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One-Dimensional Condensation of Mo_6 Octahedral Clusters: A New Cluster, Mo_{12}, and a New Building Block, $Mo_{12}S_{14}$, in $M_2Mo_9S_{11}$

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

Université de Rennes, Laboratoire de Chimie Minérale B, Laboratoire Associé au CNRS n° 254, Avenue du Général Leclerc, 35042 Rennes Cedex, France

AND M. DECROUX AND Ø. FISCHER

Université de Genève, Département de Physique de la Matière Condensée 132, boulevard d'Yvoy, 1211 Genève 4, Suisse

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Two new Mo compounds, $Tl_2Mo_9S_{11}$ and $K_2Mo_9S_{11}$, have been found. The structure of these compounds is characterized by the presence of a completely new building block, $Mo_{12}S_{14}$, in addition to the well-known Mo_6S_8 unit as in the $PbMo_6S_8$-type compounds. The new cluster, Mo_{12}, contained in the $Mo_{12}S_{14}$ unit can be considered as a one-dimensional condensation of three Mo_6 octahedral clusters. These new materials, the structure of which resembles that of $PbMo_6S_8$, are metallic but are not superconducting above 2.1°K.

Introduction

In earlier publications, we have reported the synthesis and structure of several new ternary molybdenum chalcogenides. These new compounds are all characterized by the presence of Mo clusters: in the $M_xMo_6X_8$-type materials (M=metal; X = S, Se, Te) (*1*), one finds Mo_6 octahedral clusters (*2*), and in $In_3Mo_{15}Se_{19}$ (*3*) and $M_2Mo_{15}X_{19}$ (to be published), a combination of Mo_6 and Mo_9 clusters. The Mo_9 cluster which belongs to a Mo_9X_{11} building block can be viewed as a condensation of two Mo_6 clusters along a face.

In the present work, we present two new compounds, $Tl_2Mo_9S_{11}$ and $K_2Mo_9S_{11}$, which have structures very similar to that of $In_2Mo_{15}Se_{19}$ but where the Mo_9S_{11} unit is replaced by a $Mo_{12}S_{14}$ unit. The latter unit contains a completely new type of cluster Mo_{12}.

Preparation

The two compounds were prepared starting from the elements in a glove box under deoxygenized, dry-argon atmosphere. The reactions were performed in evacuated silica tubes and special care was taken in order to avoid any contact of the initial mixtures with the silica (refractory crucible). The first reactions were carried out at 850°C for 12 hr followed by an annealing at 1000–1100°C for another 12 hr. The compounds thus obtained are black and stable in air. Small single crystals in the form of elongated rhombohedra were obtained after a prolonged annealing.

Results of the X-Ray Analysis

The two compounds were characterized by the usual methods (*1*). The analysis of powder diagrams showed a single-phase

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material for the composition $M_2Mo_9S_{11}$ (M = K, Tl). Deviations from this composition always gave new X-ray lines, indicating that $Tl_2Mo_9S_{11}$ and $K_2Mo_9S_{11}$ are two definite compounds without a homogeneity domain.

A preliminary structural study was carried out on single crystals of the two materials. This analysis showed that the compounds crystallize in a hexagonal–rhombohedral lattice with space group $R\bar{3}$ (Laue group $\bar{3}$) and allowed us to determine the lattice parameters of the two compounds (Table I).

A complete structural study was then carried out on $Tl_2Mo_9S_{11}$ (*4*). In Fig. 1, we show the X-ray diagram of this compound, and in Table II, we give the corresponding lattice spacings with the hexagonal and the rhombohedral *hkl* indices, as well as the observed intensities.

Description of the Structure (of $Tl_2Mo_9S_{11}$)

The complete structural study revealed the existence of a new type of cluster Mo_{12}, built into $Mo_{12}S_{14}$ units, in addition to the well-known Mo_6S_8 units. In Fig. 2, we present a projection of this structure onto the $(11\bar{2}0)$ plane. From this figure, one can see that we may describe the structure as made up of linear chains with the sequence (Mo_6S_8)–Tl–Tl–($Mo_{12}S_{14}$)–Tl–Tl–(Mo_6S_8) . . . . These chains are parallel to the hexagonal c-axis and are equivalent modulo translations by $c_{hex}/3$. A similar stacking has been found in $M_2Mo_{15}X_{19}$ (to be published) where the sequence is Mo_6X_8–M–Mo_9X_{11}–M–Mo_6X_8 . . . ; the MMo_6X_8 compounds may also be considered to be of this type. In fact, these latter materials may be considered as composed of linear chains running in the hexagonal c-direction and having the sequence Mo_6X_8–M–Mo_6X_8–M–Mo_6X_8 . . .

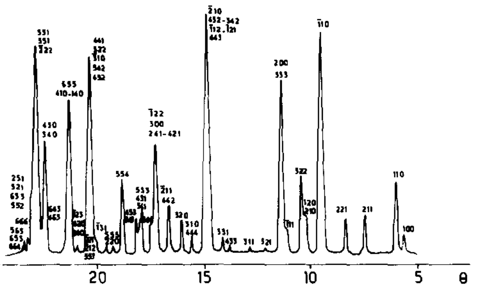

FIG. 1. X-Ray diffraction pattern of $Tl_2Mo_9S_{11}$ (λ Cu$K\bar{\alpha}$ = 1.541 Å) with rhombohedral *hkl*.

The two Tl^+ ions are situated on the ternary axis and are surrounded by three $Mo_{12}S_{14}$ units and three Mo_6S_8 units belonging to other chains. On the same chain there is one $Mo_{12}S_{14}$ unit on one side and one Mo_6S_8 unit on the other side. The environment of the two Tl^+ ions is thus 14 sulfur atoms (3×3 S (3 $Mo_{12}S_{14}$) + 3 S (3 Mo_6S_8) + 1 S (Mo_6S_8) + 1 S ($Mo_{12}S_{14}$)).

The projection shown in Fig. 2 also demonstrated the existence of channels running in the direction of the rhombohedral axes, similar to those found in the MMo_6S_8-type materials (*2*).

The Mo_{12} cluster can be considered as the linear condensation of three octahedral Mo_6 clusters. It is formed by a stacking of four

TABLE I

CRYSTALLOGRAPHIC DATA FOR $M_2Mo_9S_{11}$ (M = K, Tl)

$M_2Mo_9S_{11}$	Symmetry hexag./rhomb.	Space group: $R\bar{3}$ Laue group: $\bar{3}$ $Z_{rh} = 2$	
$K_2Mo_9S_{11}$	$a_R = 13.13(1)$ Å $a_H = 9.27(1)$ Å	$\alpha_R = 41°34(1)$ $c_H = 35.97(1)$ Å	$V_R = 892.4$ Å^3 $d_{th} = 4.67$
$Tl_2Mo_9S_{11}$	$a_R = 12.95$ (1) Å $a_H = 9.30(1)$ Å	$\alpha_R = 42°09(1)$ $c_H = 35.37(1)$ Å	$V_R = 883.3$ Å^3 $d_{th} = 5.34$

TABLE II

LATTICE SPACINGS WITH HEXAGONAL AND RHOMBOHEDRAL INDICES AND THE OBSERVED X-RAY INTENSITIES FOR $Tl_2Mo_9S_{11}$

hkl_{rh}	hkl_{hex}	d_{obs}	d_{calc}	I_{obs}
100	101	7.899	7.856	5
110	012	7.374	7.332	18
211	104	5.985	5.955	9
221	015	5.372	5.316	8
$\bar{1}10$	110	4.665	4.652	86
120–210	$2\bar{1}3$–113	4.320	4.327	11
322	107	4.270	4.280	19
$\bar{1}11$	021	3.934	4.002	58
333	009		3.929	
200	202		3.928	
321	116	3.642	3.652	1
311	205	3.495	3.501	1
433	10.10	3.236	3.238	2
331	027	3.153	3.150	4
$\bar{2}10$	211	2.999	3.034	100
432–342	119–$2\bar{1}9$		3.002	
$\bar{1}12$–$\bar{1}21$	$3\bar{2}2$–122		3.001	
443	01.11		2.986	
444	00.12	2.875	2.947	5
310	214		2.879	
320	125	2.801	2.797	8
$\bar{2}11$	300	2.687	2.686	12
442	02.10		2.686	
$\bar{1}22$–300	303	2.602	2.619	34
421–241	217–$3\bar{1}7$		2.608	
544	10.13		2.577	
533	20.11	2.506	2.513	12
431–341	128–328		2.508	
453	21.12	2.487	2.490	8
543	11.12		2.489	
554	01.12	2.405	2.409	19
555	00.15	2.349	2.358	21
220	220	2.324	2.326	2
$\bar{1}31$	223	2.208	2.282	72
553	02.13		2.254	
$\bar{2}12$–$\bar{2}21$	$4\bar{3}1$–131		2.230	
441–522	039–309		2.217	
$\bar{3}10$	$4\bar{1}2$		2.217	
542–452	12.11–$3\bar{2}$.11		2.211	
$\bar{1}23$	$4\bar{3}4$	2.160	2.167	2
420–240	226–$4\bar{2}6$		2.164	
655	10.16	2.128	2.132	53
410–140	315–415		2.131	
430–340	137–437	2.030	2.044	36
643–463	21.12–31.13		2.029	
665	01.17		2.014	
531–351	229–$4\bar{2}9$		2.002	
$\bar{2}22$	042	1.999	2.001	79

TABLE II—*Continued*

hkl_{rh}	hkl_{hex}	d_{obs}	d_{cal}	I_{obs}
521–251	318–$4\bar{1}8$		1.994	
633	30.12	1.984	1.985	11
552	03.12		1.985	
666	00.18	1.960	1.965	2
653–563	12.14–$3\bar{2}$.14	1.937	1.944	2
664	02.16		1.938	

Mo_3 triangles in staggered positions. The sulfurs in the $Mo_{12}S_{14}$ unit are of two types: eight sulfurs face a triangular face of Mo atoms and six sulfurs face two triangular Mo faces having one common edge. The six Mo atoms in extremal positions are each further bonded to one sulfur atom on a neighboring Mo_6S_8 unit (Fig. 3).

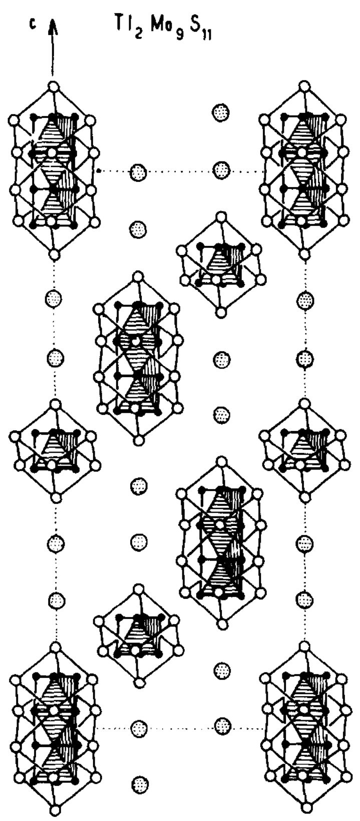

FIG. 2. Projection onto the hexagonal plane (11$\bar{2}$0) of $Tl_2Mo_9S_{11}$.

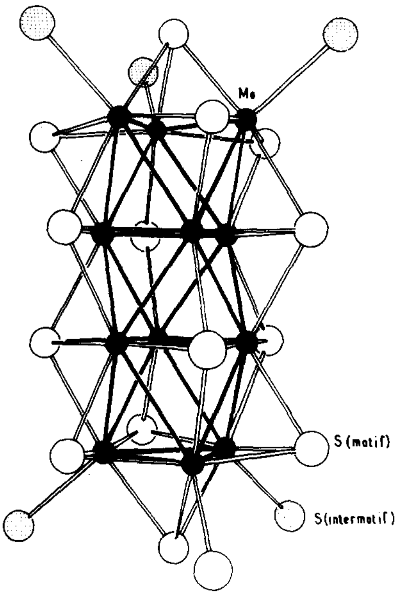

FIG. 3. The $Mo_{12}S_{14}$ unit with the Mo_{12} cluster. The stippled atoms are the nearest sulfurs on the neighboring units, and show the interunit Mo–S bonds.

The point symmetries of the $Mo_{12}S_{14}$ and the Mo_6S_8 block units are the same ($C3i$); they both have a ternary axis and an inversion center. Contrary to this, one finds for the Mo_9S_{11} block unit $D3$ point symmetry in $In_2Mo_{15}S_{19}$. Here, the inversion center is replaced by three twofold axes. The intercluster bondings around the Mo_9 cluster are then very different. In contrast, the intercluster bondings are realized in the same manner in the $Tl_2Mo_9S_{11}$ compound as in the MMo_6S_8-type compound (*2*). Each Mo atom of a Mo_6 cluster is bonded to one extremal Mo atom of a neighboring Mo_{12} cluster, and conversely each extremal Mo atom of a Mo_{12} cluster is bonded to one Mo atom of a neighboring Mo_6 cluster. The Mo–Mo intercluster distance is 3.217 Å in $Tl_2Mo_9S_{11}$ (Fig. 4).

Discussion

As we have already stressed, there is a strong similarity between the MMo_6X_8-type compounds and the two compounds presented in this work. Like the former compounds, $Tl_2Mo_9S_{11}$ and $K_2Mo_9S_{11}$ are metallic, but they do not become superconducting down to 2.1°K. This similarity is further corroborated by the average valency of Mo. Assuming a valency of −2 for S and +1 for Tl, we find a mean valency of +2.22 for Mo. There are therefore 3.78 valence electrons per Mo atom. This latter number varies between 3.33 and 4.00 in the MMo_6X_8 compounds, and is 3.66 for $PbMo_6S_8$ and 3.83 for $LaMo_6S_8$. It is well established that there is a correlation between the number of valence electrons per Mo atom and some structural parameters in the MMo_6S_8 compounds. The Mo–Mo intertriangle bond within the Mo_6S_8 unit is especially sensitive to this charge transfer and decreases as the valence electron concentration on the Mo atoms increases (*5*, *6*). If we compare these bonds with that observed in $Tl_2Mo_6S_{11}$ (Table III), we find that the latter corresponds to 3.60 valence electrons in the Mo_6 cluster of the $Tl_2Mo_9S_{11}$ compound. This suggests that there is a slight charge transfer from the Mo_6 cluster to the Mo_{12} cluster. This could then be consistent with the very short interplane distance in the central octahedron in the Mo_{12} cluster.

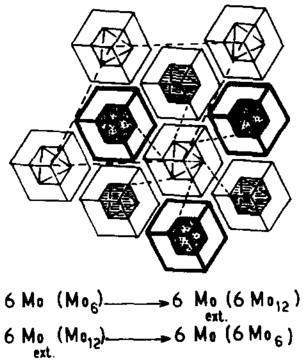

FIG. 4. Intercluster bonds in $M_2Mo_9S_{11}$ (M = Tl, K).

If we compare the three types of compounds, MMo_6X_8, $M_2Mo_{15}X_{19}$, and $M_2Mo_9S_{11}$, it is tempting to assume that a whole series of different compounds charac-

TABLE III

CHARACTERISTIC DISTANCES IN THE Mo_6 AND THE Mo_{12} CLUSTERS IN $Tl_2Mo_9S_{11}$

Mo_6S_8	$(\mathrm{Mo{-}Mo})_{\Delta}$	2.693(1) Å	Mo–Mo interplane	2.30 Å
	$\mathrm{Mo}_{\Delta}{-}\mathrm{Mo}_{\Delta}$	2.780(5) Å		
			Mo–Mo intercluster	3.217(1) Å
$Mo_{12}S_{14}$	$(\mathrm{Mo{-}Mo})_{\Delta}$ ext	2.658(1) Å	Mo–Mo interplane	2.28 Å (Mo ext–Mo in) 2.17 Å (Mo in–Mo in)
	$(\mathrm{Mo{-}Mo})_{\Delta}$ in	2.688(1) Å		
	(Mo_{Δ} ext–Mo_{Δ} in)	2.743(1) Å 2.771(1) Å		
	Mo_{Δ} in–Mo_{Δ} in	2.669(5) Å		

terized by clusters from Mo_6 to Mo_{3n} might exist. In the limit $n \rightarrow \infty$, one would then get a material containing infinite linear chains $(Mo_3)^1_\infty$ in the form of infinite staggered stackings of Mo_3 triangles. Very recently, we were able to synthesize compounds of this type: $M_2Mo_6X_6$ (M = K, Rb, Cs, X = S; and M = Na, K, Tl, In, X = Se) (*7*). These materials have hexagonal structure and the shortest Mo–Mo intercluster distance is 6.34 Å, for example, in the $Tl_2Mo_6Se_6$ compound. We expect these materials to have a strongly one-dimensional character.

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