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$In_{0.87}K_2Mo_{15}Se_{19}$: a quaternary selenide containing Mo_6 and Mo_9 clusters

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The structure of $In_{0.87}K_2Mo_{15}Se_{19}$ (indium dipotassium pentadecamolybdate nonadecaselenide), isotypic with $In_{2.9}Mo_{15}Se_{19}$, is characterized by a mixture of $Mo_6Se^i_8Se^a_6$ and $Mo_9Se^i_{11}Se^a_6$ cluster units in the ratio 1:1. Both units are interconnected through additional Mo—Se bonds. In the title compound, K^+ replaces the monovalent In positions as observed in $In_{2.9}Mo_{15}Se_{19}$. One Mo, one Se and the In atom are situated on mirror planes, and two other Se atoms are situated on threefold axes.

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(Mo–Mo) = 0.001 Å
Disorder in main residue
R factor = 0.037
wR factor = 0.040
Data-to-parameter ratio = 39.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

In 1979, Grüttner *et al.* reported the crystal structure of $In_{2.9}Mo_{15}Se_{19}$, which was the first compound containing a transition metal cluster with a nuclearity higher than six, *viz*. the Mo_9 cluster, which results from face-sharing of two Mo_6 octahedra. The Mo_9 cluster coexists with the octahedral Mo_6

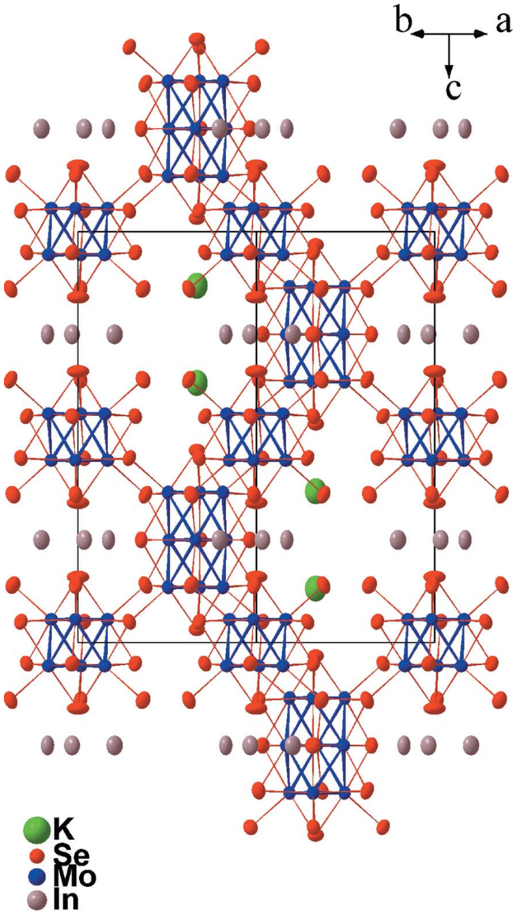

Figure 1
A view of $In_{0.87}K_2Mo_{15}Se_{19}$, along [110].

cluster in equal proportion in this structure. Another interesting feature of these compounds pertains to the In atoms, which occupy two crystallographically different positions depending on their formal oxidation state of +1 or +3. While the In^+ site is fully occupied (Wyckoff site 4f), the In^{3+} site (6h) exhibits partial occupation that leads to compositions ranging from $In_{2.9}Mo_{15}Se_{19}$ to $In_{3.3}Mo_{15}Se_{19}$. Interest in these Mo cluster compounds also lies in their physical properties, because they become superconductors with high critical magnetic fields at about 4 K. We present here the crystal structure of $In_{0.87}K_2Mo_{15}Se_{19}$, in which K^+ replaces the monovalent In positions.

The crystal structure of $In_{0.87}K_2Mo_{15}Se_{19}$ is shown in Fig. 1. The Mo–Se framework consists of equal proportions of $Mo_6Se^i_8Se^a_6$ and $Mo_9Se^i_{11}Se^a_6$ units that are interconnected through additional Mo—Se bonds (Fig. 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 core of the second unit results from the face sharing of two octahedral Mo_6 clusters. The Mo_9 cluster is surrounded by 11 Se^i atoms capping the faces of the bioctahedron and six apical Se^a ligands above the terminal Mo atoms. The Mo—Mo distances within the Mo_6 clusters are 2.6916 (6) Å for the intra-triangle distances (distances between the Mo atoms related through the threefold axis) and 2.7091 (7) Å for the inter-triangle distances. The Mo—Mo distances within the Mo_9 clusters are 2.6417 (8) and 2.7238 (8) Å for the intra-triangle distances between the Mo2 and Mo3 atoms, respectively, and 2.7132 (5) and 2.7746 (6) Å for those between the Mo_3 triangles.

The Se atoms bridge either one or two Mo triangular faces of the clusters. Moreover, the Se1 and Se2 atoms are linked to an Mo atom of a neighbouring cluster. The Mo—Se bond distances range from 2.5514 (7) to 2.6581 (6) Å within the $Mo_6Se^i_8Se^a_6$ unit and from 2.5205 (7) to 2.7004 (7) Å within the $Mo_9Se^i_{11}Se^a_6$ unit. Each $Mo_9Se^i_{11}Se^a_6$ cluster is interconnected to six $Mo_6Se^i_8Se^a_6$ clusters (and *vice versa*) *via* Mo2—Se1 bonds (respectively, Mo1—Se2), to form the three-dimensional Mo–Se framework, the connective formula of which is $Mo_9Se^i_5Se^{i-a}_{6/2}Se^{a-i}_{6/2}$, $Mo_6Se^i_2Se^{i-a}_{6/2}Se^{a-i}_{6/2}$. The result of this arrangement is that the shortest intercluster Mo1···Mo2 distance between the Mo_6 and Mo_9 units is 3.5125 (8) Å, indicating only weak metal–metal interaction.

The K^+ cations reside in the cavities of this arrangement and are seven-coordinated by Se atoms. As in $In_{2.9}Mo_{15}Se_{19}$, the In^{3+} positions are partially occupied. The distorted octahedral coordination of these atoms is accomplished by Se atoms of two $Mo_6Se^i_8Se^a_6$ and three $Mo_9Se^i_{11}Se^a_6$ units.

Experimental

Single crystals of $In_{0.87}K_2Mo_{15}Se_{19}$ were synthesized from $In_{2.9}Mo_{15}Se_{19}$ by cationic exchange reaction of K^+ for In^+. Crystals of $In_{2.9}Mo_{15}Se_{19}$ were mixed with an excess of KCl and placed at one end of a silica ampoule, which was then sealed under vacuum. The ampoule was placed in a furnace with about 3 cm of the empty end protruding out of the furnace; this end of the ampoule was thus at about room temperature. The furnace was then heated at 1073 K for 96 h. After this time, black crystals of the title compound were obtained at the hot part of the ampoule, and crystals of InCl at the cooler part.

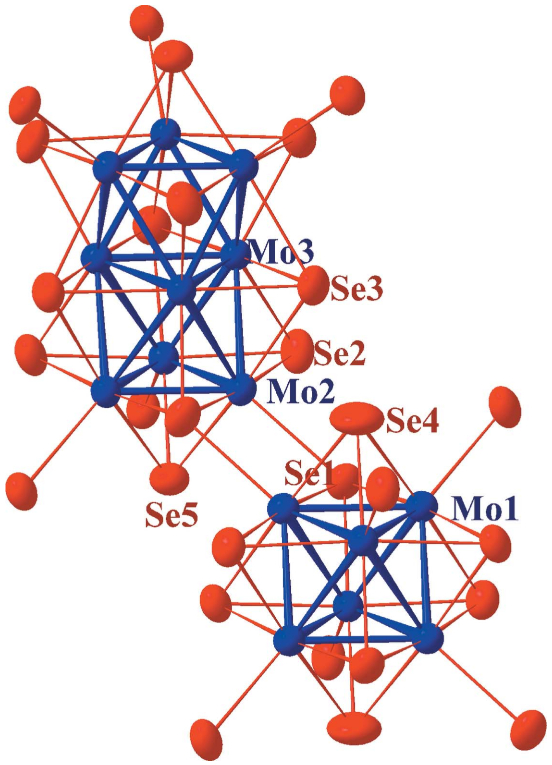

Figure 2
A view showing the atom-numbering scheme and the inter-unit linkage of the $Mo_9Se_{11}Se_6$ and $Mo_6Se_8Se_6$ clusters. Displacement ellipsoids are drawn at the 97% probability level.

Crystal data

$In_{0.875}K_2Mo_{15}Se_{19}$
$M_r = 3118$
Hexagonal, $P6_3/m$
$a = 9.80760$ (10) Å
$c = 19.6036$ (3) Å
$V = 1633.02$ (3) Å^3
$Z = 2$
$D_x = 6.339$ (1) Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 27.57$ mm^{-1}
$T = 293$ K
Irregular block, black
0.10 × 0.09 × 0.06 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: analytical (de Meulenaer & Tompa, 1965)
$T_{min} = 0.174$, $T_{max} = 0.390$
34604 measured reflections
3409 independent reflections
2628 reflections with $I > 2\sigma(I)$
$R_{int} = 0.088$
$\theta_{max} = 39.8°$

Refinement

Refinement on F
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.040$
$S = 1.15$
2628 reflections
67 parameters
$w = 1/[\sigma^2(F) + 0.0004F^2]$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 2.12$ e Å^{-3}
$\Delta\rho_{min} = -1.37$ e Å^{-3}
Extinction correction: B-C type 1 Gaussian isotropic (Becker & Coppens, 1974)
Extinction coefficient: 0.035 (6)

Acta Cryst. (2007). E**63**, i8–i10 Salloum *et al.* • $In_{0.875}K_2Mo_{15}Se_{19}$ **i9**

Table 1
Selected bond lengths (Å).

Mo1—Mo1^{i}	2.6916 (6)	Mo3—Mo3^{vi}	2.7238 (8)
Mo1—Mo1^{ii}	2.7091 (7)	Mo3—Mo3^{v}	2.7238 (8)
Mo1—Se1	2.5832 (9)	Mo3—Se2	2.5851 (5)
Mo1—Se1^{i}	2.6160 (10)	Mo3—Se2^{vii}	2.5851 (5)
Mo1—Se1^{iii}	2.5560 (6)	Mo3—Se3	2.5961 (13)
Mo1—Se2^{iv}	2.6581 (6)	Mo3—Se3^{vi}	2.5923 (16)
Mo1—Se4	2.5514 (7)	K—Se1^{viii}	3.5652 (10)
Mo2—Mo2^{v}	2.6417 (8)	K—Se2^{viii}	3.2069 (6)
Mo2—Mo3	2.7746 (6)	K—Se5	3.212 (2)
Mo2—Mo3^{v}	2.7132 (5)	In—Se2^{ix}	2.8373 (10)
Mo2—Se1	2.6874 (8)	In—Se2^{iv}	2.8373 (10)
Mo2—Se2	2.5877 (6)	In—Se3	2.759 (3)
Mo2—Se2^{v}	2.6051 (6)	In—Se3^{i}	2.984 (3)
Mo2—Se3	2.7004 (7)	In—Se4	2.5703 (12)
Mo2—Se5	2.5205 (7)	In—Se4^{x}	2.5703 (12)

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

The site-occupation factor for the In atom was refined freely [0.291 (3)[. The highest peak and the deepest hole in the final Fourier map are at 0.42 and 0.62 Å from Mo2, 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: *JANA2000* (Petříček & Dušek, 2000); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *JANA2000*.

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

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i10 Salloum *et al.* • $In_{0.875}K_2Mo_{15}Se_{19}$ *Acta Cryst.* (2007). E**63**, i8–i10