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Ternary Molybdenum Chalcogenides: A Route to New Extended Clusters*

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Within the last decade, the ternary molybdenum chalcogenides have played a major role in superconductivity: opening of the ternary superconductor range, competition between superconductivity and magnetism. It is mainly due to the pseudomolecular nature of the Mo_6X_8 unit. In these materials, the Mo_6 cluster plays the electron-acceptor role and the number of valence electrons per molybdenum atom is related to the Mo–Mo intracluster bonding. The increase of this valence electron concentration (VEC) per molybdenum in new ternary chalcogenides corresponds to larger and larger clusters. These new extended clusters belong to a very large family containing the general $Mo_{3n}X_{3n+2}$ ($n \geq 2$) block unit. The tridimensional stacking of these building blocks provides more and more large channels and leads to a more and more anisotropic character of their physical properties.

Introduction

The ternary molybdenum chalcogenides $M_xMo_6X_8$ (X = S, Se, Te; M = a cation), so called "Chevrel phases," have stimulated a great amount of interest because of their outstanding remarkable properties.

These chalcogenides were considered by Matthias *et al.* (*1*) as the first superconducting ternary system having high critical temperatures, reaching 15 K for the $PbMo_6S_8$ compound. These compounds have helped open the way to the research of new ternary superconductors. The upper critical field H_{c_2} of the Pb/Mo/S compound ($H_{c_2} \sim 60$ T) is, so far, the highest value observed in any class of superconductors; it exceeds by more than 20 T, the highest value reported for the Nb_3Ge binary (*2, 3*). Another center of interest is the interplay between superconductivity and magnetism at low temperatures in the rare earth molybdenum chalcogenides: the coexistence of superconductivity and antiferromagnetism or the competition between superconductivity and ferromagnetism. Another property is the high and reversible mobility of the M^{n+} counterions (Cu, Li, Fe, Ni . . .) allowing one to carry out reversible topotactic redox reactions (*4*). This property is used to make new metastable binary or ternary molybdenum chalcogenides (*5, 6*). The originality of this family resides in the

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fact that they are ternary cluster-based superconductors, providing the beginning for an intense activity in the field of new cluster-based materials (*7*). It seems that the clustering of the transition metal atoms has been found to be a feature common to ternary high-T_c superconductors and is therefore a contributing factor to the high critical temperatures.

The purpose of this paper is to describe briefly the structural aspects of the M_x Mo_6X_8 compounds and new extended cluster compounds and to exhibit the relationships between the valence electron concentration per molybdenum and the size of the cluster.

Structural Aspects of the $M_xMo_6X_8$ Compounds

The $M_xMo_6X_8$ ternary molybdenum chalcogenides are a very large family of compounds (more than 100 compounds where M stands for about 40 elements and X a chalcogen atom) made up from the Mo_6X_8 quasirigid building blocks (*5*):

Each Mo_6X_8 block unit is constituted from an octahedral molybdenum Mo_6 cluster (slightly elongated along the threefold axis) where the faces are bridged by eight chalcogen atoms forming a pseudocube like the Mo_6Cl_8 unit of molybdenum dichloride. These cubic units are directly interconnected via short Mo–X intercluster bonds arising from tilting of the units: every Mo atom in one octahedral cluster, located at the center of a chalcogen square face of one unit, is bonded to another chalcogen in a neighboring unit. The five Mo–X distances are nearly equal (Mo–S ~ 2.5 Å). The stacking and bridging of these Mo_6X_8 units makes possible the Mo–Mo intercluster bonding. These Mo–Mo intercluster distances depend strongly upon the nature of the M element and the X chalcogen; for instance, they vary from 3.1 to 3.3 Å in the sulfides and are 20% larger than the intracluster Mo–Mo distances (~2.7 Å) (Fig. 1).

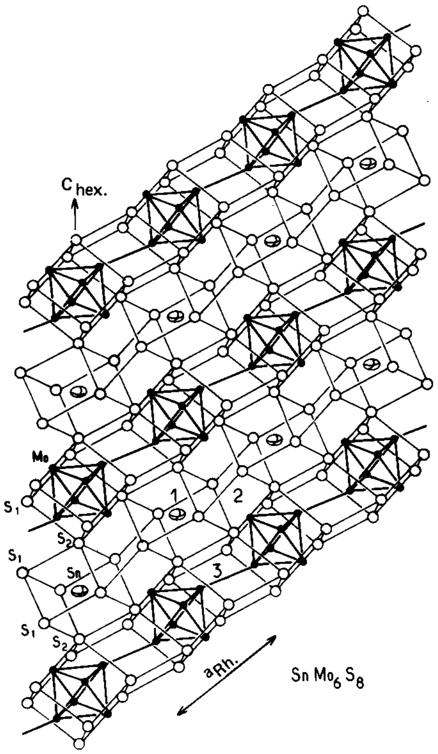

FIG. 1. Projection onto the (11$\bar{2}$0) hexagonal plane of the $SnMo_6S_8$ compound.

These Mo–Mo interactions are relatively weak as proved by band structure calculations (*7*) but are very important for electronic properties of these materials. The two main cavities form tridimensional channels running along the chains of weakly coupled octahedral clusters and are either empty (binaries) or partially filled by the counterions like tin ions.

The Valence Electron Concentration (VEC) and Related Properties

The large electronegativity differences between the two metals M and Mo and the nonmetal chalcogen imply the occurrence of the charge transfer within the structure.

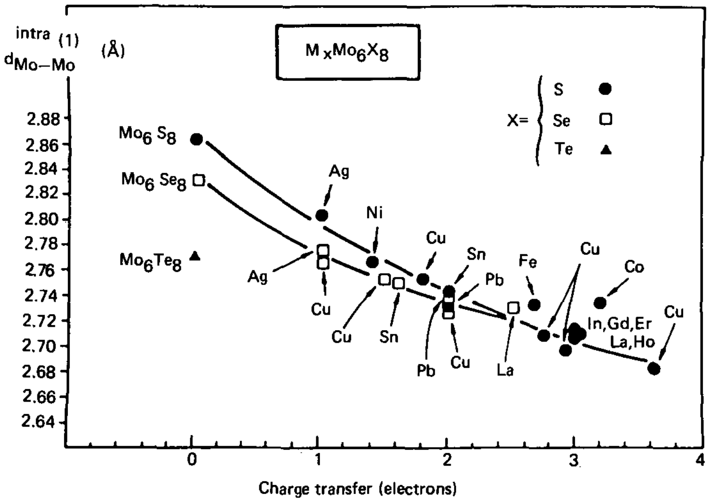

FIG. 2. The decrease of the Mo–Mo intracluster distance d_l as a function of the charge transfer (or the VEC) (after Ref. (*7*)).

We are going to consider this charge transfer from the *M* elements to the Mo_6 cluster or better, the number of the valence electrons on the molybdenum atoms, the so-called VEC (valence electron concentration), which are available for the Mo–Mo intracluster bonding (*8*). In the first approximation, for instance, in the $PbMo_6S_8$ compound, the lead atom transfers its two *p* electrons to the Mo_6S_8 unit, giving the Pb^{2+} ion, and the sulfur atoms accept 2 electrons to fill their *p*-states (S^{2-}); so there remain 22 electrons per Mo_6 cluster or a VEC equal to 3.66 electrons per molybdenum. So, in the binary Mo_6S_8, the VEC is 20 electrons per Mo_6 cluster or 3.33 e^- per Mo, the electron-poorest compound with the least regular cluster whereas in the $Cu_xMo_6S_8$ solid solution, the $Cu_4Mo_6S_8$ compound with a VEC of 24 e^- per cluster or 4 e^- per molybdenum is the electron-richest compound and has the most regular Mo_6 cluster. It seems that the counting of the VEC is also a measure of the Mo–Mo intracluster bonding. Actually, if we plot the Mo–Mo intracluster distance d_l parallel to the direction of the threefold axis versus the charge transfer or the number of valence electrons per cluster or per molybdenum (VEC), we obtain a good relationship between both variables (Fig. 2). The larger the charge transfer from the *M* element onto the cluster (from an increased content or charge of the *M* element) is or the VEC, the shorter the Mo–Mo intracluster bonding d_l becomes, and the more the Mo_6 cluster is regular. In fact, the Mo_6 cluster plays the role of an electron–acceptor.

Furthermore, the band structure calculations, related to the pseudomolecular aspect of the structure, show the Fermi level falls in narrow bands that mainly arise from the 4*d*-molybdenum character. That narrow band is completely filled with 24 electrons per cluster or 4 electrons per Mo. Thus, an increase of the VEC from 20 to 24 electrons corresponds to a gradual filling of this conduction band.

One consequence of this gradual filling is the stability of the compounds. Really, the binary Mo_6S_8 compound containing 20 e^- per cluster (the most elongated Mo_6 cluster) is a metastable compound (it decomposes at 470°C); it cannot be made through heating of its constitutive elements at high temperature, but only by deintercalation (*9*). So, if we change the VEC by substitution of two bromine or iodine atoms for two of sulfur, we obtain the pseudobinaries $Mo_6S_6Br_2$ and $Mo_6S_6I_2$ at high temperatures containing 22 electrons per cluster or a VEC equal to 3.66 electrons per Mo atom (*10*). These compounds are high-T_c superconductors (13.8 and 14 K, respectively) and have the same VEC that the two better ternary superconductors ($PbMo_6S_8$, $SnMo_6S_8$). The synthesis of new pseudobinaries at high temperatures has been carried out, for instance, for the semiconducting pseudobinary $(Mo_2Re_4)S_8$ with 24 electrons per cluster and a filled *d*-band (*11*).

New Extended Clusters in Other Ternary Molybdenum Chalcogenides

Some general conclusions can be drawn when we consider obtaining new extended clusters in the ternary molybdenum chalcogenides: the number of valence electrons (VEC) available for Mo–Mo bonding must be increased to allow an increase in the number of the metallic bonding. In other words, the formal oxidation state will be lowered; i.e., the compounds will become more and more reduced and the ratio X/Mo will become lower and lower. Of course, the VEC will be a function of the charge transfer and the number of the counterions.

A considerable number of Mo-cluster chalcogenides closely related to the Mo_6X_8 structure have been prepared at high temperatures. The syntheses of the ternary molybdenum chalcogenides have been performed using appropriate mixtures of Mo powder, MoX_2 or Mo_6X_8 chalcogenide and M element in the form of metallic grains (M = Ag, In, Tl), binary compounds (BaS), or ternary compounds (M_2MoS_4 or $M_2Mo_6X_6$) in evacuated silica tubes or sealed molybdenum crucibles.

The $M_2Mo_6S_6$ phases (M = alkali metal) can be obtained by different methods: reduction of MMoS$_2$ under H_2 flow at 950°C (*12*) or by solid–solid reaction between M_2MoS_4, MoS_2, and Mo powder in evacuated sealed silica tubes. The $M_2Mo_6X_6$ (X = Se, Te) alkali metal phases are also synthesized by cationic exchange in a temperature gradient (500°C–room temperature) according to the reaction (5, 6, 13)

$$In_2Mo_6X_6 + 2\,MCl \xrightarrow{\text{between 500 and 800°C}} M_2Mo_6X_6 + 2\,InCl\uparrow$$

The new $M_{2n-2}Mo_{6n}X_{6n+2}$ series have been prepared from mixtures of $M_2Mo_6X_6$ and Mo_6X_8 phases (X = Se) (or MoS_2 and Mo powder):

$$(n-1)M_2Mo_6X_6 + Mo_6X_8 \rightarrow M_{2n-2}Mo_{6n}X_{6n+2}$$

The reaction is carried out in sealed molybdenum crucibles at 1300–1500°C (*14*). This method allows one to obtain single crystals of these later compounds and likewise, the pseudo-one-dimensional $M_2Mo_6X_6$ alkali metal compounds. The lattice parameters and the volumes of the unit cells in the new $M_{2n-2}Mo_{6n}X_{6n+2}$ series and the $M_2Mo_6X_6$ compounds are reported in Tables I and II, respectively. The detailed structural pa-

TABLE I

RHOMBOHEDRAL AND HEXAGONAL LATTICE PARAMETERS OF THE $M_{2n-2}Mo_{6n}X_{6n+2}$ SERIES (SPACE GROUP $R\bar{3}$)

	a_{Rh} (Å)	α_{Rh} (°)	V_{Rh} (Å^3)	a_H (Å)	c_H (Å)
Mo_6S_8	6.432	91.34	265.8	9.20	10.88
$Cs_6Mo_{24}S_{26}$	17.705	30.62	1276.8	9.351	50.59
$Cs_8Mo_{30}S_{32}$	21.960	24.56	1608.7	9.423	63.83
Mo_6Se_8	6.658	91.58	294.7	9.54	11.21
$Cs_2Mo_{12}Se_{14}$	9.905	58.38	661.6	9.661	24.55
$Rb_4Mo_{18}Se_{20}$	13.896	39.94	998.9	9.492	38.31
$Rb_6Mo_{24}Se_{26}$	18.110	30.23	1333.9	9.444	51.81
$Cs_6Mo_{24}Se_{26}$	18.087	30.91	1384.7	9.639	51.63
$Cs_8Mo_{30}Se_{32}$	22.409	24.78	1738.4	9.616	65.13

TABLE II

HEXAGONAL LATTICE PARAMETERS OF THE PSEUDO-ONE-DIMENSIONAL $M_2Mo_6X_6$ COMPOUNDS (SPACE GROUP $P6_3/m$, $Z = 1$)

	a (Å)	c (Å)	V (Å^3)
$K_2Mo_6S_6$	8.72	4.41	290.3
$Rb_2Mo_6S_6$	8.96	4.41	306.6
$Cs_2Mo_6S_6$	9.26	4.42	328.6
Mo_6Se_6	8.35	4.44	268
$Ag_2Mo_6Se_6$	8.56	4.50	286
$Na_2Mo_6Se_6$	8.65	4.49	291.0
$In_2Mo_6Se_6$	8.85	4.50	306.6
$Tl_2Mo_6Se_6$	8.94	4.50	311.4
$K_2Mo_6Se_6$	9.05	4.49	318.6
$Rb_2Mo_6Se_6$	9.26	4.49	338.8
$Cs_2Mo_6Se_6$	9.54	4.50	354.9
$Ba_2Mo_6Se_6$	9.06	4.29	305
$Na_2Mo_6Te_6$	9.23	4.60	339
$In_2Mo_6Te_6$	9.35	4.59	347
$Tl_2Mo_6Te_6$	9.44	4.59	354
$K_2Mo_6Te_6$	9.60	4.60	367
$Rb_2Mo_6Te_6$	9.76	4.60	379
$Cs_2Mo_6Te_6$	10.09	4.60	405.4
$Ba_2Mo_6Te_6$	9.41	4.57	350

rameters from single crystals are available in Ref. (*14*).

The principle of cluster condensation in the ternary molybdenum chalcogenides is based on the sharing of opposite faces of the Mo-cluster octahedra when the ratio X/Mo is decreased. All of these new cluster units derive from a linear progressive condensation of the Mo_6X_8 units along the ternary axis: as shown in Fig. 3, the Mo_9X_{11} and the $Mo_{12}X_{14}$ units, the new $Mo_{18}X_{20}$, $Mo_{24}X_{26}$, $Mo_{30}X_{32}$ block units, and then the limit of the series ($n = \infty$) $|Mo_{6/2}X_{6/2}|^1_\infty$ in a one-dimensional chain.

The units all belong to the same very general unit:

$$Mo_{3n}X_{3n+2} \qquad (n \geq 2).$$

This general formula allows a fragmental decomposition of the units. In fact, the Mo_6X_8 cubic unit observed along the threefold axis can be viewed as two Mo_3X_3 star-shaped planes ($n = 2$) capped by two chalcogen atoms on the threefold axis. Then, the Mo_9X_{11} unit ($n = 3$), the $Mo_{12}X_{14}$ unit ($n = 4$), and so on . . . can be, respectively, described as a stacking of three Mo_3X_3 star-like planes, four Mo_3X_3 star-like planes, and so on . . . , always capped by two chalcogen atoms to give discrete units.

The Mo–Mo and Mo chalcogen intracluster distances in these longer clusters are like the intracluster distances in the $M_xMo_6X_8$ compounds. Apart from the infinite unit, the Mo terminal atoms (Mo_3

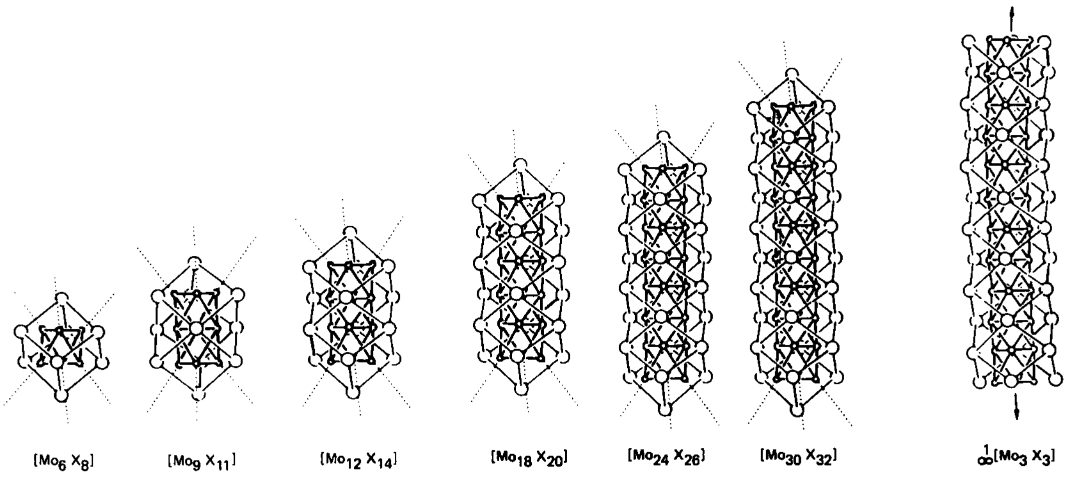

FIG. 3. The principle of cluster condensation.

TABLE III

RELATIONSHIPS BETWEEN THE VALENCE ELECTRON CONCENTRATION PER CLUSTER OR PER MOLYBDENUM ATOM (OR THE FORMAL OXIDATION STATE) AND THE SIZE OF THE EXTENDED CLUSTERS IN THE TERNARY MOLYBDENUM CHALCOGENIDES AS WELL AS THE NUMBER OF CHALCOGENS PER Mo_6 AND THE RATIO OF CHALCOGEN TO Mo

X/Mo_6	X/Mo	Compound	Cluster units	VEC/cluster	VEC/Mo	Formal oxidation number = 6 − VEC
8	1.33	$M_x\mathrm{Mo}_6X_8$	$\lvert\mathrm{Mo}_6X_8\rvert^{0\to4-}\ M_x^{n+}\ {}^{1+-4+}_{0\ -4}$	20–24 e^-	3.33–4	2.66–2
7.6	1.26_7	$\mathrm{In}_{\sim3}\mathrm{Mo}_{15}\mathrm{Se}_{19}$				
		$2\ \mathrm{In}^{+1} \sim 1\ \mathrm{In}^{3+}$	$(\mathrm{Mo}_6X_8)(\mathrm{Mo}_9X_{11})$			
		$\mathrm{In}_2^{+}\mathrm{Mo}_{15}\mathrm{Se}_{19}$	$= (\mathrm{Mo}_6X_8)^{0\to4-} + (\mathrm{Mo}_9X_{11})^{2+\to4-}$	20–24 e^-	3.33–4	2.66–2
		$\mathrm{Ba}_2^{2+}\mathrm{Mo}_{15}\mathrm{Se}_{19}$		30–36 e^-	3.33–4	2.66–2
7.33	1.22_2	$\mathrm{Ag}_{3.6}^{+}\mathrm{Mo}_9\mathrm{Se}_{11}$	$\lvert\mathrm{Mo}_9X_{11}\rvert$			
			$(\mathrm{Mo}_9\mathrm{Se}_{11})^{3.6-}$	35.6 e^-	3.95_5	2.04
		$\mathrm{Tl}_2^{+}\mathrm{Mo}_9\mathrm{S}_{11}$	$(\mathrm{Mo}_6X_8)(\mathrm{Mo}_{12}X_{14})$			
			$= (\mathrm{Mo}_6X_8)^{0\to4-} + (\mathrm{Mo}_{12}X_{14})^{4-\to0}$	20–24 e^-	3.33–4	2.66–2
				44–48 e^-	3.66–4	2.33–2
7	1.16_7	$\mathrm{Cs}_2\mathrm{Mo}_{12}\mathrm{Se}_{14}$	$\lvert\mathrm{Mo}_{12}\mathrm{Se}_{14}\rvert^{2-}$	46 e^-	3.83_3	2.16_7
6.66	1.11_1	$\mathrm{Rb}_4\mathrm{Mo}_{18}\mathrm{Se}_{20}$	$\lvert\mathrm{Mo}_{18}\mathrm{Se}_{20}\rvert^{4-}$	72 e^-	4	2
6.50	1.08_3	$\mathrm{Cs}_6\mathrm{Mo}_{24}\mathrm{Se}_{26}$	$\lvert\mathrm{Mo}_{24}\mathrm{Se}_{26}\rvert^{6-}$	98 e^-	4.08	1.92
6.40	1.06_6	$\mathrm{Cs}_8\mathrm{Mo}_{30}\mathrm{Se}_{32}$	$\lvert\mathrm{Mo}_{30}\mathrm{Se}_{32}\rvert^{8-}$	124 e^-	4.13	1.87
6	1	$\mathrm{Tl}_2\mathrm{Mo}_6\mathrm{Se}_6$	$\lvert\mathrm{Mo}_{6/2}\mathrm{Se}_{6/2}\rvert_{\infty}^{1-}$	13 e^-/Mo_3	4.33_3	1.66_6

plane) in the top and bottom layers of these finite clusters have the same surroundings as the six Mo atoms of the Mo_6X_8 unit.

Each one of the six Mo terminal atoms is located to the center of square of chalcogen atoms and is interconnected to another unit by short Mo–X intercluster bonds; this packing allows some Mo–Mo intercluster contacts. In the terminal Mo_3X_3 planes, the Mo atom has nine coordinated atoms: four Mo atoms and four X atoms of the same unit and one X chalcogen atom of a neighboring unit; the X chalcogen atom has four metal neighbors: three Mo atoms of the same unit and one Mo atom of a different unit. In the central Mo_3X_3 planes, the Mo atom has 10 coordinated atoms: six Mo atoms and four X atoms in the same unit but no contacts with any atoms in the surrounding unit; the X atom has four Mo neighboring atoms of the same unit.

We can remark that the metal-ligand environment is the same as the ligand-metal environment in the central plane: each atom is surrounded by four butterfly-shaped different atoms, this allowing one-dimensional polymerization.

The limit term of this series ($n = \infty$) (Fig. 3) is $(\mathrm{Mo}_3X_3)_\infty^1$ and contains quasi-infinite columns of face-sharing Mo_6 octahedra and contains only the central Mo_3X_3 planes.

Relationships between the VEC and the Size of the Extended Cluster

In Table III are summarized the results on the new extended clusters. It is seen that the lowering of the formal oxidation state of the Mo atom or the increase of the valence electron concentration per Mo atom together with the decrease of the ratio X/Mo and the charge transfer from the M^{n+} counterions are well related to the size of the extended clusters. We have already seen that in the first chalcogenides, the ratio X/

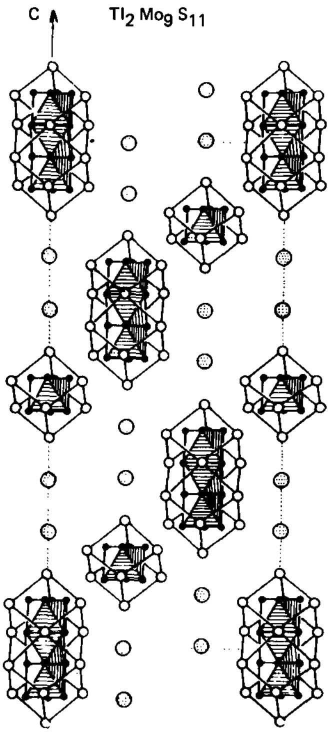

FIG. 4. Projection onto the (11$\bar{2}$0) hexagonal plane of the $Tl_2Mo_9S_{11}$ compound.

Mo is 1.33 and the charge of the Mo_6X_8 unit can vary from 0 to 4^-, corresponding to 20 and 24 electrons per Mo_6 cluster. For the ratio X/Mo equal to 1.26_7, we have two kinds of compounds in which two types of building blocks coexist: Mo_6X_8 and Mo_9X_{11} units. Based on the assumption of the variation in the negative charge (from 0 to 4) of the Mo_6X_8 unit as the $M_xMo_6X_8$ compounds, and accounting for the charge transfer of the indium or barium counterions, the formal Mo-electron number found on the Mo_9X_{11} unit will be between 30 and 36 electrons per Mo_9 cluster. This corresponds to the same range of the VEC per Mo atom as before (3.33 to 4 e^-). For the ratio 11/9 or 1.22_2, we have therefore two kinds of compounds: one containing the only Mo_9Se_{11} unit in $Ag_{3.6}Mo_9Se_{11}$ (*15*) with almost 4 electrons per Mo and the other one, $Tl_2Mo_9S_{11}$, where both Mo_6X_8 and $Mo_{12}X_{14}$ units cocrystallize. With the same assumption as before, the Mo_{12} cluster will count between 44 and 48 e^-, corresponding to a VEC range between 3.66 and 4 electrons per Mo atom.

The new condensed cluster selenides synthesized recently by Gougeon (*14*) are obtained by further reduction of the X/Mo ratio. The ratio in these lies between 1.16_7 and 1.06_6 as the new clusters become larger and larger: the Mo_{12}, Mo_{18}, Mo_{24}, and Mo_{30} clusters are more and more extended and are multiples of the primary Mo_6 octahedra. The new ($Mo_{12}Se_{14}$), ($Mo_{18}Se_{20}$), ($Mo_{24}Se_{26}$), ($Mo_{30}Se_{32}$) units have twofold, fourfold, sixfold, and eightfold negative formal charges, respectively, and a VEC per Mo atom increasing from 3.83, 4, 4.08 to 4.13, respectively. It is a stepwise condensation of the Mo_6X_8 units.

At the end of the linear condensation of these units, the infinite limit chain $|Mo_{6/2}X_{6/2}|^1_\infty$ has a 1− negative charge for each planar Mo_3X_3 unit in the $Tl_2Mo_6Se_6$ compound, and it corresponds to 13 electrons per Mo_3 plane and a VEC of 4.33 per Mo atom.

What is the structural tridimensional arrangement of these different condensed clusters? The different stacking of the Mo_6X_8 and Mo_9X_{11} block units provides two families of superconducting-type compounds: $In_2Mo_{15}Se_{19}$ and $In_{\sim 3}Mo_{15}Se_{19}$ (*16, 17*). The $M_2Mo_9S_{11}$ compounds (M = K, Tl) do not contain the Mo_9X_{11} unit but the two mixed Mo_6S_8 and $Mo_{12}S_{14}$ units where one-half of the Mo_6S_8 units are replaced by the $Mo_{12}S_{14}$ units of the same ($\bar{3}$) point symmetry (*18*). The sequence along the c hexagonal axis is Mo_6S_8–Tl–Tl–$Mo_{12}S_{14}$ (Fig. 4). The different length of the $Mo_{12}S_{14}$ unit with respect to the Mo_6S_8 unit leaves large vacant sites between two units along the c hexagonal axis where two thallium monovalent ions are located.

The new compounds in the M_{2n-2}

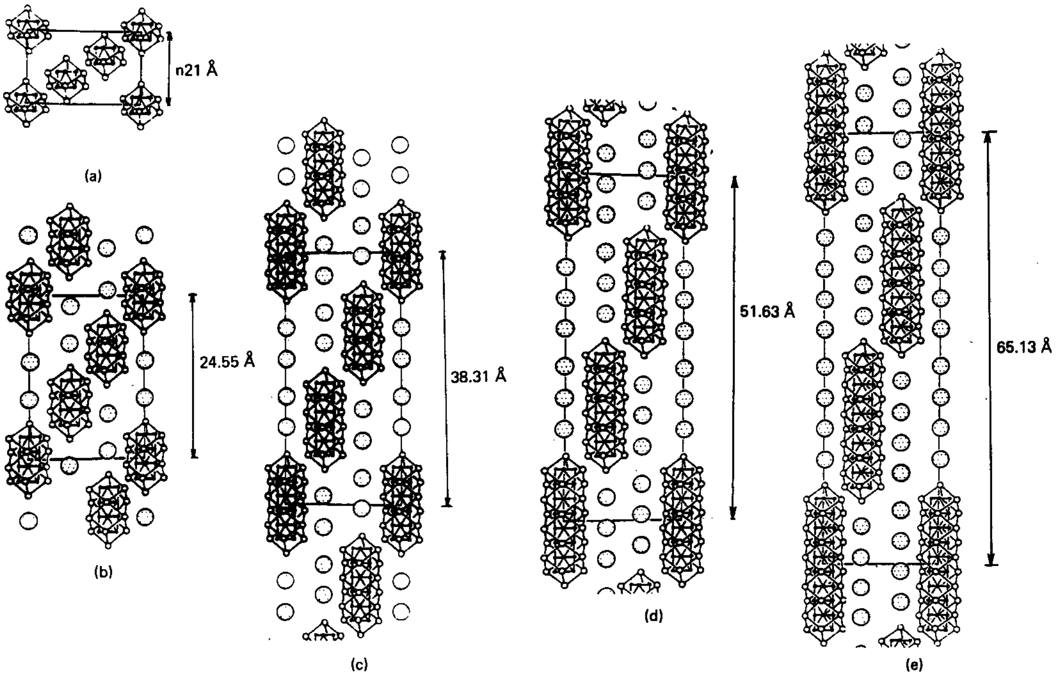

FIG. 5. Projection onto the (11$\bar{2}$0) hexagonal plane of the $M_{2n-2}Mo_{6n}X_{6n+2}$ series. Mo_6Se_8 (a), $Cs_2Mo_{12}Se_{14}$ (b), $Rb_4Mo_{18}Se_{20}$ (c), $Cs_6Mo_{24}Se_{26}$ (d), and $Cs_8Mo_{30}Se_{32}$ (e).

$Mo_{6n}X_{6n+2}$ family crystallize in the same space group $R\bar{3}$ as do the $M_xMo_6X_8$ phases. These compounds are richer and richer in molybdenum atoms (the ratio of chalcogen to Mo decreases) and contain longer and longer units with more and more extended clusters. Every Mo_6X_8 unit is replaced by the condensed $Mo_{6n}X_{6n+2}$ unit of the $\bar{3}$ same symmetry. These condensed units create larger and larger tridimensional channels which run along the three rhombohedral axes (Fig. 5). Of course, more large cations like alkali metals Rb, Cs occur in these channels along the threefold axis with increasing content.

The first results on the transport properties performed on single crystals of the $Cs_2Mo_{12}Se_{14}$ and $Cs_6Mo_{24}Se_{26}$ ternary selenides show that these exhibit superconducting transitions ($T_c \sim 4$ and 3 K, respectively) though the $Cs_6Mo_{24}S_{26}$ compound shows a drastic metal–insulator transition at 112 K in the resistivity associated with a structural transition.

This lengthening of these units leads directly to the one-dimensional compounds with the $Tl_2Mo_6Se_6$-type structure (*19, 20*). In this type of compound, there are no terminal Mo atoms because there are no capped chalcogen ligands on the threefold axis and no square-face ligands. Thus, there are no close contacts between the different chains as in the previous clusters (intercluster distances ~ 6.30 Å).

These infinite $(Mo_{6/2}Se_{6/2})^1_\infty$ chains are separated by the Tl monovalent ions and Se–Se van der Waals contacts (Fig. 6). Thus the resistivity measurements performed on single crystals indicate a very high anisotropy ($\rho_\perp/\rho_\parallel$ above 1000). This result fits with the anisotropy of the critical field of the superconducting $Tl_2Mo_6Se_6$ compound ($T_c \sim 6$ K) (*21–23*).

On the contrary, the low resistivities of

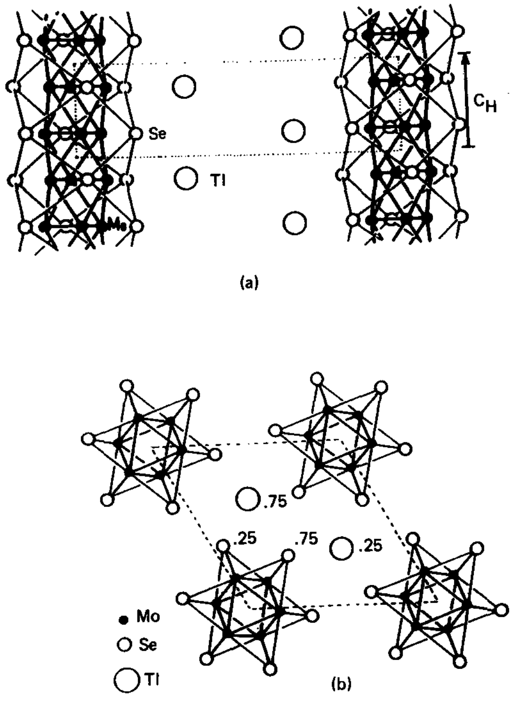

FIG. 6. Projection onto the $(11\bar{2}0)$ (a), and (0001) (b) hexagonal planes of the $Tl_2Mo_6Se_6$ structure.

the alkali metal compounds at room temperature ($\rho_{RT} \sim 0.1$ to 1 mΩ cm) increase strongly at low temperature (below 70 K) by factors of 10^3 to 10^8.

These results have opened up a lot of research on many cluster compounds. Some recent results provide hope for establishing a solution-phase chemistry such as the well-known chemistry of the $Mo_6Cl_8^{4+}$ ion.

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