

# The Chevrel phase $\text{In}_{4.07}\text{Mo}_{15}\text{S}_{11.87}\text{Se}_{7.13}$ with mixed chalcogenide occupancy

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Key indicators: single-crystal X-ray study;  $T = 295$  K; mean  $\sigma(\text{Mo}-\text{Mo}) = 0.001$  Å; disorder in main residue;  $R$  factor = 0.039;  $wR$  factor = 0.090; data-to-parameter ratio = 17.0.

The single-crystal of the title compound, indium pentadeca-molybdenum nonadeca(sulfide/selenide), was obtained by solid state reaction with an S/Se mixture. It adopts the structure type of  $\text{In}_3\text{Mo}_{15}\text{Se}_{19}$  and  $\text{In}_{3.7}\text{Mo}_{15}\text{S}_{19}$ , which are non-substituted Chevrel phases in the space group  $P6_3/m$ . The Mo, one S/Se and two In sites have point symmetry  $m..$  and two S/Se and one In atoms are in  $3..$  sites. This compound contains isolated  $\text{Mo}_6$  and  $\text{Mo}_9$  clusters. The shapes of clusters are octahedral and confacial bioctahedral, respectively, face-capped by chalcogen atoms over each triangle face. The Mo– $X$  bonds ( $X = \text{S}, \text{Se}$ ) play an important role for the constitution of the framework. The Mo– $X$  distances of 2.479 (2)–2.6687 (9) Å are within the ranges of average values of Mo–S and Mo–Se distances. The In atoms located on sites with  $m..$  symmetry are partially occupied.

## Related literature

For discussion of the crystal structures of Chevrel phases, see: Grüttner *et al.* (1979). For applications, see: Suresh *et al.* (2008); Aurbach *et al.* (2007). For the syntheses and crystal structures of Chevrel phases with various cations, see: Salloum, Gautier *et al.* (2004); Salloum, Gougeon *et al.* (2004).

## Experimental

### Crystal data

$\text{In}_{4.07}\text{Mo}_{15}\text{S}_{11.87}\text{Se}_{7.13}$   
 $M_r = 2847.4$   
 Hexagonal,  $P6_3/m$   
 $a = 9.5974$  (2) Å  
 $c = 19.1668$  (5) Å  
 $V = 1528.93$  (6) Å<sup>3</sup>

$Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 18.17$  mm<sup>−1</sup>  
 $T = 295$  K  
 $0.04 \times 0.04 \times 0.03$  mm

### Data collection

Bruker SMART CCD area-detector diffractometer  
 Absorption correction: multi-scan (*SADABS*; Bruker, 2002)  
 $T_{\min} = 0.431$ ,  $T_{\max} = 0.577$

10366 measured reflections  
 1309 independent reflections  
 1047 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.048$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$   
 $wR(F^2) = 0.090$   
 $S = 1.41$   
 1309 reflections

77 parameters  
 $\Delta\rho_{\text{max}} = 4.14$  e Å<sup>−3</sup>  
 $\Delta\rho_{\text{min}} = -4.12$  e Å<sup>−3</sup>

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *WinGX* publication routines (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BR2099).

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**supplementary materials**

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### Comment

The classical Chevrel phases, containing blocks of  $\text{Mo}_6\text{X}_8$ , have been in interest for both structural respects and application to rechargeable batteries (Suresh, *et al.*, 2008; Aurbach, *et al.*, 2007). The new Chevrel phases  $\text{In}_x\text{Mo}_{15}\text{Se}_{19}$  ( $x=2.9$  and 3.3) also have been studied by X-ray single-crystal method (Grüttner *et al.*, 1979). These were the first compound having a transition metal cluster with the isolated  $\text{Mo}_6$  and  $\text{Mo}_9$  clusters. The  $\text{Mo}_9$  cluster has the shape of a confacial bioctahedron resulting from the condensation of two octahedral  $\text{Mo}_6$  clusters. Both clusters are surrounded by face-capping Se atoms to form  $\text{Mo}_6\text{Se}_8$  and  $\text{Mo}_9\text{Se}_{11}$  cluster units, and they are interconnected through Mo—Se bonds to build the three dimensional framework (Fig. 1). On our continuous studies to develop new materials for rechargeable batteries, herein, we report the single-crystal structure of the mixed chalcogenide compound  $\text{In}_{4.07}\text{Mo}_{15}\text{S}_{11.87}\text{Se}_{7.13}$  (1). We have investigated the effect of the partial substitution of Se by S atoms in the related Chevrel phase, hoping that the building blocks of Chevrel phase would not be changed.

The crystal structure of the title compound in a unit cell is shown in Fig. 1. The framework is composed of  $\text{Mo}_6\text{X}_8$  and  $\text{Mo}_9\text{X}_{11}$  cluster units ( $X=\text{Se/S}$ ) that are interconnected through Mo—X bonds. The  $\text{Mo}_6$  cluster forms the octahedral geometry with Mo—Mo bonds between the six Mo atoms, and the eight faces on the octahedron share a chalcogen atom to create the  $\text{Mo}_6\text{X}_8$  building block (Fig. 2). The  $\text{Mo}_9$  cluster is formed by one dimensional *trans*-face sharing of two  $\text{Mo}_6$  octahedron, and surrounded by eleven face-capping chalcogen atoms. The Mo—Mo bond distance related through the threefold axis in the  $\text{Mo}_6$  clusters is 2.6728 (11) Å. And the Mo—Mo distances within the  $\text{Mo}_9$  clusters are in the range of 2.6415 (10) - 2.7540 (8) Å which are within the normal range of the other Chevrel phases (Grüttner *et al.*, 1979; Salloum, Gautier *et al.*, 2004; Salloum, Gougeon *et al.*, 2004). The amount of substitution of Se atoms by S atoms are dependent on the atomic positions with the range of 34% (for X3 atom) - 86% (for X1 atom). The higher the S atom occupation, the shorter Mo—X bond distances are.

### Experimental

The title compound was prepared from powder elemental indium (99.999 at.%), molybdenum (99.999 at.%), sulfur (99.98 at.%), and selenium (99.99 at.%) from Aldrich products in the slightly off-stoichiometric 5:15:12:7 ratio. The reaction mixture was sealed under a nitrogen atmosphere in a silica tube and heated at 1343 K for 72 h and cooled to room temperature at the rate of 10 K/h to obtain black single crystals for X-ray studies.

### Refinement

The crystal structure of the title compound was solved and refined starting from the atomic coordinates reported for  $\text{In}_{\sim 3}\text{Mo}_{15}\text{Se}_{19}$  compound (Grüttner *et al.*, 1979). In the first stage of the refinement, the positions of all atoms but In3 were

## supplementary materials

obtained reasonably. The remaining In<sub>3</sub> atom was located in subsequent difference Fourier syntheses. The maximum and minimum residual electron density peaks were located at 1.07 and 0.46 Å, respectively, from the In1 atom.

### Figures

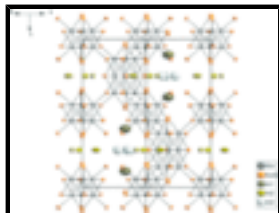


Fig. 1. View of the crystal structure of the title compound along [110], with displacement ellipsoids at the 80% probability level.

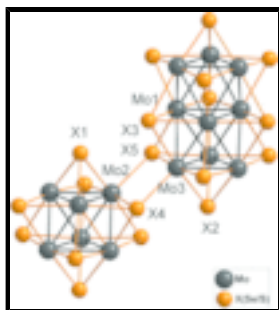


Fig. 2. Mo<sub>6</sub>X<sub>8</sub> and Mo<sub>9</sub>X<sub>11</sub> cluster units interconnected through Mo—X bonds (X=Se/S).

### indium pentadecamolybdenum nonadeca(sulfide/selenide)

#### Crystal data

In<sub>4.07</sub>Mo<sub>15</sub>S<sub>11.87</sub>Se<sub>7.13</sub>

$M_r = 2847.4$

Hexagonal,  $P6_3/m$

Hall symbol:  $-P\ 6c$

$a = 9.5974\ (2)\ \text{\AA}$

$b = 9.5974\ (2)\ \text{\AA}$

$c = 19.1668\ (5)\ \text{\AA}$

$\alpha = 90^\circ$

$\beta = 90^\circ$

$\gamma = 120^\circ$

$V = 1528.93\ (6)\ \text{\AA}^3$

$Z = 2$

$F_{000} = 2524.1$

$D_x = 6.185\ \text{Mg m}^{-3}$

Mo  $K\alpha$  radiation

$\lambda = 0.71073\ \text{\AA}$

Cell parameters from 1691 reflections

$\theta = 2.5\text{--}28.3^\circ$

$\mu = 18.17\ \text{mm}^{-1}$

$T = 295\ \text{K}$

Block, black

$0.04 \times 0.04 \times 0.03\ \text{mm}$

#### Data collection

Bruker SMART CCD area-detector diffractometer

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan (SADABS; Bruker, 2002)

$T_{\min} = 0.431$ ,  $T_{\max} = 0.577$

10366 measured reflections

1309 independent reflections

$R_{\text{int}} = 0.048$

$\theta_{\text{max}} = 28.3^\circ$

$\theta_{\text{min}} = 2.1^\circ$

$h = -12 \rightarrow 12$

$k = -9 \rightarrow 12$

$l = -25 \rightarrow 25$

1047 reflections with  $I > 2\sigma(I)$

*Refinement*

Refinement on $F^2$	77 parameters
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0327P)^2]$
	where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.039$	$(\Delta/\sigma)_{\max} < 0.001$
$wR(F^2) = 0.090$	$\Delta\rho_{\max} = 4.14 \text{ e } \text{\AA}^{-3}$
$S = 1.41$	$\Delta\rho_{\min} = -4.12 \text{ e } \text{\AA}^{-3}$
1309 reflections	Extinction correction: none

*Special details*

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Mo1	0.16177 (10)	0.50528 (10)	0.25	0.0084 (2)	
Mo2	0.01379 (7)	0.16724 (7)	0.05730 (3)	0.00754 (18)	
Mo3	0.31869 (7)	0.50095 (7)	0.13306 (3)	0.00801 (18)	
Se1	0	0	0.15855 (13)	0.0164 (9)	0.140 (9)
S1	0	0	0.15855 (13)	0.0164 (9)	0.860 (9)
Se2	0.3333	0.6667	0.03438 (13)	0.0137 (9)	0.142 (9)
S2	0.3333	0.6667	0.03438 (13)	0.0137 (9)	0.858 (9)
Se3	0.31626 (16)	0.34882 (16)	0.25	0.0139 (5)	0.658 (8)
S3	0.31626 (16)	0.34882 (16)	0.25	0.0139 (5)	0.342 (8)
Se4	0.71167 (14)	0.03659 (14)	0.05076 (5)	0.0122 (4)	0.437 (6)
S4	0.71167 (14)	0.03659 (14)	0.05076 (5)	0.0122 (4)	0.563 (6)
Se5	0.01082 (16)	0.38207 (15)	0.13790 (6)	0.0149 (5)	0.328 (6)
S5	0.01082 (16)	0.38207 (15)	0.13790 (6)	0.0149 (5)	0.672 (6)
In1	0.6667	0.3333	0.10758 (9)	0.0837 (6)	
In2	0.2155 (3)	0.0510 (3)	0.25	0.0331 (8)	0.468 (4)
In3	0.5545 (8)	0.2420 (7)	0.25	0.055 (2)	0.224 (4)

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Mo1	0.0086 (4)	0.0086 (4)	0.0080 (4)	0.0043 (4)	0	0
Mo2	0.0079 (3)	0.0083 (3)	0.0066 (3)	0.0041 (3)	-0.0002 (2)	-0.0006 (2)
Mo3	0.0083 (3)	0.0085 (3)	0.0072 (3)	0.0042 (3)	-0.0002 (2)	-0.0005 (2)
Se1	0.0198 (11)	0.0198 (11)	0.0098 (13)	0.0099 (6)	0	0
S1	0.0198 (11)	0.0198 (11)	0.0098 (13)	0.0099 (6)	0	0

## supplementary materials

Se2	0.0132 (10)	0.0132 (10)	0.0146 (14)	0.0066 (5)	0	0
S2	0.0132 (10)	0.0132 (10)	0.0146 (14)	0.0066 (5)	0	0
Se3	0.0143 (8)	0.0136 (8)	0.0129 (7)	0.0064 (6)	0	0
S3	0.0143 (8)	0.0136 (8)	0.0129 (7)	0.0064 (6)	0	0
Se4	0.0108 (6)	0.0127 (6)	0.0107 (6)	0.0041 (5)	0.0031 (4)	0.0006 (4)
S4	0.0108 (6)	0.0127 (6)	0.0107 (6)	0.0041 (5)	0.0031 (4)	0.0006 (4)
Se5	0.0197 (8)	0.0110 (7)	0.0136 (7)	0.0073 (6)	-0.0028 (5)	-0.0045 (5)
S5	0.0197 (8)	0.0110 (7)	0.0136 (7)	0.0073 (6)	-0.0028 (5)	-0.0045 (5)
In1	0.0967 (10)	0.0967 (10)	0.0579 (10)	0.0483 (5)	0	0
In2	0.0608 (17)	0.0434 (14)	0.0201 (10)	0.0446 (13)	0	0
In3	0.072 (4)	0.043 (4)	0.060 (4)	0.037 (3)	0	0

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

Mo1—Mo3	2.7123 (7)	Mo3—S3	2.6687 (9)
Mo1—Mo3 <sup>i</sup>	2.7540 (8)	Mo3—S4 <sup>vii</sup>	2.6034 (12)
Mo2—Mo2 <sup>ii</sup>	2.6728 (11)	Mo3—S5 <sup>iii</sup>	2.4976 (14)
Mo3—Mo3 <sup>iii</sup>	2.6415 (10)	Mo3—S5	2.5827 (15)
Mo1—S3	2.5844 (16)	In1—In3	2.904 (3)
Mo1—S3 <sup>i</sup>	2.5681 (16)	In2—In3	2.825 (7)
Mo1—S5 <sup>iv</sup>	2.5299 (13)	In2—Mo1 <sup>viii</sup>	2.862 (2)
Mo2—S1	2.479 (2)	In1—S2 <sup>ix</sup>	2.721 (3)
Mo2—S4 <sup>v</sup>	2.5093 (12)	In2—S1 <sup>iv</sup>	2.564 (2)
Mo2—S4 <sup>vi</sup>	2.5219 (13)	In2—S3	2.518 (3)
Mo2—S4 <sup>vii</sup>	2.6101 (13)	In2—S5 <sup>viii</sup>	2.8445 (18)
Mo2—S5	2.5880 (13)	In3—S3	2.937 (6)
Mo3—S2	2.430 (2)	In3—S5 <sup>viii</sup>	3.055 (4)
Mo2 <sup>ii</sup> —Mo2—Mo2 <sup>viii</sup>	60.0	S1—Mo2—Mo2 <sup>ii</sup>	57.39 (3)
Mo3 <sup>iii</sup> —Mo3—Mo3 <sup>i</sup>	60.0	S4 <sup>v</sup> —Mo2—Mo2 <sup>ii</sup>	120.33 (3)
Mo3—Mo1—Mo3 <sup>iv</sup>	111.46 (4)	S4 <sup>vi</sup> —Mo2—Mo2 <sup>ii</sup>	60.24 (4)
Mo3—Mo1—Mo3 <sup>i</sup>	57.79 (2)	S4 <sup>vii</sup> —Mo2—Mo2 <sup>ii</sup>	116.94 (3)
Mo3 <sup>x</sup> —Mo1—Mo3 <sup>i</sup>	108.95 (4)	S4 <sup>v</sup> —Mo2—Mo2 <sup>viii</sup>	118.11 (3)
Mo3—Mo1—Mo3 <sup>x</sup>	144.30 (4)	S4 <sup>vi</sup> —Mo2—Mo2 <sup>viii</sup>	120.16 (4)
S5—Mo1—S5 <sup>iv</sup>	116.27 (7)	S4 <sup>vii</sup> —Mo2—Mo2 <sup>viii</sup>	57.01 (3)
S5—Mo1—S3 <sup>i</sup>	87.54 (4)	S5—Mo2—Mo2 <sup>ii</sup>	131.12 (4)
S5—Mo1—S3	95.12 (4)	S5—Mo2—Mo2 <sup>viii</sup>	136.62 (4)
S3 <sup>i</sup> —Mo1—S3	174.93 (5)	S2—Mo3—S3	173.60 (5)
S5—Mo1—Mo3	58.91 (3)	S2—Mo3—S5 <sup>iii</sup>	91.81 (3)
S5 <sup>iv</sup> —Mo1—Mo3	152.53 (5)	S5 <sup>iii</sup> —Mo3—S5	175.03 (5)
S3 <sup>i</sup> —Mo1—Mo3	117.85 (3)	S5 <sup>iii</sup> —Mo3—S3	86.03 (4)
S3—Mo1—Mo3	60.45 (2)	S5 <sup>iii</sup> —Mo3—S4 <sup>vii</sup>	86.33 (4)
S5—Mo1—Mo3 <sup>x</sup>	145.74 (5)	S5—Mo3—S4 <sup>vii</sup>	98.34 (4)
S5 <sup>iv</sup> —Mo1—Mo3 <sup>x</sup>	56.23 (3)	S2—Mo3—Mo3 <sup>iii</sup>	57.07 (3)

S3 <sup>i</sup> —Mo1—Mo3 <sup>x</sup>	60.07 (2)	S3 <sup>iii</sup> —Mo3—Mo3	116.82 (3)
S3—Mo1—Mo3 <sup>x</sup>	118.08 (2)	S3 <sup>i</sup> —Mo3—Mo3	119.14 (3)
S5 <sup>iv</sup> —Mo1—Mo3 <sup>i</sup>	145.74 (5)	S4 <sup>vii</sup> —Mo3—Mo3 <sup>i</sup>	136.62 (3)
S3 <sup>i</sup> —Mo1—Mo3 <sup>i</sup>	60.07 (2)	S4 <sup>vii</sup> —Mo3—Mo3 <sup>iii</sup>	130.06 (4)
S1—Mo2—S4 <sup>v</sup>	175.41 (5)	S5 <sup>iii</sup> —Mo3—Mo3 <sup>iii</sup>	60.26 (4)
S1—Mo2—S4 <sup>vi</sup>	92.35 (3)	S5 <sup>iii</sup> —Mo3—Mo3 <sup>i</sup>	120.21 (4)
S1—Mo2—S4 <sup>vii</sup>	90.27 (3)	Mo1 <sup>iii</sup> —S3—Mo1	65.07 (5)
S1—Mo2—S5	91.73 (5)	Mo1 <sup>iii</sup> —S3—Mo3 <sup>iv</sup>	63.42 (3)
S4 <sup>v</sup> —Mo2—S5	92.56 (4)	Mo1—S5—Mo3	64.07 (4)
S4 <sup>vi</sup> —Mo2—S5	87.58 (4)	Mo2 <sup>ii</sup> —S1—Mo2 <sup>viii</sup>	65.23 (6)
S4 <sup>v</sup> —Mo2—S4 <sup>vii</sup>	87.51 (3)	Mo2 <sup>xi</sup> —S4—Mo2 <sup>xii</sup>	64.49 (4)
S4 <sup>vi</sup> —Mo2—S4 <sup>vii</sup>	173.73 (5)	Mo2 <sup>xi</sup> —S4—Mo3 <sup>xiii</sup>	131.31 (5)
S4 <sup>v</sup> —Mo2—S4 <sup>vi</sup>	89.47 (3)	Mo2 <sup>xii</sup> —S4—Mo3 <sup>xiii</sup>	127.85 (5)
S5—Mo2—S4 <sup>vii</sup>	98.04 (4)		

Symmetry codes: (i)  $-x+y, -x+1, z$ ; (ii)  $-y, x-y, z$ ; (iii)  $-y+1, x-y+1, z$ ; (iv)  $x, y, -z+1/2$ ; (v)  $y, -x+y+1, -z$ ; (vi)  $x-1, y, z$ ; (vii)  $-x+y+1, -x+1, z$ ; (viii)  $-x+y, -x, z$ ; (ix)  $-x+1, -y+1, -z$ ; (x)  $-x+y, -x+1, -z+1/2$ ; (xi)  $x-y+1, x, -z$ ; (xii)  $x+1, y, z$ ; (xiii)  $-y+1, x-y, z$ .

Fig. 1

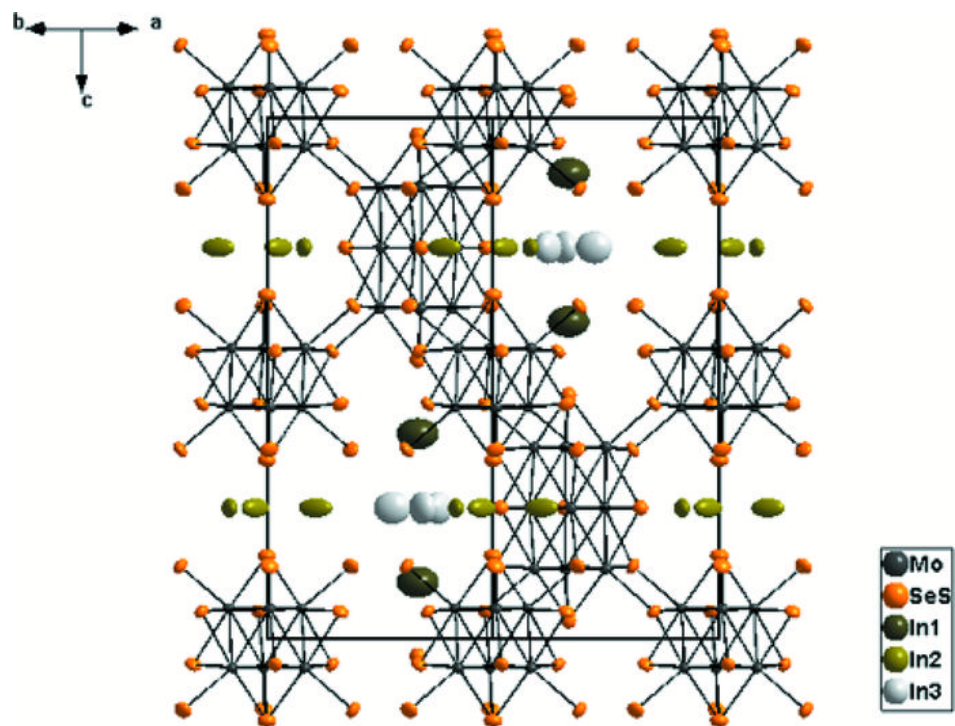




Fig. 2

