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# $CuSm_3Se_4[Se_2]$: a new ternary copper(I) rare-earth(III) selenide with mono- and diselenide units

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**Abstract**

Single crystals of $CuSm_3Se_6$ develop by reaction of the elements (Cu, Sm and Se; molar ratio: 1:3:6) after 7 days at 973 K. As the formula indicates, the crystal structure of $CuSm_3Se_4[Se_2]$ (orthorhombic, *Pbcm*; $a = 709.53(6)$, $b = 783.91(7)$, $c = 1689.98(9)$ pm, $Z = 4$) contains both mono- ($Se^{2-}$) and diselenide anions ($[Se_2]^{2-}$). The latter are surrounded by six $Sm^{3+}$ cations. If the diselenide units serve as one fragment, they form irregular $\{[Se_2]Sm_6\}^{16+}$ octahedra, which produce chains running along [010]. Together with $[SeSm_4]^{10+}$ tetrahedra they build up a two-dimensional layer parallel to (001) according to $^2_\infty\{(Sm_3Se[Se_2])^{5+}\}$. Vertex-, edge- and face-shared $[CuSe_4]^{7-}$ tetrahedra compose chains running along [010] as well. Since the distance between the two central cations of a face-shared bitetrahedron ($d$(Cu–Cu) = 115 pm) is much too short, the copper position is only half occupied. A three-dimensional network is created by stacking $^2_\infty\{(Sm_3Se[Se_2])^{5+}\}$ layers and $^1_\infty\{(CuSe_3)^{5-}\}$ chains parallel to (001).

*Keywords:* Copper; Samarium; Selenides; Diselenide units

## 1. Introduction

Many rare-earth polyselenides with different selenide arrangement are known (e.g. Refs. [1–7]). For example, the compound $KCeSe_4$ [1] contains polyselenide units as anions exclusively. There $[Se_2]^{2-}$ dumbbells build the anionic framework. The same $[Se_2]^{2-}$ dumbbells as well as monoselenide units ($Se^{2-}$) exist in $LaSe_2$ [2], $La_4O_4Se_3$ [3], $Ce_4O_4Se_3$ [4], $Pr_4O_4Se_3$ [5] and $KCuCe_2Se_6$ [6,7]. Thus in the latter, selenium occurs simultaneously in two oxidation states. With $CuSm_3Se_4[Se]_2$, it was possible to synthesize another copper(I) rare-earth(III) selenide containing $[Se_2]^{2-}$ and $Se^{2-}$ anions beneath copper(I) cations. In the following the synthesis and crystal structure of this new ternary compound is reported.

## 2. Experimental

### 2.1. Synthesis

The title compound $CuSm_3Se_6$ is formed by reaction of the elements (Cu: ChemPur, 99.9%; Sm: ChemPur, 99.9% and Se: Retorte, 99.9%) in a molar ratio of 1:3:6. To obtain single crystals a mixture of 100 mg samarium and the corresponding amounts of copper and selenium plus an additional quantity of CsI as flux are filled into silica tubes under an argon atmosphere in a glove box. They are torch-sealed under vacuum and placed in a furnace. After 7 days at 973 K an almost quantitative amount of dark red, cubic shaped single crystals is obtained. At temperatures higher than 1023 K the diselenide units are destroyed and $CuSmSe_2$ [8] results. Washing the product with water and drying it in air atmosphere yields isolated crystals.

### 2.2. Structure determination

Single-crystal X-ray diffraction data were collected on a STOE IPDS diffractometer with the use of graphite-monochromatized Mo*Kα* radiation ($\lambda = 71.07$ pm). A face-indexed absorption correction was performed numerically with the program X-SHAPE [9]. To solve the structure the direct methods program SHELXS [10] was applied. The refinement was made with help of the full-matrix least-squares program SHELXL [10]. For details see Table 1. In space group *Pbcm* the $Cu^+$ cations occupy one crystallographic site (8*e*), which

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leads to a much too short $Cu^+$–$Cu^+$ distance of 115 pm. Refining the site occupancy factor for copper as a free parameter gets it to a numerical value of 0.494(5). Thus the copper position is only half occupied. Yet a refinement in the space group $Pbc2_1$ ($\equiv Pca2_1$) provides no ordered arrangement for the $Cu^+$ cations.

Table 1
Crystal data and structure determination and refinement for $CuSm_3Se_4[Se_2]$

| | |
|---|---|
| Crystal system | Orthorhombic |
| Space group | *Pbcm* (no. 57) |
| *Z* | 4 |
| Lattice constants | |
| *a* (pm) | 709.53(6) |
| *b* (pm) | 783.91(7) |
| *c* (pm) | 1689.98(9) |
| Molar volume, $V_m$ ($cm^3\,mol^{-1}$) | 141.515 |
| Calculated density, $D_x$ ($g\,cm^{-3}$) | 6.984 |
| Diffractometer | Single crystal diffractometer IPDS (Fa. Stoe) |
| Wavelength (pm) | Mo$K\alpha$: $\lambda = 71.07$ (graphite-monochromatized) |
| Index range | $-10 \leqslant h \leqslant 10$; $-11 \leqslant k \leqslant 11$; $-23 \leqslant l \leqslant 23$ |
| $\theta$ range | $1° \leqslant \theta \leqslant 33°$ |
| *F*(000) | 1676 |
| Linear absorption coefficient, $\mu$ ($mm^{-1}$) | 43.85 |
| $R_{int}$ ($R_\sigma$) | 0.055 (0.034) |
| Collected reflections | 13071 |
| Observed reflections with $\lvert F_o \rvert \geqslant 4\sigma(F_o)$ | 1198 |
| Unique reflections | 1694 |
| Structure solution and refinement | Program package SHELX [10] |
| Scattering factors | International Tables, Vol. C [13] |
| $R_1$ ($R_1$ with $4\sigma$-barrier) | 0.056 (0.036) |
| $wR_2$ | 0.087 |
| Goodness of fit (GooF) | 0.936 |
| Extinction (g) | 0.0023(1) |
| Residual electron density $\rho(e^-)$ [$10^6\,pm^3$] | max: 3.72; min: −4.03 |

Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-412446.

Although the crystallographic site 8*e* in *Pbcm* splits into two positions ($2 \times 4a$) in space group $Pca2_1$, merely a statistic distribution for copper is found. In addition the Flack *x* parameter of 0.49(2) indicates that the higher symmetry *Pbcm* is required. However, there is no indication for a supercell. On the contrary, this structure is already a superstructure with three times the *c* axis of an observed subcell. Positional parameters in space group *Pbcm* and equivalent isotropic displacement parameters are shown in Table 2 whereas in Table 3 selected bond distances are listed.

## 3. Results and discussion

As shown in Fig. 1 the crystal structure of $CuSm_3Se_4[Se_2]$ contains diselenide units ($[Se_2]^{2-}$, $d$(Se–Se) = 248 pm). This distance corresponds fairly well with the Se–Se distances known in other polyselenide compounds with large cations, e.g. $LaSe_2$ [2], $Pr_4O_4Se_3$ [4], $Ce_4O_4Se_3$ [5], $Rb_2Se_2$ [11] ($d$(Se–Se) = 245–247 pm). The $[Se_2]^{2-}$ units are surrounded by six $Sm^{3+}$ cations. Two samarium cations (Sm1) bridge both $Se^-$ fragments of a dumbbell and two out of four (Sm2) are coordinated to only one $Se^-$ half each. Thus, if the diselenide units are considered as one entity, they form distorted $\{[Se_2]Sm_6\}^{16+}$ octahedra, which are connected via *trans*-oriented faces to produce infinite chains running

Table 3
Selected bond lengths (pm) for $CuSm_3Se_4[Se_2]$

| | | | |
|---|---|---|---|
| Cu–Se1 | 237.2 | Sm2–Se3 | 293.0 |
| Cu–Se3 | 237.9 | Sm2–Se2 | 293.2 |
| Cu–Se3′ | 254.0 | Sm2–Se3′ | 294.3 |
| Cu–Se3″ | 258.3 | Sm2–Se1 | 302.6 |
| | | Sm2–Se4 | 304.1 |
| Sm1–Se2 | 281.7 | Sm2–Se4′ | 306.6 |
| Sm1–Se2′ | 282.4 | Sm2–Se1′ | 307.2 |
| Sm1–Se3 | 298.1 (2×) | Sm2–Se3″ | 308.4 |
| Sm1–Se4 | 302.9 (2×) | | |
| Sm1–Se4′ | 310.5 (2×) | Se4–Se4 | 248.4 |

Table 2
Atomic coordinates and equivalent isotropic displacement parameters for $CuSm_3Se_4[Se_2]$

| Atom type | Wyckoff position | *x/a* | *y/b* | *z/c* | $U_{eq}$[a] ($pm^2$) |
|---|---|---|---|---|---|
| Cu[b] | 8*e* | 0.3946(4) | 0.2919(3) | 0.0279(2) | 382(11) |
| Sm1 | 4*d* | 0.26476(7) | 0.55516(6) | $\frac{1}{4}$ | 91(1) |
| Sm2 | 8*d* | 0.23484(5) | 0.94139(4) | 0.08815(2) | 97(1) |
| Se1 | 4*c* | 0.0702(1) | 1/4 | 0 | 89(2) |
| Se2 | 4*d* | 0.3767(1) | 0.9009(1) | $\frac{1}{4}$ | 96(2) |
| Se3 | 8*d* | 0.38643(9) | 0.59401(8) | 0.08210(4) | 90(2) |
| Se4 | 8*d* | 0.07565(9) | 0.24712(8) | 0.17652(4) | 96(2) |

[a] $U_{eq} = \frac{1}{3}[U_{11} + U_{22} + U_{33}]$.
[b] Site occupation probability: 0.494(5).

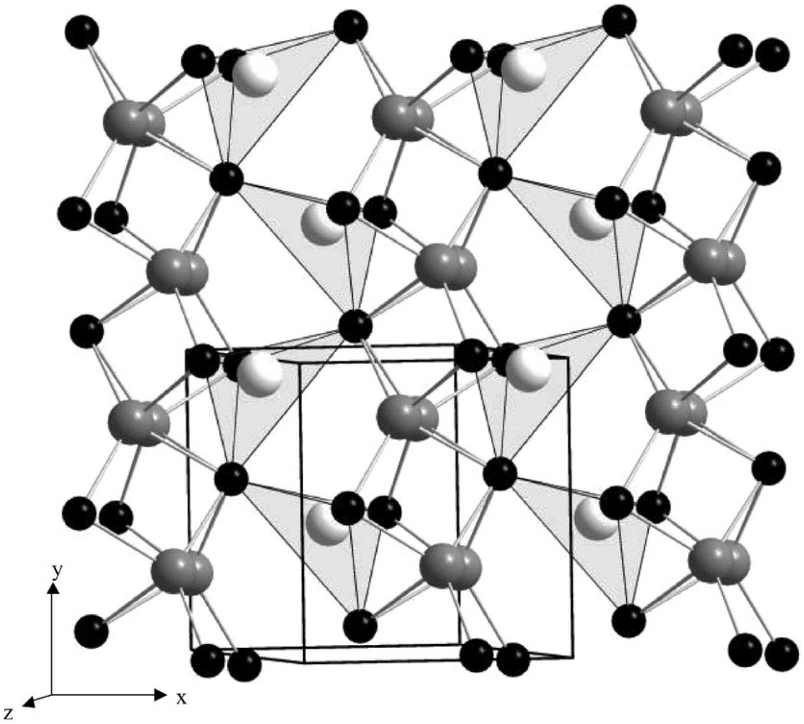

Fig. 1. $^{2}_{\infty}\{(\mathrm{Sm_3Se[Se_2]})^{5+}\}$ layer parallel to (001); $\mathrm{Sm^{3+}}$: black, $\mathrm{Se^{2-}}$: white, $[\mathrm{Se_2}]^{2-}$: gray; $\{[\mathrm{Se_2}]\mathrm{Sm_6}\}^{16+}$ octahedra are marked by bonds, whereas the $[\mathrm{SeSm_4}]^{10+}$ tetrahedra appear as closed polyhedra.

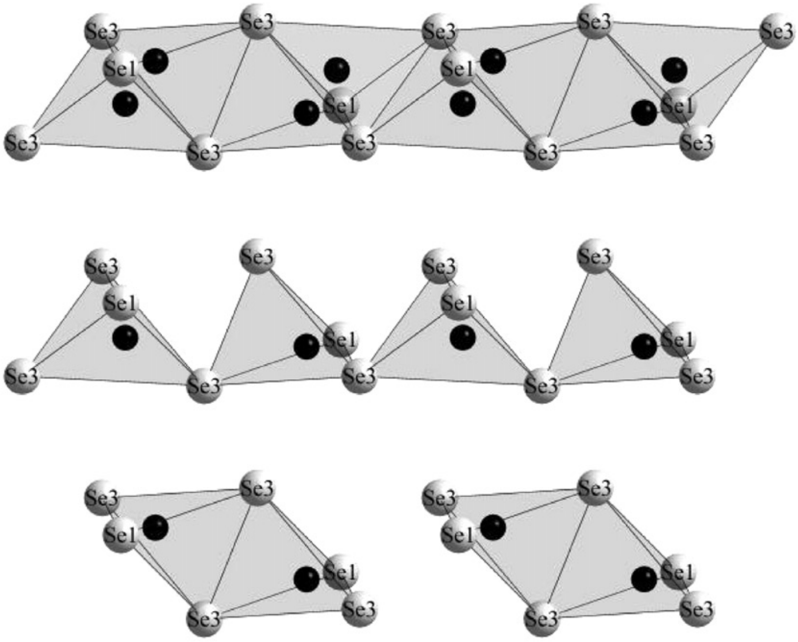

Fig. 2. $^{1}_{\infty}\{(\mathrm{CuSe_3})^{5-}\}$ chain along [010]; $\mathrm{Cu^{+}}$: black, $\mathrm{Se^{2-}}$: gray; *above*: chain of vertex-, edge- and face-shared tetrahedra, *mid*: ordering variation one: chain of vertex-shared tetrahedra, *below*: ordering variation two: discrete edge-shared bitetrahedra.

along [010]. Together with chains of vertex-linked $[\mathrm{SeSm_4}]^{10+}$ tetrahedra, which consist of $(\mathrm{Se2})^{2-}$, $(\mathrm{Sm1})^{3+}$ and $(\mathrm{Sm2})^{3+}$, they build up a two-dimensional layer parallel to (001) according to $^{2}_{\infty}\{(\mathrm{Sm_3Se[Se_2]})^{5+}\}$ (Fig. 1). The $\mathrm{Cu^{+}}$ cations are surrounded by four $\mathrm{Se^{2-}}$ anions with copper-selenium distances between 237 and 258 pm. Hence they form chains of vertex-, edge- and face-shared $[\mathrm{CuSe_4}]^{7-}$ tetrahedra running along [010] as well. Since the distance between the two central cations of a face-shared bitetrahedron is much too short ($d(\mathrm{Cu–Cu}) = 115$ pm), the copper position is only half occupied. To avoid these short $\mathrm{Cu^{+}}$–$\mathrm{Cu^{+}}$ distances two

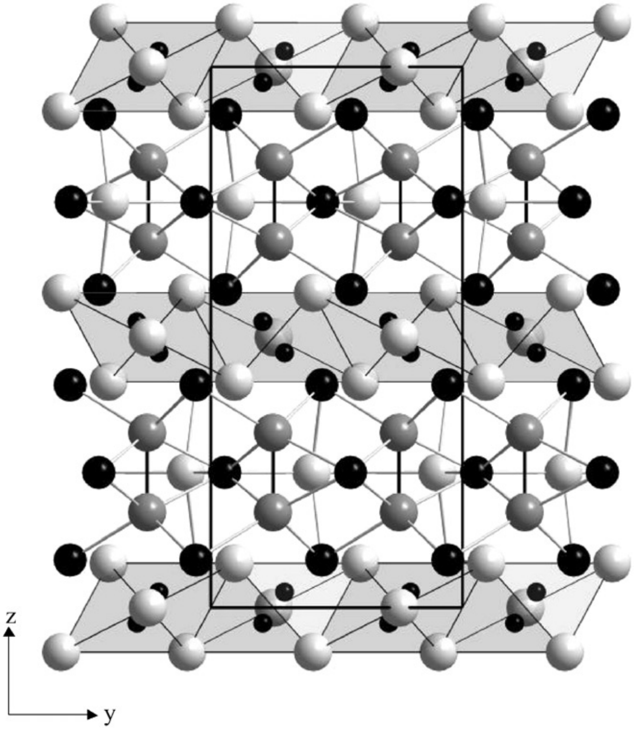

Fig. 3. Stacking of $^1_\infty\{(CuSe_3)^{5-}\}$ chains and $^2_\infty\{(Sm_3Se[Se_2])^{5+}\}$ layers parallel to (001); $Cu^+$: small black, $Sm^{3+}$: large black, $Se^{2-}$: open, $[Se_2]^{2-}$: gray spheres.

ordered configurations can be imagined, either isolated tetrahedral pairs formed by edge-sharing or a chain of vertex-shared $[CuSe_4]$ tetrahedra running along [010] (Fig. 2). However, no indication for those ordered formations is given in the X-ray diffraction data. A three-dimensional network is created by stacking $^1_\infty\{(CuSe_3)^{5-}\}$ chains and $^2_\infty\{(Sm_3Se[Se_2])^{5+}\}$ layers parallel to (001) (Fig. 3). As for the vicinity of the two crystallographically different $Sm^{3+}$ cations, it can be described as a bicapped trigonal prism for both. Sm1 and Sm2 coordinate to two $[Se_2]^{2-}$ anions each. Whereas for Sm2 only one end of a diselenide unit is coordinated, Sm1 bridges both atoms of the dumbbell (Fig. 4). The eight samarium-selenium distances range between 281 and 310 pm which are a bit shorter than the distances observed in other samarium selenides, e.g. $Sm_2Se_3$ [12] ($d$(Sm–Se) = 291–347 pm). This could be the result of the two different oxidation states of selenium. On account of the weaker Coulomb interactions between $Sm^{3+}$ and $Se^-$ the distances between $[Se_2]^{2-}$ and $(Sm1)^{3+}$ extend, whereas the distances between $(Sm1)^{3+}$ and $Se^{2-}$ reduce.

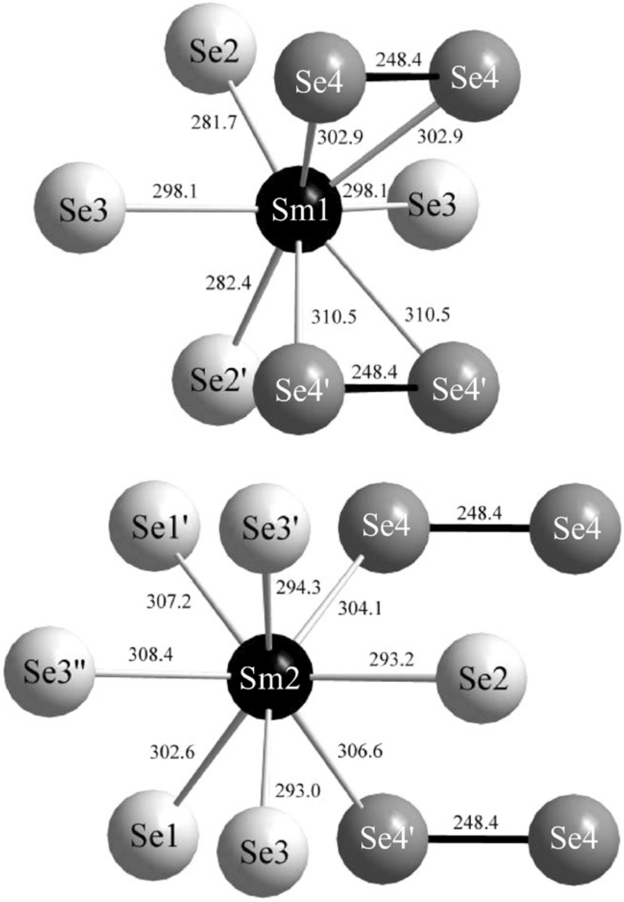

Fig. 4. Coordination spheres for the two crystallographically different $Sm^{3+}$ cations (bond lengths in pm).

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