

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

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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Received 20 February 2009; accepted 28 February 2009

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 Mo_6 and 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) Å³

$Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 18.17$ mm⁻¹
 $T = 295$ 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⁻³
 $\Delta\rho_{\text{min}} = -4.12$ e Å⁻³

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).

This study was financially supported by the research fund of Chungnam National University in 2008.

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

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supporting information

Acta Cryst. (2009). E65, i26 [doi:10.1107/S1600536809007351]

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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S1. Comment

The classical Chevrel phases, containing blocks of Mo_6X_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 Mo_6 and Mo_9 clusters. The Mo_9 cluster has the shape of a confacial bioctahedron resulting from the condensation of two octahedral Mo_6 clusters. Both clusters are surrounded by face-capping Se atoms to form Mo_6Se_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 Mo_6X_8 and Mo_9X_{11} cluster units ($X=\text{Se/S}$) that are interconnected through Mo—X bonds. The 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 Mo_6X_8 building block (Fig. 2). The Mo_9 cluster is formed by one dimensional *trans*-face sharing of two Mo_6 octahedron, and surrounded by eleven face-capping chalcogen atoms. The Mo—Mo bond distance related through the threefold axis in the Mo_6 clusters is 2.6728 (11) Å. And the Mo—Mo distances within the 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.

S2. 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.

S3. Refinement

The crystal structure of the title compound was solved and refined starting from the atomic coordinates reported for $\text{In}_3\text{Mo}_{15}\text{Se}_{19}$ compound (Grüttner *et al.*, 1979). In the first stage of the refinement, the positions of all atoms but In3 were obtained reasonably. The remaining In3 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.

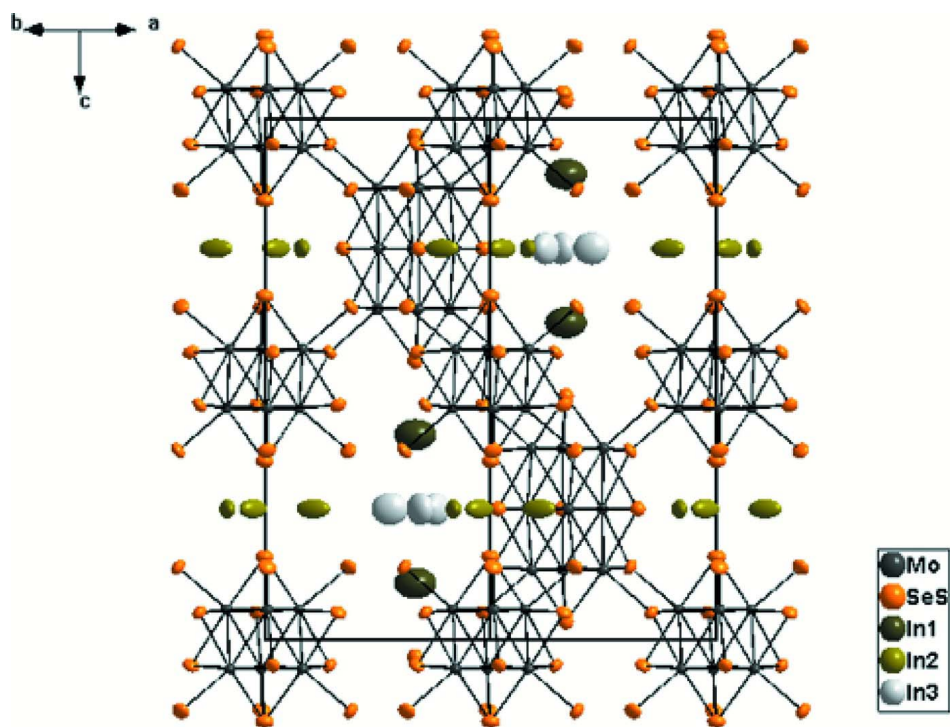
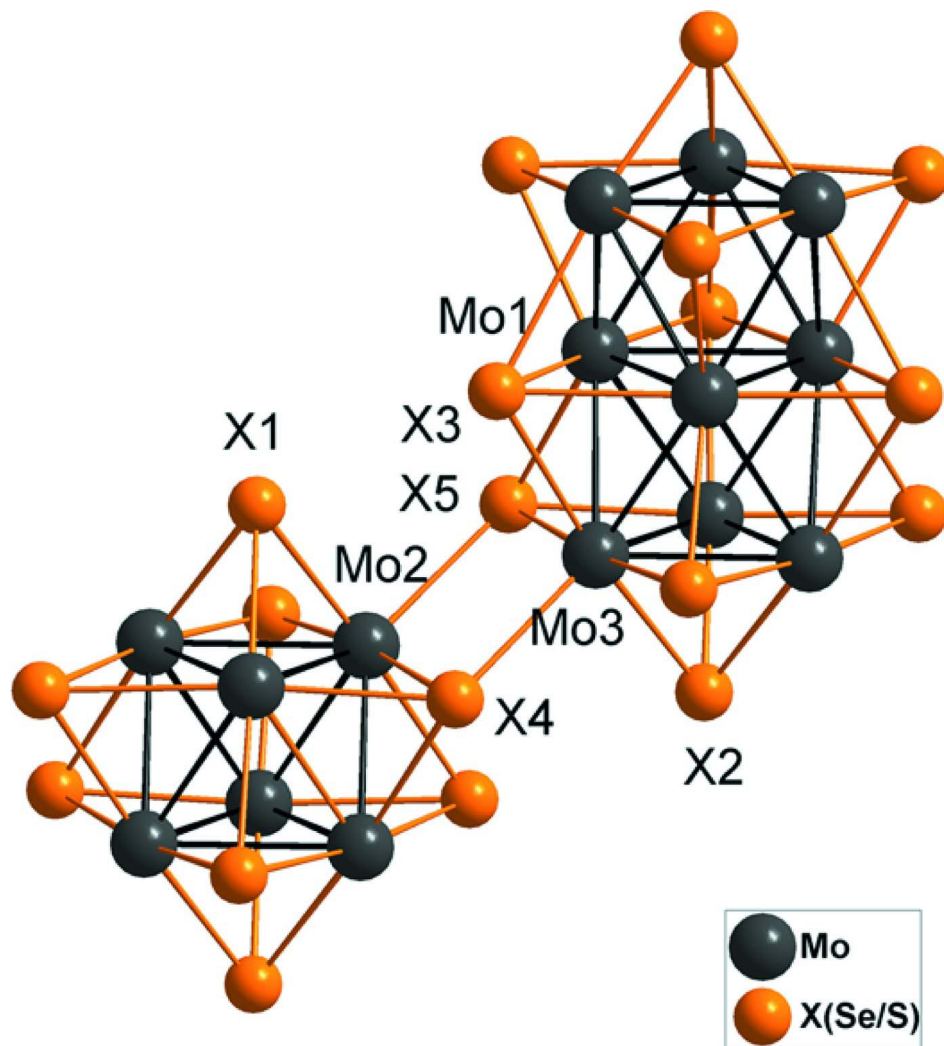


Figure 1

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

**Figure 2**

Mo_6X_8 and Mo_9X_{11} cluster units interconnected through Mo—X bonds (X=Se/S).

indium pentadecamolybdenum nonadeca(sulfide/selenide)

Crystal data

$\text{In}_{4.07}\text{Mo}_{15}\text{S}_{11.87}\text{Se}_{7.13}$

$M_r = 2847.4$

Hexagonal, $P6_3/m$

Hall symbol: $-P\ 6c$

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

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

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

$Z = 2$

$F(000) = 2524.1$

Data collection

Bruker SMART CCD area-detector
diffractometer

φ and ω scans

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

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

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

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

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

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

$\theta_{\text{max}} = 28.3^\circ$, $\theta_{\text{min}} = 2.1^\circ$
 $h = -12 \rightarrow 12$
 $k = -9 \rightarrow 12$
 $l = -25 \rightarrow 25$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.090$
 $S = 1.41$
 1309 reflections
 77 parameters

0 restraints
 $w = 1/[\sigma^2(F_o^2) + (0.0327P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 4.14 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -4.12 \text{ e } \text{\AA}^{-3}$

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 (\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 (\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
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 (Å, °)

Mo1—Mo3	2.7123 (7)	Mo3—S3	2.6687 (9)
Mo1—Mo3 ⁱ	2.7540 (8)	Mo3—S4 ^{vii}	2.6034 (12)
Mo2—Mo2 ⁱⁱ	2.6728 (11)	Mo3—S5 ⁱⁱⁱ	2.4976 (14)
Mo3—Mo3 ⁱⁱⁱ	2.6415 (10)	Mo3—S5	2.5827 (15)
Mo1—S3	2.5844 (16)	In1—In3	2.904 (3)
Mo1—S3 ⁱ	2.5681 (16)	In2—In3	2.825 (7)
Mo1—S5 ^{iv}	2.5299 (13)	In2—Mo1 ^{viii}	2.862 (2)
Mo2—S1	2.479 (2)	In1—S2 ^{ix}	2.721 (3)
Mo2—S4 ^v	2.5093 (12)	In2—S1 ^{iv}	2.564 (2)
Mo2—S4 ^{vi}	2.5219 (13)	In2—S3	2.518 (3)
Mo2—S4 ^{vii}	2.6101 (13)	In2—S5 ^{viii}	2.8445 (18)
Mo2—S5	2.5880 (13)	In3—S3	2.937 (6)
Mo3—S2	2.430 (2)	In3—S5 ^{viii}	3.055 (4)
Mo2 ⁱⁱ —Mo2—Mo2 ^{viii}	60.0	S1—Mo2—Mo2 ⁱⁱ	57.39 (3)
Mo3 ⁱⁱⁱ —Mo3—Mo3 ⁱ	60.0	S4 ^v —Mo2—Mo2 ⁱⁱ	120.33 (3)
Mo3—Mo1—Mo3 ^{iv}	111.46 (4)	S4 ^{vi} —Mo2—Mo2 ⁱⁱ	60.24 (4)
Mo3—Mo1—Mo3 ⁱ	57.79 (2)	S4 ^{vii} —Mo2—Mo2 ⁱⁱ	116.94 (3)
Mo3 ^x —Mo1—Mo3 ⁱ	108.95 (4)	S4 ^v —Mo2—Mo2 ^{viii}	118.11 (3)
Mo3—Mo1—Mo3 ^x	144.30 (4)	S4 ^{vi} —Mo2—Mo2 ^{viii}	120.16 (4)
S5—Mo1—S5 ^{iv}	116.27 (7)	S4 ^{vii} —Mo2—Mo2 ^{viii}	57.01 (3)
S5—Mo1—S3 ⁱ	87.54 (4)	S5—Mo2—Mo2 ⁱⁱ	131.12 (4)
S5—Mo1—S3	95.12 (4)	S5—Mo2—Mo2 ^{viii}	136.62 (4)
S3 ⁱ —Mo1—S3	174.93 (5)	S2—Mo3—S3	173.60 (5)
S5—Mo1—Mo3	58.91 (3)	S2—Mo3—S5 ⁱⁱⁱ	91.81 (3)
S5 ^{iv} —Mo1—Mo3	152.53 (5)	S5 ⁱⁱⁱ —Mo3—S5	175.03 (5)
S3 ⁱ —Mo1—Mo3	117.85 (3)	S5 ⁱⁱⁱ —Mo3—S3	86.03 (4)
S3—Mo1—Mo3	60.45 (2)	S5 ⁱⁱⁱ —Mo3—S4 ^{vii}	86.33 (4)
S5—Mo1—Mo3 ^x	145.74 (5)	S5—Mo3—S4 ^{vii}	98.34 (4)
S5 ^{iv} —Mo1—Mo3 ^x	56.23 (3)	S2—Mo3—Mo3 ⁱⁱⁱ	57.07 (3)
S3 ⁱ —Mo1—Mo3 ^x	60.07 (2)	S3 ⁱⁱⁱ —Mo3—Mo3	116.82 (3)
S3—Mo1—Mo3 ^x	118.08 (2)	S3 ⁱ —Mo3—Mo3	119.14 (3)
S5 ^{iv} —Mo1—Mo3 ⁱ	145.74 (5)	S4 ^{vii} —Mo3—Mo3 ⁱ	136.62 (3)
S3 ⁱ —Mo1—Mo3 ⁱ	60.07 (2)	S4 ^{vii} —Mo3—Mo3 ⁱⁱⁱ	130.06 (4)
S1—Mo2—S4 ^v	175.41 (5)	S5 ⁱⁱⁱ —Mo3—Mo3 ⁱⁱⁱ	60.26 (4)
S1—Mo2—S4 ^{vi}	92.35 (3)	S5 ⁱⁱⁱ —Mo3—Mo3 ⁱ	120.21 (4)

S1—Mo2—S4 ^{vii}	90.27 (3)	Mo1 ⁱⁱⁱ —S3—Mo1	65.07 (5)
S1—Mo2—S5	91.73 (5)	Mo1 ⁱⁱⁱ —S3—Mo3 ^{iv}	63.42 (3)
S4 ^v —Mo2—S5	92.56 (4)	Mo1—S5—Mo3	64.07 (4)
S4 ^{vi} —Mo2—S5	87.58 (4)	Mo2 ⁱⁱ —S1—Mo2 ^{viii}	65.23 (6)
S4 ^v —Mo2—S4 ^{vii}	87.51 (3)	Mo2 ^{xi} —S4—Mo2 ^{xii}	64.49 (4)
S4 ^{vi} —Mo2—S4 ^{vii}	173.73 (5)	Mo2 ^{xi} —S4—Mo3 ^{xiii}	131.31 (5)
S4 ^v —Mo2—S4 ^{vi}	89.47 (3)	Mo2 ^{xii} —S4—Mo3 ^{xiii}	127.85 (5)
S5—Mo2—S4 ^{vii}	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) $-y+1, x-y, z$.