughbanks & Hoffmann, 1983). Since this peak is roughly half-occupied, the MEC of the Mo₆ unit is close to 22 ME. The two DOS peaks that lie above the Fermi level are derived mainly from the Mo₉ cluster. These peaks show some Mo—Mo antibonding character within the bioctahedral cluster, whereas the occupied bands show an overall Mo—Mo character within the same cluster. This means that the MEC of the Mo₆ unit in this compound must be close to the optimal value. In fact, assuming an MEC of 22 for the Mo₉ cluster, the MEC per Mo₆ unit is (93 — 22)/2 = 35.5. This distribution differs slightly from that resulting from the analysis of Mo—Mo distances within the clusters. However, this difference cannot be considered significant since: (i) the quantum periodic calculations we have carried out are semi-empirical, (ii) Ag and Tl atoms have been neglected within the calculations because of the lack of reliable EH parameters for Tl, and (iii) the MEC values resulting from the empirical distance analysis show significant uncertainties.

**Experimental**

Single crystals of Ag₂₄Tl₂Mo₉Se₁₅ were prepared from a mixture of Ag, MoSe₂, TlSe and Mo with the nominal composition Ag₂₄Tl₂-Mo₉Se₁₅. Before use, Mo powder was reduced under flowing H₂ gas at 1273 K for 10 h in order to eliminate any trace of oxygen. The MoSe₂ and TlSe binaries were obtained by heating stoichiometric mixtures of the elements in sealed evacuated silica tubes for about 2 d at 1073 and 573 K, respectively. All handling of materials was carried out in an argon-filled glove-box. The initial mixture (ca 5 g) was cold pressed and loaded into a molybdenum crucible, which was sealed under a low argon pressure using an arc-welding system. The charge was heated at a rate of 300 K h⁻¹ to 1523 K, held at that temperature for 48 h, cooled at a rate of 100 K h⁻¹ to 1373 K, and finally furnace cooled.

**Crystal data**

<table>
<thead>
<tr>
<th>Crystal data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag₂₄Mo₉Se₁₅Tl₂</td>
</tr>
</tbody>
</table>
| Mᵣ = 3017.9 | Z = 2  
| Trigonal, P3 | Mo Kα radiation  
| a = 9.9962 (1) Å | μ = 39.41 mm⁻¹  
| c = 15.5564 (3) Å | T = 293 K  
| V = 1344.47 (3) Å³ | 0.07 × 0.06 × 0.03 mm  

**Data collection**

<table>
<thead>
<tr>
<th>Data collection</th>
</tr>
</thead>
</table>
| Nonius KappaCCD area-detector diffractometer | 31332 measured reflections  
| Absorption correction: analytical (de Meulenaer & Tompa, 1965) | 5641 independent reflections  
| | 4029 reflections with I > 2σ(I)  
| T_max = 0.104, T_min = 0.346 | R_abs = 0.097 |
inorganic compounds

### Table 1
Selected bond lengths (Å).

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo1—Mo1'</td>
<td>2.6879 (10)</td>
</tr>
<tr>
<td>Mo1—Mo1''</td>
<td>2.7007 (7)</td>
</tr>
<tr>
<td>Mo2—Mo2'</td>
<td>3.6041 (10)</td>
</tr>
<tr>
<td>Mo1—Se1</td>
<td>2.5914 (8)</td>
</tr>
<tr>
<td>Mo1—Se1''</td>
<td>2.6153 (6)</td>
</tr>
<tr>
<td>Mo1—Se1''</td>
<td>2.5741 (9)</td>
</tr>
<tr>
<td>Mo2—Se2'</td>
<td>2.6457 (11)</td>
</tr>
<tr>
<td>Mo2—Se7</td>
<td>2.5492 (9)</td>
</tr>
<tr>
<td>Mo2—Mo2''</td>
<td>2.6374 (6)</td>
</tr>
<tr>
<td>Mo3—Se2'</td>
<td>2.6896 (8)</td>
</tr>
<tr>
<td>Mo2—Mo3</td>
<td>2.7757 (7)</td>
</tr>
<tr>
<td>Mo2—Se1</td>
<td>2.7085 (10)</td>
</tr>
<tr>
<td>Mo2—Se2</td>
<td>2.6523 (8)</td>
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<tr>
<td>Mo2—Se2''</td>
<td>2.5787 (6)</td>
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<tr>
<td>Mo3—Se3</td>
<td>2.6652 (9)</td>
</tr>
<tr>
<td>Mo3—Se6</td>
<td>2.5319 (9)</td>
</tr>
<tr>
<td>Mo3—Mo3''</td>
<td>2.7346 (7)</td>
</tr>
<tr>
<td>Mo3—Mo4</td>
<td>2.7475 (8)</td>
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<tr>
<td>Mo3—Mo4''</td>
<td>2.6628 (8)</td>
</tr>
<tr>
<td>Mo3—Mo5</td>
<td>2.6275 (7)</td>
</tr>
<tr>
<td>Mo3—Se3</td>
<td>2.5765 (11)</td>
</tr>
<tr>
<td>Mo3—Mo3''</td>
<td>2.5839 (13)</td>
</tr>
</tbody>
</table>

### Refinement

\[ R(F^2) = 2\sqrt{2} R(F^2) = 0.079 \]

\[ wR(F^2) = 0.079 \]

\[ S = 1.28 \]

\[ \Delta \rho_{\text{max}} = 3.78 \text{ e Å}^{-3} \]

\[ \Delta \rho_{\text{min}} = -2.71 \text{ e Å}^{-3} \]

641 reflections

The structure was solved in the space group \( P\bar{3} \) using SIR97 (Altomare et al., 1999), which revealed all atoms. The final model was refined down to \( R = 0.169 \). Analysis of the data with the TwinRotMat procedure implemented in PLATON (Spek, 2009) revealed that the crystal investigated was merohedrally twinned. Introduction of the twinning matrix (010, 100, 00) lowered the factor to 0.059. At this stage, the difference Fourier map revealed significant electron densities near atoms Tl1 (5.10 and \(-2.45 \text{ e Å}^{-3} \)), Tl2 (7.75 and \(-8.06 \text{ e Å}^{-3} \)) and Ag1 (5.59 and \(-3.85 \text{ e Å}^{-3} \)). Fourth-order tensors in the Gram–Charlier expansion (Johnson & Levy, 1974) of the probability density function maps of Tl1, Tl2 and Ag1 did not show significant negative regions, indicating that the refined model can be considered valid (Bachmann & Schulz, 1984). Fig. 6 shows the isosurfaces of the probability density for the Ag and Tl atoms. The twin volume ratio was refined to 0.338 (1):0.662 (1). Refinement of the occupancy factor of atom Ag1 led to the final stoichiometry \( \text{Ag}_{2.55(9)}\text{Tl}_{1.20(2)} \).

Data collection: COLLECT (Nonius, 1998); cell refinement: COLLECT; data reduction: EVALCCD (Duisenberg, 1998); program(s) used to solve structure: SIR97 (Altomare et al., 1999); program(s) used to refine structure: JANA2006 (Petříček et al., 2006); molecular graphics: DIAMOND (Brandenburg, 2001); software used to prepare material for publication: JANA2006.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FN3050). Services for accessing these data are described at the back of the journal.

### References


Petrˇí´cekA, 668–675.


