Crystal and electronic structure of the ternary monoclinic selenide $Tl_{2.59}Sb_{8.41}Se_{14}$ ($TlSb_3Se_5$)

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The ternary selenide $Tl_{2.59}Sb_{8.41}Se_{14}$ crystallizes with a monoclinic structure in space group $P2_1/m$ where the atoms are located on 2e sites (site symmetry m). The structure of the title compound is closely related to the strongly disordered structure of $K_{2.5}Sb_{8.5}Se_{14}$. The coordination polyhedra of the thallium atoms are trigonal prisms with additional selenium atoms centering lateral faces. All the antimony atoms are coordinated by slightly deformed Se_6 octahedra. Three types of polyhedron: octahedron, trigonal bipyramid and tetrahedron, are observed for the selenium atoms. The crystal chemical analysis and electronic structure calculations by the TB-LMTO-ASA method show that the antimony and selenium atoms form a polyanionic network the negative charge of which is compensated by the thallium cations.

Selenide / Crystal structure / Electronic structure

Introduction

The ternary selenides Tl₉SbSe₆, TlSbSe₂, and TlSb₃Se₅ were detected during an investigation of the (Tl₂Se)_{3x}–(Sb₂Se₃)_{1-x} system by DTA and XRD [1]. Among these compounds, only Tl₉SbSe₆ melts congruently (at 629 K), the others melting incongruently (at 723 and 743 K, respectively). The TlSbSe₂ selenide undergoes a polymorphic transition at 658 K. According to this work TlSb₃Se₅ forms by peritectic reaction at 743 K due to the interaction of the melt with Sb₂Se₃. A similar description of the above-mentioned phases was later presented by Gotko *et al.* [2].

According to Babanly *et al.* [3], the formation of four intermediate ternary compounds, Tl₉SbSe, TlSbSe₂, Tl₅SbSe₄, and TlSb₃Se₅, was observed in the Tl₂Se–Sb₂Se₃ section. The Tl₉SbSe₆ and TlSbSe₂ phases melt congruently at 740 and 750 K, respectively, and Tl₅SbSe₄ and TlSb₃Se₅ are formed by peritectic reactions at 625 and 740 K, respectively. For the ternary selenide TlSbSe₂ the polymorphic transition temperature was estimated to 665 K.

Some other results are given in [4,5]. Four ternary compounds, Tl₉SbSe₆, Tl₃SbSe₃ (new phase), TlSbSe₂,

and TlSb₃Se₅, were found in the Tl₂Se-Sb₂Se₃ system. Only two of them, Tl₉SbSe₆ (at 725 K) and TlSbSe₂ (at 730 K), melt congruently. rest of the The ternary phases, Tl₃SbSe₃ TlSb₃Se₅, melt incongruently and at 625 K 725 K, respectively. For the intermediate Tl₃SbSe₃ and TlSbSe₂ transformation were observed at 575 and 665 K, respectively.

According to the most recent literature data [6], four individual intermediate compounds, Tl_9SbSe_6 , $Tl_{26}Sb_4Se_{19}$ (new phase), $TlSbSe_2$, and $TlSb_3Se_5$, exist in the $Tl_2Se_-Sb_2Se_3$ section. Congruent melting was observed for Tl_9SbSe_6 (at 730 K) and $TlSbSe_2$ (at 727.6 K). $Tl_{26}Sb_4Se_{19}$ (at 650.1 K) and $TlSb_3Se_5$ (at 722.4 K) form by peritectic reactions. The $Tl_{26}Sb_4Se_{19}$ and $TlSbSe_2$ phases undergo polymorphic transformations at 570 and 669.7 K, respectively.

Although the $TlSb_3Se_5$ compound has been known for nearly twenty years, its crystal structure was first investigated in 2008 ($Tl_{2.35}Sb_{8.65}Se_{14}$) [7]. In this paper we present the results of a redetermination of the crystal structure and results of electronic structure calculations.

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Experimental section

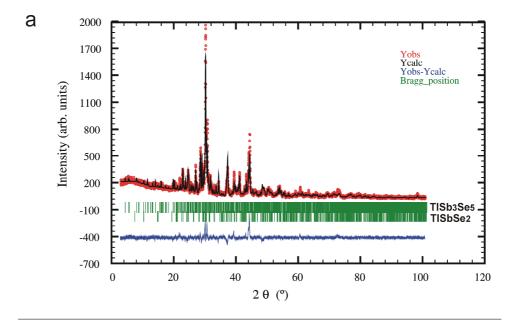
Alloys of the Tl₂Se-Sb₂Se₃ section were prepared by the direct temperature method in evacuated quartz ampoules, using appropriate amounts of binary thallium(I) and antimony(III) selenides. composition of the ternary alloys corresponded to the individual $TlSbSe_2$ and $TlSb_3Se_5$ phases. The maximum temperature for synthesis was 950 K. To achieve equilibrium and a homogeneous state, the alloys were annealed at 700 K for 290 h, and then quenched. The reaction products were examined by X-ray diffraction (XRD), differential thermal analysis (DTA), scanning electron microscopy (SEM), wavelength-dispersive spectrometry (WDS), and electron probe microanalysis (EPMA). For the X-ray powder diffraction (XRD) analysis the samples were ground in an agate mortar. X-ray powder diffraction of the samples was carried out using a STOE STADI P powder diffractometer (Cu-radiation, step scanning). Rietveld refinements of the data were performed using the FULLPROF program [8]. A TESCAN electron microscope equipped with WDS/EDXS detectors was used for the analysis of the phase content of the synthesized alloys. For the structure investigation a prismatic single crystal, of metallic gray appearance, was isolated from the TlSb₃Se₅ alloy by mechanical fragmentation. Single-crystal diffraction data were collected at room temperature using a four-circle diffractometer (Xcalibur Oxford Diffraction) with a CCD detector (graphite-monochromatized Mo Kαradiation, $\lambda = 0.071073$ nm). Scans were made in the ω -mode; empirical absorption corrections were made by CrysAlis RED [9]. The crystal structure of the ternary compound investigated in the present work was successfully solved by direct methods and refined using SHELX-97 package programs [10]. The composition refined from the single-crystal X-ray data was $Tl_{10.3}Sb_{33.7}Se_{56.00}$. composition Tl_{11.2}Sb_{34.6}Se_{54.2} obtained by EPMA agrees well with the XRD data, the difference being less than 2 at.%

Results and discussion

A detailed investigation of the crystal structure was carried out on an alloy of the composition $Tl_{11}Sb_{33}Se_{56}$. According to the phase analysis by X-ray powder diffraction, scanning electron microscopy and electron probe microanalysis, the prepared alloy consisted of two phases: $TlSbSe_2$ and $TlSb_3Se_5$ (Fig. 1a,b). The DTA curve of the sample (Fig. 2) exhibits two endothermic peaks at 705 K and 739 K. The first peak is likely to correspond to the peritectic reaction $TlSb_3Se_5 \leftrightarrow L + Sb_2Se_3$. The second peak, at 739 K, corresponds to primary crystallization of the Sb_2Se_3 phase. The crystal structure of the $TlSbSe_2$ phase is monoclinic with space group $P2_1$ and

the unit cell parameters refined by X-ray powder diffraction were: a = 9.1356(8) Å, b = 4.0924(4) Å, $c = 12.617(1) \text{ Å}, \quad \beta = 110.503(7)^{\circ}.$ The crystal structure of TlSb₃Se₅ was investigated by singlecrystal X-ray diffraction. The obtained single crystal data (Table 1) showed that the title compound crystallizes with a monoclinic structure (space group $P2_1/m$) in which all the atoms are located on sites in Wyckoff position 2e. The refined positional and thermal displacement parameters are given Table 2 and Table 3. The structure of the title compound is closely related to the structure of K_{2.5}Sb_{8.5}Se₁₄ [11], in which several sites are positionally disordered with the following ratios: Sb5/K1 (16/84); Sb7/K3 (48/52); Se2/Se2' (62/38); Se4/Se4' (70/30); Se6/Se6' (48/52). The potassium and antimony atoms form statistical mixtures, while part of the selenium atoms occupy pairs of split positions. Compared to the structure of K_{2.5}Sb_{8.5}Se₁₄, the structure of the title compound is more ordered, because the selenium atoms do not form split positions. Sb4/Tl4 and Sb5/Tl5 form statistical mixtures with the occupation ratio 86/14. The pairs Tl2/Sb2 (67/33) and Tl3/Sb3 (64/36) also form split positions. It should be noted that this disordered model provides better refinements than the structure model proposed by Xu Jianxiao et al., which has only two split Tl/Sb positions [7]. The content of one unit cell and the coordination polyhedra of the atoms are shown in Fig. 3. The coordination polyhedra around the thallium atoms are trigonal prisms with two or three additional selenium atoms that center lateral faces. All of the antimony atoms are enclosed in deformed Se₆ octahedra. The arrangement of the polyhedra described above is shown in Fig. 4. The selenium atoms have three kinds of coordination polyhedron: octahedron (Se12, Se14, Se19 and Se21), trigonal bipyramid (Se17 and Se18), and tetrahedron (the rest of the Se atoms). The arrangement of these polyhedra in the unit cell is shown in Fig. 5. The interatomic distances are given in Table 4.

As in the case of other selenides of thallium and antimony, for TlSb₃Se₅ the following formal charges should be assigned: 1+ for the thallium atoms, 3+ for the antimony atoms and 2- for the selenium atoms. Hence, the charge-balanced formula can be written as $[(Tl^+)(Sb^{3+})_3][(Se^{2-})_5]$. The crystal chemical analysis shows that the selenium and bismuth atoms form a negatively charged polyanionic network, the charge of which is compensated by the thallium cations (Fig. 6). This assumption is confirmed by the results of calculations of the electronic structure. The data of electronic structure calculations using the TB-LMTO-ASA approach [12] show high values of the electron localization function (ELF) around the selenium and antimony atoms and much lower ELF values around the thallium atoms (Fig. 7a). Isosurfaces of the electron localization function for the title compound are shown in Fig. 7b. Strong chemical bonding exists within the network of Sb-Se interactions with



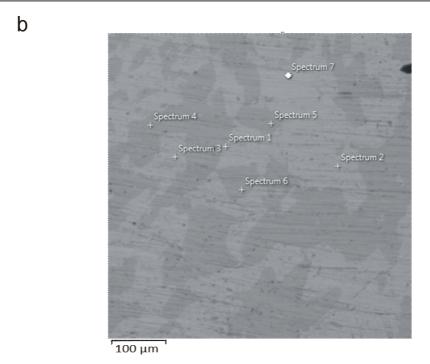


Fig. 1 X-ray powder diffraction pattern (a), scanning electron microscopy and electron probe microanalysis data (b): gray phase - TlSb₃Se₅, dark gray phase - TlSbSb₂.

interatomic distances ranging from $d=2.602\,\text{Å}$ to $d=2.761\,\text{Å}$, where the integrated crystal orbital Hamilton population (iCOHP) takes values between -iCOHP = $3.004\,\text{eV}$ and -iCOHP = $1.457\,\text{eV}$ (Fig. 8). The interaction between Tl and Se atoms for the range of interatomic distances from $d=3.114\,\text{Å}$ to $d=3.283\,\text{Å}$ is much weaker and iCOHP varies from -iCOHP = $0.347\,\text{eV}$ to -iCOHP = $0.294\,\text{eV}$. These data confirm our assumption that the selenium and antimony atoms form a complex polyanion.

Acknowledgements

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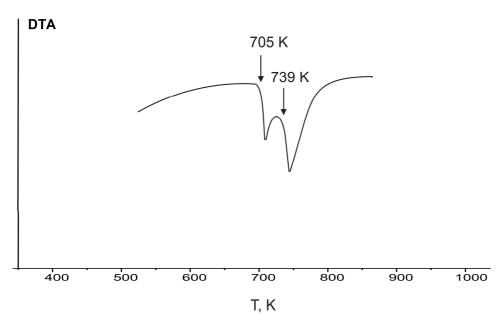


Fig. 2 DTA curve of the TlSb₃Se₅ sample.

Table 1 Structure data and data collection.

Crystal data				
$Tl_{2.59}Sb_{8.41}Se_{14}$	F(000) = 2229			
$M_{\rm r} = 5316.41$	$D_{\rm x} = 6.312 \; {\rm Mg \; m^{-3}}$			
Monoclinic, $P2_1/m$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ Å}$			
a = 17.1847(5) Å	Cell parameters from 2874 reflections			
b = 4.07227(17) Å	$\theta = 2.0 - 25.2^{\circ}$			
c = 21.1856(7) Å	$\mu = 41.02 \text{ mm}^{-1}$			
$\beta = 109.381(4)^{\circ}$	T = 293 K			
$V = 1398.57 (9) \text{ Å}^3$	Prism, metallic grey			
<u>Z</u> = 1	$0.14 \times 0.06 \times 0.04 \text{ mm}$			

Data collection				
Oxford Diffraction Xcalibur3 CCD diffractometer	2874 independent reflections			
Radiation source: fine-focus sealed tube	2545 reflections with $I > 2\sigma(I)$			
Graphite monochromator	$R_{\rm int} = 0.025$			
ω scans	$\theta_{\text{max}} = 25.2^{\circ}, \ \theta_{\text{min}} = 2.0^{\circ}$			
Absorption correction: analytical [9]	$h = -20 \rightarrow 20$			
	$k = -4 \rightarrow 4$ $l = -25 \rightarrow 25$			
5748 measured reflections	$l = -25 \rightarrow 25$			

Refinement				
Refinement on F^2	Primary atom site location: structure-invariant direct			
	methods			
Least-squares matrix: full	Secondary atom site location: difference Fourier map			
$R[F^2 > 2\sigma(F^2)] = 0.033$	$w = 1/[\sigma^2(F_0^2) + (0.0333P)^2]$, where $P = (F_0^2 + 2F_c^2)/3$			
$wR(F^2) = 0.079$	$(\Delta/\sigma)_{\text{max}} = 0.001$			
S = 1.02	$\Delta \rho_{\text{max}} = 1.63 \text{ e Å}^{-3}$			
2874 reflections	$\Delta \rho_{\min} = -1.99 \text{ e Å}^{-3}$			
163 parameters	Extinction correction [10]:			
	$k[1 + 0.001 \times F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$			
0 restraints	Extinction coefficient: 0.00086(5)			

Table 2 Fractional positional coordinates and equivalent isotropic displacement parameters (\mathring{A}^2).

Atom	X	у	z	$U_{ m eq}$	Occ. (<1)
T11	0.92490(3)	1/4	0.85792(3)	0.02391(16)	
T12	0.16139(4)	1/4	0.78867(6)	0.0172(3)	0.666(3)
Sb2	0.15552(17)	1/4	0.8175(2)	0.0172(3)	0.334(3)
T13	0.64374(7)	1/4	0.69453(5)	0.0201(3)	0.637(3)
Sb3	0.6831(2)	1/4	0.71075(16)	0.0201(3)	0.363(3)
Sb4	0.37100(4)	1/4	0.11827(4)	0.01317(18)	0.86
T14	0.37100(4)	1/4	0.11827(4)	0.01317(18)	0.14
Sb5	0.61126(4)	1/4	0.07252(4)	0.01260(18)	0.86
T15	0.61126(4)	1/4	0.07252(4)	0.01260(18)	0.14
Sb6	0.42310(4)	1/4	0.77521(4)	0.01105(19)	
Sb7	0.15778(5)	1/4	0.35737(4)	0.0144(2)	
Sb8	0.83525(4)	1/4	0.01892(4)	0.01014(19)	
Sb9	0.02687(4)	1/4	0.58937(4)	0.01257(19)	
Sb10	0.40633(5)	1/4	0.50879(5)	0.0155(2)	
Sb11	0.77531(5)	1/4	0.43449(5)	0.0184(2)	
Se12	0.71113(9)	1/4	0.56659(9)	0.0300(4)	
Se13	0.46776(6)	1/4	0.24332(6)	0.0114(3)	
Se14	0.28665(7)	1/4	0.94550(6)	0.0139(3)	
Se15	0.68340(6)	1/4	0.20166(6)	0.0115(3)	
Se16	0.48405(7)	1/4	0.41796(6)	0.0130(3)	
Se17	0.72279(7)	1/4	0.86086(6)	0.0144(3)	
Se18	0.95589(8)	1/4	0.69860(7)	0.0195(3)	
Se19	0.50815(6)	1/4	0.91103(6)	0.0119(3)	
Se20	0.08290(6)	1/4	0.01128(6)	0.0119(3)	
Se21	0.09482(6)	1/4	0.48387(6)	0.0121(3)	
Se22	0.86110(7)	1/4	0.34541(6)	0.0173(3)	
Se23	0.32993(9)	1/4	0.62818(8)	0.0276(3)	
Se24	0.92748(7)	1/4	0.14729(6)	0.0161(3)	
Se25	0.20855(7)	1/4	0.25316(7)	0.0162(3)	

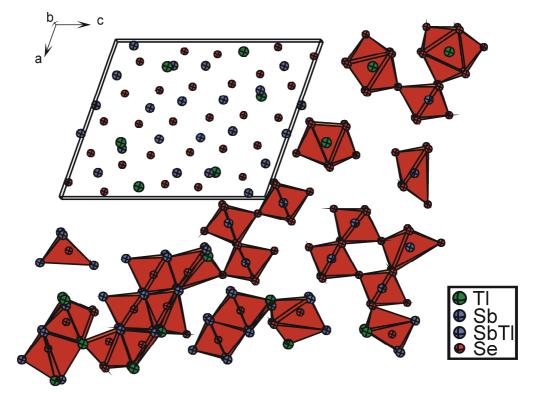


Fig. 3 Projection of the unit cell content and coordination polyhedra of the atoms.

Table 3 Atomic displacement parameters (\mathring{A}^2).

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
T11	0.0183(2)	0.0284(3)	0.0243(3)	0	0.0060(2)	0
T12	0.0150(3)	0.0213(4)	0.0151(6)	0	0.0047(3)	0
Sb2	0.0150(3)	0.0213(4)	0.0151(6)	0	0.0047(3)	0
T13	0.0153(6)	0.0259(4)	0.0164(5)	0	0.0016(4)	0
Sb3	0.0153(6)	0.0259(4)	0.0164(5)	0	0.0016(4)	0
Sb4	0.0092(3)	0.0179(4)	0.0104(4)	0	0.0004(3)	0
T14	0.0092(3)	0.0179(4)	0.0104(4)	0	0.0004(3)	0
Sb5	0.0084(3)	0.0176(4)	0.0103(4)	0	0.0012(3)	0
T15	0.0084(3)	0.0176(4)	0.0103(4)	0	0.0012(3)	0
Sb6	0.0075(3)	0.0155(4)	0.0083(4)	0	0.0000(3)	0
Sb7	0.0113(3)	0.0191(5)	0.0140(4)	0	0.0060(3)	0
Sb8	0.0074(3)	0.0098(4)	0.0154(4)	0	0.0068(3)	0
Sb9	0.0089(3)	0.0174(4)	0.0104(4)	0	0.0020(3)	0
Sb10	0.0127(4)	0.0179(5)	0.0174(4)	0	0.0069(3)	0
Sb11	0.0140(4)	0.0202(5)	0.0189(5)	0	0.0027(3)	0
Se12	0.0237(6)	0.0280(8)	0.0368(9)	0	0.0078(6)	0
Se13	0.0083(5)	0.0160(6)	0.0106(6)	0	0.0040(4)	0
Se14	0.0094(5)	0.0171(6)	0.0174(6)	0	0.0072(4)	0
Se15	0.0064(5)	0.0190(7)	0.0066(6)	0	-0.0013(4)	0
Se16	0.0090(5)	0.0185(7)	0.0089(6)	0	-0.0005(4)	0
Se17	0.0080(5)	0.0185(7)	0.0147(6)	0	0.0012(4)	0
Se18	0.0187(6)	0.0242(8)	0.0137(6)	0	0.0027(5)	0
Se19	0.0082(5)	0.0164(7)	0.0082(6)	0	-0.0013(4)	0
Se20	0.0076(5)	0.0127(6)	0.0166(6)	0	0.0057(4)	0
Se21	0.0076(5)	0.0143(6)	0.0150(6)	0	0.0045(4)	0
Se22	0.0147(5)	0.0253(7)	0.0097(6)	0	0.0010(4)	0
Se23	0.0231(6)	0.0355(9)	0.0227(8)	0	0.0057(5)	0
Se24	0.0156(5)	0.0198(7)	0.0129(6)	0	0.0048(5)	0
Se25	0.0140(5)	0.0195(7)	0.0162(6)	0	0.0065(5)	0

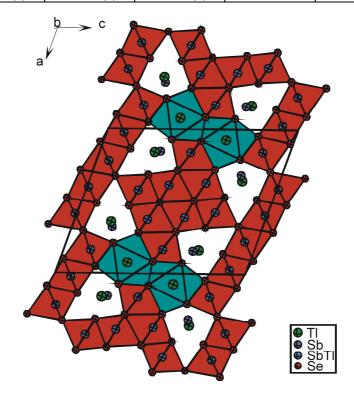


Fig. 4 Arrangement of [(Sb,Tl)Se₆] octahedra and [TlSe₉] tricapped trigonal prisms in the structure of $Tl_{2.59}Sb_{8.41}Se_{14}$.

Table 4 Geometric parameters (Å, °).

T11—Se24 ⁱⁱ 3.2833(10) Sb10—Se16 ^{vi} 2.8570(10) T11—Se24 ⁱⁱⁱ 3.2833(10) Sb10—Se16 ^{vi} 2.8571(10) T12—Se24 ⁱⁱⁱ 3.1136(13) Sb10—Se12 ^{vi} 2.9379(12) T12—Se14 3.3056(16) Sb11—Se22 ^{vii} 2.7533(16) T12—Se15 3.3074(11) Sb11—Se23 ^{vii} 2.7542(11) Sb2—Se24 ⁱⁱⁱ 2.728(3) Se12—Sb10 ^{vii} 2.9379(12) Sb2—Se24 ^{ivii} 2.728(3) Se12—Sb10 ^{vii} 2.9379(12) Sb2—Se24 ^{viii} 2.728(3) Se12—Sb10 ^{vii} 2.9379(12) Sb2—Se24 ^{viii} 2.728(3) Se12—Sb10 ^{vii} 2.9379(12) Sb2—Se24 ^{viii} 2.728(3) Se12—Sb10 ^{viii} 2.9379(12) Sb2—Se24 ^{viii} 2.728(3) Se12—Sb10 ^{viii} 2.9379(12) Sb2—Se24 ^{viiii} 3.1662(12) Se13—Sb6 ^{viiii} 3.0671(12) T13—Se25 ^{viiii} 3.1662(12) Se13—Sb6 ^{viiii} 2.882(19) T13—Se25 ^{viiii} 3.1662(12) Se13—Sb6 ^{viiii} 2.882(19) Sb3—Se25 ^{viiiii} 3.2821(19) Se14—T15 ^{viiii} 2.7954(9) Sb3—Se25 ^{viiiii} 3.033(3) Se14—Sb6 ^{viiii} 2.8862(10) Sb3—Se25 ^{viiiii} 3.023(3) Se15—Sb6 ^{viiiii} 2.8862(10) Sb3—Se27 ^{viiiii} 3.023(3) Se15—Sb6 ^{viiiii} 2.8862(10) Sb4—Se17 ^{viiiii} 2.72226(9) Se16—Sb10 ^{viiii} 2.8862(10) Sb4—Se17 ^{viiiiii} 2.72226(9) Se16—Sb10 ^{viiiii} 2.877(110) Sb5—Se14 ^{viiiii} 2.7953(9) Se17—Tb4 ^{viiiiii} 2.7226(9) Sb5—Se15 ^{viiiii} 2.7992(10) Se18—Sb9 ^{viiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiii}				
T12—Sc24 ^{III} T12—Sc24 ^{IV} 3.1136(13) Sb10—Sc12 ^{IV} 2.9379(12) T12—Sc14 3.3056(16) Sb11—Sc22 ^{III} 3.3056(11) Sb11—Sc23 ^{IV} 2.7533(16) T12—Sc15 3.3074(11) Sb11—Sc23 ^{IV} 3.15(11) Sb1—Sc23 ^{IVI} 2.7542(11) Sb2—Sc24 ^{IVI} 2.728(3) Sc12—Sb10 ^{IVI} 2.9379(12) Sb2—Sc24 ^{IVI} 2.728(3) Sc12—Sb10 ^{IVI} 2.9379(12) Sb2—Sc24 ^{IVI} 2.728(3) Sc12—Sb10 ^{IVI} 2.9379(12) Sb2—Sc14 2.895(4) Sc12—Sb10 ^{IVI} 3.0671(12) Sb2—Sc25 3.1662(12) Sc12—T13 ^{IVI} 3.2820(19) T13—Sc25 3.1662(12) Sc13—Sb6 ^{IVI} 3.2820(19) Sb3—Sc25 2.703(3) Sc14—Sb5 ^{IVI} 2.7954(9) Sb3—Sc25 2.703(3) Sc15—Sb6 ^{IVI} 2.8862(10) Sb3—Sc17 3.033(3) Sc15—Sb6 ^{IVI} 2.8862(10) Sb4—Sc17 2.7225(9) Sc16—Sb10 ^{IVI} 2.851(11) Sb4—Sc17 2.7225(9) Sc16—Sb10 ^{IVI} 2.851(10) Sb5—Sc15 2.6020(14) Sc15—T12 ^{IVI} 3.3075(11) Sb5—Sc15 2.6020(14) Sc15—T12 ^{IVI} 2.7226(9) Sb5—Sc14 2.7953(9) Sc16—Sb10 ^{IVI} 2.7226(9) Sb5—Sc14 2.7953(9) Sc16—Sb10 ^{IVI} 2.7226(9) Sb5—Sc19 ^{IVI} 2.7922(9) Sb13—Sc19 Sc10—Sc19 ^{IVI} 2.7922(9) Sc16—Sb10 ^{IVI} 2.7226(9) Sb5—Sc19 Sc10—Sc19 ^{IVI} 2.7922(9) Sc16—Sb10 ^{IVI} 2.7983(10) Sb5—Sc19 2.9921(10) Sb6—Sc19 2.9921(10) Sc18—Sb9 ^{IVI} 2.9920(10) Sb6—Sc13 2.8822(9) Sc19—T15 ^{IVI} 2.9920(10) Sb6—Sc13 2.8822(9) Sc19—Sb5 ^{IVI} 2.8862(10) Sc10—Sb5 ^{IVI} 2.8862(10) Sc21—Sb9 ^{IVI} 2.9920(10) Sb6—Sc13 2.8862(10) Sc22—Sb8 ^{IVI} 2.9920(10) Sb7—Sc18 2.7983(10) Sc22—Sb9 ^{IVI} 2.9920(10) Sb7—Sc18 2.7983(10) Sc22—Sb9 ^{IVI} 2.953(11) Sb7—Sc18 2.7983(10) Sc22—Sb9 ^{IVI} 2.7953(11) Sb7—Sc12 3.0671(12) Sc22—Sb9 ^{IVI} 2.7953(11) Sc23—Sb9 ^{IVI} 2.7953(11) Sb7—Sc12 3.0671(12) Sc22—Sb9 ^{IVI} 2.7953(11) Sc23—Sb9 ^{IVI} 2.7953(11) Sb7—Sc12 3.0671(12) Sc23—Sb9 ^{IVI} 2.79543(11) Sb8—Sc20 2.66347(15) Sc23—Sb9 ^{IVI} 2.66547(15)	T11—Se24 ⁱ	3.2833(10)	Sb10—Se16	2.8570(10)
T12—Se24 ^{lv} 3.1136(13) Sb10—Se12 st 2.9379(12) T12—Se14 3.3056(16) Sb11—Se22 ^{still} 2.75533(16) T12—Se15 3.3074(11) Sb11—Se23 ^{still} 2.7542(11) Sb2—Se24 ^{lill} 2.728(3) Se12—Sb10 ^{still} 2.9379(12) Sb2—Se24 ^{lill} 2.728(3) Se12—Sb10 ^{still} 2.9379(12) Sb2—Se24 ^{lill} 2.895(4) Se12—Sb10 ^{still} 3.0671(12) Sb2—Se14 2.895(4) Se12—Sb7 ^{still} 3.0671(12) T13—Se25 3.1662(12) Se13—Sb6 ^{still} 2.8821(9) T13—Se25 ^v 3.1662(12) Se13—Sb6 ^v 2.8821(9) T13—Se25 ^v 3.2821(19) Se14—T15 ^v 2.7954(9) Sb3—Se25 2.703(3) Se15—Sb6 ^{lv} 2.8862(10) Sb3—Se25 2.703(3) Se15—Sb6 ^{lv} 2.8862(10) Sb3—Se17 3.023(3) Se15—Sb6 ^{lv} 2.8862(10) Sb4—Se17 2.7225(9) Se16—Sb10 ^{lv} 2.8862(10) Sb4—Se17 2.7225(9) Se16—Sb10 ^{lv} 2.6818(15) Sb4—Se17 2.7225(9) Se16—Sb10 ^{lv} 2.851(10) Sb5—Se15 2.6020(14) Se17—T14 ^{still} 2.7226(9) Sb5—Se14 2.7953(9) Se17—Sb4 ^{still} 2.7226(9) Sb5—Se14 2.7953(9) Se18—Sb7 ^v 2.7983(10) Sb5—Se19 2.9921(10) Se18—Sb7 ^v 2.7983(10) Sb5—Se19 2.9921(10) Se18—Sb7 ^v 2.9920(10) Sb6—Se13 2.8822(9) Se19—T15 ^{lvill} 3.1144(10) Sb6—Se13 2.8822(9) Se19—T15 ^{lvill} 3.1144(10) Sb6—Se13 2.8822(9) Se19—T15 ^{lvill} 3.1144(10) Sb6—Se15 2.8862(10) Se20—Sb8 ^{lvill} 2.9920(10) Sb6—Se15 2.8862(10) Se21—Sb5 ^{lvill} 2.9920(10) Sb6—Se15 2.8862(10) Se21—Sb9 ^{lvill} 3.1144(10) Sb6—Se15 2.8862(10) Se21—Sb9 ^{lvill} 2.9920(10) Sb6—Se15 2.8862(10) Se22—Sb9 ^{lvill} 2.9920(10) Sb6—Se15 2.668(15) Se21—Sb9 ^{lvill} 3.1144(10) Sb6—Se25 3.668(15) Se21—Sb9 ^{lvill} 2.9920(10) Sb7—Se18 2.7983(10) Se22—Sb9 ^{lvill} 2.9619(10) Sb7—Se18 2.7983(10) Se22—Sb9 ^{lvill} 2.9619(10) Sb7—Se18 2.7983(10) Se22—Sb9 ^{lvill} 2.8277(9) Sb8—Se20 2.66704(9) Se23—Sb11 ^{lvill} 2.7543(11) Sb8—Se20 2.		3.2833(10)	Sb10—Se16 ^{vi}	2.8571(10)
T12—Se14 T12—Se15 T12—Se16 T12—Se24 T12—Se24 T12—Se24 T13—Se25 T13—Se26 T13—Se26 T13—Se26 T13—Se26 T13—Se26 T13—Se26 T13—Se26 T13—Se26 T13—Se27 T2754(9) T2754(10) T2754(Tl2—Se24 ⁱⁱⁱ	3.1136(13)	Sb10—Se12 ^{xi}	2.9379(12)
T12—Se15	Tl2—Se24 ^{iv}	3.1136(13)	Sb10—Se12 ^x	2.9379(12)
T12—Se15 ^v Sb2—Se24 ⁱⁱⁱ Sb2—Se24 ^{ivi} Sb2—Se24 ^{ivi} Sb2—Se14 Sb2—Se14 Se12—Sb10 ^{vi} Sb2—Se15 Se12—Sb10 ^{vi} Se12—T13 ^{vi} Se25v Se13—Se25v Se13—Se25v Se13—Se25v Se14—Sb5 ^{vi} Se14—Sb5 ^{vi} Se14—Sb5 ^{vi} Se14—Se15v Se15—Se6iii Se15—Se6iii Se15—Se6iii Se15—Se6iii Se15—Se6iii Se15—Se6iii Se15—Se6iii Se16—Se10v Se15—T12 ^{vi} Se15—T12 ^{vi} Se15—T12 ^{vi} Se15—Se15v Se16—Se10v Se16—Se10v Se16—Se10v Se16—Se10v Se17—Se14 ^{vi} Se17—Se14 ^{vi} Se17—Se14 ^{vi} Se17—Se14 ^{vi} Se17—Se14 ^{vi} Se2725(9) Se18—Se17 Se18—Se19 ^{vi} Se19=Se10v Se19=T15 ^{vii} Se19=Se10v Se19=T15 ^{vii} Se2920(10) Se18—Se19 Se6—Se13 Se282(9) Se19—T15 ^{vii} Se19=Se15 ^{vii} Se29920(10) Se6—Se13 Se282(9) Se19—Se15 ^{vii} Se19=Se15 ^{vii} Se29920(10) Se6—Se13 Se282(9) Se19—Se15 ^{viii} Se29920(10) Se6—Se15 ^{viii} Se2882(10) Se20—Se8 ^{viii} Se21—Se9 ^{viii} Se29Se10(10) Se6—Se15 ^{viii} Se28Se20v Se22—Se11 ^{viii} Se2753(16) Se22—Se11 ^{viii} Se2753(16) Se22—Se11 ^{viii} Se2753(16) Se22—Se11 ^{viii} Se2753(16) Se27—Se18v Se277(10) Se27580 ^{viii} Se27580 ^{viii} Se27580 ^{viiii} Se27580 ^{viii} Se2758	T12—Se14	3.3056(16)	Sb11—Se22 ^{xii}	2.7533(16)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Tl2—Se15	3.3074(11)	Sb11—Se23 ^x	2.7542(11)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Tl2—Se15 ^v	3.3075(11)	Sb11—Se23 ^{vii}	2.7542(11)
Sb2—Se14 2.895(4) Se12—Sb7 ^{vi} 3.0671(12) T13—Se25 3.1662(12) Se12—T13 ^{vi} 3.2820(19) T13—Se25 ^{vi} 3.1662(12) Se13—Sb6 ^{vi} 2.8821(9) T13—Se25 ^{vi} 3.2821(19) Se14—T15 ^{vi} 2.7954(9) Sb3—Se25 ^{vi} 2.703(3) Se14—Sb5 ^{vi} 2.7954(9) Sb3—Se25 ^{vi} 2.703(3) Se15—Sb6 ^{vii} 2.8862(10) Sb4—Se17 3.023(3) Se15—Sb6 ^{viii} 2.8862(10) Sb4—Se13 2.6192(14) Se15—T1 ^{viii} 3.3075(11) Sb4—Se17 2.7226(9) Se16—Sb10 ^{viii} 2.6818(15) Sb4—Se17 ^{viii} 2.7226(9) Se16—Sb10 ^{viii} 2.8871(10) Sb5—Se15 2.6020(14) Se17—T14 ^{viiii} 2.7226(9) Sb5—Se14 ^{viiii} 2.7953(9) Se18—Sb7 ^{viii} 2.7983(10) Sb5—Se19 ^{viiii} 2.9921(10) Se18—Sb9 ^{viii} 2.9923(16) Sb6—Se19 ^{viiii} 2.9921(10) Se19—T15 ^{viii} 2.9920(10) Sb6—Se13 ^{viii} 2.8862(10) Se19—T15 ^{viiii} 2.9920(10) Sb	Sb2—Se24 ⁱⁱⁱ	2.728(3)	Se12—Sb10 ^{xi}	2.9379(12)
TI3—Se25 TI3—Se25' 3.1662(12) Se13—Sb6' Se14—TI5' Se12" Se32821(19) Se14—TI5' Se33—Se25' Se33—Se25 Se33—Se25 Se33—Se25' Se33—Se25' Se33—Se25' Se33—Se25' Se33—Se25' Se33—Se26' Se33—Se26' Se34—Se36' Se34—Se36' Se34—Se36' Se34—Se36' Se3882(10) Sb3—Se27' Se34—Se36' Se3882(10) Sb3—Se17 Se303(3) Se15—Sb6'' Se3882(10) Sb4—Se13 Se15—Sb6'' Se3882(10) Sb4—Se13 Se16—Sb10' Se15—TI2'' Se4—Se17 Se4—Se17' Se4—Se17' Se4—Se17' Se4—Se17' Se4—Se17' Se4—Se17' Se5—Se16—Sb10' Se5—Se15 Se5—Se14 Se7—Sb4'' Se17—TI4'' Se7—Sb4'' Se7—Se44'' Se30—Se36' Se38—Sb7' Se30—Se36' Se5—Se19'' Se30—Se36' Se30—Se49' Se4—Se59'' Se30—TI5'' Se4—Se50'' Se4—Se50'' Se6—Se13 Se30—TI5'' Se4—Se50'' Se6—Se13 Se30—Se40(10) Se40—TI5'' Se6—Se13 Se6—Se13'' Se822(9) Se19—Sb5'' Se19—Sb5'' Se9920(10) Sb6—Se13 Se822(9) Se19—Sb5'' Se9920(10) Sb6—Se13'' Se822(9) Se19—Sb5'' Se19—Sb5'' Se9920(10) Sb6—Se15'' Se6—Se15'' Se820—Sb8'' Se30—Sb8'' Se30—Sb8'' Se44(15) Sb7—Se25 Se30—Sb8'' Se44(15) Sb7—Se25 Se30—Sb8'' Se21—Sb9''' Se3—Se17'' Se33(10) Sb7—Se18 Se7—Se12' Se30-Sb11''' Se22—Sb9''' Se23—Sb11''' Sb8—Se20' Se3—Sb11''' Se23—Sb11''' Sb8—Se20 Se3—Sb11''' Se23—Sb11''' Se3—Se37(11) Sb8—Se20' Se3—Sb11''' Se24—Sb8''' Se24—Sb8''' Se3—Sb11''' Se3—Se3—Sb11''' Se25—Sb9''' Se23—Sb11''' Se25—Sb9''' Se23—Sb11''' Se25—Sb9''' Se23—Sb11''' Se3—Sb11''' Se3—Se3—Sb11''' Se3—Se3—	Sb2—Se24 ^{iv}	2.728(3)	Se12—Sb10 ^x	2.9379(12)
T13—Se25°	Sb2—Se14	2.895(4)	Se12—Sb7 ^{vi}	3.0671(12)
T13—Se12 ^v Sb3—Se25 Sb3—Se25 Sc2703(3) Se14—Sb5 ^v Se14—Sb6 ^v Sb3—Se25 Sc2703(3) Se15—Sb6 ⁱⁱⁱ Sb3—Se17 Sc28862(10) Sb3—Se17 Sb4—Se13 Sc4—Sc5 ^v Sc4—Sb6 ⁱⁱⁱ Sb4—Se17 Sc4—Sc5 ^v Sc5—Sc6 ⁱⁱⁱ Sc6—Sc618(15) Sb4—Se17 Sc6—Sc6—Sc6—Sc6—Sc6—Sc6—Sc6—Sc6—Sc6—Sc6—	Tl3—Se25	3.1662(12)	Se12—Tl3 ^{vi}	3.2820(19)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Tl3—Se25 ^v	3.1662(12)	Se13—Sb6 ^v	2.8821(9)
Sb3—Se25° 2.703(3) Se15—Sb6 ^{iiv} 2.8862(10) Sb3—Se17 3.023(3) Se15—Sb6 ⁱⁱⁱ 2.8862(10) Sb4—Se13 2.6192(14) Se15—Tl2 ^{vi} 3.3075(11) Sb4—Se17 2.7225(9) Se16—Sb10 ^x 2.6818(15) Sb4—Se17 ^v 2.7226(9) Se16—Sb10 ^v 2.8571(10) Sb5—Se15 2.6020(14) Se17—Tl4 ^{vi} 2.7226(9) Sb5—Se14 2.7953(9) Se18—Sb7 ^{vi} 2.7226(9) Sb5—Se14 ^{vii} 2.7953(9) Se18—Sb9 ⁱⁱⁱ 2.7983(10) Sb5—Se19 ^{ivii} 2.9921(10) Se18—Sb9 ⁱⁱⁱ 2.9523(16) Sb5—Se19 ^{iviii} 2.9921(10) Se19—Tl5 ^{iviii} 2.9920(10) Sb6—Se19 2.7613(14) Se19—Sb5 ^{iviii} 2.9920(10) Sb6—Se13 ^{viiii} 2.8822(9) Se19—Tl5 ^{ivii} 2.9920(10) Sb6—Se15 ^{ivii} 2.8862(10) Se19—Sb5 ^{iviii} 2.9920(10) Sb6—Se15 ^{ivii} 2.8862(10) Se21—Sb8 ^{viii} 2.6704(9) Sb7—Se18 2.7983(10) Se21—Sb9 ^{viii} 2.8446(15) Sb7—Se18 </td <td>T13—Se12^v</td> <td>3.2821(19)</td> <td>Se14—Tl5^v</td> <td>2.7954(9)</td>	T13—Se12 ^v	3.2821(19)	Se14—Tl5 ^v	2.7954(9)
Sb3—Se17 3.023(3) Se15—Sb6 ⁱⁱⁱ 2.8862(10) Sb4—Se13 2.6192(14) Se15—Tl2 ^{vi} 3.3075(11) Sb4—Se17 2.7225(9) Se16—Sb10 ^x 2.6818(15) Sb4—Se17 ^v 2.7226(9) Se16—Sb10 ^v 2.8571(10) Sb5—Se15 2.6020(14) Se17—Tl4 ^{vi} 2.7226(9) Sb5—Se14 2.7953(9) Se17—Sb4 ^{vi} 2.7226(9) Sb5—Se19 ^{iv} 2.7953(9) Se18—Sb7 ^v 2.7983(10) Sb5—Se19 ^{ivi} 2.9921(10) Se18—Sb9 ⁱⁱⁱ 2.9523(16) Sb5—Se19 ^{ivi} 2.9921(10) Se19—Tl5 ^{ivi} 2.9920(10) Sb6—Se19 2.7613(14) Se19—Sb5 ^{ivi} 2.9920(10) Sb6—Se13 2.8822(9) Se19—Tl5 ^{ivi} 2.9920(10) Sb6—Se13 ^{viiii} 2.8862(10) Se19—Sb5 ^{iviii} 2.9920(10) Sb6—Se15 ^{viiiii} 2.8862(10) Se19—Tl4 ^{viiiii} 3.1144(10) Sb6—Se23 2.9928(17) Se21—Sb9 ^{iviii} 2.8446(15) Sb7—Se18 ^{viiii} 2.7983(10) Se21—Sb9 ^{iviii} 2.9619(10) Sb7—Se18 <td>Sb3—Se25</td> <td>2.703(3)</td> <td>Se14—Sb5^v</td> <td>2.7954(9)</td>	Sb3—Se25	2.703(3)	Se14—Sb5 ^v	2.7954(9)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Sb3—Se25 ^v	2.703(3)	Se15—Sb6 ^{iv}	2.8862(10)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Sb3—Se17	3.023(3)	Se15—Sb6 ⁱⁱⁱ	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Sb4—Se13	2.6192(14)	Se15—Tl2 ^{vi}	3.3075(11)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Sb4—Se17	2.7225(9)	Se16—Sb10 ^x	2.6818(15)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Sb4—Se17 ^v	2.7226(9)	Se16—Sb10 ^v	2.8571(10)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Sb5—Se15	2.6020(14)	Se17—Tl4 ^{vi}	2.7226(9)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Sb5—Se14	2.7953(9)		2.7226(9)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Sb5—Se14 ^{vi}	2.7953(9)	Se18—Sb7 ^v	2.7983(10)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Sb5—Se19 ^{iv}	2.9921(10)	Se18—Sb9 ⁱⁱ	2.9523(16)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Sb5—Se19 ⁱⁱⁱ	2.9921(10)	Se19—Tl5 ^{iv}	2.9920(10)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Sb6—Se19	2.7613(14)	Se19—Sb5 ^{iv}	2.9920(10)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Sb6—Se13	2.8822(9)	Se19—T15 ⁱⁱⁱ	2.9920(10)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Sb6—Se13 ^{vi}	2.8822(9)	Se19—Sb5 ⁱⁱⁱ	2.9920(10)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Sb6—Se15 ^{iv}	2.8862(10)	Se19—Tl4 ^{vi}	3.1144(10)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Sb6—Se15 ⁱⁱⁱ	2.8862(10)		2.6704(9)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Sb6—Se23	2.9928(17)	Se21—Sb9 ^{vii}	2.8446(15)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Sb7—Se25	2.6189(15)	Se21—Sb9 ⁱⁱ	2.9619(10)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Sb7—Se18 ^{vi}	2.7983(10)	Se21—Sb9 ^{xiii}	2.9619(10)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Sb7—Se18	2.7983(10)	Se22—Sb11 ^{xiv}	2.7533(16)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Sb7—Se12 ^v	3.0671(12)	Se22—Sb9 ⁱⁱⁱ	2.8277(10)
Sb8—Se20 2.6704(9) Se23—Sb11 ^{vii} 2.7543(11) Sb8—Se20 ^v 2.6704(9) Se24—Sb8 ^{iv} 2.6547(15)	Sb7—Se12	3.0671(12)	Se22—Sb9 ^{iv}	2.8277(9)
Sb8—Se20 ^v 2.6704(9) Se24—Sb8 ^{iv} 2.6547(15)	Sb8—Se24 ^{iv}	2.6547(15)	Se23—Sb11 ^x	2.7543(11)
	Sb8—Se20	2.6704(9)	Se23—Sb11 ^{vii}	2.7543(11)
Sb9—Se22 ⁱⁱⁱ 2.8277(9) Se24—Sb2 ⁱⁱⁱ 2.728(3)	Sb8—Se20 ^v	2.6704(9)	Se24—Sb8 ^{iv}	2.6547(15)
	Sb9—Se22 ⁱⁱⁱ	2.8277(9)		2.728(3)
Sb9—Se22 ^{iv} 2.8277(9) Se24—Sb2 ^{iv} 2.728(3)	Sb9—Se22 ^{iv}	2.8277(9)		2.728(3)
Sb9—Se21 ^{vii} 2.8445(15) Se24—Tl2 ⁱⁱⁱ 3.1135(13)		2.8445(15)		3.1135(13)
Sb9—Se18 ^{viii} 2.9523(16) Se24—Tl2 ^{iv} 3.1135(12)		2.9523(16)	Se24—T12 ^{iv}	3.1135(12)
Sb9—Se21 ^{viii} 2.9619(10) Se24—T11 ^{xv} 3.2833(10)				3.2833(10)
Sb9—Se21 ^{ix} 2.9619(10) Se24—T11 ^{viii} 3.2833(10)		2.9619(10)		3.2833(10)
Sb10—Se16 ^x 2.6819(15) Se25—Sb3 ^{vi} 2.703(3)	Sb10—Se16 ^x	2.6819(15)		2.703(3)
Se25—T13 ^{vi} 3.1662(12)			Se25—T13 ^{vi}	3.1662(12)

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

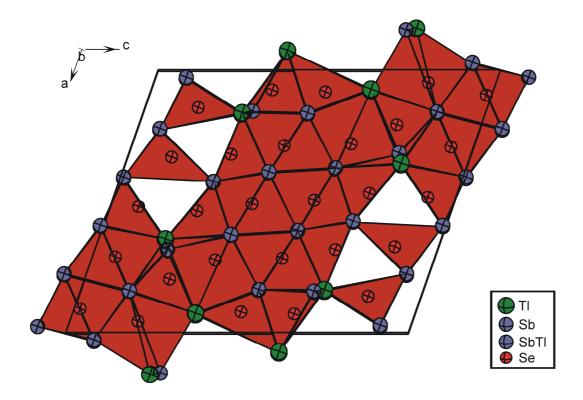


Fig. 5 Arrangement of Se-centered octahedra (Se12, Se14, Se19, and Se21), trigonal bipyramids (Se17 and Se18) and tetrahedra (remaining Se atoms) in the unit cell.

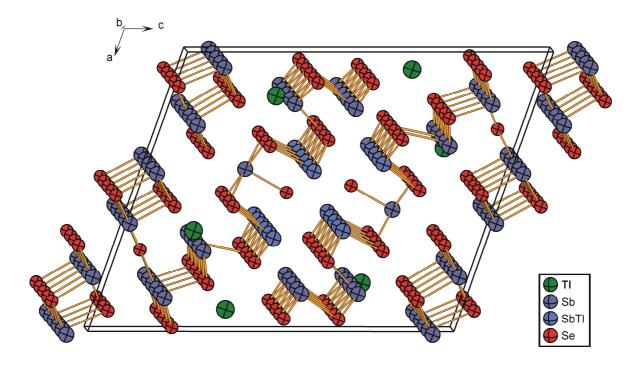
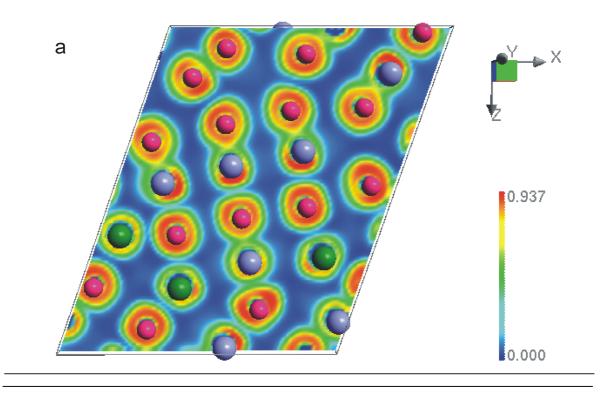


Fig. 6 Polyanionic 3D-network of selenium and antimony atoms.



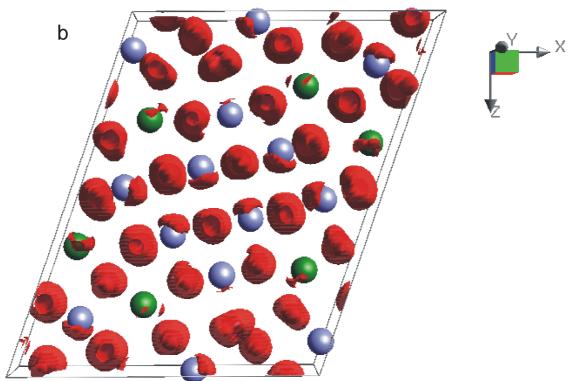


Fig. 7 Electron localization function (ELF) mapping (a) and isosurfaces of the electron localization function around the atoms (b) for the title compound.

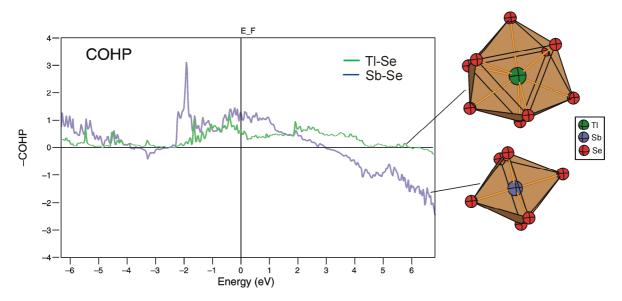


Fig. 8 -iCOHP curves from TB-LMTO-ASA calculations. It is shown polyhedra for which examined the interaction between atoms.

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