

Cs₃Sm₇Se₁₂

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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{Sm}-\text{Se}) = 0.001$ Å; disorder in main residue; R factor = 0.035; wR factor = 0.072; data-to-parameter ratio = 29.7.

The title compound, tricaesium heptasamarium(III) dodecateselenide, is setting a new starting point for realization of the channel structure of the Cs₃M₇Se₁₂ series, now with $M = \text{Sm}, \text{Gd}-\text{Er}$. This Cs₃Y₇Se₁₂-type arrangement is structurally based on the Z-type sesquiselenides M₂Se₃ adopting the Sc₂S₃ structure. Thus, the structural set-up of Cs₃Sm₇Se₁₂ consists of edge- and vertex-connected [SmSe₆]⁹⁻ octahedra [$d_{\text{O}}(\text{Sm}^{3+} - \text{Se}^{2-}) = 2.931$ Å], forming a rock-salt-related network [Sm₇Se₁₂]³⁻ with channels along [001] that are apt to take up monovalent cations (here Cs⁺) with coordination numbers of 7 + 1 for one and of 6 for the second cation. The latter cation has a trigonal-prismatic coordination and shows half-occupancy, resulting in an impossible short distance [2.394 (4) Å] between symmetrically coupled Cs⁺ cations of the same kind. While one Sm atom occupies *Wyckoff* position 2*b* with site symmetry $\cdot 2/m$, all other 11 crystallographically different atoms (namely 2 × Cs, 3 × Sm and 6 × Se) are located at *Wyckoff* positions 4*g* with site symmetry $\cdot m$.

Related literature

For prototypic Cs₃Y₇Se₁₂ or Rb₃Yb₇Se₁₂, see: Folchnandt & Schleid (1996); Kim *et al.* (1996). For other representatives of the A₃M₇Ch₁₂ series, see: Folchnandt & Schleid (1997, 1998, 2000); Tougaït *et al.* (2001); Lissner *et al.* (2002). A detailed description of the relation between the crystal structures of the Cs₃M₇Se₁₂ series and Z-type Sc₂Ch₃ (Dismukes & White, 1964) is provided by Folchnandt & Schleid (1998).

Experimental

Crystal data

Cs₃Sm₇Se₁₂
 $M_r = 2398.70$

Orthorhombic, *Pnmm*
 $a = 13.0387$ (9) Å

$b = 26.6742$ (19) Å
 $c = 4.2351$ (3) Å
 $V = 1472.95$ (18) Å³
 $Z = 2$

Mo $K\alpha$ radiation
 $\mu = 32.19$ mm⁻¹
 $T = 293$ K
 $0.10 \times 0.07 \times 0.05$ mm

Data collection

Stoe IPDS-I diffractometer
Absorption correction: numerical
(*X-SHAPE*; Stoe & Cie, 1999)
 $T_{\text{min}} = 0.115$, $T_{\text{max}} = 0.216$

15080 measured reflections
2135 independent reflections
1587 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.065$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.072$
 $S = 0.97$
2135 reflections

72 parameters
 $\Delta\rho_{\text{max}} = 2.09$ e Å⁻³
 $\Delta\rho_{\text{min}} = -1.78$ e Å⁻³

Table 1
Selected bond lengths (Å).

Cs1—Se4 ⁱ	3.6071 (12)	Cs1—Se1	4.5421 (14)
Cs1—Se4 ⁱⁱ	3.6071 (12)	Cs2—Se2 ⁱⁱ	3.5286 (16)
Cs1—Se6 ⁱⁱ	3.7129 (12)	Cs2—Se2 ⁱ	3.5286 (16)
Cs1—Se6 ⁱ	3.7129 (12)	Cs2—Se2 ^v	3.6917 (17)
Cs1—Se3 ⁱⁱⁱ	3.7639 (14)	Cs2—Se2 ^{vi}	3.6917 (17)
Cs1—Se5 ⁱ	3.8053 (12)	Cs2—Se5 ⁱⁱⁱ	3.719 (2)
Cs1—Se5 ⁱⁱ	3.8053 (12)	Cs2—Se6 ⁱⁱⁱ	3.924 (2)

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

Data collection: *DIF4* (Stoe & Cie, 1992); cell refinement: *DIF4*; data reduction: *REDU4* (Stoe & Cie, 1992); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2561).

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supplementary materials

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Cs₃Sm₇Se₁₂

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Comment

Cs₃Sm₇Se₁₂ crystallizes isotypically to the large family of ternary $A_3M_7Ch_{12}$ representatives with a channel-like structure. For $Ch = S$, $A = K, Rb$, $M = Er$, see: Lissner *et al.* (2002); for $Ch = Se$, $A = Rb$, $M = Dy, Yb$, see: Folchnandt & Schleid (2000), Kim *et al.* (1996); for $Ch = Se$, $A = Cs$, $M = Y, Gd - Er$, see: Folchnandt & Schleid (1996, 1997, 1998); for $Ch = Te$, $A = Cs$, $M = Sm, Gd, Tb$, see: Tougaït *et al.* (2001).

In the title compound, [SmSe₆]⁹⁻ octahedra ($d(\text{Sm}^{3+}-\text{Se}^{2-}) = 2.8578(9)-3.0614(13) \text{ \AA}$) are connected via edges and corners to form a [Sm₇Se₁₂]³⁻ network with triple-channels occupied by Cs⁺ cations (Fig. 1). This network represents a defect rock-salt-type structure strongly related to that of the *Z*-type sesquiselenides $M_2\text{Se}_3$ (Dismukes & White, 1964) according to the formula $[\square]_4[M]_8[\text{Se}]_{12}$. In tricaesium heptasamarium(III) dodecaselenide three Cs⁺ cations replace one Sm³⁺ for charge balance. The triple-channels are arranged in a herringbone pattern and run through the structure parallel to [001]. They are filled with two crystallographically different Cs⁺ cations (Fig. 2). While Cs1⁺ exhibits a coordination number of 7+1 with an extra secondary contact ($d(\text{Cs}1^+-\text{Se}^{2-}) = 3.6071(12)-3.8053(12) \text{ \AA}$ and $4.5421(14) \text{ \AA}$; Fig. 2, *left*), the Cs2⁺ cations have only six selenide anions as nearest neighbours in the shape of a trigonal prism ($d(\text{Cs}2^+-\text{Se}^{2-}) = 3.5286(16) - 3.924(2) \text{ \AA}$; Fig. 2, *right*). Owing to the very close distances between these Cs2⁺ cations ($d(\text{Cs}2^+\cdots\text{Cs}2^+) = 2.394(4) \text{ \AA}$) only a half-occupation of this position is possible (Fig. 2, *right* and Fig. 3) and stoichiometrically meaningful.

Experimental

Yellow, transparent, needle-shaped single crystals of Cs₃Sm₇Se₁₂ were obtained as the main product of a reaction between 0.10 g Sm, 0.08 g Se and 0.50 g CsCl added as flux and caesium source upon heating at 1073 K for 10 days in a sealed, evacuated fused-silica vessel.

Refinement

In the final difference Fourier map the highest peak is 1.24 Å away from Se2 and the deepest hole is located 0.83 Å away from Sm2.

Figures

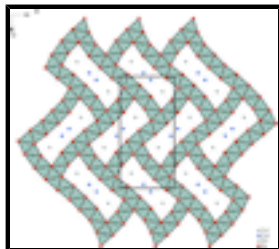


Fig. 1. Channel-structure representation of $\text{Cs}_3\text{Sm}_7\text{Se}_{12}$ as octahedral framework with indicated unit cell.

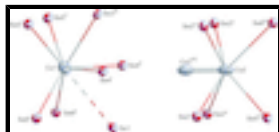


Fig. 2. Coordination spheres of the $\text{Cs}1^+$ (left) and $\text{Cs}2^+$ (right) cations in $\text{Cs}_3\text{Sm}_7\text{Se}_{12}$. Displacement ellipsoids are drawn at the 90% probability level. Symmetry codes: (i) $-x+1/2, y-1/2, z+1/2$; (ii) $-x+1/2, y-1/2, z-1/2$; (iii) $-x+1, -y+1, -z$; (viii) $-x+1, -y, -z$; (ix) $x+1/2, -y+1/2, -z-1/2$; (x) $x+1/2, -y+1/2, -z+1/2$.

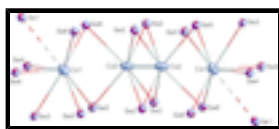


Fig. 3. Interplay of the Cs^+ cations situated in the triple-channels of the crystal structure of $\text{Cs}_3\text{Sm}_7\text{Se}_{12}$. Displacement ellipsoids are drawn at the 90% probability level.

tricaesium heptasamarium(III) dodecaselenide

Crystal data

$\text{Cs}_3\text{Sm}_7\text{Se}_{12}$

$M_r = 2398.70$

Orthorhombic, $Pnmm$

Hall symbol: $-P\ 2\ 2n$

$a = 13.0387\ (9)\ \text{\AA}$

$b = 26.6742\ (19)\ \text{\AA}$

$c = 4.2351\ (3)\ \text{\AA}$

$V = 1472.95\ (18)\ \text{\AA}^3$

$Z = 2$

$F(000) = 2014$

$D_x = 5.408\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71069\ \text{\AA}$

Cell parameters from 5000 reflections

$\theta = 2.1\text{--}29.3^\circ$

$\mu = 32.19\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Needle, yellow

$0.10 \times 0.07 \times 0.05\ \text{mm}$

Data collection

Stoe IPDS-I
diffractometer

Radiation source: fine-focus sealed tube
graphite

imaging plate detector system scans

Absorption correction: numerical
($X\text{-SHAPE}$; Stoe & Cie, 1999)

$T_{\min} = 0.115, T_{\max} = 0.216$

15080 measured reflections

2135 independent reflections

1587 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.065$

$\theta_{\max} = 29.0^\circ, \theta_{\min} = 2.8^\circ$

$h = -17 \rightarrow 17$

$k = -36 \rightarrow 36$

$l = -5 \rightarrow 5$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.035$	$w = 1/[\sigma^2(F_o^2) + (0.0371P)^2]$
$wR(F^2) = 0.072$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.97$	$(\Delta/\sigma)_{\max} = 0.014$
2135 reflections	$\Delta\rho_{\max} = 2.09 \text{ e } \text{\AA}^{-3}$
72 parameters	$\Delta\rho_{\min} = -1.78 \text{ e } \text{\AA}^{-3}$
0 restraints	Extinction correction: <i>SHELXL97</i> (Sheldrick, 2008), $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
	Extinction coefficient: 0.00017 (4)

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2 , conventional R-factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Cs1	0.28796 (6)	0.36600 (3)	0.0000	0.0252 (2)	
Cs2	0.56532 (14)	0.03154 (7)	0.0000	0.0311 (5)	0.50
Sm1	0.0000	0.0000	0.5000	0.0124 (2)	
Sm2	0.21848 (5)	0.08314 (2)	0.0000	0.01316 (15)	
Sm3	0.40590 (4)	0.71214 (2)	0.0000	0.01224 (15)	
Sm4	0.07792 (5)	0.68240 (2)	0.0000	0.01271 (15)	
Se1	0.25592 (8)	0.19644 (4)	0.0000	0.0125 (3)	
Se2	0.12980 (9)	0.57736 (4)	0.0000	0.0142 (3)	
Se3	0.43019 (9)	0.60350 (4)	0.0000	0.0129 (3)	
Se4	0.05307 (8)	0.78890 (4)	0.0000	0.0133 (3)	
Se5	0.15051 (9)	0.98065 (4)	0.0000	0.0142 (3)	
Se6	0.42742 (9)	0.82140 (4)	0.0000	0.0133 (3)	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cs1	0.0214 (4)	0.0295 (4)	0.0247 (6)	-0.0002 (3)	0.000	0.000
Cs2	0.0266 (9)	0.0273 (9)	0.0393 (14)	0.0114 (7)	0.000	0.000

supplementary materials

Sm1	0.0147 (4)	0.0109 (4)	0.0116 (6)	-0.0030 (3)	0.000	0.000
Sm2	0.0153 (3)	0.0135 (3)	0.0107 (4)	-0.0027 (2)	0.000	0.000
Sm3	0.0137 (3)	0.0117 (3)	0.0113 (4)	-0.0018 (2)	0.000	0.000
Sm4	0.0131 (3)	0.0130 (3)	0.0121 (4)	0.0034 (2)	0.000	0.000
Se1	0.0123 (5)	0.0153 (5)	0.0101 (7)	-0.0004 (4)	0.000	0.000
Se2	0.0147 (6)	0.0142 (5)	0.0137 (8)	0.0007 (4)	0.000	0.000
Se3	0.0154 (5)	0.0096 (5)	0.0138 (7)	0.0007 (4)	0.000	0.000
Se4	0.0144 (5)	0.0128 (5)	0.0126 (8)	0.0000 (4)	0.000	0.000
Se5	0.0155 (5)	0.0129 (5)	0.0141 (8)	-0.0004 (4)	0.000	0.000
Se6	0.0140 (5)	0.0134 (5)	0.0124 (8)	0.0008 (4)	0.000	0.000

Geometric parameters (Å, °)

Cs1—Se4 ⁱ	3.6071 (12)	Sm1—Se5 ^{xi}	2.9328 (8)
Cs1—Se4 ⁱⁱ	3.6071 (12)	Sm1—Se5 ^{xii}	2.9328 (8)
Cs1—Se6 ⁱⁱ	3.7129 (12)	Sm1—Se5 ^{xiii}	2.9328 (8)
Cs1—Se6 ⁱ	3.7129 (12)	Sm2—Se5 ^{xiii}	2.8738 (13)
Cs1—Se3 ⁱⁱⁱ	3.7639 (14)	Sm2—Se2 ⁱ	2.9020 (10)
Cs1—Se5 ⁱ	3.8053 (12)	Sm2—Se2 ⁱⁱ	2.9020 (10)
Cs1—Se5 ⁱⁱ	3.8053 (12)	Sm2—Se3 ⁱⁱ	2.9217 (9)
Cs1—Se1	4.5421 (14)	Sm2—Se3 ⁱ	2.9217 (9)
Cs1—Cs1 ^{iv}	4.2351 (3)	Sm2—Se1	3.0614 (13)
Cs1—Cs1 ^v	4.2351 (3)	Sm3—Se4 ^{xiv}	2.8578 (9)
Cs2—Cs2 ^{vi}	2.394 (4)	Sm3—Se4 ^{xv}	2.8578 (9)
Cs2—Se2 ⁱⁱ	3.5286 (16)	Sm3—Se3	2.9152 (13)
Cs2—Se2 ⁱ	3.5286 (16)	Sm3—Se6	2.9279 (13)
Cs2—Se2 ^{vii}	3.6917 (17)	Sm3—Se1 ^{xvi}	3.0185 (9)
Cs2—Se2 ^{viii}	3.6917 (17)	Sm3—Se1 ^{xvii}	3.0185 (9)
Cs2—Se5 ⁱⁱⁱ	3.719 (2)	Sm4—Se4	2.8591 (13)
Cs2—Se6 ⁱⁱⁱ	3.924 (2)	Sm4—Se2	2.8823 (13)
Cs2—Sm2 ^{vi}	4.1597 (18)	Sm4—Se6 ^{xviii}	2.8888 (9)
Sm1—Se3 ⁱ	2.9070 (11)	Sm4—Se6 ^{xix}	2.8888 (9)
Sm1—Se3 ^{ix}	2.9070 (11)	Sm4—Se1 ^{xvii}	3.0526 (9)
Sm1—Se5 ^x	2.9328 (8)	Sm4—Se1 ^{xvi}	3.0526 (9)
Se4 ⁱ —Cs1—Se4 ⁱⁱ	71.90 (3)	Se2 ⁱⁱ —Sm2—Se1	86.77 (3)
Se4 ⁱ —Cs1—Se6 ⁱⁱ	125.93 (3)	Se3 ⁱⁱ —Sm2—Se1	85.54 (3)
Se4 ⁱⁱ —Cs1—Se6 ⁱⁱ	85.24 (2)	Se3 ⁱ —Sm2—Se1	85.54 (3)
Se4 ⁱ —Cs1—Se6 ⁱ	85.24 (2)	Se4 ^{xiv} —Sm3—Se4 ^{xv}	95.63 (4)
Se4 ⁱⁱ —Cs1—Se6 ⁱ	125.93 (3)	Se4 ^{xiv} —Sm3—Se3	85.26 (3)
Se6 ⁱⁱ —Cs1—Se6 ⁱ	69.55 (3)	Se4 ^{xv} —Sm3—Se3	85.26 (3)
Se4 ⁱ —Cs1—Se3 ⁱⁱⁱ	64.04 (3)	Se4 ^{xiv} —Sm3—Se6	86.87 (3)
Se4 ⁱⁱ —Cs1—Se3 ⁱⁱⁱ	64.04 (3)	Se4 ^{xv} —Sm3—Se6	86.87 (3)
Se6 ⁱⁱ —Cs1—Se3 ⁱⁱⁱ	143.874 (16)	Se3—Sm3—Se6	168.27 (4)

Se6 ⁱ —Cs1—Se3 ⁱⁱⁱ	143.874 (16)	Se4 ^{xiv} —Sm3—Se1 ^{xvi}	171.05 (4)
Se4 ⁱ —Cs1—Se5 ⁱ	90.60 (2)	Se4 ^{xv} —Sm3—Se1 ^{xvi}	87.03 (2)
Se4 ⁱⁱ —Cs1—Se5 ⁱ	131.59 (3)	Se3—Sm3—Se1 ^{xvi}	86.44 (3)
Se6 ⁱⁱ —Cs1—Se5 ⁱ	137.25 (3)	Se6—Sm3—Se1 ^{xvi}	101.84 (3)
Se6 ⁱ —Cs1—Se5 ⁱ	95.72 (2)	Se4 ^{xiv} —Sm3—Se1 ^{xvii}	87.03 (2)
Se3 ⁱⁱⁱ —Cs1—Se5 ⁱ	67.69 (3)	Se4 ^{xv} —Sm3—Se1 ^{xvii}	171.05 (4)
Se4 ⁱ —Cs1—Se5 ⁱⁱ	131.59 (3)	Se3—Sm3—Se1 ^{xvii}	86.44 (3)
Se4 ⁱⁱ —Cs1—Se5 ⁱⁱ	90.60 (2)	Se6—Sm3—Se1 ^{xvii}	101.84 (3)
Se6 ⁱⁱ —Cs1—Se5 ⁱⁱ	95.72 (2)	Se1 ^{xvi} —Sm3—Se1 ^{xvii}	89.10 (3)
Se6 ⁱ —Cs1—Se5 ⁱⁱ	137.25 (3)	Se4—Sm4—Se2	172.93 (4)
Se3 ⁱⁱⁱ —Cs1—Se5 ⁱⁱ	67.69 (3)	Se4—Sm4—Se6 ^{xviii}	87.59 (3)
Se5 ⁱ —Cs1—Se5 ⁱⁱ	67.63 (2)	Se2—Sm4—Se6 ^{xviii}	97.20 (3)
Se2 ⁱⁱ —Cs2—Se2 ^{vii}	95.31 (3)	Se4—Sm4—Se6 ^{xix}	87.59 (3)
Se2 ⁱ —Cs2—Se2 ^{vii}	141.35 (6)	Se2—Sm4—Se6 ^{xix}	97.20 (3)
Se2 ⁱⁱ —Cs2—Se2 ^{viii}	141.35 (6)	Se6 ^{xviii} —Sm4—Se6 ^{xix}	94.28 (4)
Se2 ⁱ —Cs2—Se2 ^{viii}	95.31 (3)	Se4—Sm4—Se1 ^{xvii}	87.63 (3)
Se2 ^{vii} —Cs2—Se2 ^{viii}	70.00 (4)	Se2—Sm4—Se1 ^{xvii}	87.29 (3)
Se2 ⁱⁱ —Cs2—Se5 ⁱⁱⁱ	138.46 (3)	Se6 ^{xviii} —Sm4—Se1 ^{xvii}	174.23 (4)
Se2 ⁱ —Cs2—Se5 ⁱⁱⁱ	138.46 (3)	Se6 ^{xix} —Sm4—Se1 ^{xvii}	88.74 (2)
Se2 ^{vii} —Cs2—Se5 ⁱⁱⁱ	72.81 (4)	Se4—Sm4—Se1 ^{xvi}	87.63 (3)
Se2 ^{viii} —Cs2—Se5 ⁱⁱⁱ	72.81 (4)	Se2—Sm4—Se1 ^{xvi}	87.29 (3)
Se2 ⁱⁱ —Cs2—Se6 ⁱⁱⁱ	70.80 (4)	Se6 ^{xviii} —Sm4—Se1 ^{xvi}	88.74 (2)
Se2 ⁱ —Cs2—Se6 ⁱⁱⁱ	70.80 (4)	Se6 ^{xix} —Sm4—Se1 ^{xvi}	174.23 (4)
Se2 ^{vii} —Cs2—Se6 ⁱⁱⁱ	141.36 (3)	Se1 ^{xvii} —Sm4—Se1 ^{xvi}	87.85 (3)
Se2 ^{viii} —Cs2—Se6 ⁱⁱⁱ	141.36 (3)	Sm3 ⁱⁱ —Se1—Sm3 ⁱ	89.10 (3)
Se5 ⁱⁱⁱ —Cs2—Se6 ⁱⁱⁱ	93.63 (5)	Sm3 ⁱⁱ —Se1—Sm4 ⁱ	178.80 (4)
Se3 ⁱ —Sm1—Se3 ^{ix}	180.000 (14)	Sm3 ⁱ —Se1—Sm4 ⁱ	91.519 (12)
Se3 ⁱ —Sm1—Se5 ^x	92.43 (3)	Sm3 ⁱⁱ —Se1—Sm4 ⁱⁱ	91.519 (12)
Se3 ^{ix} —Sm1—Se5 ^x	87.57 (3)	Sm3 ⁱ —Se1—Sm4 ⁱⁱ	178.80 (4)
Se3 ⁱ —Sm1—Se5 ^{xi}	87.57 (3)	Sm4 ⁱ —Se1—Sm4 ⁱⁱ	87.85 (3)
Se3 ^{ix} —Sm1—Se5 ^{xi}	92.43 (3)	Sm3 ⁱⁱ —Se1—Sm2	91.46 (3)
Se5 ^x —Sm1—Se5 ^{xi}	180.00 (4)	Sm3 ⁱ —Se1—Sm2	91.46 (3)
Se3 ⁱ —Sm1—Se5 ^{xii}	92.43 (3)	Sm4 ⁱ —Se1—Sm2	89.55 (3)
Se3 ^{ix} —Sm1—Se5 ^{xii}	87.57 (3)	Sm4 ⁱⁱ —Se1—Sm2	89.55 (3)
Se5 ^x —Sm1—Se5 ^{xii}	92.44 (3)	Sm4—Se2—Sm2 ^{xvii}	96.22 (3)
Se5 ^{xi} —Sm1—Se5 ^{xii}	87.56 (3)	Sm4—Se2—Sm2 ^{xvi}	96.22 (3)
Se3 ⁱ —Sm1—Se5 ^{xiii}	87.57 (3)	Sm2 ^{xvii} —Se2—Sm2 ^{xvi}	93.72 (4)
Se3 ^{ix} —Sm1—Se5 ^{xiii}	92.43 (3)	Sm1 ^{viii} —Se3—Sm3	167.99 (5)
Se5 ^x —Sm1—Se5 ^{xiii}	87.56 (3)	Sm1 ^{viii} —Se3—Sm2 ^{xvi}	91.79 (3)
Se5 ^{xi} —Sm1—Se5 ^{xiii}	92.44 (3)	Sm3—Se3—Sm2 ^{xvi}	96.47 (3)
Se5 ^{xii} —Sm1—Se5 ^{xiii}	180.0	Sm1 ^{viii} —Se3—Sm2 ^{xvii}	91.79 (3)

supplementary materials

Se5 ^{xiii} —Sm2—Se2 ⁱ	99.19 (3)	Sm3—Se3—Sm2 ^{xvii}	96.47 (3)
Se5 ^{xiii} —Sm2—Se2 ⁱⁱ	99.19 (3)	Sm2 ^{xvi} —Se3—Sm2 ^{xvii}	92.90 (4)
Se2 ⁱ —Sm2—Se2 ⁱⁱ	93.72 (4)	Sm3 ^{xviii} —Se4—Sm3 ^{xix}	95.63 (4)
Se5 ^{xiii} —Sm2—Se3 ⁱⁱ	88.41 (3)	Sm3 ^{xviii} —Se4—Sm4	93.81 (3)
Se2 ⁱ —Sm2—Se3 ⁱⁱ	172.31 (4)	Sm3 ^{xix} —Se4—Sm4	93.81 (3)
Se2 ⁱⁱ —Sm2—Se3 ⁱⁱ	86.18 (2)	Sm2 ^{xx} —Se5—Sm1 ^{xxi}	92.23 (3)
Se5 ^{xiii} —Sm2—Se3 ⁱ	88.41 (3)	Sm2 ^{xx} —Se5—Sm1 ^{xx}	92.23 (3)
Se2 ⁱ —Sm2—Se3 ⁱ	86.18 (2)	Sm1 ^{xxi} —Se5—Sm1 ^{xx}	92.44 (3)
Se2 ⁱⁱ —Sm2—Se3 ⁱ	172.31 (4)	Sm4 ^{xiv} —Se6—Sm4 ^{xv}	94.28 (4)
Se3 ⁱⁱ —Sm2—Se3 ⁱ	92.90 (4)	Sm4 ^{xiv} —Se6—Sm3	91.72 (3)
Se5 ^{xiii} —Sm2—Se1	171.21 (4)	Sm4 ^{xv} —Se6—Sm3	91.72 (3)
Se2 ⁱ —Sm2—Se1	86.77 (3)		

Symmetry codes: (i) $-x+1/2, y-1/2, z+1/2$; (ii) $-x+1/2, y-1/2, z-1/2$; (iii) $-x+1, -y+1, -z$; (iv) $x, y, z-1$; (v) $x, y, z+1$; (vi) $-x+1, -y, -z$; (vii) $x+1/2, -y+1/2, -z-1/2$; (viii) $x+1/2, -y+1/2, -z+1/2$; (ix) $x-1/2, -y+1/2, -z+1/2$; (x) $-x, -y+1, -z$; (xi) $x, y-1, z+1$; (xii) $-x, -y+1, -z+1$; (xiii) $x, y-1, z$; (xiv) $x+1/2, -y+3/2, -z+1/2$; (xv) $x+1/2, -y+3/2, -z-1/2$; (xvi) $-x+1/2, y+1/2, z-1/2$; (xvii) $-x+1/2, y+1/2, z+1/2$; (xviii) $x-1/2, -y+3/2, -z-1/2$; (xix) $x-1/2, -y+3/2, -z+1/2$; (xx) $x, y+1, z$; (xxi) $x, y+1, z-1$.

Fig. 1

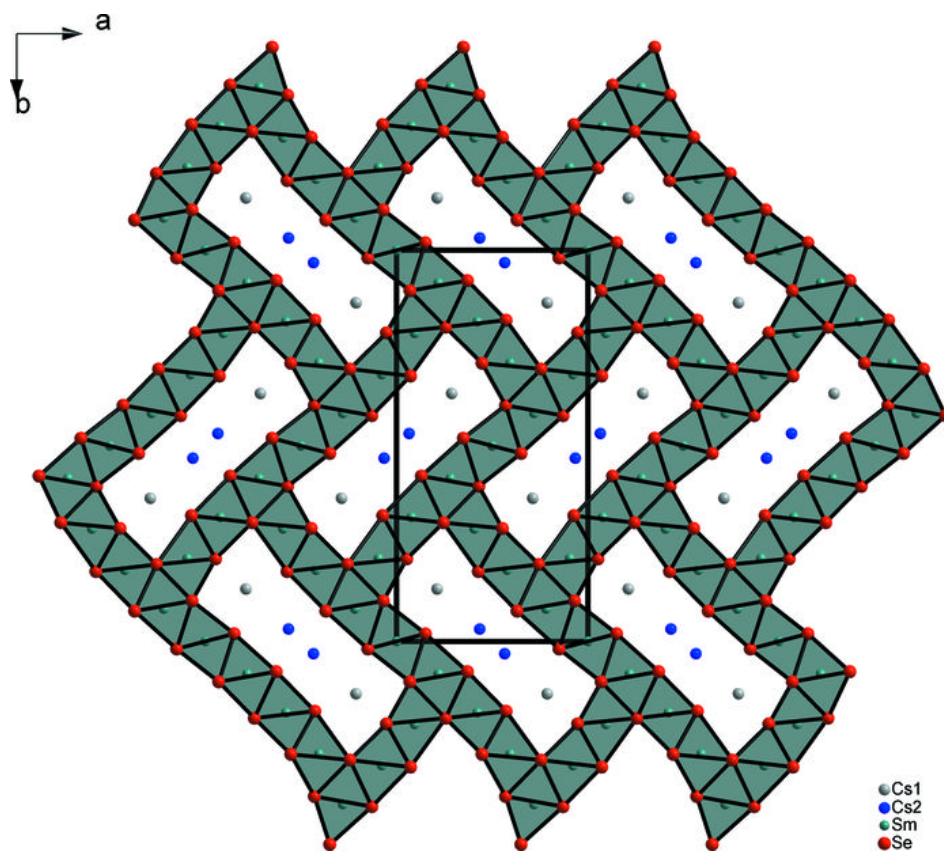


Fig. 2

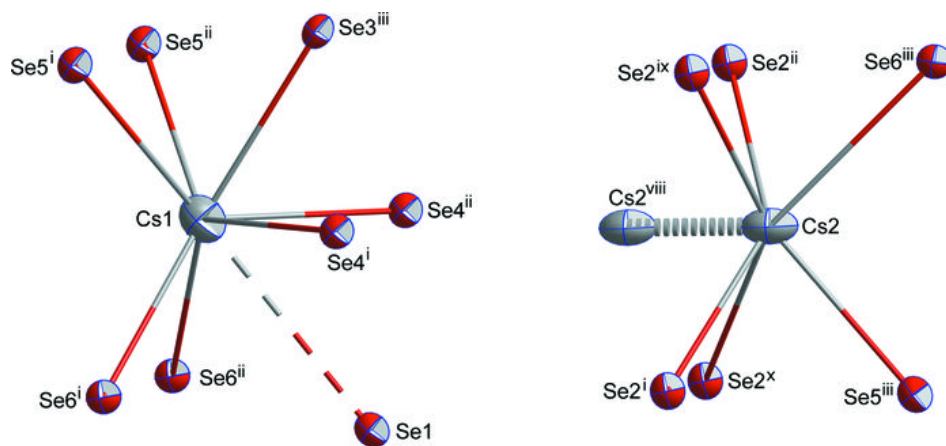


Fig. 3

