JOURNAL OF SOLID STATE CHEMISTRY 35, 286–290 (1980)

New Pseudo-One-Dimensional Metals: $M_2Mo_6Se_6$ (M = Na, In, K, Tl), $M_2Mo_6S_6$ (M = K, Rb, Cs), $M_2Mo_6Te_6$ (M = In, Tl)

M. POTEL, R. CHEVREL, AND M. SERGENT

Université de Rennes, Laboratoire de Chimie Minérale B, Laboratoire Associé au C.N.R.S. No. 254, Avenue du Général Leclerc, 35042 Rennes Cedex, France

AND J. C. ARMICI, M. DECROUX, AND Ø. FISCHER

Université de Genève, Département de Physique de la Matière Condensée, 32, Boulevard d'Yvoy, 1211 Geneva 4, Switzerland

Received December 12, 1979; in final form February 25, 1980

We present a new series of ternary chalcogenides, derived from divalent molybdenum: $M_2Mo_6X_6$. These compounds crystallize in a hexagonal lattice with $a \approx 9$ Å, $c \approx 4.5$ Å, and space group $P6_3/m$. The compounds are characterized by clusters $(Mo_3)^1_\infty$ in the form of linear chains, resulting from a linear condensation of Mo_6 octahedral clusters. The $(Mo_3)^1_\infty$ clusters are well separated from each other, with the shortest Mo–Mo intercluster distance larger than 6 Å. The resulting pseudo-one-dimensional structures show remarkable anisotropy of physical properties.

Introduction

The structure of the ternary chalcogenides derived from divalent molybdenum is characterized by the presence of octahedral Mo_6 clusters in Mo_6X_8 units (X = chalcogens). These are connected by Mo–Mo intercluster bonds varying between 3.10 and 3.60 Å (*1*). These compounds which have the general formula $M_xMo_6X_8$ (M = metal, $0 < x < 4$, X = chalcogen) (*2*) are in most cases metallic and several of them are high field superconductors (*3–5*).

In several recent publications we have shown that it is possible to obtain new clusters as a result of a one-dimensioned condensation of several Mo_6 clusters, realized by common faces. The condensation of two clusters Mo_6 gives a new cluster Mo_9 in a unit Mo_9X_{11} (*6–7*), the uniaxial condensation of three Mo_6 clusters gives another new cluster Mo_{12} in a unit $Mo_{12}X_{14}$ (*8*). This progressive condensation is followed by a lowering of the chalcogen to molybdenum ratio giving the Mo atoms a more and more metallic character (*9*). In this work we present the preparation and the structural characterization of a new series of ternary molybdenum chalcogenides $M_2Mo_6X_6$ whose ratio X/Mo (=1) is the lowest one presently known.

Preparation

The compounds $M_2Mo_6Se_6$ (M = Na, K, In, Tl) and $M_2Mo_6Te_6$ (M = In, Tl) were prepared from the elements: Na, In, K, and

0022-4596/80/140286-05$02.00/0

TABLE I

CRYSTALLOGRAPHIC DATA AND LATTICE PARAMETERS FOR $M_2Mo_6X_6$ COMPOUNDS

$M_2Mo_6X_6$	Hexagonal Symmetry	Space group $P6_3/m$ Laue group $6/m$ $Z = 1$	
$Tl_2Mo_6Se_6$ Ref. *11*	$a_H = 8.9398(7)$ Å	$c_H = 4.4997(4)$ Å	$V_H = 311.4$ Å^3
$K_2Mo_6Se_6$	$a_H = 9.01(1)$ Å	$c_H = 4.50(1)$ Å	$V_H = 316.4$ Å^3
$In_2Mo_6Se_6$	$a_H = 8.88(1)$ Å	$c_H = 4.49(1)$ Å	$V_H = 306.6$ Å^3
$Na_2Mo_6Se_6$	$a_H = 8.74(1)$ Å	$c_H = 4.42(1)$ Å	$V_H = 296.4$ Å^3
$Tl_2Mo_6Te_6$	$a_H = 9.44(1)$ Å	$c_H = 4.59(1)$ Å	$V_H = 354.2$ Å^3
$In_2Mo_6Te_6$	$a_H = 9.38(1)$ Å	$c_H = 4.58(1)$ Å	$V_H = 349.0$ Å^3
$Cs_2Mo_6S_6$	$a_H = 8.96(1)$ Å	$c_H = 4.46(1)$ Å	$V_H = 310.1$ Å^3
$Rb_2Mo_6S_6$	$a_H = 8.82(1)$ Å	$c_H = 4.44(1)$ Å	$V_H = 299.1$ Å^3
$K_2Mo_6S_6$	$a_H = 8.76(1)$ Å	$c_H = 4.42(1)$ Å	$V_H = 243.7$ Å^3

Tl in the form of lumps, Mo in the form of powder, Se and Te in the form of grains. All manipulations were carried out in a glove box under dry argon atmosphere.

The elements were reacted in evacuated silica tubes at 850°C for 12 hr. During this reaction the samples were placed in Al_2O_3 crucibles in order to avoid contamination by the silica. A subsequent heat treatment at 1000–1200°C for 12 hr was necessary in order to obtain single phase samples. A prolongated annealing at 1150–1200°C allowed us to obtain single crystals in the form of long black needles.

The compounds $M_2Mo_6S_6$ (M = K, Rb, Cs) have to date been obtained only by reduction of the compounds M_xMoS_2 under hydrogen atmosphere at 800°C (*10*). All new compounds are black and are stable in air.

Characterization of the New Compounds

The new compounds have been characterized as described earlier (*2*). Powder-diagrams revealed the existence of a single phase material for the composition $M_2Mo_6X_6$. All deviations from this composition resulted in supplementary diffraction lines indicating that no finite homogeneity domain exists.

A preliminary structural study was carried out on a single crystal of $Tl_2Mo_6Se_6$. The crystal structure is hexagonal with space group $P6_3/m$. The lattice parameters are a_H = 8.9398 Å, c_H = 4.4997 Å. The other compounds are isostructural with $Tl_2Mo_6Se_6$ and their X-ray powder diffraction patterns were indexed by analogy to that of $Tl_2Mo_6Se_6$. The results are summarized in Table I, and Fig. 1 shows the powder diffraction pattern of $Tl_2Mo_6Se_6$. In Table II we have listed the calculated and the observed lattice spacings as well as the observed intensities.

Structural Description

A complete structural determination has been carried out on a single crystal of

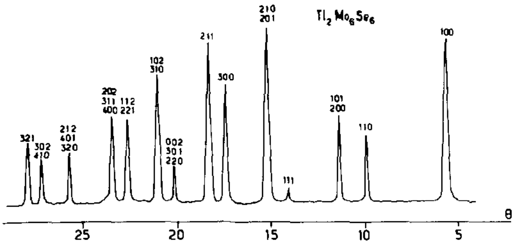

FIG. 1 Powder diffraction pattern for $Tl_2Mo_6Se_6$ (λ Cu$K\bar{\alpha}$ = 1.541 Å).

TABLE II

OBSERVED AND CALCULATED LATTICE SPACINGS AND OBSERVED INTENSITIES FOR $\mathrm{Tl_2Mo_6Se_6}$

Observed intensity	$(hkl)_{\mathrm{Hex.}}$	$d_{\mathrm{obs.}}$	$d_{\mathrm{calc.}}$
90	100	7.810	7.742
43	110	4.486	4.470
57	101 200	3.881	3.890 3.870
7	111	3.171	3.173
100	201 210	2.928	2.934 2.926
64	300	2.581	2.581
85	211	2.453	2.453
20	002 301 220	2.248	2.250 2.239 2.235
69	102 310	2.147	2.160 2.147
40	112 221	2.001	2.010 2.002
41	202 311 400	1.937	1.945 1.938 1.936
28	212 401 320	1.776	1.784 1.778 1.776
25	302 410	1.688	1.696 1.689
32	321	1.650	1.652

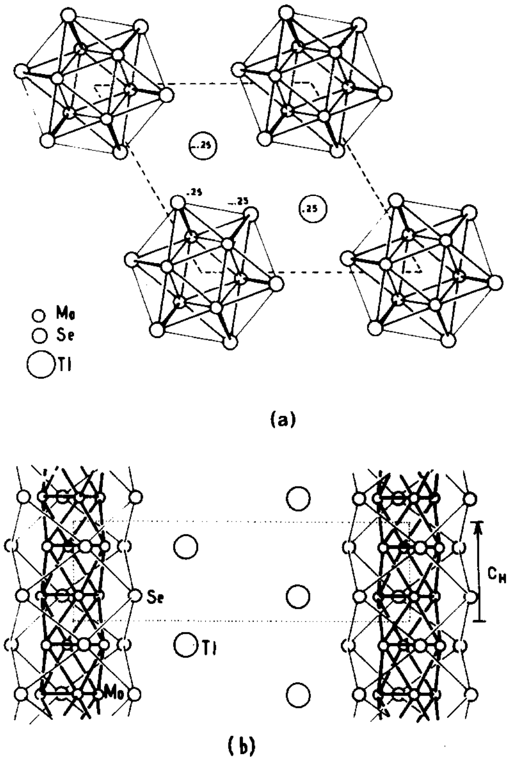

FIG. 2 Projection of the structure of $\mathrm{Tl_2Mo_6Se_6}$ onto the (001) plane (a) and the $(11\bar{2}0)$ plane (b).

$\mathrm{Tl_2Mo_6Se_6}$ (*11*). The new structure is mainly characterized by the presence of one-dimensional chains $(\mathrm{Mo}_3X_3)^1_\infty$ running in the direction of the hexagonal *c* axis and separated by parallel chains of *M* atoms (Fig. 2). The $(\mathrm{Mo}_3X_3)^1_\infty$ chain is formed by an infinite stack of Mo_3 and X_3 triangles in staggered positions and may be viewed as the result of a linear condensation of an infinite number of Mo_6X_6 units. The $(\mathrm{Mo}_3X_3)^1_\infty$ chain is therefore the last member of the series Mo_6X_8, Mo_9X_{11}, $\mathrm{Mo}_{12}X_{14}$ . . . resulting from the progressive polymerization of the Mo_6X_8 units. So far only the three first and the last member of this series have been found, but it seems likely that compounds containing units like $\mathrm{Mo}_{15}X_{17}$ or $\mathrm{Mo}_{18}X_{20}$ etc. can be synthesized.

It is interesting to note that the environments of the molybdenum and the chalcogens are geometrically similar. In fact, the Mo atom faces four chalcogens forming two triangles with a common edge, and conversely each chalcogen atom faces two Mo triangles having a common edge.

The intrachain Mo–Mo bonds are very close to the intracluster bonds observed in other ternary molybdenum chalcogenides and also very close to the nearest neighbor distance of Mo metal (Mo–Mo = 2.723 Å). In $\mathrm{Tl_2Mo_6Se_6}$, the Mo–Mo intratriangle and intertriangle distances are 2.663 and 2.725 Å, respectively. The interplane distance ($\mathrm{Mo_3}$–$\mathrm{Mo_3}$) is 2.25 Å.

The M-element is situated in a 9-prismatic site on chains between the $(Mo_3X_3)^1_\infty$ units.

So far the ternary metal atoms are all monovalent and this leads for the first time to chalcogenides where Mo has a valence lower than 2. In fact the formal number of electrons on each Mo atom is 4.33. This constitutes an essential difference with other ternary molybdenum chalcogenides where this number was always situated below 4.

Another difference with the other chalcogenides comes from the fact that there is no chalcogen situated on the "ternary" axis in $M_2Mo_6X_6$. In the other chalcogenides the chalcogen situated on the ternary axis created three square chalcogen faces on each side of a cluster from which the bond to the next cluster was realized (Fig. 3a). In the new linear chain materials these latter bonds are absent and the shortest Mo–Mo interchain distance is greater than 6 Å (6.34 Å in $Tl_2Mo_6Se_6$) (Fig. 3b). There is therefore practically no direct interchain 4*d*–4*d* overlap, and the electronic interchain coupling must pass through two Se atoms. From structural considerations we therefore expect these materials to be highly anisotropic. Note also that the Tl–Mo distance is as large as 3.759 Å.

Physical Properties

A detailed study of some physical properties has been carried out on single crystals of $Tl_2Mo_6Se_6$ (*12*). This compound shows metallic behavior but the resistivity is strongly anisotropic. The residual resistivity at 4.2 K parallel to the *c* axis is about 30 $\mu\Omega$cm, whereas the perpendicular resistivity is several hundred times larger. At 3 K, $Tl_2Mo_6Se_6$ becomes superconducting, and the anisotropy of the resistivity shows up in a strong anisotropy of the upper critical field H_{c2}. The ratio $H^{\parallel}_{c2}/H^{\perp}_{c2}$ was found to be larger than 20. This corresponds to a mass anisotropy of at least 400, which is of the same order of magnitude as the one observed in certain organic materials (*13*).

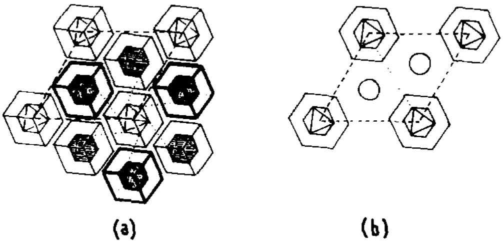

FIG. 3 (a) intercluster bonds shown in the projection on the (001) plane of M Mo_6X_8, $M_2Mo_{15}X_{19}$, and $M_2Mo_9X_{11}$; (b) the same projection for $M_2Mo_6X_6$. The dotted line show the shortest Mo–Mo intercluster distance.

Conclusions

The new class of materials $M_2Mo_6X_6$ described here may be considered as the last member of the series of new materials MMo_6X_8, $M_2Mo_{15}X_{19}$, $M_2Mo_9X_{11}$ containing Mo_6 clusters, Mo_6 and Mo_9 clusters, and Mo_6 and Mo_{12} clusters, respectively. The series Mo_6, Mo_9, Mo_{12} . . . may be viewed as resulting from a progressive linear condensation of Mo_6 clusters. The last member in this series is an infinite chain $(Mo_3)^1_\infty$ of Mo_3 triangles, as found in the new materials described in this work. The presence of these chains gives these materials, both in the structure as well as in the physical properties, a strongly anisotropic character.

Note: A new ternary compound $Tl_2Fe_6Te_6$ of similar structure has been recently isolated (*14*).

References

1. J. GUILLEVIC, These d'état, University of Rennes (1974).
2. R. CHEVREL, These d'état, University of Rennes (1974).

3. B. T. Matthias, M. Marezio, E. Corenzwit, A. S. Cooper, H. E. Barz, *Science* **175**, 1465 (1972).
4. R. Odermatt, Ø. Fischer, H. Jones, and Bongi, *J. Phys.* **C7**, L13 (1974).
5. For a review of physical properties see Ø. Fischer, *Appl. Phys.* **16**, 1 (1978).
6. R. Chevrel, M. Sergent, B. Seeber, Ø. Fischer, A. Grüttner, and K. Yvon, *Mat. Res. Bull.* **14**, 567 (1979); A. Grüttner, K. Yvon, R. Chevrel, M. Potel, M. Sergent, and B. Seeber, *Acta Cryst.* **B35**, 285 (1979); B. Seeber, M. Decroux, Ø. Fischer, R. Chevrel, M. Sergent, and A. Grüttner, *Solid State Commun.* **29**, 419 (1979).
7. R. Chevrel, M. Potel, M. Sergent, M. Decroux, and Ø. Fischer, *Mat. Res. Bull.* **15**, 867 (1980); M. Potel, R. Chevrel, and M. Sergent, *Acta Cryst.*, in press.
8. R. Chevrel, M. Potel, M. Sergent, M. Decroux, and Ø. Fischer, *J. Solid State Chem.* **34**, 247 (1980); M. Potel, R. Chevrel, and M. Sergent, *Acta Cryst.* **B36**, 1319 (1980).
9. M. Potel, R. Chevrel, M. Sergent, M. Decroux, and Ø. Fischer, *C. R. Acad. Sci. Paris* **288**, 429 (1979).
10. M. Sergent, Thesis University of Rennes (1969).
11. M. Potel, R. Chevrel, and M. Sergent, Acta Cryst. **B36**, 1545 (1980).
12. J. C. Armici, M. Decroux, Ø. Fischer, M. Potel, R. Chevrel, and M. Sergent, *Solid State Comm.*, **33**, 607 (1980).
13. See for instance H. J. Keller (Ed.), "Chemistry and Physics of One Dimensional Metals." Plenum Press, New York (1977).
14. K. Klepp and H. Boller, *Mh. Chem.* **110**, 677 (1979).