

In_{~3}Mo₁₅Se₁₉, Containing Isolated Mo₆ and Mo₉ Clusters

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(Received 26 June 1978; accepted 9 October 1978)

Abstract

The structure of In_{~3}Mo₁₅Se₁₉ has been determined by single-crystal X-ray diffraction analysis and refined for two different In concentrations. Space group $P6_3/m$, $Z = 2$, $a = 9.804$ (5) and 9.830 (5) Å, $c = 19.49$ (1) and 19.40 (1) Å, for In_{2.9}Mo₁₅Se₁₉ and In_{3.3}Mo₁₅Se₁₉, respectively. The key structural elements are Mo₆Se₈ and Mo₉Se₁₁ building blocks which are stacked in the sequence *ABAC* and are separated by In atoms occupying statistically two types of interstices in the Se-atom network. While the geometry of the Mo₆Se₈ unit is identical to the one found in the rhombohedral $M\text{Mo}_6X_8$ compounds ($M = \text{metal}$, $X = \text{S, Se, Te}$), the Mo₉Se₁₁ unit represents a new structural element which may be regarded as resulting from the fusion of two Mo₆Se₈ units. It contains a Mo-atom cluster which is formed by nine Mo atoms occupying the vertices of a slightly elongated confacial bioctahedron. The variation of the In concentration leads to significant changes in the metal–metal bond lengths of the Mo₆ and Mo₉ clusters.

Introduction

Transition elements are known to have a marked propensity for the formation of homonuclear bonds (Schäfer & von Schnering, 1964; Cotton & Wilkinson, 1972; King, 1972; Vahrenkamp, 1977). Compounds in which such interactions occur often contain the metal atoms in the form of clusters, of which the formation is favoured by a low formal oxidation state of the transition element. Mo is a typical representative

showing this behaviour (Cotton, 1977), for its low-valent chemistry is characterized by numerous metal–metal bonded compounds which contain Mo clusters of various sizes such as Mo₂ dumb-bells [MoCl₃ (von Schnering & Wöhrle, 1963); MoS₂Cl₃ (Marcoll, Rabenau, Mootz & Wunderlich, 1974)], Mo₃ triangles [Zn₂Mo₃O₈ (Ansell & Katz, 1966); MoN (Vandenberg & Matthias, 1974); Mo₃S₇Cl₄ (Marcoll, Rabenau, Mootz & Wunderlich, 1974)], Mo₄ tetrahedra [GaMo₄S₈ (Perrin, Chevrel & Sergent, 1975*a*; Vandenberg & Brasen, 1975); MoSBr (Perrin, Chevrel & Sergent, 1975*b*)], Mo₅ square-pyramids [(*n*-C₄H₉)₄N]₂Mo₅Cl₁₃ (Jödden, von Schnering & Schäfer, 1975)] and Mo₆ octahedra [MoCl₂ (Schäfer, von Schnering, Tillack, Kuhn, Wöhrle & Baumann, 1967); Mo₃Se₄ (Bars, Guillevic & Grandjean, 1973)]. Compounds with clusters containing more than six Mo atoms, however, have not been found so far, and neither have substances been reported in which more than one transition-metal cluster species occurs in the same compound. Very recently a new ternary compound has been synthesized in the In–Mo–Se system (Seeber, Decroux, Fischer, Chevrel, Sergent & Grüttner, 1978; Chevrel, Sergent, Seeber, Fischer, Grüttner & Yvon, 1978). The purpose of this communication is to report on the crystal structure of this compound which is the first example of the simultaneous occurrence of two types of Mo-atom clusters; one consisting of six nuclei and having the shape of an octahedron and the other consisting of nine nuclei and having the shape of a confacial bioctahedron.

Experimental

Two crystals were investigated in this work; one at the University of Geneva and the other at the University of Rennes. The crystal studied in Geneva (*G*) had the

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Table 1. *Crystallographica data for In_{~3}Mo₁₅Se₁₉*

	In _{2.9} Mo ₁₅ Se ₁₉	In _{3.3} Mo ₁₅ Se ₁₉
Space group	<i>P</i> 6 ₃ / <i>m</i>	<i>P</i> 6 ₃ / <i>m</i> (No. 176)
<i>a</i>	9.804 (5) Å	9.830 (5) Å
<i>c</i>	19.49 (1)	19.40 (1)
<i>V</i>	1622 Å ³	1624 Å ³
<i>Z</i>	2	2
<i>F</i> (000)	2836	2879
<i>D_x</i>	6.72 Mg m ⁻³	6.79 Mg m ⁻³
<i>μ</i> (Mo <i>Kα</i>)	28.81 mm ⁻¹	29.69 mm ⁻¹

composition In_{2.9}Mo₁₅Se₁₉ and was taken from a sample prepared from Mo₃Se₄ powder reacted with In in evacuated quartz tubes at 1300 K. The crystal studied in Rennes (*R*) had a higher In concentration. Its composition was In_{3.3}Mo₁₅Se₁₉ and it was prepared by reaction of In₂Se₃ with Mo and Se in the presence of an excess of In (1400 K, 5 d). Both crystals were small (*G*: 40 μm, irregularly shaped; *R*: 30 × 100 μm, needle shaped) and were analysed on computer-controlled four-circle diffractometers. The unit cell was found to be hexagonal (for crystal data see Table 1) and the Laue group (6/*m*) and the systematically absent reflexions (00*l*, *l* odd) indicated the possible space groups *P*6₃ and *P*6₃/*m*. Integrated intensities (*G*: 1844, *R*: 2238 reflexions) were recorded to a limit of sin θ/λ = 0.48 (*G*) and 0.53 (*R*) Å⁻¹ of which 451 (*G*) and 461 (*R*) unique reflexions were retained. The structure was solved from a Patterson map which was very similar to that of the rhombohedral *MMo₆Se₈* phases except that it showed a strong accumulation of peaks along the [00*w*] direction. This indicated that the compound contained the well known Mo₆Se₈ building blocks which were probably related to each other by mirror planes perpendicular to the *c* direction. This model was correct and could be refined in space group *P*6₃/*m* by a least-squares program (XRAY system, 1976). Atomic scattering factors and correction terms for anomalous

dispersion were taken from *International Tables for X-ray Crystallography* (1974). The In positions were obtained from an electron density difference map and their occupancy was refined together with all other parameters in a final least-squares cycle. The consistency index *R* (= ∑ |Δ*F*|/∑ |*F*_o|) calculated from 234 (*G*) and 423 (*R*) reflexions (*F* > 2σ|*F*|) with isotropic thermal parameters was 0.09 (*G*) and 0.07 (*R*).* The positional, occupational and thermal parameters have been summarized in Table 2 and a list of the low-angle reflexions with X-ray powder intensities will be given elsewhere (Chevrel, Sergent, Seeber, Fischer, Grüttner & Yvon, 1978).

Description of the structure

In the following section the overall structural features of this compound will be described and compared with those of the rhombohedral *MMo₆X₈* compounds (*M* = metal, *X* = chalcogen; Chevrel, Sergent & Prigent, 1971; Sergent & Chevrel, 1973). For this purpose the two crystals studied in this work are considered together and will be referred to as having the approximate formula In_{~3}Mo₁₅Se₁₉.

The Mo₆Se₈ and Mo₉Se₁₁ building blocks

From a structural chemistry point of view one can consider the crystal as being built up of molecular units which represent two types of building blocks. One is a Mo₆Se₈ unit which has the same atom configuration

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33989 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Fractional atomic coordinates (× 10⁴), isotropic thermal parameters (Å²) and occupancy factors for In_{~3}Mo₁₅Se₁₉*

		In _{2.9} Mo ₁₅ Se ₁₉					In _{3.3} Mo ₁₅ Se ₁₉				
Equipoint	Occu- pancy	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)	Occu- pancy	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)	
Mo(1)	6(<i>h</i>)	1.00	1692 (10)	5127 (10)	2500 (–)	0.5 (2)	1.00	1661 (8)	5092 (8)	2500 (–)	0.28 (12)
Mo(2)	12(<i>i</i>)	1.00	142 (7)	1647 (6)	571 (4)	1.2 (2)	1.00	145 (6)	1646 (6)	564 (2)	0.36 (8)
Mo(3)	12(<i>i</i>)	1.00	3185 (6)	5035 (7)	1334 (4)	0.8 (2)	1.00	3186 (5)	5039 (5)	1336 (2)	0.19 (8)
Se(1)	4(<i>e</i>)	1.00	0 (–)	0 (–)	1617 (10)	2.5 (4)	1.00	0 (–)	0 (–)	1605 (5)	0.37 (17)
Se(2)	4(<i>f</i>)	1.00	3333 (–)	6667 (–)	297 (9)	1.0 (3)	1.00	3333 (–)	6667 (–)	307 (4)	0.30 (17)
Se(3)	6(<i>h</i>)	1.00	3136 (12)	3543 (13)	2500 (–)	1.0 (2)	1.00	3178 (8)	3544 (10)	2500 (–)	0.10 (14)
Se(4)	12(<i>i</i>)	1.00	7142 (8)	340 (9)	509 (6)	1.2 (2)	1.00	7133 (7)	342 (6)	522 (2)	0.04 (9)
Se(5)	12(<i>i</i>)	1.00	91 (9)	3794 (8)	1393 (5)	1.2 (2)	1.00	113 (6)	3812 (7)	1376 (2)	0.22 (10)
In(1)	4(<i>f</i>)	1.00	6667 (–)	3333 (–)	1288 (9)	4.5 (4)	1.00	6667 (–)	3333 (–)	1259 (4)	2.96 (9)
In(2)	6(<i>h</i>)	0.29 (5)	2127 (29)	458 (27)	2500 (–)	Not positive definite	0.44 (2)	2254 (15)	472 (16)	2500 (–)	1.23 (36)

The e.s.d.'s are in parentheses and the Debye–Waller factor, *B*, is defined as exp(–*B* sin²θ/λ²).

and point-group symmetry ($\bar{3}$) as the known building block of the $M\text{Mo}_6\text{Se}_8$ compounds ($M = \text{Pb}, \text{Sn}, \text{La}, \text{Cu}, \text{etc.}$) (Guillevic, Lestrat & Grandjean, 1976; Yvon, 1978a), *i.e.* it consists of an octahedron-shaped Mo-atom cluster whose faces are bridged by eight Se atoms occupying the vertices of an almost regular cube (see upper drawing of Fig. 1a). The other is a $\text{Mo}_9\text{Se}_{11}$ unit which represents a previously unknown building block and constitutes the most intriguing structural aspect of the present compound. It has $3/m$ symmetry (Fig. 1b) and contains a cluster of nine close-packed Mo atoms which occupy the vertices of a confacial bioctahedron. The configuration of the Se atoms surrounding this cluster resembles that of the Mo_6Se_8 unit insofar as each face of the biocuboctahedron is bridged by a chalcogen atom. It is therefore appropriate to consider the $\text{Mo}_9\text{Se}_{11}$ unit as resulting from a fusion of two pseudocubic Mo_6Se_8 units along the $[111]$ direction in the way which has been illustrated in Fig. 1. Since the Mo_6Se_8 and $\text{Mo}_9\text{Se}_{11}$ building blocks occur in equal proportions, the overall Mo to Se ratio of the compound corresponds to the formula ' $\text{Mo}_{15}\text{Se}_{19}$ ', *i.e.* it is very close to the 3:4 ratio of the rhombohedral compounds. The relative arrangement of these building blocks in the structure has been represented in Figs. 2 and 3, where it is also compared with the arrangement of the Mo_6Se_8 units in the rhombohedral InMo_6S_8 compound (Chevrel, Sergent & Yvon, 1978). From these figures one can see how these two structures are related to one another.

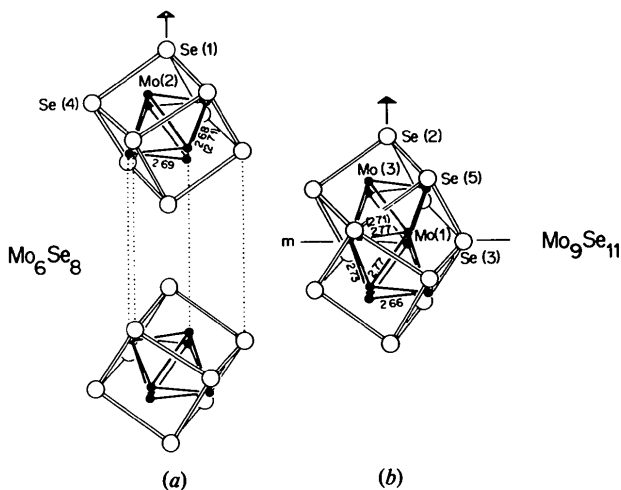


Fig. 1. (a) The Mo_6Se_8 and (b) $\text{Mo}_9\text{Se}_{11}$ building blocks of $\text{In}_{\sim 3}\text{Mo}_{15}\text{Se}_{19}$. The Mo_6Se_8 unit (symmetry $\bar{3}$) consists of an almost regular metal octahedron whose faces are bridged by Se atoms. The $\text{Mo}_9\text{Se}_{11}$ unit (symmetry $3/m$) contains a cluster of nine Mo atoms having the shape of a slightly elongated biocuboctahedron, whose faces are all bridged by Se atoms. This unit can be considered as resulting from the fusion of two Mo_6Se_8 units as illustrated by the dotted lines. The numbers on the metal-atom clusters indicate the Mo—Mo bond lengths in Å. The values in parentheses indicate those Mo—Mo distances of the In-poor compound $\text{In}_{2.9}\text{Mo}_{15}\text{Se}_{19}$ which are significantly different from the corresponding ones in the In-rich compound $\text{In}_{3.3}\text{Mo}_{15}\text{Se}_{19}$.

Their projections on to the hexagonal base plane actually look almost identical, *i.e.* the building blocks all have a similar orientation with respect to the unit-cell vectors and are centred above the same points of the base-plane section (Fig. 2).

Their projections on to the $11\bar{2}0$ plane, however, differ markedly (Fig. 3). Due to the increased length and the particular stacking of the $\text{Mo}_9\text{Se}_{11}$ units the c parameter of the hexagonal compound is about twice as long as that of the rhombohedral compound in the hexagonal setting. Yet both structure types have a common building principle and can be derived from each other by a periodic unit-cell twinning operation. This will be shown in the following way. Let the stacking sequence of the Mo_6Se_8 units in the rhombohedral structure be $ABCABC \text{ etc.}$ (Fig. 3a). Introducing now a mirror plane, m , perpendicular to the ternary axis such as to change the stacking sequence to $AB_mBAC_mCAB_mB \text{ etc.}$ and grouping the Mo_6Se_8 units of positions B and C together by pairs such as are illustrated in Fig. 1, one obtains the new stacking sequence $ABACABAC \text{ etc.}$ This sequence corresponds exactly to the arrangement of the Mo_6Se_8 units (position A) and the $\text{Mo}_9\text{Se}_{11}$ units (positions B and C) in the hexagonal $\text{In}_{\sim 3}\text{Mo}_{15}\text{Se}_{19}$ compound (Fig. 3b).

Thus one can consider this substance as being built up of infinite structural slabs which are cut out from a hypothetical InMo_6Se_8 structure of trigonal symmetry (see dashed lines in Fig. 3) and are stacked along the c direction such as to be related to one another by mirror planes. Consequently the atom coordinations in the two structure types are very similar. The Mo(2) and Mo(3) atoms, for instance, have five Se atoms as nearest neighbours, of which four form an approximately square-planar configuration around the metal atom, and the fifth, which belongs to an adjacent building

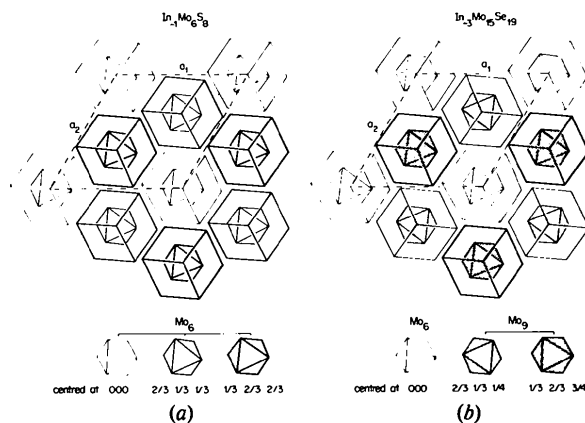


Fig. 2. The projection of the Mo_6Se_8 (containing a non-dotted metal-atom octahedron) and $\text{Mo}_9\text{Se}_{11}$ building blocks (containing dotted metal-atom biocuboctahedron) onto the base plane of (a) the rhombohedral InMo_6S_8 and (b) the hexagonal $\text{In}_{\sim 3}\text{Mo}_{15}\text{Se}_{19}$ compound. Like atoms in the building blocks are joined by lines and the In atoms have been omitted for clarity.

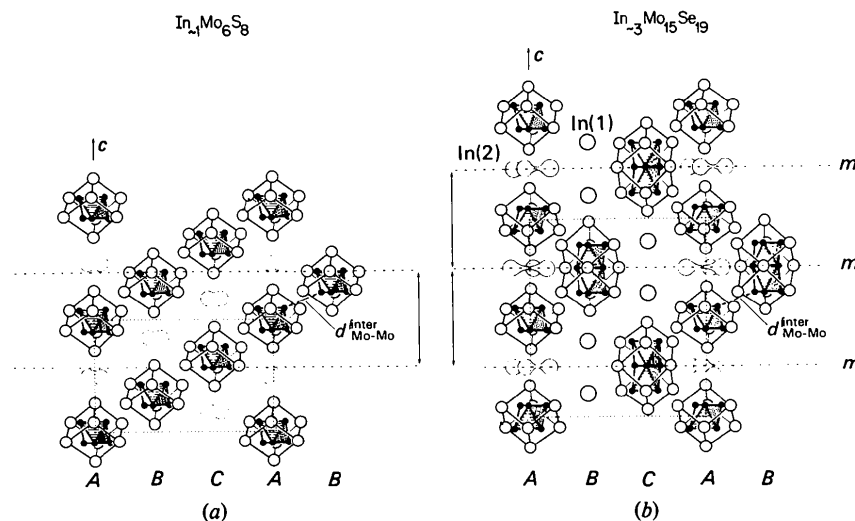


Fig. 3. The projection of (a) InMo_6S_8 and (b) $\text{In}_3\text{Mo}_{15}\text{Se}_{19}$ on to the hexagonal $(11\bar{2}0)$ plane. The structure of $\text{In}_3\text{Mo}_{15}\text{Se}_{19}$ can be derived by cutting structural slabs out of the InMo_6S_8 structure (see dotted lines) and by stacking them perpendicular to c according to a periodic unit-cell twinning operation. The dotted electron density clouds represent In atoms which undergo strong thermal motion.

block, is off the plane and opposite the metal atom. Adding the four adjacent Mo atoms of the metal cluster to their coordination sphere leads to a liganacy of 9 and to an atomic environment which is practically identical to the one around the Mo atoms in the rhombohedral structure. The Mo(1) atoms which lie on the mirror plane bisecting the Mo₉ cluster, however, have a different though closely related ligand set. It can be derived from the previous one simply by replacing a Se atom belonging to the square-planar configuration by two additional Mo atoms. The liganacy of these particular Mo atoms is therefore equal to 10.

The In atoms

With respect to the In atoms, two crystallographically different positions exist in the structure. One position [In(1), point symmetry 3] corresponds to a large seven-coordinated cavity in the chalcogen atom network which is formed by three Mo₆Se₈ and four Mo₉Se₁₁ units. These cavities have the form of open cages which are grouped together by pairs and face each other along the c direction (Fig. 3b). In both crystals each cavity is occupied by one In atom. These atoms undergo a large thermal motion and are well separated from one another [$d_{\text{In}(1)-\text{In}(1)} = 4.8 \text{ \AA}$ (R)]. The other position [In(2), point symmetry m] corresponds to a triangular group of six-coordinated cavities which are formed by two Mo₆Se₈ and three Mo₉Se₁₁ units (see dotted electron density clouds on the mirror plane in Fig. 3b). Similar to the rhombohedral $\text{In}_{-1}\text{Mo}_6\text{S}_8$ phase these cavities are only partially occupied (0.9 and 1.3 In atoms per triangular group, for crystals G and R , respectively). These occupancies led to the assignment

of the formulae $\text{In}_{2.9}\text{Mo}_{15}\text{Se}_{19}$ and $\text{In}_{3.3}\text{Mo}_{15}\text{Se}_{19}$ to crystals G and R , respectively. However, due to the correlation between the thermal vibrational parameters and the occupancy factors of the In(2) atoms in the least-squares refinement and in view of the presumably strong anharmonic motion of these atoms (Yvon, 1978b) the true In concentration of both crystals may be slightly different. Yet this uncertainty will not affect the conclusions with regard to the bonding situation as long as one can assume that crystal R is richer in In than crystal G . One also has to be aware of the fact that the quality of the structure refinements as indicated by the R values of 7 and 9% is not very good. The same difficulty has already appeared earlier during a study of the rhombohedral selenides $M\text{Mo}_6\text{Se}_8$ and is probably due to a high concentration of crystal imperfections rather than to a deficiency of the structural model or of the method of refinement (Yvon, 1978a).

Interatomic distances

In this section the structural features which are common to $\text{In}_{-3}\text{Mo}_{15}\text{Se}_{19}$ and the rhombohedral selenides $M\text{Mo}_6\text{Se}_8$ will be described in more detail. Also the structural changes which occur as a function of the In concentration will be examined.

Mo—Mo bonds

Of particular interest for the bonding situation are the metal—metal distances within the Mo-atom clusters. As can be seen from Fig. 1 the Mo—Mo bond lengths of the Mo₆ octahedron are practically equal to the corre-

sponding distances in the rhombohedral compounds (LaMo_6Se_8 : 2.68 Å in the plane perpendicular and 2.73 Å in the plane parallel to the ternary axis; Yvon, 1978a). These distances are longer than the sum of the 'single-bond metallic radii' ($2r_{\text{Mo}} = 2.592$ Å) but shorter than the sum of the 'maximum-valence single-bond radii' ($2r_{\text{Mo}} = 2.78$ Å) given by Pauling (1960 and 1975, respectively). Most interesting is the fact that the metal octahedron of the In-poor crystal is not regular but elongated along the *c* direction, and that it has an almost regular shape and a smaller volume in the In-rich crystal. This apparent contraction of the Mo_6 octahedron has already been observed in the rhombohedral $\text{Cu}_{4-x}\text{Mo}_6\text{S}_8$ compounds (Yvon, Paoli, Flükiger & Chevrel, 1977) for which it was found to be proportional to the Cu concentration. The same trend also exists in the other $M\text{Mo}_6X_8$ compounds for which the contraction is proportional to the oxidation state of the cation *M* (Yvon & Paoli, 1977; Yvon, 1978a).

With respect to the Mo_9 biotetrahedron the observed Mo—Mo bond lengths are somewhat longer but are still close to single-bond distances. In contrast to the Mo_6 octahedron, however, this cluster did not become smaller as the In-concentration was increased. In fact it was found to expand slightly. As can be seen from Fig. 1(b) the expansion is not uniform since it affects only the Mo—Mo distances between the three Mo atoms which are median to the Mo_9 cluster, all other Mo—Mo distances remaining essentially unchanged.

Of particular interest for the electronic properties are the Mo—Mo distances between the metal-atom clusters. The only distance shorter than 4.2 Å is that between the Mo(2) atoms of the Mo_6 octahedron and the Mo(3) atoms of the Mo_9 biotetrahedron ($d_{\text{Mo-Mo}}^{\text{inter}}$ in Fig. 3b). It measures 3.50 Å in the In-poor and 3.51 Å in the In-rich crystal, which shows that the metal-atom clusters are well separated from one another and that the In concentration has only a very small influence on their separation. Intercluster distances of the same magnitude occur also in the rhombohedral compounds. In LaMo_6Se_8 , for instance, the shortest Mo—Mo separation between adjacent Mo_6 clusters was found to be 3.45 Å (Yvon, 1978a).

Mo—Se and Se—Se distances

A comparison of all the other interatomic distances in the present hexagonal compound with the analogous distances in the rhombohedral selenides confirms their close bonding relationship. The average Mo—Se bond lengths, for instance, are equal in both types of compounds ($\bar{d}_{\text{Mo-Se}} = 2.6$ Å) and correspond roughly to the sum of the covalent radii ($r_{\text{Mo}} + r_{\text{Se}} = 2.5$ Å; Pauling, 1960). On the other hand their average Se—Se distances are also the same ($\bar{d}_{\text{Se-Se}} = 3.7$ Å) and correspond to a shortened Se^{2-} — Se^{2-} separation ($2r_{\text{Se}^{2-}} = 4.0$ Å; Shannon, 1976). Notable differences between

the two structure types only occur with respect to the separation of the Mo_6Se_8 building blocks along the *c* axis and with respect to the shortest separation of the Mo and In atoms. In the present compound the Mo_6Se_8 units come much closer to each other along the unique axis than in any of the rhombohedral compounds [$d_{\text{Se(1)-Se(1)}} = 3.47$ Å in $\text{In}_{3.3}\text{Mo}_{15}\text{Se}_{19}$, compared to 4.40 Å in $\text{Cu}_2\text{Mo}_6\text{Se}_8$; Yvon, 1978a]. As a consequence the In atoms separating these units are shifted much further away from the unique axis in the hexagonal compound than in the rhombohedral compound (2 Å in $\text{In}_{3.3}\text{Mo}_{15}\text{Se}_{19}$, compared to 0.7 Å in $\text{In}_1\text{Mo}_6\text{S}_8$). This delocalization corresponds to an average separation of about 3 Å for the three symmetry equivalent In(2) sites. A pair formation of the In atoms is therefore unlikely.

With respect to the separation of the In and Mo atoms, however, a rather short distance occurs between the statistically occupied In(2) sites and those Mo atoms which are median to the Mo_9 cluster. This distance is 3.0 Å in the In-poor compound and decreases even further as the occupancy of the In(2) site is increased. The In—Mo distances in the sulphur based InMo_6S_8 compound, by comparison, are much longer ($d_{\text{Mo-In}} = 3.7$ Å; Chevrel, Sergent & Yvon, 1978).

Bonding and electronic structure

In view of the close structural resemblance between the present compound and the $M\text{Mo}_6X_8$ phases it is natural to assume a similar bonding mechanism for the two structure types. For the latter phases the bonding situation has already been examined in detail both by a valence-bond approach (Yvon & Paoli, 1977; Yvon, 1978a) and by molecular-orbital and band-structure calculations (Mattheiss & Fong, 1977; Bullett, 1977; Andersen, Klose & Nohl, 1978). The main results which are relevant for the discussion of the present compound can be summarized as follows. Within the valence-bond model one can consider the edges of the Mo_6 octahedron as representing 12 covalent, two-centre, metal—metal bonds. The electron requirement of this cluster is therefore equal to 24 valence electrons and the formal oxidation states of the isolated Mo_6X_8 building block can be expressed by the ionic formula $[\text{Mo}_6^{2+}X_8^{2-}]^{4-}$. In most of the $M\text{Mo}_6X_8$ compounds, however, the cations *M* do not completely balance the fourfold negative formal charge of this unit. This results in an electron deficit on the Mo_6 cluster and explains why the Mo—Mo bond lengths were found to increase as the concentration and the formal oxidation state of the *M* atom decreased. It also explains why these substances show metallic behaviour.

The molecular-orbital and band-structure calculations, by comparison, did not predict any trends for the variation of the metal—metal bond lengths.

However, they did provide a detailed view on the energy distribution of the electronic states and thus allowed a much better understanding of the physical properties. In fact all the calculations predict a stable electronic configuration and a forbidden energy gap if 24 Mo spin states per Mo₆X₈ unit are occupied. The existence of this gap has been confirmed very recently for the isostructural compound Re₄Mo₂S₈ which was found to be semi-conducting (Perrin, Sergent & Fischer, 1978). As shown in detail by Andersen, Klose & Nohl (1978), the electronic states of the MMo₆X₈ compounds around the Fermi level are derived from the molecular-orbital levels of the Mo₆ octahedron. These states are confined into sub-bands which are rather narrow mainly because the metal-atom clusters in the structure are far away from one another. This localized character of the Mo wavefunctions is generally believed to be responsible for some of the unusual physical properties which are typical of these substances, such as their very high critical magnetic fields or the possible coexistence of superconductivity with magnetic long-range order (for a review see Fischer, 1978). Another important result of the theoretical calculations is the fact that the conduction bands may contain only a few electrons. This explains why charge-transfer effects and small deviations from ideal stoichiometry have a strong influence on the electronic properties such as the superconducting transition temperature (Yvon & Paoli, 1977).

In view of these findings one expects that very similar electronic properties will also be found with the present compounds or with other compounds having this structure type. A structural detail which suggests that these properties could again depend primarily on the Mo atoms is the fact that the Mo₆ octahedron becomes smaller as the In concentration is increased.

This apparent contraction can be interpreted by a valence-bond model similar to that used for the MMo₆X₈ compounds. According to this model the In-poor crystals contain electron-deficient Mo₆ clusters having partially filled Mo bonding orbitals. As the In concentration is increased the number of valence electrons available for the formation of covalent metal-metal bonds increases because of charge transfer. Thus the Mo-Mo bonds become shorter and the Mo₆ octahedron contracts. At the upper phase limit (In_{3.4}Mo₁₅Se₁₉; Chevrel, Sergent, Seeber, Fischer, Grüttner & Yvon, 1978) all the bonding orbitals of the Mo₆ cluster could be filled and the Mo-Mo distances could correspond to two-electron bonds. Thus one expects generally metallic behaviour for these substances. The conduction bands should contain electronic states which have predominantly Mo *d* character and they should become gradually filled as the In concentration is increased. These bands could be rather narrow mainly because the Mo₆ and Mo₉ clusters are well separated from one another and they

should contain only a few electron holes (about 1 electron hole per formula unit, as indicated by the homogeneity range with respect to In). Thus the electronic properties of the compounds having this new structure are expected to be even more sensitive to small compositional variations than those of compounds having the rhombohedral structure.

Some of the physical properties which have been measured in the meantime tend to support the above point of view. In particular it has now been established that the In_xMo₁₅Se₁₉ compounds are all metallic (Seeber, Decroux, Fischer, Chevrel, Sergent & Grüttner, 1978). Some of them are even superconducting and have critical temperatures of up to 4.3 K. They also have high critical magnetic fields and extremely high initial slopes. The latter property especially correlates well with the presumed localized character of the conducting electrons. Interestingly enough, both the magnetic susceptibility and the critical temperature were found to decrease as the In concentration was increased. This correlates well with the assumption of a conduction band becoming gradually filled.

With respect to the crystal chemistry of this compound, however, several questions have yet to be answered. One concerns the electron requirement of the Mo₉Se₁₁ building block and in particular the formal oxidation state of the Mo atoms. In fact the upper limit of the In concentration (In_{3.4}Mo₁₅Se₁₉) and the relatively long Mo-Mo bond lengths of the Mo₉ bioctahedron indicate that the formation of this cluster requires much less than 42 electrons, a value suggested by the possible formation of 21 covalent bonds across all the edges of the bioctahedron. It is likely that this cluster already forms with 36 or 38 valence electrons, depending essentially on whether the In atoms occupying the In(1) position have a formal oxidation number of +1 or +3, respectively. An indication in favour of a monovalent In⁺⁽¹⁾ atom is the relatively long distances of this atom to its seven nearest Se atoms as compared to the much shorter distances of the In³⁺⁽²⁾ atom to its six nearest Se atoms (see Table 3). If this assumption is correct, Mo would have the same formal oxidation state as in the rhombohedral selenides MMo₆Se₈, *i.e.* a value close to +2. The compound could then be described by an arrangement of pseudo ions [Mo₆²⁺Se₈²⁻]⁴⁻ and [Mo₉²⁺Se₁₁²⁻]⁴⁻ whose fourfold negative formal charges are balanced by the positive formal charges of the In atoms. However, one has to admit that these formulae can only be valid at the In-rich phase limit and that they do not take into account a possible reduction of the 2- formal charge of the Se atoms due to covalency effects. Another intriguing question to be also answered is why the present structure appears to form only in this particular ternary system and why a rhombohedral InMo₆Se₈ phase has not been found as yet. Theoretical calculations, such as molecular-orbital schemes, and further experimental

Table 3. *Interatomic distances (Å) up to 4.2 Å for In_{2.9}Mo₁₅Se₁₉*The first column in each block refers to In_{2.9}Mo₁₅Se₁₉, and the second column to In_{3.3}Mo₁₅Se₁₉. The e.s.d.'s are given in parentheses.

Mo(1)–Mo(3)	2 × 2.729 (10)	2 × 2.725 (7)	Se(1)–Mo(2)	3 × 2.561 (17)	3 × 2.547 (9)
Mo(1)	2 × 2.705 (13)	2 × 2.768 (10)	Se(1)	3.442 (28)	3.473 (14)
Mo(3)	2 × 2.770 (8)	2 × 2.771 (7)	Se(4)	3 × 3.682 (15)	3 × 3.663 (8)
Mo(3)	2 × 3.839 (8)	2 × 3.860 (6)	Se(5)	3 × 3.702 (9)	3 × 3.720 (7)
Se(3)	2.575 (13)	2.584 (14)	Se(3)	3 × 3.715 (12)	3 × 3.745 (10)
Se(5)	2 × 2.603 (10)	2 × 2.596 (5)	In(2)	3 × 2.564 (25)	3 × 2.667 (11)
Se(3)	2.572 (19)	2.609 (14)	Se(2)–Mo(3)	3 × 2.537 (16)	3 × 2.517 (7)
In(2)	2.965 (23)	2.857 (14)	Se(4)	3 × 3.558 (13)	3 × 3.577 (8)
Mo(2)–Mo(2)	2 × 2.712 (9)	2 × 2.683 (7)	Se(5)	3 × 3.694 (13)	3 × 3.649 (7)
Mo(2)	2 × 2.684 (7)	2 × 2.688 (7)	Se(4)	3 × 3.693 (6)	3 × 3.699 (5)
Mo(3)	3.498 (8)	3.512 (8)	In(1)	3.089 (25)	3.038 (11)
Mo(2)	3.816 (10)	3.797 (6)	Se(3)–Mo(1)	2.575 (13)	2.584 (14)
Se(1)	2.561 (17)	2.547 (9)	Mo(1)	2.572 (19)	2.609 (14)
Se(4)	2.547 (13)	2.557 (6)	Mo(3)	2 × 2.690 (11)	2 × 2.692 (5)
Se(4)	2.557 (10)	2.573 (11)	Se(5)	2 × 3.589 (10)	2 × 3.583 (10)
Se(4)	2.616 (10)	2.628 (11)	Se(1)	2 × 3.715 (12)	2 × 3.745 (10)
Se(5)	2.666 (12)	2.661 (6)	Se(5)	2 × 3.790 (15)	2 × 3.834 (7)
In(2)	3.807 (9)	3.818 (5)	Se(4)	2 × 3.944 (12)	2 × 3.897 (5)
Mo(3)–Mo(3)	2 × 2.654 (11)	2 × 2.655 (7)	In(2)	2.671 (29)	2.684 (22)
Mo(1)	2.729 (10)	2.725 (7)	In(2)	3.502 (25)	3.108 (14)
Mo(1)	2.770 (8)	2.771 (7)	Se(4)–Mo(2)	2.547 (13)	2.557 (7)
Mo(2)	3.498 (8)	3.512 (8)	Mo(2)	2.557 (10)	2.573 (11)
Mo(1)	3.839 (8)	3.860 (6)	Mo(2)	2.616 (10)	2.628 (11)
Se(2)	2.537 (16)	2.517 (7)	Mo(3)	2.677 (10)	2.665 (6)
Se(5)	2.579 (8)	2.568 (10)	Se(2)	3.558 (13)	3.577 (8)
Se(5)	2.647 (10)	2.635 (10)	Se(5)	3.618 (13)	3.582 (9)
Se(4)	2.677 (10)	2.665 (6)	Se(5)	3.606 (11)	3.601 (6)
Se(3)	2.690 (11)	2.692 (5)	Se(4)	2 × 3.582 (14)	2 × 3.620 (6)
In(2)	4.126 (17)	4.095 (16)	Se(1)	3.682 (15)	3.663 (8)
In(1)–Se(2)	3.089 (25)	3.038 (22)	Se(2)	3.693 (6)	3.699 (5)
Se(5)	3 × 3.162 (10)	3 × 3.186 (7)	Se(5)	3.780 (15)	3.754 (6)
Se(4)	3 × 3.535 (12)	3 × 3.500 (8)	Se(3)	3.944 (12)	3.897 (5)
In(2)–Mo(1)	2.965 (23)	2.857 (14)	Se(5)	3.986 (13)	3.962 (9)
Mo(2)	2 × 3.807 (9)	2 × 3.818 (5)	In(1)	3.535 (12)	3.500 (8)
Mo(3)	2 × 4.126 (17)	2 × 4.095 (16)	Se(5)–Mo(3)	2.579 (8)	2.568 (10)
Se(1)	2 × 2.564 (25)	2 × 2.667 (11)	Mo(1)	2.603 (10)	2.596 (5)
Se(3)	2.671 (29)	2.684 (22)	Mo(3)	2.647 (10)	2.635 (10)
Se(5)	2 × 2.857 (20)	2 × 2.814 (11)	Mo(2)	2.666 (12)	2.661 (6)
Se(3)	3.052 (25)	3.108 (14)	Se(4)	3.618 (13)	3.582 (9)
In(2)	2 × 3.293 (31)	2 × 3.506 (21)	Se(3)	3.589 (10)	3.583 (10)
			Se(4)	3.606 (11)	3.601 (6)
			Se(2)	3.694 (13)	3.649 (7)
			Se(1)	3.702 (9)	3.720 (7)
			Se(4)	3.780 (15)	3.754 (6)
			Se(3)	3.790 (15)	3.834 (7)
			Se(4)	3.986 (13)	3.962 (9)
			In(2)	2.857 (20)	2.814 (11)
			In(1)	3.162 (10)	3.186 (7)

work such as the synthesis of new isostructural compounds are therefore desirable.

Stimulating discussions with Professors Ø. K. Andersen, Ø. Fischer, E. Parthé and H. G. von Schnering are gratefully acknowledged.

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Structure Cristalline de la Forme de Haute Température du Polyphosphate de Cadmium Cd(PO₃)₂β

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(Reçu le 21 juin 1978, accepté le 16 octobre 1978)

Abstract

β-Cd(PO₃)₂ is the high-temperature form of cadmium polyphosphate. It has an orthorhombic unit cell $P2_12_12_1$ with $a = 7.418$ (2), $b = 7.360$ (2), $c = 8.564$ (2) Å. The crystal structure was solved from single-crystal diffractometer data measured at room temperature. The final R value is 0.052 for 1399 reflexions (0.044 for 1382 reflexions with $||F_o| - |F_c||/\sigma < 6$). The unit cell is crossed by two (PO₃)_∞ chains, running in the b direction. CdO₆ octahedra are edge-linked and form chains parallel to the b direction. The poor thermal stability of the compound accounts for the high temperature factor values.

Introduction

Cd(PO₃)₂β est la forme de haute température du polyphosphate de cadmium. Elle a été signalée pour la première fois par Brown & Hummel (1964); ses

caractéristiques cristallines ont été mesurées par Laügt, Bagieu-Beucher & Grenier (1972), qui décrivent sa préparation.

Parmi les phosphates condensés de cadmium, la forme de basse température du polyphosphate Cd(PO₃)₂α est aussi connue. Ses caractéristiques cristallines ont été mesurées par Beucher & Tordjman (1968) qui ont ensuite résolu sa structure (Tordjman, Beucher, Guitel & Bassi, 1968) et l'ont affinée ultérieurement (Bagieu-Beucher, Guitel, Tordjman & Durif, 1974).

On connaît aussi un tétramétaphosphate de cadmium. Les paramètres de maille de la forme anhydre Cd₂P₄O₁₂ ont été mesurés par Laügt, Durif & Averbuch-Pouchot (1973). Ce sel est isotype des tétramétaphosphates de cations bivalents M₂^{II}P₄O₁₂ avec M^{II} = Mg, Mn, Co, Ni, Cu, Zn (Beucher & Grenier, 1968; Laügt, Guitel, Tordjman & Bassi, 1972; Nord & Börje-Lindberg, 1975).

Par ailleurs, deux variétés hydratées de trimétaphosphate de cadmium sont connues: il s'agit de