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Key indicators

Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{Mo}-\text{Se}) = 0.007\text{ \AA}$
Disorder in main residue
 R factor = 0.040
 wR factor = 0.088
Data-to-parameter ratio = 36.9For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>. $\text{Ho}_{0.76}\text{In}_{1.68}\text{Mo}_{15}\text{Se}_{19}$

The structure of holmium indium molybdenum selenide, $\text{Ho}_{0.76}\text{In}_{1.68}\text{Mo}_{15}\text{Se}_{19}$, isotypic with $\text{In}_{2.9}\text{Mo}_{15}\text{Se}_{19}$ [Grüttner, Yvon, Chevrel, Potel, Sergent & Seeber (1979). *Acta Cryst. B* **35**, 285–292], is characterized by two cluster units $\text{Mo}_6\text{Se}_8^i\text{Se}_6^a$ and $\text{Mo}_9\text{Se}_{11}^i\text{Se}_6^a$ (where i = inner and a = apical) that are present in a 1:1 ratio. The cluster units are centered at Wyckoff positions $2b$ and $2c$ and have point-group symmetry $\bar{3}$ and $\bar{6}$, respectively. The clusters are interconnected through additional Mo–Se bonds. In the title compound, Ho^{3+} cations replace the trivalent indium observed in $\text{In}_{2.9}\text{Mo}_{15}\text{Se}_{19}$, and a deficiency is observed on the monovalent indium site.

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Comment

In 1979, Grüttner *et al.* reported the crystal structures of $\text{In}_{2.9}\text{Mo}_{15}\text{Se}_{19}$ and $\text{In}_{3.3}\text{Mo}_{15}\text{Se}_{19}$ as the first compounds containing a transition metal cluster with a nuclearity higher than 6, *viz.* the bioctahedral Mo_9 cluster. The latter cluster, which results from the face-sharing of two Mo_6 octahedra, coexists with the octahedral Mo_6 cluster in equal proportions. Another interesting feature in these compounds concerns the In atoms that occupy two crystallographically different positions depending on their formal oxidation state of +I or +III, respectively. While the In^{I} site is fully occupied, the In^{III} site

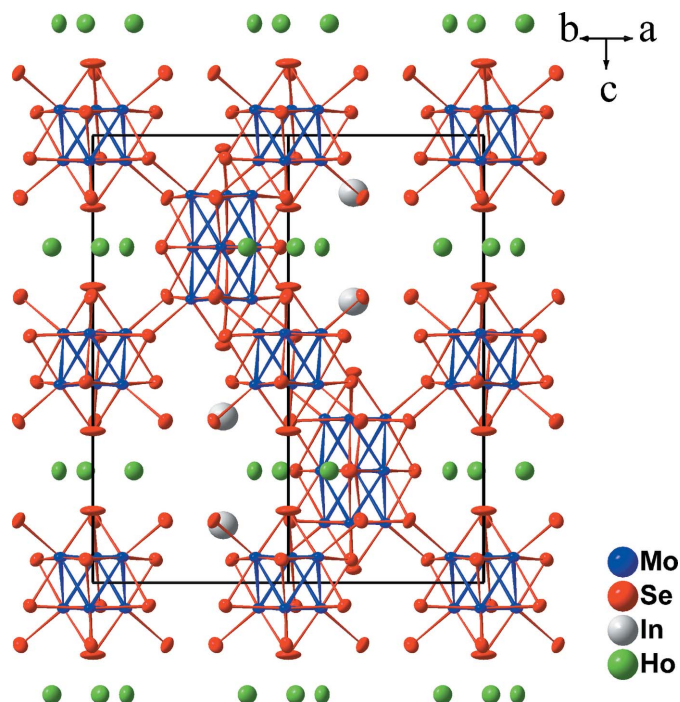


Figure 1
View of $\text{Ho}_{0.76}\text{In}_{1.68}\text{Mo}_{15}\text{Se}_{19}$ along $[110]$.

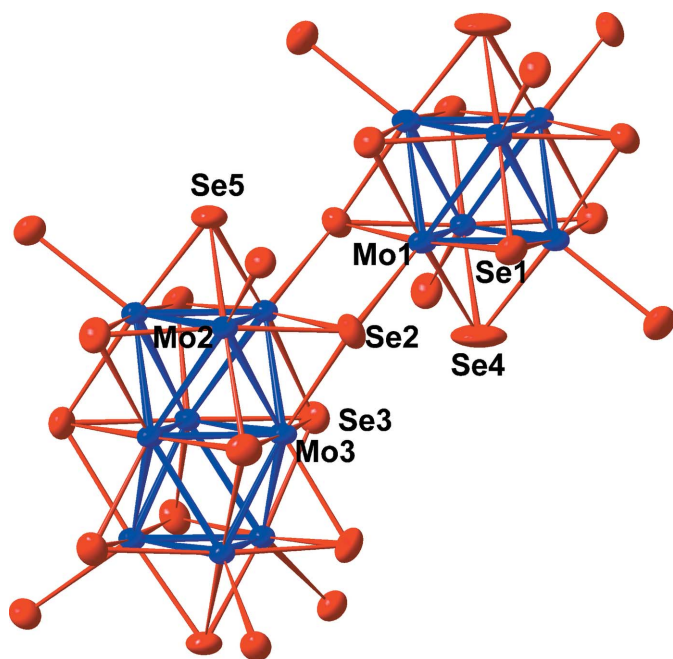


Figure 2

Plot showing the atom-numbering scheme and the inter-unit linkage of the $\text{Mo}_9\text{Se}_{11}\text{Se}_6$ and $\text{Mo}_6\text{Se}_8\text{Se}_6$ cluster units. Displacement ellipsoids are drawn at the 97% probability level.

presents a non-stoichiometry that leads to broad composition ranges from $\text{In}_{2.9}\text{Mo}_{15}\text{Se}_{19}$ to $\text{In}_{3.3}\text{Mo}_{15}\text{Se}_{19}$. We present here the crystal structure of $\text{Ho}_{0.76}\text{In}_{1.68}\text{Mo}_{15}\text{Se}_{19}$ in which Ho replaces the trivalent In site.

The Mo–Se framework of the title compound consists of the cluster units $\text{Mo}_6\text{Se}_8\text{Se}_6^a$ and $\text{Mo}_9\text{Se}_{11}\text{Se}_6^a$ in a 1:1 ratio. These units are interconnected through additional Mo–Se bonds (Figs. 1 and 2); for details of the *i*- and *a*-type ligand notation, see Schäfer & von Schnering (1964). The first unit can be described as an Mo_6 octahedron surrounded by eight face-capping inner Se^i and six apical Se^a ligands. The Mo_9 cluster is surrounded by 11 Se^i atoms capping the faces of the bioctahedron and six Se^a ligands above the apical Mo atoms. The $\text{Mo}_6\text{Se}_8\text{Se}_6^a$ and $\text{Mo}_9\text{Se}_{11}\text{Se}_6^a$ units are centered at Wyckoff positions $2b$ and $2c$ and have point-group symmetry $\bar{3}$ and $\bar{6}$, respectively. The Mo–Mo distances within the Mo_6 cluster are 2.7001 (7) Å for the distances of the Mo_3 triangles formed by the Mo atoms related through the threefold axis, and 2.7104 (8) Å for the distances between these triangles. The Mo–Mo distances within the Mo_9 clusters are 2.6470 (7) and 2.719 (1) Å for the intra-triangle distances between atoms Mo2 and Mo3, respectively, and 2.7179 (5) and 2.7673 (6) Å for those between the Mo_3 triangles. The Se atoms bridge either one (Se1, Se2, Se4 and Se5) or two (Se3) triangular faces of the Mo clusters. Moreover, atoms Se1 and Se2 are linked to an Mo atom of a neighboring cluster. The Mo–Se bond distances range from 2.5469 (9) to 2.6587 (7) Å within the $\text{Mo}_6\text{Se}_8\text{Se}_6^a$ unit, and from 2.5290 (8) to 2.6928 (6) Å within the $\text{Mo}_9\text{Se}_{11}\text{Se}_6^a$ unit. Each $\text{Mo}_9\text{Se}_{11}\text{Se}_6^a$ cluster is interconnected to six $\text{Mo}_6\text{Se}_8\text{Se}_6^a$ units (and *vice versa*) via Mo2–S1 bonds (and Mo1–S2 bonds, respectively), forming the three-dimensional Mo–S framework, the connective formula of

which is $\text{Mo}_9\text{Se}_{11}\text{Se}_6^i\text{Se}_6^{i-a}\text{Se}_6^{a-i}$, $\text{Mo}_6\text{Se}_8\text{Se}_6^i\text{Se}_6^{i-a}\text{Se}_6^{a-i}$. It results from this arrangement that the shortest intercluster Mo1–Mo2 distance is 3.4666 (6) Å, indicating only weak metal–metal interaction. The In^+ cations are surrounded by seven Se atoms forming a distorted tricapped tetrahedron, as is the case in $\text{In}_{2.9}\text{Mo}_{15}\text{Se}_{19}$. The Se5 and Se2 atoms forming the tetrahedron are at 3.0647 (15) and 3.1591 (5) Å from the In atom, and the capping Se1 atoms are at 3.5079 (7) Å. While in $\text{In}_{2.9}\text{Mo}_{15}\text{Se}_{19}$ the latter site is fully occupied by monovalent In, in the title compound it is only 0.842 (3) occupied. This probably results from the higher temperature used during the crystal-growth process which led to a loss of InSe because of its high volatility at 1773 K. The Ho^{3+} cations, as the In^{3+} cations in the $\text{In}_{3\pm x}\text{Mo}_{15}\text{Se}_{19}$ compounds, occupy partially [25.5 (2)%] occupied distorted octahedral cavities around the threefold axis, which are formed by two $\text{Mo}_6\text{Se}_8\text{Se}_6^a$ and three $\text{Mo}_9\text{Se}_{11}\text{Se}_6^a$ units. The Ho–Se distances are in the range 2.5689 (13)–2.9690 (16) Å.

Experimental

Single crystals of $\text{Ho}_{0.76}\text{In}_{1.68}\text{Mo}_{15}\text{Se}_{19}$ were prepared from a mixture of Ho_2Se_3 , MoSe_2 , InSe and Mo with the nominal composition $\text{HoIn}_2\text{Mo}_{15}\text{Se}_{19}$. Before use, Mo powder was reduced under flowing H_2 gas at 1273 K over a period 10 h in order to eliminate any trace of oxygen. The binaries Ho_2Se_3 , MoSe_2 , InSe were obtained by heating stoichiometric mixtures of the elements in sealed evacuated silica tubes over a period of about 2 d. All handling of materials was carried out in an argon-filled glove-box. The initial mixture (*ca* 5 g) was cold-pressed and loaded into a molybdenum crucible, which was sealed under a low argon pressure using an arc-welding system. The charge was heated at a rate of 300 K h^{-1} up to 1773 K, the temperature which was held there for 48 h, then cooled at a rate of 100 K h^{-1} to 1373 K and finally allowed to cool in the switched-off furnace. On the basis of the X-ray powder diagram, the product was a single phase.

Crystal data

$\text{Ho}_{0.76}\text{In}_{1.68}\text{Mo}_{15}\text{Se}_{19}$
 $M_r = 3258.98$
 Hexagonal, $P6_3/m$
 $a = 9.7969$ (1) Å
 $c = 19.3973$ (4) Å
 $V = 1612.31$ (4) Å³
 $Z = 2$
 $D_x = 6.713$ Mg m^{-3}

Mo $K\alpha$ radiation
 Cell parameters from 31521 reflections
 $\theta = 2.0$ – 35.0°
 $\mu = 30.08$ mm^{-1}
 $T = 293$ (2) K
 Irregular block, black
 $0.08 \times 0.05 \times 0.03$ mm

Data collection

Nonius KappaCCD diffractometer
 φ and ω scans
 Absorption correction: analytical
 (de Meulenaer & Tompa, 1965)
 $T_{\min} = 0.094$, $T_{\max} = 0.345$
 28264 measured reflections
 2436 independent reflections

1625 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.092$
 $\theta_{\max} = 35.1^\circ$
 $h = -11 \rightarrow 15$
 $k = -15 \rightarrow 15$
 $l = -31 \rightarrow 31$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.088$
 $S = 1.07$
 2436 reflections
 66 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0398P)^2 + 0.2653P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 2.64$ e Å⁻³
 $\Delta\rho_{\min} = -2.69$ e Å⁻³

Table 1
Selected bond lengths (Å).

Mo1—Se4	2.5469 (9)	Mo2—Mo3	2.7673 (5)
Mo1—Se1 ⁱ	2.5526 (7)	Mo3—Se3 ^v	2.5836 (9)
Mo1—Se1	2.5765 (7)	Mo3—Se2	2.5851 (6)
Mo1—Se1 ⁱⁱ	2.6163 (6)	Mo3—Se2 ^{vii}	2.5851 (6)
Mo1—Se2	2.6587 (7)	Mo3—Se3	2.5908 (9)
Mo1—Mo1 ⁱⁱⁱ	2.7001 (7)	Mo3—Mo3 ^{viii}	2.7193 (10)
Mo1—Mo1 ^{iv}	2.7104 (8)	In—Se5	3.0647 (15)
Mo2—Se5	2.5290 (8)	In—Se2 ^{ix}	3.1591 (5)
Mo2—Se2	2.5862 (6)	In—Se1 ^{ix}	3.5079 (7)
Mo2—Se2 ^v	2.6275 (7)	Ho—Se4 ^{vii}	2.5689 (13)
Mo2—Mo2 ^v	2.6470 (7)	Ho—Se3 ⁱⁱ	2.7270 (16)
Mo2—Se1 ^{vi}	2.6675 (7)	Ho—Se2 ⁱⁱⁱ	2.8314 (11)
Mo2—Se3 ^v	2.6928 (6)	Ho—Se2 ^s	2.8314 (11)
Mo2—Mo3 ^v	2.7179 (5)	Ho—Se3 ⁱⁱⁱ	2.9690 (16)

Symmetry codes: (i) $x - y, x, -z + 1$; (ii) $-y, x - y, z$; (iii) $-x + y, -x, z$; (iv) $y, -x + y, -z + 1$; (v) $-y + 1, x - y, z$; (vi) $-x + y + 1, -x, z$; (vii) $x, y, -z + \frac{3}{2}$; (viii) $-x + y + 1, -x + 1, z$; (ix) $-x + 1, -y, -z + 1$; (x) $-x + y, -x, -z + \frac{1}{2}$.

The occupation factors for the Ho and In atoms were refined freely. The highest peak and the deepest hole in the final Fourier map are located 0.20 Å from In and 0.64 Å from Se4, respectively.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *COLLECT*; data reduction: *EVALCCD* (Duisenberg *et al.*, 2003);

program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *SHELXL97*.

Intensity data were collected on the Nonius KappaCCD X-ray diffractometer system of the Centre de diffractométrie de l'Université de Rennes I (URL: www.cdifx.univ-rennes1.fr).

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