

An ordered polymorph of copper trismarium
hexaselenide, CuSm_3Se_6

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Key indicators

Single-crystal X-ray study
 $T = 153 \text{ K}$
Mean $\sigma(\text{Se}-\text{Se}) = 0.002 \text{ \AA}$
 R factor = 0.039
 wR factor = 0.103
Data-to-parameter ratio = 24.8For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

An ordered polymorph of CuSm_3Se_6 crystallizes in the monoclinic space group $P2_1/m$. The structure, which contains both monoselenide (Se^{2-}) and diselenide (Se_2^{2-}) units, comprises a three-dimensional network built from SmSe_8 polyhedra and distorted CuSe_4 tetrahedra.

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Comment

The CuSm_3Se_6 polymorph reported here crystallizes in the monoclinic space group $P2_1/m$ in a cell of dimensions $a = 7.1357(10) \text{ \AA}$, $b = 16.986(3) \text{ \AA}$, $c = 7.8957(12) \text{ \AA}$, $\beta = 90.585(2)^\circ$ and $V = 957.0(2) \text{ \AA}^3$ at 153 K. The cell lengths are remarkably close to those previously reported (Strobel & Schleid, 2003) for orthorhombic CuSm_3Se_6 [$a = 7.0953(6) \text{ \AA}$, $b = 7.8391(7) \text{ \AA}$, $c = 16.8998(9) \text{ \AA}$ and $V = 939.98(13) \text{ \AA}^3$, presumably determined at 298 K]. The present structure is ordered; the latter structure, which crystallizes in the orthorhombic space group $Pbcm$, has Cu disordered over two sites. Otherwise, the metrical details of the two structures are similar. Differences in synthetic routes, rather than the temperature of data collection, are probably the reason for the difference in the crystallographic symmetry of the two structures.

Views of the monoclinic structure and asymmetric unit are given in Figs. 1 and 2, respectively. The structure contains diselenide Se_2^{2-} units, with Se–Se distances of 2.479(2) and 2.494(2) \AA . Consequently, the formula of the compound may be written as $\text{CuSm}_3\text{Se}_4[\text{Se}_2]$ and charge balance is achieved with Cu^+ and Sm^{3+} . Each of the four independent Sm atoms is formally eight-coordinate, with Sm–Se distances ranging

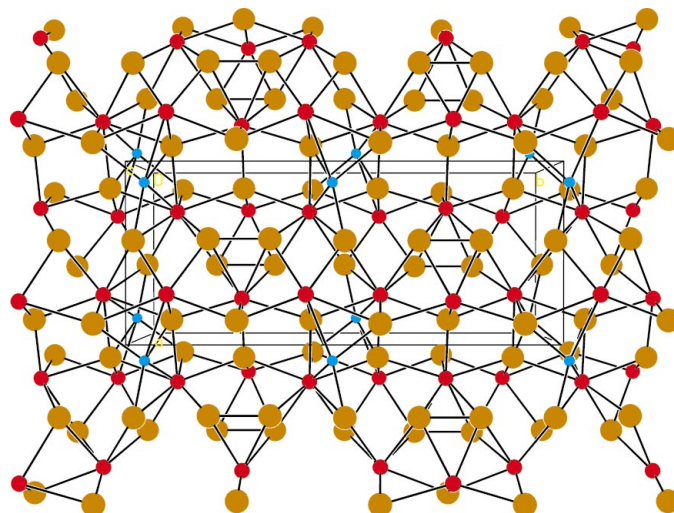
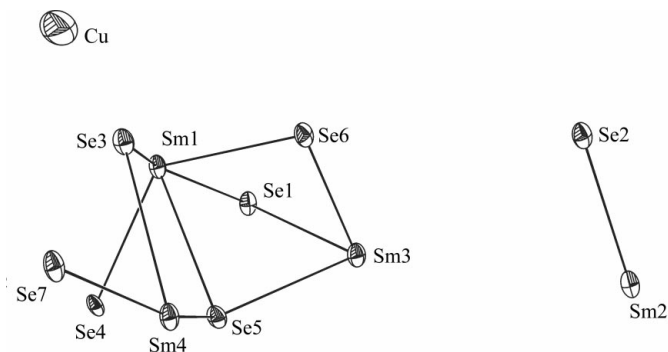


Figure 1

The structure of CuSm_3Se_6 , viewed down $[001]$. The smallest circles are Cu, the intermediate circles are Sm, and the largest circles are Se atoms.


Figure 2

The view of the asymmetric unit of CuSm_3Se_6 , with displacement ellipsoids drawn at the 90% probability level.

from 2.8381 (16) to 3.1536 (11) Å. The coordination about atoms Sm1 and Sm2 can be described somewhat subjectively as square antiprismatic and bicapped trigonal prismatic, respectively. The coordination about atoms Sm3 and Sm4, each of which lies on a mirror plane, can be considered octahedral if the diselenide units are replaced by their centers. The Cu atom is pseudo-tetrahedrally coordinated by four Se atoms, with Cu–Se distances ranging from 2.384 (2) to 2.608 (2) Å.

Experimental

Dark red square needles of CuSm_3Se_6 were obtained from a solid-state reaction of 100 mg Sm (Alfa, 99.9%), 100 mg Cu (Aldrich, 99.999%), and 100 mg of Se (Aldrich, 99.5%). The reactants were loaded into a fused-silica tube under an argon atmosphere in a glove-box. The tube was sealed under a 10^{-4} Torr atmosphere and then placed in a computer-controlled furnace. The sample was heated to 923 K over 48 h, kept at 923 K for 3 d, and then cooled at 70 K h^{-1} to room temperature. The tube was opened under argon, the contents were ground, about 300 mg of KBr were added, and the mixture was resealed in a second tube that was then evacuated. This tube was heated to 1173 K over a period of 30 h, kept at 1173 K for 42 h, then cooled to 963 K over a period of 99 h and then cooled to room temperature over a period of 6.5 h.

Crystal data

CuSm_3Se_6	$D_x = 6.860 \text{ Mg m}^{-3}$
$M_r = 988.35$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/m$	Cell parameters from 4189 reflections
$a = 7.1357 (10) \text{ \AA}$	$\theta = 2.6\text{--}29.0^\circ$
$b = 16.986 (3) \text{ \AA}$	$\mu = 43.07 \text{ mm}^{-1}$
$c = 7.8957 (12) \text{ \AA}$	$T = 153 (2) \text{ K}$
$\beta = 90.585 (2)^\circ$	Needle, red
$V = 957.0 (2) \text{ \AA}^3$	$0.24 \times 0.05 \times 0.04 \text{ mm}$
$Z = 4$	

Data collection

Bruker SMART 1000 CCD diffractometer	2435 independent reflections
ω scans	1976 reflections with $I > 2\sigma(I)$
Absorption correction: numerical face indexed (<i>SHELXTL</i>)	$R_{\text{int}} = 0.048$
$T_{\text{min}} = 0.029$, $T_{\text{max}} = 0.210$	$\theta_{\text{max}} = 29.0^\circ$
11410 measured reflections	$h = -9 \rightarrow 9$
	$k = -22 \rightarrow 23$
	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.103$
 $S = 1.05$
 2435 reflections
 98 parameters

$$w = 1/[\sigma^2(F_o^2) + (0.04P)^2 + 34P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.002$
 $\Delta\rho_{\text{max}} = 5.31 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -3.74 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXTL*
 Extinction coefficient: 0.00117 (8)

Table 1

Selected bond distances (Å).

Sm1–Se1	2.9400 (12)	Sm3–Se1 ⁱⁱ	2.9969 (10)
Sm1–Se2 ⁱ	2.9606 (12)	Sm3–Se3 ^{ix}	3.0563 (12)
Sm1–Se6	2.9611 (8)	Sm3–Se3 ^x	3.0563 (12)
Sm1–Se2 ⁱⁱ	3.0512 (11)	Sm3–Se5	3.1047 (12)
Sm1–Se4	3.0643 (11)	Sm3–Se5 ⁱⁱ	3.1047 (12)
Sm1–Se3	3.0662 (11)	Sm4–Se6 ^{xi}	2.8368 (16)
Sm1–Se4 ⁱⁱⁱ	3.0909 (11)	Sm4–Se7	2.8426 (16)
Sm1–Se5	3.1062 (11)	Sm4–Se2 ^{xii}	2.9956 (10)
Sm2–Se7 ^{iv}	2.9300 (8)	Sm4–Se2 ^{iv}	2.9957 (10)
Sm2–Se2	2.9676 (12)	Sm4–Se5	3.0374 (12)
Sm2–Se1 ^v	2.9682 (12)	Sm4–Se5 ⁱⁱ	3.0374 (12)
Sm2–Se4 ⁱⁱ	3.0263 (11)	Sm4–Se3	3.1320 (12)
Sm2–Se5 ^{vi}	3.0544 (11)	Sm4–Se3 ⁱⁱ	3.1320 (12)
Sm2–Se3 ^{vii}	3.0667 (11)	Cu–Se2 ⁱ	2.3840 (18)
Sm2–Se4 ^{viii}	3.0920 (11)	Cu–Se4 ⁱⁱⁱ	2.4063 (18)
Sm2–Se1 ⁱⁱ	3.1536 (11)	Cu–Se1 ^{xiii}	2.516 (2)
Sm3–Se7 ^{viii}	2.8381 (16)	Cu–Se1 ^{xiv}	2.608 (2)
Sm3–Se6	2.8461 (16)	Se3–Se3 ⁱⁱ	2.479 (2)
Sm3–Se1	2.9968 (10)	Se5–Se5 ⁱⁱ	2.494 (2)

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

The symmetry of the diffraction pattern is monoclinic, not orthorhombic. The highest residual electron density of 5.3 e \AA^{-3} is 1.17 \AA from the Cu site; the second highest residual electron density of 3.1 e \AA^{-3} is 0.95 \AA from this same site. The deepest hole of -3.7 e \AA^{-3} is 0.64 \AA from the Cu site. The Cu atom displays a moderately large value of U^{22} of $0.0418 (10) \text{ \AA}^2$. Clearly, there is some disorder around the Cu site. However, the height of the Cu peak itself is 60.1 e \AA^{-3} . Therefore, any disorder of the Cu-atom position is slight.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2003); program(s) used to refine structure: *SHELXTL*; molecular graphics: *XP* in *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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