

The crystal structure of the selenide-based synthetic sulfosalt $\text{CuPbSb}_3\text{Se}_6$

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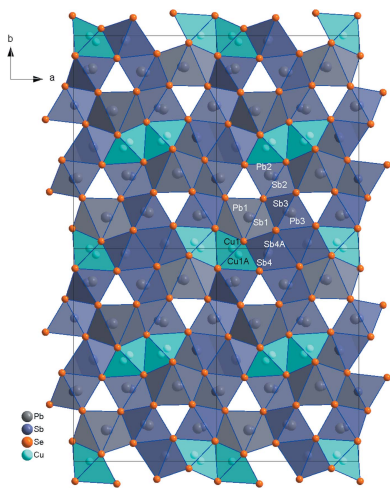
Keywords: crystal structure; sulfosalt; selenide; disorder.**CCDC reference:** 2236460**Supporting information:** this article has supporting information at journals.iucr.org/e

Single crystals of copper lead triantimony hexaselenide, $\text{CuPbSb}_3\text{Se}_6$, were obtained as a minor phase during systematic studies of the formation conditions of selenide-based sulfosalts. The crystal structure is an unusual representative of the family of sulfosalts. Instead of the expected galena-like slabs with octahedral coordination, it features mono and double-capped trigonal–prismatic (Pb), square-pyramidal (Sb) and trigonal–bipyramidal (Cu) coordination. All metal positions are occupationally and/or positionally disordered.

1. Chemical context

Sulfosalts (Moëlo *et al.*, 2008) are promising candidates as thermoelectric materials owing to their high electrical conductivity paired with a low thermal conductivity. Inspired by natural sulfur-based sulfosalts, we attempted to further increase the electrical conductivity by substituting Se for S. During systematic studies of the formation conditions of sulfosalts of the andorite structure type (Moëlo *et al.*, 2008), we obtained crystals of the title compound, $\text{CuPbSb}_3\text{Se}_6$, as a minor phase, by heating the precursor selenides Cu_2Se , PbSe and Sb_2Se_3 in evacuated fused silica ampoules. Surprisingly, the title compound does not follow the expected crystal chemistry of the structural family. In fact, crystals of the andorite family are modular structures, which are composed of galena-like slabs, with octahedral coordination of the metal atoms. This coordination is not observed for $\text{CuPbSb}_3\text{Se}_6$. Nevertheless, certain structural relationships can be established, as will be shown below. These structural relationships are reflected by andorite-like compounds of the $\text{Sn}_3\text{Bi}_2\text{S}_6$ structure type (Chen & Lee, 2010) with very similar cell parameters yet a different space-group symmetry. The structure with the closest matching cell parameters is $\text{SnPb}_2\text{Bi}_2\text{S}_6$ (Li *et al.*, 2019) with $a = 20.5458(12)$ Å, $b = 4.0925(4)$ Å and $c = 13.3219(10)$ Å, whereby the axes have been cyclically permuted with respect to the cell of $\text{CuPbSb}_3\text{Se}_6$ presented here. $\text{SnPb}_2\text{Bi}_2\text{S}_6$ crystallizes in a lillianite-type ^4L (Moëlo *et al.*, 2008) structure and was investigated by the authors for its thermoelectric performance, sporting a figure of merit ZT of 0.3. Since $\text{CuPbSb}_3\text{Se}_6$ shows strongly disordered positions, it is possible that it exhibits similar thermoelectric properties.

It should be noted that from a structural point of view, lillianites and andorites are interchangeable terms. However, in a mineralogical context, they define distinct sulfosalt mineral groups because the Sb that replaces Bi from the lillianite structure in andorite forms electron-pair micelles that distort the structure (Makovicky & Topa, 2014).



2. Structural commentary

Crystals of the title compound crystallize in the *Pnmm* space group. All atoms are located on or disordered about (in the case of Sb4A) the reflection plane parallel to (001), which corresponds to the Wyckoff position 4g. The crystal structure is comprised of three mixed Pb/Sb positions, one Sb and one Cu position (Fig. 1). There are three different kinds of coordination polyhedra, with the interatomic distances compiled in Table 1. The predominantly Pb Pb1/Sb1 position is coordinated by Se atoms, forming a double-capped trigonal prism. The predominantly Sb Sb2/Pb2 and Sb3/Pb3 positions and the disordered Sb4/Sb4A are quadratic pyramids in the case of Sb and mono-capped trigonal prisms in the case of Pb. Finally, the disordered Cu1/Cu1A position features trigonal-bipyramidal coordination. Whereas the [PbSe₈] double-capped trigonal prisms of the Pb1/Sb1 position are a defining feature of lillianite-type structures and form where the galena-like slabs meet, the remaining two coordinations are unexpected in this structural family.

It has to be noted that the description of the coordination polyhedra of the Sb2/Pb2, Sb3/Pb3 and Sb4/Sb4A positions as quadratic pyramids and capped trigonal prisms is not completely unambiguous. Both variants based on the central atom are shown in Fig. 2 for Sb3 and Pb3. Since the distance from Sb3 to the two farther Se6 atoms is 3.7015 (19) Å and the

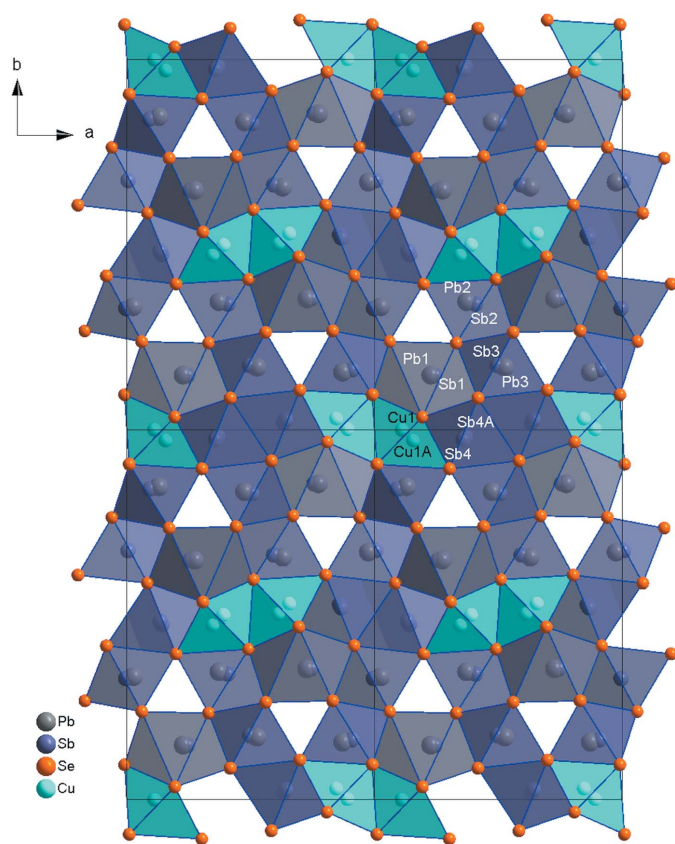


Figure 1
CuPbSb₃Se₆ viewed down [001]. Pb and Pb/Sb are represented by grey, Sb by dark blue, Cu by cyan spheres of arbitrary radius.

Table 1
Selected bond lengths (Å).

Pb1—Se1	3.0553 (15)	Pb2—Se4 ⁱ	2.900 (7)
Pb1—Se1 ⁱ	3.0553 (15)	Pb2—Se6 ⁱ	3.283 (8)
Pb1—Se2	2.9124 (17)	Pb2—Se6 ^{vii}	3.283 (8)
Pb1—Se3 ⁱⁱ	3.5754 (15)	Sb3—Se1	2.587 (2)
Pb1—Se3 ⁱⁱⁱ	3.5754 (15)	Sb3—Se2 ^{vi}	2.9293 (15)
Pb1—Se4 ⁱⁱ	3.4061 (16)	Sb3—Se2	2.9293 (15)
Pb1—Se5 ^{iv}	3.1205 (17)	Sb3—Se3	2.8835 (14)
Pb1—Se5 ^v	3.1205 (17)	Sb3—Se3 ⁱ	2.8835 (14)
Sb1—Se1	2.95 (2)	Sb3—Se6 ^{viii}	3.7015 (19)
Sb1—Se1 ⁱ	2.95 (2)	Sb3—Se6 ^{ix}	3.7015 (19)
Sb1—Se2	2.68 (3)	Pb3—Se1	3.02 (4)
Sb1—Se3 ⁱⁱ	3.75 (2)	Pb3—Se2 ^{vi}	3.05 (3)
Sb1—Se3 ⁱⁱⁱ	3.75 (2)	Pb3—Se2	3.05 (3)
Sb1—Se4 ⁱⁱ	3.65 (2)	Pb3—Se3	2.86 (3)
Sb1—Se5 ^{iv}	3.16 (3)	Pb3—Se3 ⁱ	2.86 (3)
Sb1—Se5 ^v	3.16 (3)	Pb3—Se6 ^{viii}	3.35 (3)
Sb1—Cu1 ^v	3.54 (3)	Pb3—Se6 ^{ix}	3.35 (3)
Sb2—Se1 ^{vi}	3.1563 (14)	Sb4—Se2 ^x	3.166 (3)
Sb2—Se1	3.1563 (14)	Sb4—Se2 ^{xi}	3.166 (3)
Sb2—Se3	2.6135 (19)	Sb4—Se5	2.595 (3)
Sb2—Se4	2.7090 (12)	Sb4—Se6	2.723 (2)
Sb2—Se4 ⁱ	2.7090 (12)	Sb4—Se6 ⁱ	2.723 (2)
Sb2—Se6 ⁱ	3.6962 (17)	Sb4a—Se2 ^x	3.30 (3)
Sb2—Se6 ^{vii}	3.6962 (17)	Sb4a—Se2 ^{xi}	2.77 (3)
Pb2—Se1 ^{vi}	3.114 (7)	Sb4a—Se2 ⁱⁱ	3.66 (2)
Pb2—Se1	3.114 (7)	Sb4a—Se5	2.633 (19)
Pb2—Se3	3.094 (10)	Sb4a—Se6	3.15 (3)
Pb2—Se4	2.900 (7)	Sb4a—Se6 ⁱ	2.59 (3)

Symmetry codes: (i) $x, y, z + 1$; (ii) $x - \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{3}{2}$; (iii) $x - \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{5}{2}$; (iv) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (v) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; (vi) $x, y, z - 1$; (vii) $x, y, z + 2$; (viii) $x + \frac{1}{2}, -y + \frac{1}{2}, -z - \frac{1}{2}$; (ix) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{1}{2}$; (x) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (xi) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$.

corresponding calculated bond valence, using the parameters $R_0 = 2.60$ Å and $b = 0.37$, is only 0.05, they are considered not to coordinate with Sb3. In contrast, the Se2 and Se3 atoms at the base of the pyramid are located at 2.9293 (15) Å and 2.8835 (14) Å, respectively. The Se1 atom at the apex of the pyramid is located at 2.587 (2) Å from the Sb3 atom. This is different for Pb3, where the two distant Se6 atoms are much closer, with the atomic distances changed to 3.35 (3) Å. The other Se atoms are further away with 3.05 (3) Å for Se2, 2.86 (2) Å for Se3 and 3.02 (4) Å for Se1. Note that the large standard uncertainties (s.u.s) of the Pb—Se distances here are due to Pb3 being a minor position in close proximity to Se3. Thus, in the case of the Pb3 atoms, the coordination is clearly a

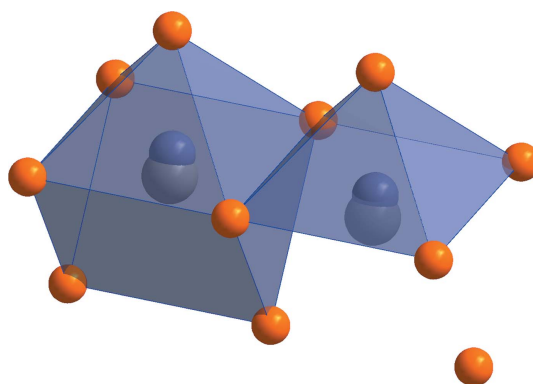


Figure 2
Graphical comparison of the two different coordination polyhedra of Sb3 and Pb3. Colours as in Fig. 1.

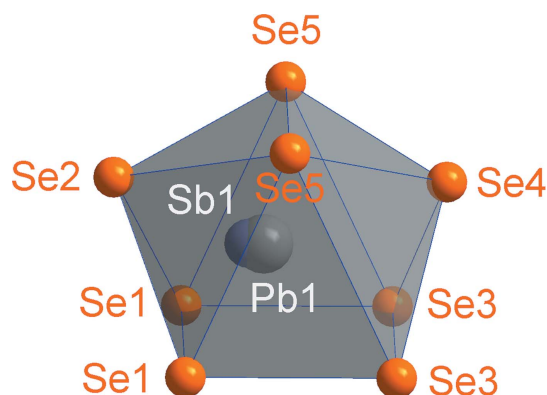


Figure 3
The coordination polyhedron of Pb1/Sb1. Colours as in Fig. 1

capped trigonal prism, whereas for Sb3 it is better described as quadratic pyramidal. When considering the electron lone-pair of the Sb^{III} atoms, the coordination might also be seen as ψ^1 -octahedral.

For the Sb2/Pb2 position, the same observation is made with slightly changed distances. The extended coordination environment of Sb2 possesses two far Se6 atoms at 3.6962 (17) Å, Se1 and Se4 atoms at the square base at 3.1563 (14) Å and 2.7090 (12) Å and an apex Se3 atom at 2.6135 (19) Å. For Pb2 these distances change to 3.283 (6) Å, 3.114 (7) Å, 2.900 (7) Å and 3.094 (10) Å, respectively.

On the Sb4/Sb4A position, the Sb atom is sometimes located on the $\dots m$ position [Sb4, 83 (3)%] and sometimes to both sides of the reflection plane [Sb4A, 2×8.4 (15)%]. The

coordination of Sb4 is similar to those of Sb2 and Sb3. The coordination polyhedron can be considered as a quadratic pyramid with the bond lengths being 2×2.723 (2) Å (Se6), 2×3.166 (3) Å (Se2) and 2.595 (3) Å (Se5, located at the apex). The next Se atom is Se2 located 3.875 (2) Å from Sb4, which can be considered as non-coordinating. The coordination of Sb4A is very similar, as it is located only 0.44 (3) Å from Sb4.

As for the other discussed coordination polyhedra, one might also see the double-capped trigonal prisms that surround the Pb1/Sb1 position (Fig. 3) as quadratic pyramids in the case of Sb because the metal atoms do not lie in the centre of the polyhedron. If the Sb1 atom is realized, one might rather think of a fivefold instead of an eightfold coordination, again with the atoms forming a quadratic pyramid. Here, the bond distances involving the Pb1 atom are 3.0553 (15) Å and 3.1205 (17) Å for the quadratic base (Se1 and Se5) and 2.9124 (14) Å to the apex (Se2). The two Se3 atoms are located at 3.5754 (15) Å from the Pb1 atom and the last Se4 atom, which forms the second cap of the prism at a distance of 3.4061 (16) Å. The coordination of Sb1 is very similar [distance to Pb1 = 0.26 (2) Å], with a slightly more pronounced quadratic pyramidal coordination.

The (double-)capped trigonal prism is, as stated above, a defining structural element of the lillianite family. It is interesting to note that whereas the 90° angles of all the prisms are perfectly realized owing to the $\dots m$ reflection plane, the triangular bases deviate significantly from an ideal trigonal symmetry. The prism around Pb1/Sb1 is formed from a triangle with 48.31 (2), 66.60 (3) and 65.09 (3)° angles. The

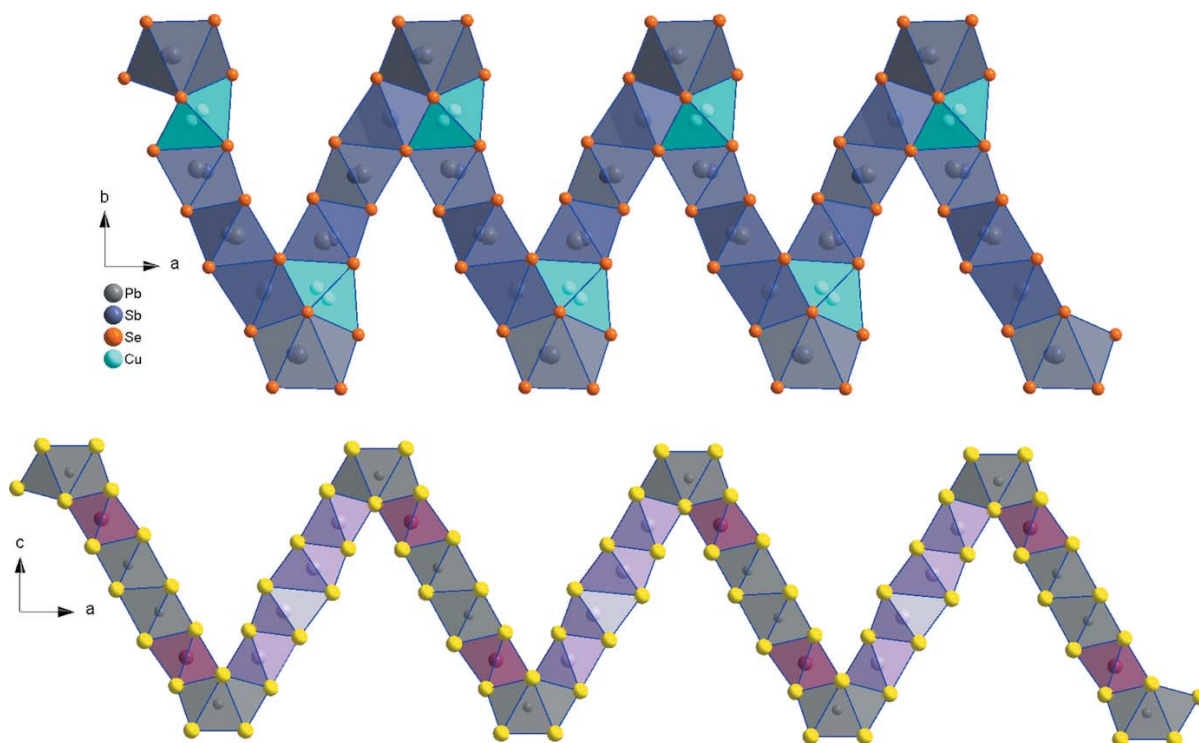


Figure 4
Comparison of four-polyhedra-long chains delimited by the Pb1/Sb1 position in (top) $\text{CuPbSb}_3\text{Se}_6$ and (bottom) the lillianite ^4L -type structure of $\text{SnPb}_2\text{Bi}_2\text{S}_6$. Colour codes: Bi red, Pb grey, Bi/Sn pink, S yellow.

other prisms are closer to regular, with the angles deviating the most from 60° being 54.53 (3)° for Pb2 and 65.57 (3)° for Pb3.

Finally, the trigonal–bipyramidal coordination of Cu is unusual as Cu is usually encountered as coordinated tetrahedrally or in a planar square. This is still somewhat true for Cu1/Cu1A, as the disordering takes place over the trigonal base of the pyramids, placing them both in their own tetrahedron. However, the position closer to the base (Cu1), *i.e.* with the more trigonal–bipyramidal-like coordination, has a higher occupancy [59.5 (17)%] than the position further removed from the centre of the trigonal bipyramid (Cu1A).

Despite the clearly different coordination polyhedra, CuPbSb₃Se₆ can nevertheless be described as a distorted ⁴L andorite-type structure, since there are four polyhedra between two double-capped trigonal prisms as shown in Fig. 4. However, the spatial distribution of the Se/S atoms is fundamentally different, leading not only to different coordination polyhedra, as described above, but also an altered connectivity of the polyhedra.

3. Database survey

No compounds containing only copper, lead, antimony and selenium have been deposited in the Inorganic Crystal Structure Database (ICSD; Bergerhoff & Brown, 1987) as of Fall 2022.

4. Synthesis and crystallization

40.0mg of Cu₂Se, 47.6mg of PbSe and 125mg of Sb₂Se were mixed thoroughly and transferred into a fused silica ampoule, which was sealed under vacuum. The ampoule was heated at 1223 K for 2 h, cooled to 873 K over 7 h and held at that temperature for 149 h. After cooling to 473 K over 5 h and quenching in air, the ampoule was opened and the obtained ingot crushed. Among other phases in the andorite family, single crystals of the title compound CuPbSbSe₃ were isolated.

5. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 2. All atoms were refined with anisotropic atomic displacement parameters (ADPs). It was necessary to model the Cu-atom position as positionally disordered to avoid non-positive definite (NPD) ADP tensors. Modelling the positions of Pb1, Sb2 and Sb3 as mixed Pb/Sb positions as well as the position of Sb4 as positionally disordered improved the residuals significantly. The pairs Pb1/Sb1, Sb2/Pb2, Sb3/Pb3 and Sb4/Sb4A were refined with identical ADP tensor elements, though distinct coordinates. Furthermore, the site occupancies were constrained to full occupancy and the Pb occupancies were restrained to fit the sum formula CuPbSb₃Se₆, corresponding to an electroneutral structure.

Table 2
Experimental details.

Crystal data	
Chemical formula	CuPbSb ₃ Se ₆
<i>M_r</i>	1109.7
Crystal system, space group	Orthorhombic, <i>Pnmm</i>
Temperature (K)	300
<i>a</i> , <i>b</i> , <i>c</i> (Å)	13.7217 (5), 20.5149 (8), 4.0716 (2)
<i>V</i> (Å ³)	1146.15 (8)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	42.44
Crystal size (mm)	0.08 × 0.06 × 0.04 × 0.03 (radius)
Data collection	
Diffractometer	Stoe Stadivari
Absorption correction	Multi-scan [absorption correction by scaling of reflection intensities followed by a spherical absorption correction (<i>LANA</i> ; Koziskova <i>et al.</i> , 2016)]
<i>T_{min}</i> , <i>T_{max}</i>	0.428, 0.654
No. of measured, independent and observed [<i>I</i> > 3σ(<i>I</i>)] reflections	15049, 2534, 1472
<i>R_{int}</i>	0.079
(sin θ/λ) _{max} (Å ⁻¹)	0.792
Refinement	
<i>R</i> [<i>F</i> > 3σ(<i>F</i>)], <i>wR</i> (<i>F</i>), <i>S</i>	0.042, 0.110, 1.40
No. of reflections	2534
No. of parameters	86
Δρ _{max} , Δρ _{min} (e Å ⁻³)	2.96, −2.68

Computer programs: *X-AREA Pilatus3_SV*, *Recipe*, *Integrate* and *LANA* (Stoe & Cie, 2021), *SHELXT* (Sheldrick, 2015), *JANA2006* (Petříček *et al.*, 2014), *DIAMOND* (Putz & Brandenburg, 2021) and *publCIF* (Westrip, 2010).

Funding information

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Computing details

Data collection: *X-AREA* Pilatus3_SV 1.31.175.0 (Stoe & Cie, 2021); cell refinement: *X-AREA* Recipe 1.37.0.0 (Stoe & Cie, 2021); data reduction: *X-AREA* Integrate 2.5.1.0 (Stoe & Cie, 2021) *X-AREA* LANA 2.6.2.0 (Stoe & Cie, 2021); program(s) used to solve structure: SHELXT (Sheldrick, 2015); program(s) used to refine structure: *JANA2006* (Petříček *et al.*, 2014); molecular graphics: *DIAMOND* (Putz & Brandenburg, 2021); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Copper lead triantimony hexaselenide

Crystal data

$\text{CuPbSb}_3\text{Se}_6$

$M_r = 1109.7$

Orthorhombic, *Pnmm*

Hall symbol: -P -2xabc;-2yabc;-2z

$a = 13.7217$ (5) Å

$b = 20.5149$ (8) Å

$c = 4.0716$ (2) Å

$V = 1146.15$ (8) Å³

$Z = 4$

$F(000) = 1872$

$D_x = 6.431$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 17463 reflections

$\theta = 2.5\text{--}33.5^\circ$

$\mu = 42.44$ mm⁻¹

$T = 300$ K

Fragment, black

$0.08 \times 0.06 \times 0.04 \times 0.03$ (radius) mm

Data collection

Stoe Stadivari
diffractometer

Radiation source: Axo_Mo

Graded multilayer mirror monochromator

Detector resolution: 13.33 pixels mm⁻¹

rotation method, ω scans

Absorption correction: multi-scan

[absorption correction by scaling of reflection intensities followed by a spherical absorption correction (*LANA*; Koziskova *et al.*, 2016)]

$T_{\min} = 0.428$, $T_{\max} = 0.654$

15049 measured reflections

2534 independent reflections

1472 reflections with $I > 3\sigma(I)$

$R_{\text{int}} = 0.079$

$\theta_{\max} = 34.3^\circ$, $\theta_{\min} = 2.5^\circ$

$h = -21 \rightarrow 19$

$k = -32 \rightarrow 17$

$l = -6 \rightarrow 4$

Refinement

Refinement on F^2

$R[F > 3\sigma(F)] = 0.042$

$wR(F) = 0.110$

$S = 1.40$

2534 reflections

86 parameters

0 restraints

24 constraints

Weighting scheme based on measured s.u.'s $w =$

$1/(\sigma^2(I) + 0.0016I^2)$

$(\Delta/\sigma)_{\max} = 0.028$

$\Delta\rho_{\max} = 2.96$ e Å⁻³

$\Delta\rho_{\min} = -2.68$ e Å⁻³

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Pb1	0.22598 (7)	0.14687 (9)	1.5	0.0286 (2)	0.897 (4)
Sb1	0.2448 (17)	0.1462 (17)	1.5	0.0286 (2)	0.103 (4)
Sb2	0.40745 (12)	0.33892 (6)	0.5	0.0247 (3)	0.923 (3)
Pb2	0.3710 (7)	0.3449 (5)	0.5	0.0247 (3)	0.077 (3)
Sb3	0.49573 (14)	0.17280 (7)	1	0.0411 (4)	0.974 (5)
Pb3	0.527 (3)	0.1673 (19)	1	0.0411 (4)	0.026 (5)
Sb4	0.14104 (17)	0.47308 (17)	−0.5	0.0307 (11)	0.83 (3)
Sb4a	0.1341 (12)	0.4816 (13)	−0.402 (6)	0.0307 (11)	0.084 (15)
Se1	0.33027 (8)	0.23328 (6)	1	0.0199 (3)	
Se2	0.41682 (9)	0.08474 (6)	1.5	0.0228 (4)	
Se3	0.55995 (8)	0.26260 (6)	0.5	0.0209 (3)	
Se4	0.49064 (9)	0.40595 (6)	0	0.0214 (4)	
Se5	0.30698 (8)	0.53372 (6)	−0.5	0.0208 (3)	
Se6	0.19799 (9)	0.39357 (7)	−1	0.0297 (4)	
Cu1a	0.3449 (8)	0.4703 (6)	0	0.050 (3)	0.405 (17)
Cu1	0.3896 (5)	0.4990 (3)	0	0.0341 (14)	0.595 (17)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pb1	0.0292 (5)	0.0306 (3)	0.0260 (3)	−0.0027 (5)	0	0
Sb1	0.0292 (5)	0.0306 (3)	0.0260 (3)	−0.0027 (5)	0	0
Sb2	0.0228 (6)	0.0241 (5)	0.0272 (5)	0.0007 (5)	0	0
Pb2	0.0228 (6)	0.0241 (5)	0.0272 (5)	0.0007 (5)	0	0
Sb3	0.0267 (6)	0.0335 (7)	0.0632 (8)	0.0089 (6)	0	0
Pb3	0.0267 (6)	0.0335 (7)	0.0632 (8)	0.0089 (6)	0	0
Sb4	0.0212 (5)	0.0344 (9)	0.037 (3)	−0.0042 (5)	0	0
Sb4a	0.0212 (5)	0.0344 (9)	0.037 (3)	−0.0042 (5)	0	0
Se1	0.0185 (5)	0.0209 (6)	0.0205 (6)	−0.0003 (5)	0	0
Se2	0.0183 (5)	0.0262 (7)	0.0241 (6)	−0.0016 (5)	0	0
Se3	0.0196 (5)	0.0208 (7)	0.0223 (6)	0.0003 (5)	0	0
Se4	0.0182 (5)	0.0220 (7)	0.0239 (6)	−0.0016 (4)	0	0
Se5	0.0197 (5)	0.0225 (7)	0.0200 (6)	−0.0012 (5)	0	0
Se6	0.0221 (6)	0.0257 (7)	0.0415 (8)	0.0009 (5)	0	0
Cu1a	0.044 (5)	0.057 (6)	0.048 (3)	0.025 (5)	0	0
Cu1	0.034 (3)	0.036 (3)	0.0331 (17)	0.009 (2)	0	0

Geometric parameters (\AA , $^\circ$)

Pb1—Sb1	0.26 (2)	Pb3—Sb4a ^{viii}	3.41 (5)
Pb1—Se1	3.0553 (15)	Pb3—Sb4a ^{ix}	3.41 (5)
Pb1—Se1 ⁱ	3.0553 (15)	Pb3—Se1	3.02 (4)
Pb1—Se2	2.9124 (17)	Pb3—Se2 ^{vi}	3.05 (3)
Pb1—Se3 ⁱⁱ	3.5754 (15)	Pb3—Se2	3.05 (3)
Pb1—Se3 ⁱⁱⁱ	3.5754 (15)	Pb3—Se3	2.86 (3)

Pb1—Se4 ⁱⁱ	3.4061 (16)	Pb3—Se3 ⁱ	2.86 (3)
Pb1—Se5 ^{iv}	3.1205 (17)	Pb3—Se6 ^x	3.35 (3)
Pb1—Se5 ^v	3.1205 (17)	Pb3—Se6 ^{viii}	3.35 (3)
Pb1—Cu1a ^v	3.751 (13)	Sb4—Sb4a ^{vi}	3.68 (3)
Pb1—Cu1 ^v	3.423 (6)	Sb4—Sb4a	0.44 (3)
Sb1—Se1	2.95 (2)	Sb4—Sb4a ^{xi}	0.44 (3)
Sb1—Se1 ⁱ	2.95 (2)	Sb4—Sb4a ^{xii}	3.68 (3)
Sb1—Se2	2.68 (3)	Sb4—Se2 ^{xiii}	3.166 (3)
Sb1—Se3 ⁱⁱ	3.75 (2)	Sb4—Se2 ^{xiv}	3.166 (3)
Sb1—Se3 ⁱⁱⁱ	3.75 (2)	Sb4—Se5	2.595 (3)
Sb1—Se4 ⁱⁱ	3.65 (2)	Sb4—Se6	2.723 (2)
Sb1—Se5 ^{iv}	3.16 (3)	Sb4—Se6 ⁱ	2.723 (2)
Sb1—Se5 ^v	3.16 (3)	Sb4—Cu1a ^{vi}	3.461 (9)
Sb1—Cu1 ^v	3.54 (3)	Sb4—Cu1a	3.461 (9)
Sb2—Pb2	0.515 (10)	Sb4a—Sb4a ^{xv}	3.76 (2)
Sb2—Se1 ^{vi}	3.1563 (14)	Sb4a—Sb4a ^{xi}	0.79 (4)
Sb2—Se1	3.1563 (14)	Sb4a—Sb4a ^{xii}	3.28 (4)
Sb2—Se3	2.6135 (19)	Sb4a—Se2 ^{xiii}	3.30 (3)
Sb2—Se4	2.7090 (12)	Sb4a—Se2 ^{xiv}	2.77 (3)
Sb2—Se4 ⁱ	2.7090 (12)	Sb4a—Se2 ⁱⁱ	3.66 (2)
Sb2—Se6 ⁱ	3.6962 (17)	Sb4a—Se5	2.633 (19)
Sb2—Se6 ^{vii}	3.6962 (17)	Sb4a—Se6	3.15 (3)
Sb2—Cu1a	3.485 (10)	Sb4a—Se6 ⁱ	2.59 (3)
Sb2—Cu1a ⁱ	3.485 (10)	Sb4a—Cu1a ^{vi}	3.79 (2)
Pb2—Se1 ^{vi}	3.114 (7)	Sb4a—Cu1a	3.33 (2)
Pb2—Se1	3.114 (7)	Se1—Se3	3.7999 (14)
Pb2—Se3	3.094 (10)	Se1—Se3 ⁱ	3.7999 (14)
Pb2—Se4	2.900 (7)	Se1—Se3 ⁱⁱ	3.7101 (16)
Pb2—Se4 ⁱ	2.900 (7)	Se1—Se6 ^{vii}	3.7560 (19)
Pb2—Se6 ⁱ	3.283 (8)	Se3—Se4	3.7009 (15)
Pb2—Se6 ^{vii}	3.283 (8)	Se3—Se4 ⁱ	3.7009 (15)
Pb2—Cu1a	3.300 (12)	Se3—Se6 ^x	3.7219 (19)
Pb2—Cu1a ⁱ	3.300 (12)	Se4—Se5 ^{xvi}	3.6590 (14)
Pb2—Cu1	3.770 (9)	Se4—Se5 ^{xvii}	3.6590 (14)
Pb2—Cu1 ⁱ	3.770 (9)	Se4—Cu1a	2.395 (12)
Sb3—Pb3	0.44 (4)	Se4—Cu1a ^{xvi}	3.397 (12)
Sb3—Sb4 ^{viii}	3.596 (4)	Se4—Cu1	2.360 (6)
Sb3—Sb4a ^{viii}	3.71 (2)	Se4—Cu1 ^{xvi}	2.550 (6)
Sb3—Sb4a ^{ix}	3.71 (2)	Se5—Cu1a ^{vi}	2.472 (7)
Sb3—Se1	2.587 (2)	Se5—Cu1a	2.472 (7)
Sb3—Se2 ^{vi}	2.9293 (15)	Se5—Cu1 ^{vi}	2.436 (4)
Sb3—Se2	2.9293 (15)	Se5—Cu1	2.436 (4)
Sb3—Se3	2.8835 (14)	Se6—Cu1a ^{vi}	2.558 (12)
Sb3—Se3 ⁱ	2.8835 (14)	Se6—Cu1 ^{vi}	3.405 (6)
Sb3—Se6 ^x	3.7015 (19)	Cu1a—Cu1	0.851 (13)
Sb3—Se6 ^{viii}	3.7015 (19)	Cu1a—Cu1 ^{xvi}	3.696 (13)
Pb3—Sb4 ^{viii}	3.28 (4)	Cu1—Cu1 ^{xvi}	3.030 (9)

Se1—Pb1—Se1 ⁱ	83.57 (5)	Se2 ^{vi} —Sb3—Se6 ^x	70.61 (4)
Se1—Pb1—Se2	80.37 (4)	Se2 ^{vi} —Sb3—Se6 ^{viii}	115.63 (6)
Se1—Pb1—Se3 ⁱⁱ	67.52 (4)	Se2—Sb3—Se3	176.06 (8)
Se1—Pb1—Se3 ⁱⁱⁱ	112.11 (6)	Se2—Sb3—Se3 ⁱ	90.93 (3)
Se1—Pb1—Se4 ⁱⁱ	128.95 (3)	Se2—Sb3—Se6 ^x	115.63 (6)
Se1—Pb1—Se5 ^{iv}	93.71 (3)	Se2—Sb3—Se6 ^{viii}	70.61 (4)
Se1—Pb1—Se5 ^v	159.10 (5)	Se3—Sb3—Se3 ⁱ	89.82 (5)
Se1 ⁱ —Pb1—Se2	80.37 (4)	Se3—Sb3—Se6 ^x	67.52 (4)
Se1 ⁱ —Pb1—Se3 ⁱⁱ	112.11 (6)	Se3—Sb3—Se6 ^{viii}	113.22 (6)
Se1 ⁱ —Pb1—Se3 ⁱⁱⁱ	67.52 (4)	Se3 ⁱ —Sb3—Se6 ^x	113.22 (6)
Se1 ⁱ —Pb1—Se4 ⁱⁱ	128.95 (3)	Se3 ⁱ —Sb3—Se6 ^{viii}	67.52 (4)
Se1 ⁱ —Pb1—Se5 ^{iv}	159.10 (5)	Se6 ^x —Sb3—Se6 ^{viii}	66.73 (4)
Se1 ⁱ —Pb1—Se5 ^v	93.71 (3)	Se1—Pb3—Se2 ^{vi}	78.8 (8)
Se2—Pb1—Se3 ⁱⁱ	143.15 (2)	Se1—Pb3—Se2	78.8 (8)
Se2—Pb1—Se3 ⁱⁱⁱ	143.15 (2)	Se1—Pb3—Se3	80.5 (8)
Se2—Pb1—Se4 ⁱⁱ	135.50 (7)	Se1—Pb3—Se3 ⁱ	80.5 (8)
Se2—Pb1—Se5 ^{iv}	78.74 (5)	Se1—Pb3—Se6 ^x	142.5 (4)
Se2—Pb1—Se5 ^v	78.74 (5)	Se1—Pb3—Se6 ^{viii}	142.5 (4)
Se3 ⁱⁱ —Pb1—Se3 ⁱⁱⁱ	69.42 (3)	Se2 ^{vi} —Pb3—Se2	83.8 (9)
Se3 ⁱⁱ —Pb1—Se4 ⁱⁱ	63.97 (3)	Se2 ^{vi} —Pb3—Se3	89.0 (2)
Se3 ⁱⁱ —Pb1—Se5 ^{iv}	85.56 (3)	Se2 ^{vi} —Pb3—Se3 ⁱ	159.1 (13)
Se3 ⁱⁱ —Pb1—Se5 ^v	131.72 (4)	Se2 ^{vi} —Pb3—Se6 ^x	74.6 (5)
Se3 ⁱⁱⁱ —Pb1—Se4 ⁱⁱ	63.97 (3)	Se2 ^{vi} —Pb3—Se6 ^{viii}	123.1 (12)
Se3 ⁱⁱⁱ —Pb1—Se5 ^{iv}	131.72 (4)	Se2—Pb3—Se3	159.1 (13)
Se3 ⁱⁱⁱ —Pb1—Se5 ^v	85.56 (3)	Se2—Pb3—Se3 ⁱ	89.0 (2)
Se4 ⁱⁱ —Pb1—Se5 ^{iv}	68.04 (4)	Se2—Pb3—Se6 ^x	123.1 (12)
Se4 ⁱⁱ —Pb1—Se5 ^v	68.04 (4)	Se2—Pb3—Se6 ^{viii}	74.6 (5)
Se5 ^{iv} —Pb1—Se5 ^v	81.45 (5)	Se3—Pb3—Se3 ⁱ	90.8 (11)
Se1—Sb1—Se1 ⁱ	87.2 (8)	Se3—Pb3—Se6 ^x	73.2 (5)
Se1—Sb1—Se2	86.2 (6)	Se3—Pb3—Se6 ^{viii}	125.2 (12)
Se1—Sb1—Se3 ⁱⁱ	66.0 (4)	Se3 ⁱ —Pb3—Se6 ^x	125.2 (12)
Se1—Sb1—Se3 ⁱⁱⁱ	110.0 (9)	Se3 ⁱ —Pb3—Se6 ^{viii}	73.2 (5)
Se1—Sb1—Se4 ⁱⁱ	123.9 (6)	Se6 ^x —Pb3—Se6 ^{viii}	74.9 (7)
Se1—Sb1—Se5 ^{iv}	94.99 (14)	Se2 ^{xiii} —Sb4—Se2 ^{xiv}	80.04 (8)
Se1—Sb1—Se5 ^v	167.5 (10)	Se2 ^{xiii} —Sb4—Se5	82.71 (8)
Se1 ⁱ —Sb1—Se2	86.2 (6)	Se2 ^{xiii} —Sb4—Se6	91.41 (3)
Se1 ⁱ —Sb1—Se3 ⁱⁱ	110.0 (9)	Se2 ^{xiii} —Sb4—Se6 ⁱ	170.44 (11)
Se1 ⁱ —Sb1—Se3 ⁱⁱⁱ	66.0 (4)	Se2 ^{xiv} —Sb4—Se5	82.71 (8)
Se1 ⁱ —Sb1—Se4 ⁱⁱ	123.9 (6)	Se2 ^{xiv} —Sb4—Se6	170.44 (11)
Se1 ⁱ —Sb1—Se5 ^{iv}	167.5 (10)	Se2 ^{xiv} —Sb4—Se6 ⁱ	91.41 (3)
Se1 ⁱ —Sb1—Se5 ^v	94.99 (14)	Se5—Sb4—Se6	92.03 (7)
Se2—Sb1—Se3 ⁱⁱ	146.2 (3)	Se5—Sb4—Se6 ⁱ	92.03 (7)
Se2—Sb1—Se3 ⁱⁱⁱ	146.2 (3)	Se6—Sb4—Se6 ⁱ	96.76 (11)
Se2—Sb1—Se4 ⁱⁱ	134.8 (12)	Se2 ^{xiii} —Sb4a—Se2 ^{xiv}	83.9 (7)
Se2—Sb1—Se5 ^{iv}	81.6 (7)	Se2 ^{xiii} —Sb4a—Se2 ⁱⁱ	113.3 (5)
Se2—Sb1—Se5 ^v	81.6 (7)	Se2 ^{xiii} —Sb4a—Se5	79.6 (6)
Se3 ⁱⁱ —Sb1—Se3 ⁱⁱⁱ	65.7 (5)	Se2 ^{xiii} —Sb4a—Se6	81.8 (6)
Se3 ⁱⁱ —Sb1—Se4 ⁱⁱ	60.0 (3)	Se2 ^{xiii} —Sb4a—Se6 ⁱ	170.0 (9)

Se3 ⁱⁱ —Sb1—Se5 ^{iv}	82.1 (3)	Se2 ^{xiv} —Sb4a—Se2 ⁱⁱ	79.3 (5)
Se3 ⁱⁱ —Sb1—Se5 ^v	124.2 (7)	Se2 ^{xiv} —Sb4a—Se5	90.4 (8)
Se3 ⁱⁱⁱ —Sb1—Se4 ⁱⁱ	60.0 (3)	Se2 ^{xiv} —Sb4a—Se6	164.8 (10)
Se3 ⁱⁱⁱ —Sb1—Se5 ^{iv}	124.2 (7)	Se2 ^{xiv} —Sb4a—Se6 ⁱ	104.1 (9)
Se3 ⁱⁱⁱ —Sb1—Se5 ^v	82.1 (3)	Se2 ⁱⁱ —Sb4a—Se5	162.1 (9)
Se4 ⁱⁱ —Sb1—Se5 ^{iv}	64.6 (5)	Se2 ⁱⁱ —Sb4a—Se6	111.0 (7)
Se4 ⁱⁱ —Sb1—Se5 ^v	64.6 (5)	Se2 ⁱⁱ —Sb4a—Se6 ⁱ	74.6 (6)
Se5 ^{iv} —Sb1—Se5 ^v	80.3 (8)	Se5—Sb4a—Se6	82.3 (6)
Se1 ^{vi} —Sb2—Se1	80.33 (4)	Se5—Sb4a—Se6 ⁱ	94.2 (6)
Se1 ^{vi} —Sb2—Se3	81.80 (4)	Se6—Sb4a—Se6 ⁱ	89.7 (7)
Se1 ^{vi} —Sb2—Se4	90.30 (3)	Se3—Se1—Se3 ⁱ	64.79 (2)
Se1 ^{vi} —Sb2—Se4 ⁱ	167.07 (5)	Se3—Se1—Se3 ⁱⁱ	145.65 (2)
Se1 ^{vi} —Sb2—Se6 ⁱ	65.93 (4)	Se3—Se1—Se6 ^{vii}	105.20 (4)
Se1 ^{vi} —Sb2—Se6 ^{vii}	107.62 (5)	Se3 ⁱ —Se1—Se3 ⁱⁱ	145.65 (2)
Se1—Sb2—Se3	81.80 (4)	Se3 ⁱ —Se1—Se6 ^{vii}	105.20 (4)
Se1—Sb2—Se4	167.07 (5)	Se3 ⁱⁱ —Se1—Se6 ^{vii}	59.80 (3)
Se1—Sb2—Se4 ⁱ	90.30 (3)	Se1 ^{vi} —Se3—Se1	64.79 (2)
Se1—Sb2—Se6 ⁱ	107.62 (5)	Se1 ^{vi} —Se3—Se1 ^{xviii}	146.387 (17)
Se1—Sb2—Se6 ^{vii}	65.93 (4)	Se1 ^{vi} —Se3—Se4	67.54 (3)
Se3—Sb2—Se4	88.09 (5)	Se1 ^{vi} —Se3—Se4 ⁱ	101.97 (4)
Se3—Sb2—Se4 ⁱ	88.09 (5)	Se1 ^{vi} —Se3—Se6 ^x	106.61 (4)
Se3—Sb2—Se6 ⁱ	143.55 (3)	Se1—Se3—Se1 ^{xviii}	146.387 (17)
Se3—Sb2—Se6 ^{vii}	143.55 (3)	Se1—Se3—Se4	101.97 (4)
Se4—Sb2—Se4 ⁱ	97.44 (5)	Se1—Se3—Se4 ⁱ	67.54 (3)
Se4—Sb2—Se6 ⁱ	76.10 (3)	Se1—Se3—Se6 ^x	106.61 (4)
Se4—Sb2—Se6 ^{vii}	125.99 (5)	Se1 ^{xviii} —Se3—Se4	103.82 (4)
Se4 ⁱ —Sb2—Se6 ⁱ	125.99 (5)	Se1 ^{xviii} —Se3—Se4 ⁱ	103.82 (4)
Se4 ⁱ —Sb2—Se6 ^{vii}	76.10 (3)	Se1 ^{xviii} —Se3—Se6 ^x	60.71 (3)
Se6 ⁱ —Sb2—Se6 ^{vii}	66.84 (3)	Se4—Se3—Se4 ⁱ	66.75 (3)
Se1 ^{vi} —Pb2—Se1	81.7 (2)	Se4—Se3—Se6 ^x	144.56 (2)
Se1 ^{vi} —Pb2—Se3	75.5 (2)	Se4 ⁱ —Se3—Se6 ^x	144.56 (2)
Se1 ^{vi} —Pb2—Se4	87.72 (9)	Se3 ^{vi} —Se4—Se3	66.75 (3)
Se1 ^{vi} —Pb2—Se4 ⁱ	151.4 (4)	Se3 ^{vi} —Se4—Se5 ^{xvi}	76.57 (3)
Se1 ^{vi} —Pb2—Se6 ⁱ	71.86 (13)	Se3 ^{vi} —Se4—Se5 ^{xvii}	112.32 (4)
Se1 ^{vi} —Pb2—Se6 ^{vii}	120.0 (3)	Se3—Se4—Se5 ^{xvi}	112.32 (4)
Se1—Pb2—Se3	75.5 (2)	Se3—Se4—Se5 ^{xvii}	76.57 (3)
Se1—Pb2—Se4	151.4 (4)	Se5 ^{xvi} —Se4—Se5 ^{xvii}	67.61 (3)
Se1—Pb2—Se4 ⁱ	87.72 (9)	Se4 ^{xix} —Se5—Se4 ^{xvi}	67.61 (3)
Se1—Pb2—Se6 ⁱ	120.0 (3)	Se1 ^{xx} —Se6—Se3 ^{xxi}	59.49 (3)
Se1—Pb2—Se6 ^{vii}	71.86 (13)	Se4—Cu1a—Se4 ^{xvi}	81.8 (3)
Se3—Pb2—Se4	76.2 (2)	Se4—Cu1a—Se5	117.8 (3)
Se3—Pb2—Se4 ⁱ	76.2 (2)	Se4—Cu1a—Se5 ⁱ	117.8 (3)
Se3—Pb2—Se6 ⁱ	140.54 (13)	Se4—Cu1a—Se6 ⁱ	108.6 (5)
Se3—Pb2—Se6 ^{vii}	140.54 (13)	Se4 ^{xvi} —Cu1a—Se5	75.3 (3)
Se4—Pb2—Se4 ⁱ	89.2 (3)	Se4 ^{xvi} —Cu1a—Se5 ⁱ	75.3 (3)
Se4—Pb2—Se6 ⁱ	80.94 (12)	Se4 ^{xvi} —Cu1a—Se6 ⁱ	169.6 (5)
Se4—Pb2—Se6 ^{vii}	135.5 (3)	Se5—Cu1a—Se5 ⁱ	110.9 (5)
Se4 ⁱ —Pb2—Se6 ⁱ	135.5 (3)	Se5—Cu1a—Se6 ⁱ	99.1 (3)

Se4 ⁱ —Pb2—Se6 ^{vii}	80.94 (12)	Se5 ⁱ —Cu1a—Se6 ⁱ	99.1 (3)
Se6 ⁱ —Pb2—Se6 ^{vii}	76.7 (2)	Se4—Cu1—Se4 ^{xvi}	103.9 (2)
Se1—Sb3—Se2 ^{vi}	88.36 (6)	Se4—Cu1—Se5	120.65 (13)
Se1—Sb3—Se2	88.36 (6)	Se4—Cu1—Se5 ⁱ	120.65 (13)
Se1—Sb3—Se3	87.81 (5)	Se4—Cu1—Se6 ⁱ	86.53 (17)
Se1—Sb3—Se3 ⁱ	87.81 (5)	Se4 ^{xvi} —Cu1—Se5	94.39 (16)
Se1—Sb3—Se6 ^x	146.549 (19)	Se4 ^{xvi} —Cu1—Se5 ⁱ	94.39 (16)
Se1—Sb3—Se6 ^{viii}	146.549 (19)	Se4 ^{xvi} —Cu1—Se6 ⁱ	169.6 (2)
Se2 ^{vi} —Sb3—Se2	88.05 (5)	Se5—Cu1—Se5 ⁱ	113.3 (2)
Se2 ^{vi} —Sb3—Se3	90.93 (3)	Se5—Cu1—Se6 ⁱ	79.99 (16)
Se2 ^{vi} —Sb3—Se3 ⁱ	176.06 (8)	Se5 ⁱ —Cu1—Se6 ⁱ	79.99 (16)

Symmetry codes: (i) $x, y, z+1$; (ii) $x-1/2, -y+1/2, -z+3/2$; (iii) $x-1/2, -y+1/2, -z+5/2$; (iv) $-x+1/2, y-1/2, -z+1/2$; (v) $-x+1/2, y-1/2, -z+3/2$; (vi) $x, y, z-1$; (vii) $x, y, z+2$; (viii) $x+1/2, -y+1/2, -z+1/2$; (ix) $x+1/2, -y+1/2, z+3/2$; (x) $x+1/2, -y+1/2, -z-1/2$; (xi) $x, y, -z-1$; (xii) $x, y, -z$; (xiii) $-x+1/2, y+1/2, -z+1/2$; (xiv) $-x+1/2, y+1/2, -z+3/2$; (xv) $-x, -y+1, z$; (xvi) $-x+1, -y+1, z$; (xvii) $-x+1, -y+1, z+1$; (xviii) $x+1/2, -y+1/2, -z+3/2$; (xix) $-x+1, -y+1, z-1$; (xx) $x, y, z-2$; (xxi) $x-1/2, -y+1/2, -z-1/2$.