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Thallium(I) copper(I) thorium(IV) triselenide, TlCuThSe_3

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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{Se}-\text{Cu}) = 0.001$ Å; R factor = 0.021; wR factor = 0.046; data-to-parameter ratio = 19.8.

Thallium(I) copper(I) thorium(IV) triselenide, TlCuThSe_3 , crystallizes with four formula units in the space group $Cmcm$ in the KCuZrS_3 structure type. There is one crystallographically independent Th, Tl, and Cu atom at a site of symmetry $2/m..$, $m2m$, and $m2m$, respectively. There are two crystallographically independent Se atoms at sites of symmetry $m..$ and $m2m$. The structure consists of sheets of edge-sharing ThSe_6 octahedra and CuSe_4 tetrahedra stacked parallel to the (010) face, separated by layers filled with chains of Tl running parallel to [100]. Each Tl is coordinated by a trigonal prism of Se atoms.

Related literature

For compounds of type $AMM'Q_3$, see: Pell & Ibers (1996); Klepp & Gurtner (1996) for $A = \text{Tl}$; Pell *et al.* (1997); Yao *et al.* (2008); Wells *et al.* (2009) for $M = \text{Ag}$; Bugaris & Ibers (2009) for $M = \text{Au}$; Mansuetto *et al.* (1993); Pell & Ibers (1996) for $M' = \text{Ti}$; Mansuetto *et al.* (1992, 1993); Huang *et al.* (2001); Pell *et al.* (1997) for $M' = \text{Zr}$; Klepp & Sturmayer (1997, 1998); Pell *et al.* (1997) for $M' = \text{Hf}$; Seldy *et al.* (2005); Narducci & Ibers (2000) for $M' = \text{Th}$; Yao *et al.* (2008); Sutorik *et al.* (1996); Bugaris & Ibers (2009); Huang *et al.* (2001); Cody & Ibers (1995) for $M' = \text{U}$; Wells *et al.* (2009) for $M' = \text{Np}$. For computational details, see: Gelato & Parthé (1987). For additional synthetic details, see: Witt *et al.* (1956).

Experimental

Crystal data

TlCuThSe_3	$V = 643.02(5) \text{ \AA}^3$
$M_r = 736.83$	$Z = 4$
Orthorhombic, $Cmcm$	Mo $K\alpha$ radiation
$a = 4.1678(2) \text{ \AA}$	$\mu = 68.19 \text{ mm}^{-1}$
$b = 14.2227(7) \text{ \AA}$	$T = 100 \text{ K}$
$c = 10.8476(5) \text{ \AA}$	$0.10 \times 0.07 \times 0.02 \text{ mm}$

Data collection

Bruker APEXII CCD diffractometer	7476 measured reflections
Absorption correction: numerical (<i>SADABS</i> ; Sheldrick, 2008b)	474 independent reflections
$T_{\min} = 0.101$, $T_{\max} = 0.489$	451 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.032$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.021$	24 parameters
$wR(F^2) = 0.046$	$\Delta\rho_{\max} = 2.01 \text{ e \AA}^{-3}$
$S = 1.59$	$\Delta\rho_{\min} = -1.34 \text{ e \AA}^{-3}$
474 reflections	

Table 1

Selected bond lengths (Å).

Th1—Se2 ⁱ	2.8844 (4)	Tl1—Se1 ^{viii}	3.3564 (6)
Th1—Se2	2.8844 (4)	Tl1—Se1 ^{vi}	3.3564 (6)
Th1—Se1 ⁱⁱ	2.9057 (5)	Tl1—Se1 ^{ix}	3.3564 (6)
Th1—Se1 ⁱⁱⁱ	2.9057 (5)	Tl1—Se1 ^{vii}	3.3564 (6)
Th1—Se1 ^{iv}	2.9057 (5)	Cu1—Se1	2.4617 (11)
Th1—Se1 ^v	2.9057 (5)	Cu1—Se1 ^x	2.4617 (11)
Tl1—Se2 ^{vi}	3.2831 (9)	Cu1—Se2 ^{vii}	2.5517 (11)
Tl1—Se2 ^{vii}	3.2831 (9)	Cu1—Se2 ^{vi}	2.5517 (11)

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

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008a); molecular graphics: *CrystalMaker* (Palmer, 2009); 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: WM2644).

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supporting information

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Thallium(I) copper(I) thorium(IV) triselenide, TlCuThSe_3

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S1. Comment

Thallium(I) copper(I) thorium(IV) triselenide, TlCuThSe_3 , crystallizes in the KCuZrS_3 structure type. The structure (Figs. 1, 2) is layered and consists of sheets of edge-sharing ThSe_6 octahedra and CuSe_4 tetrahedra stacked parallel to the (010) face separated by layers filled with chains of Tl running parallel to [100]. Each Tl is coordinated by a trigonal prism of Se atoms. Because there are no Se—Se bonds in the structure, oxidation states can be assigned as Tl^+ , Cu^+ , Th^{4+} , and Se^{2-} .

The compound TlCuThSe_3 is of the type $AMM'Q_3$, where A is an alkali metal or thallium, M is a coinage metal, M' is a tetravalent group IV metal or an actinide, and Q is a chalcogen. Including the title compound, 39 such compounds are known (Pell & Ibers, 1996; Klepp & Gurtner, 1996; Pell *et al.*, 1997; Yao *et al.*, 2008; Wells *et al.*, 2009; Bugaris & Ibers, 2009; Sutorik *et al.*, 1996; Huang *et al.*, 2001; Cody & Ibers, 1995; Mansuetto *et al.*, 1993, 1992; Klepp & Sturmayer, 1997, 1998; Seldy *et al.*, 2005; Narducci & Ibers, 2000). In all cases, crystallographic data have been collected on single crystals. Most often, the A site contains an alkali metal and only 6 Tl analogues are known (Pell & Ibers, 1996; Klepp & Gurtner, 1996). The M site contains Cu in 28 analogues, Ag in 7 analogues (Pell *et al.*, 1997; Yao *et al.*, 2008; Wells *et al.*, 2009), and Au in 4 analogues (Bugaris & Ibers, 2009). The tetravalent metal is most often U with 14 analogues (Yao *et al.*, 2008; Sutorik *et al.*, 1996; Bugaris & Ibers, 2009; Huang *et al.*, 2001; Cody & Ibers, 1995), followed by Zr with 9 analogues (Mansuetto *et al.*, 1992, 1993; Huang *et al.*, 2001; Pell *et al.*, 1997), Hf with 5 analogues (Klepp & Sturmayer, 1997, 1998; Pell *et al.*, 1997), Np with 5 analogues (Wells *et al.*, 2009), Th with 4 analogues (Seldy *et al.*, 2005; Narducci & Ibers, 2000), and Ti with 2 analogues (Mansuetto *et al.*, 1993; Pell & Ibers, 1996). This is the first compound of the type $AMM'Q_3$ to contain both Tl and Th.

The compounds fall into three structure types. All the Na analogues, except for NaCuZrS_3 , are of the NaCuTiS_3 type (space group $Pnma$) (Mansuetto *et al.*, 1993; Klepp & Sturmayer, 1997); the compounds TlCuTiTe_3 and RbAgHfTe_3 are of the TlCuTiTe_3 type (space group $P2_1/m$) (Pell & Ibers, 1996; Pell *et al.*, 1997); and the remaining compounds are of the KCuZrS_3 type (space group $Cmcm$).

Interatomic distances in TlCuThSe_3 are listed in Table 1 and are nearly identical to those in the analogues $ACuThSe_3$ ($A = \text{K}, \text{Cs}$) (Narducci & Ibers, 2000). The TlCuThSe_3 Th—Se distances of 2.8844 (4) and 2.9057 (5) Å match those in KCuThSe_3 (2.893 (1) and 2.900 (1) Å) and CsCuThSe_3 (2.878 (1) and 2.906 (1) Å). The Cu—Se distances of 2.4617 (11) and 2.5517 (11) Å also match those in KCuThSe_3 (2.459 (2) and 2.545 (2) Å) and CsCuThSe_3 (2.464 (2) and 2.556 (2) Å).

S2. Experimental

Cu (Aldrich, 99.5%), Tl_2Se (Aldrich, 99.999%), and Se (Cerac, 99.999%) were used as received. Th chunks were powdered according to a literature procedure (Witt *et al.*, 1956). A fused-silica tube was loaded with Th (30 mg, 0.129 mmol), Cu (7.0 mg, 0.110 mmol), Tl_2Se (36.6 mg, 0.075 mmol), and Se (20.4 mg, 0.258 mmol), evacuated to near 10^{-4} Torr, flame sealed, and placed in a computer-controlled furnace. It was heated to 597 K in 3 h, kept at 597 K for 24 h,

heated to 1073 K in 24 h, kept at 1073 K for 96 h, cooled to 597 K in 96 h, cooled to 547 K in 24 h, and then rapidly cooled to 298 K in 3 h. The reaction produced orange-red plates of TlCuThSe_3 . The elemental composition of the crystals was determined to be Tl/Cu/Th/Se in an approximate ratio of 1/1/1/3 on an EDX-equipped Hitachi S-3400 SEM.

S3. Refinement

The structure was standardized by means of the program *STRUCTURE TIDY* (Gelato & Parthé, 1987). The highest peak ($2.0(3) \text{ e } \text{\AA}^{-3}$) is 0.98 \AA from atom Tl1 and the deepest hole ($-1.3(3) \text{ e } \text{\AA}^{-3}$) is 1.96 \AA from atom Se1.

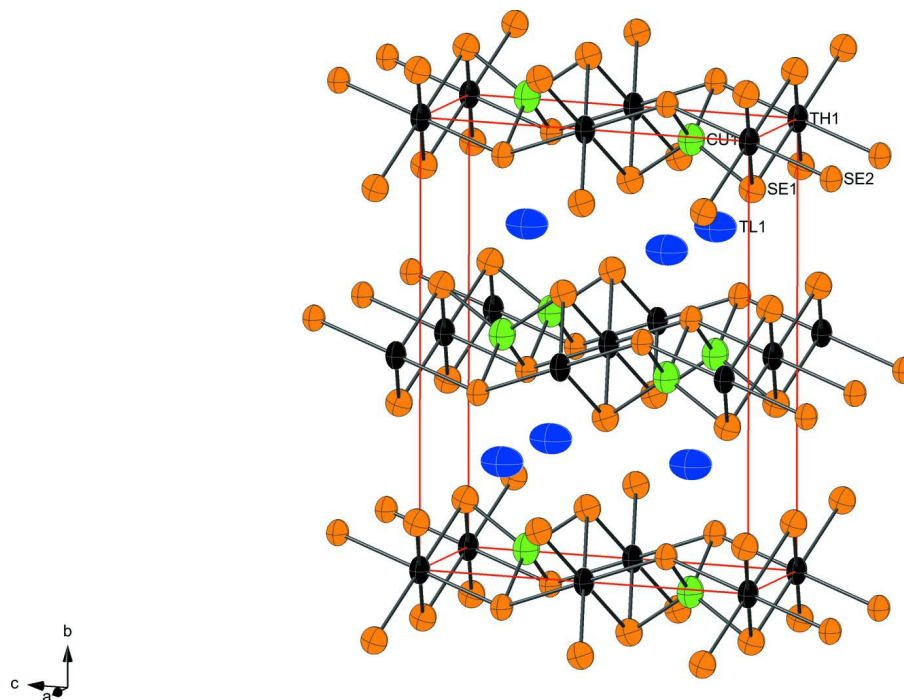


Figure 1

Structure of TlCuThSe_3 viewed approximately down the a -axis. The 95% probability displacement ellipsoids are depicted with the unit cell outlined in red. Color key: black – Th, green – Cu, blue – Tl, orange – Se.

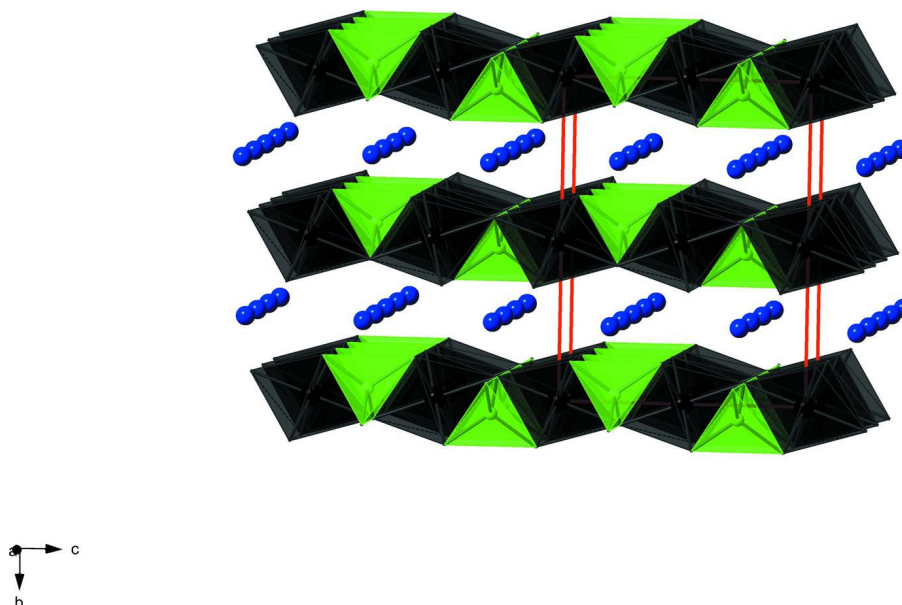


Figure 2

Polyhedral view of TICuThSe₃ showing sheets of edge-sharing ThSe₆ octahedra (black) and CuSe₄ tetrahedra (green) separated by voids filled with Tl (blue). The unit cell is outlined in red.

Thallium(I) copper(I) thorium(IV) triselenide

Crystal data

TiCuThSe₃

$M_r = 736.83$

Orthorhombic, *Cmcm*

Hall symbol: -C 2c 2

$a = 4.1678 (2) \text{ \AA}$

$b = 14.2227 (7) \text{ \AA}$

$c = 10.8476 (5) \text{ \AA}$

$V = 643.02 (5) \text{ \AA}^3$

$Z = 4$

$F(000) = 1208$

$D_x = 7.611 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 1794 reflections

$\theta = 2.9\text{--}28.2^\circ$

$\mu = 68.19 \text{ mm}^{-1}$

$T = 100 \text{ K}$

Rectangular plate, orange

$0.10 \times 0.07 \times 0.02 \text{ mm}$

Data collection

Bruker APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: numerical

(*SADABS*; Sheldrick, 2008*b*)

$T_{\min} = 0.101$, $T_{\max} = 0.489$

7476 measured reflections

474 independent reflections

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

$R_{\text{int}} = 0.032$

$\theta_{\max} = 28.5^\circ$, $\theta_{\min} = 2.9^\circ$

$h = -5 \rightarrow 5$

$k = -18 \rightarrow 18$

$l = -14 \rightarrow 13$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.021$

$wR(F^2) = 0.046$

$S = 1.59$

474 reflections

24 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

$[1.00000 + 0.00000\exp(0.00(\sin\theta/\lambda)^2)] / [\sigma^2(F_o^2) + 0.0000 + 0.0000*P + (0.0193P)^2 + 0.0000\sin\theta/\lambda]$
 where $P = 1.00000F_o^2 + 0.00000F_c^2$
 $(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 2.01 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -1.34 \text{ e } \text{\AA}^{-3}$
 Extinction correction: *SHELXL97* (Sheldrick, 2008a), $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.00066 (7)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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 $F^2 > \sigma(F^2)$ 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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Th1	0.0000	0.0000	0.0000	0.00558 (15)
Tl1	0.0000	0.74746 (3)	0.2500	0.01247 (16)
Se1	0.0000	0.36628 (5)	0.06410 (7)	0.0067 (2)
Se2	0.0000	0.06909 (8)	0.2500	0.0059 (2)
Cu1	0.0000	0.46554 (10)	0.2500	0.0085 (3)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Th1	0.0050 (2)	0.0078 (2)	0.0040 (2)	0.000	0.000	-0.00012 (14)
Tl1	0.0101 (3)	0.0092 (3)	0.0181 (3)	0.000	0.000	0.000
Se1	0.0062 (4)	0.0071 (4)	0.0067 (4)	0.000	0.000	-0.0002 (3)
Se2	0.0069 (5)	0.0064 (5)	0.0043 (5)	0.000	0.000	0.000
Cu1	0.0100 (7)	0.0096 (7)	0.0060 (6)	0.000	0.000	0.000

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

Th1—Se2 ⁱ	2.8844 (4)	Se1—Th1 ^{ix}	2.9057 (5)
Th1—Se2	2.8844 (4)	Se1—Th1 ^{viii}	2.9057 (5)
Th1—Se1 ⁱⁱ	2.9057 (5)	Se1—Tl1 ^v	3.3564 (6)
Th1—Se1 ⁱⁱⁱ	2.9057 (5)	Se1—Tl1 ⁱⁱⁱ	3.3564 (6)
Th1—Se1 ^{iv}	2.9057 (5)	Se1—Tl1 ^{xii}	3.7717 (8)
Th1—Se1 ^v	2.9057 (5)	Se1—Tl1 ^{xiv}	5.6211 (6)
Th1—Cu1 ^{iv}	3.4550 (2)	Se1—Tl1 ^{xv}	5.6211 (6)
Th1—Cu1 ^v	3.4550 (2)	Se2—Cu1 ⁱⁱⁱ	2.5517 (11)
Th1—Cu1 ⁱⁱ	3.4550 (2)	Se2—Cu1 ^v	2.5517 (11)
Th1—Cu1 ⁱⁱⁱ	3.4550 (2)	Se2—Th1 ^{xvi}	2.8844 (4)
Th1—Th1 ^{vi}	4.1678 (2)	Se2—Tl1 ^v	3.2831 (9)
Th1—Th1 ^{vii}	4.1678 (2)	Se2—Tl1 ⁱⁱⁱ	3.2831 (9)
Tl1—Se2 ^{viii}	3.2831 (9)	Se2—Tl1 ^{xvii}	4.5744 (12)
Tl1—Se2 ^{ix}	3.2831 (9)	Cu1—Se1	2.4617 (11)

Tl1—Se1 ^x	3.3564 (6)	Cu1—Se1 ^{xviii}	2.4617 (11)
Tl1—Se1 ^{viii}	3.3564 (6)	Cu1—Se2 ^{ix}	2.5517 (11)
Tl1—Se1 ^{xi}	3.3564 (6)	Cu1—Se2 ^{viii}	2.5517 (11)
Tl1—Se1 ^{ix}	3.3564 (6)	Cu1—Th1 ^{xix}	3.4550 (2)
Tl1—Cu1 ^{ix}	3.7368 (13)	Cu1—Th1 ^{viii}	3.4550 (2)
Tl1—Cu1 ^{viii}	3.7368 (13)	Cu1—Th1 ^{xx}	3.4550 (2)
Tl1—Se1 ^{xii}	3.7717 (8)	Cu1—Th1 ^{ix}	3.4550 (2)
Tl1—Se1 ^{xiii}	3.7717 (8)	Cu1—Tl1 ⁱⁱⁱ	3.7368 (13)
Tl1—Cu1	4.0095 (16)	Cu1—Tl1 ^v	3.7368 (13)
Tl1—Tl1 ^{vii}	4.1678 (2)		
Se2 ⁱ —Th1—Se2	180.0	Th1 ^{ix} —Se1—Tl1 ^v	91.607 (8)
Se2 ⁱ —Th1—Se1 ⁱⁱ	89.89 (2)	Th1 ^{viii} —Se1—Tl1 ^v	156.72 (3)
Se2—Th1—Se1 ⁱⁱ	90.11 (2)	Cu1—Se1—Tl1 ⁱⁱⁱ	78.26 (3)
Se2 ⁱ —Th1—Se1 ⁱⁱⁱ	90.11 (2)	Th1 ^{ix} —Se1—Tl1 ⁱⁱⁱ	156.72 (3)
Se2—Th1—Se1 ⁱⁱⁱ	89.89 (2)	Th1 ^{viii} —Se1—Tl1 ⁱⁱⁱ	91.607 (8)
Se1 ⁱⁱ —Th1—Se1 ⁱⁱⁱ	180.00 (4)	Tl1 ^v —Se1—Tl1 ⁱⁱⁱ	76.761 (17)
Se2 ⁱ —Th1—Se1 ^{iv}	89.89 (2)	Cu1—Se1—Tl1 ^{xii}	170.40 (4)
Se2—Th1—Se1 ^{iv}	90.11 (2)	Th1 ^{ix} —Se1—Tl1 ^{xii}	93.702 (18)
Se1 ⁱⁱ —Th1—Se1 ^{iv}	91.64 (2)	Th1 ^{viii} —Se1—Tl1 ^{xii}	93.702 (18)
Se1 ⁱⁱⁱ —Th1—Se1 ^{iv}	88.36 (2)	Tl1 ^v —Se1—Tl1 ^{xii}	109.076 (17)
Se2 ⁱ —Th1—Se1 ^v	90.11 (2)	Tl1 ⁱⁱⁱ —Se1—Tl1 ^{xii}	109.076 (17)
Se2—Th1—Se1 ^v	89.89 (2)	Cu1—Se1—Tl1 ^{xiv}	131.422 (8)
Se1 ⁱⁱ —Th1—Se1 ^v	88.36 (2)	Th1 ^{ix} —Se1—Tl1 ^{xiv}	125.11 (2)
Se1 ⁱⁱⁱ —Th1—Se1 ^v	91.64 (2)	Th1 ^{viii} —Se1—Tl1 ^{xiv}	60.762 (10)
Se1 ^{iv} —Th1—Se1 ^v	180.00 (4)	Tl1 ^v —Se1—Tl1 ^{xiv}	132.816 (19)
Se2 ^{viii} —Tl1—Se2 ^{ix}	78.80 (3)	Tl1 ⁱⁱⁱ —Se1—Tl1 ^{xiv}	76.051 (8)
Se2 ^{viii} —Tl1—Se1 ^x	141.551 (14)	Tl1 ^{xii} —Se1—Tl1 ^{xiv}	47.856 (6)
Se2 ^{ix} —Tl1—Se1 ^x	89.713 (15)	Cu1—Se1—Tl1 ^{xv}	131.422 (9)
Se2 ^{viii} —Tl1—Se1 ^{viii}	89.713 (15)	Th1 ^{ix} —Se1—Tl1 ^{xv}	60.763 (10)
Se2 ^{ix} —Tl1—Se1 ^{viii}	141.551 (14)	Th1 ^{viii} —Se1—Tl1 ^{xv}	125.11 (2)
Se1 ^x —Tl1—Se1 ^{viii}	119.54 (3)	Tl1 ^v —Se1—Tl1 ^{xv}	76.051 (8)
Se2 ^{viii} —Tl1—Se1 ^{xi}	89.713 (15)	Tl1 ⁱⁱⁱ —Se1—Tl1 ^{xv}	132.816 (19)
Se2 ^{ix} —Tl1—Se1 ^{xi}	141.551 (14)	Tl1 ^{xii} —Se1—Tl1 ^{xv}	47.856 (6)
Se1 ^x —Tl1—Se1 ^{xi}	76.760 (17)	Tl1 ^{xiv} —Se1—Tl1 ^{xv}	95.712 (12)
Se1 ^{viii} —Tl1—Se1 ^{xi}	73.86 (2)	Cu1 ⁱⁱⁱ —Se2—Cu1 ^v	109.50 (7)
Se2 ^{viii} —Tl1—Se1 ^{ix}	141.551 (14)	Cu1 ⁱⁱⁱ —Se2—Th1	78.662 (19)
Se2 ^{ix} —Tl1—Se1 ^{ix}	89.713 (15)	Cu1 ^v —Se2—Th1	78.662 (19)
Se1 ^x —Tl1—Se1 ^{ix}	73.86 (2)	Cu1 ⁱⁱⁱ —Se2—Th1 ^{xvi}	78.662 (19)
Se1 ^{viii} —Tl1—Se1 ^{ix}	76.760 (17)	Cu1 ^v —Se2—Th1 ^{xvi}	78.662 (19)
Se1 ^{xi} —Tl1—Se1 ^{ix}	119.54 (3)	Th1—Se2—Th1 ^{xvi}	140.17 (4)
Se2 ^{viii} —Tl1—Se1 ^{xii}	70.645 (11)	Cu1 ⁱⁱⁱ —Se2—Tl1 ^v	164.65 (4)
Se2 ^{ix} —Tl1—Se1 ^{xii}	70.645 (11)	Cu1 ^v —Se2—Tl1 ^v	85.85 (3)
Se1 ^x —Tl1—Se1 ^{xii}	139.351 (12)	Th1—Se2—Tl1 ^v	105.262 (13)
Se1 ^{viii} —Tl1—Se1 ^{xii}	70.924 (17)	Th1 ^{xvi} —Se2—Tl1 ^v	105.262 (13)
Se1 ^{xi} —Tl1—Se1 ^{xii}	139.351 (11)	Cu1 ⁱⁱⁱ —Se2—Tl1 ⁱⁱⁱ	85.85 (3)
Se1 ^{ix} —Tl1—Se1 ^{xii}	70.924 (17)	Cu1 ^v —Se2—Tl1 ⁱⁱⁱ	164.65 (4)
Cu1 ^{ix} —Tl1—Se1 ^{xii}	110.855 (11)	Th1—Se2—Tl1 ⁱⁱⁱ	105.262 (13)

Cu1 ^{viii} —Tl1—Se1 ^{xii}	110.855 (11)	Th1 ^{xvi} —Se2—Tl1 ⁱⁱⁱ	105.262 (13)
Se2 ^{viii} —Tl1—Se1 ^{xiii}	70.645 (11)	Tl1 ^v —Se2—Tl1 ⁱⁱⁱ	78.80 (3)
Se2 ^{ix} —Tl1—Se1 ^{xiii}	70.645 (11)	Cu1 ⁱⁱⁱ —Se2—Tl1 ^{xvii}	54.75 (3)
Se1 ^x —Tl1—Se1 ^{xiii}	70.924 (17)	Cu1 ^v —Se2—Tl1 ^{xvii}	54.75 (3)
Se1 ^{viii} —Tl1—Se1 ^{xiii}	139.351 (11)	Th1—Se2—Tl1 ^{xvii}	70.08 (2)
Se1 ^{xi} —Tl1—Se1 ^{xiii}	70.924 (17)	Th1 ^{xvi} —Se2—Tl1 ^{xvii}	70.08 (2)
Se1 ^{ix} —Tl1—Se1 ^{xiii}	139.351 (11)	Tl1 ^v —Se2—Tl1 ^{xvii}	140.600 (14)
Cu1 ^{ix} —Tl1—Se1 ^{xiii}	110.855 (11)	Tl1 ⁱⁱⁱ —Se2—Tl1 ^{xvii}	140.600 (14)
Cu1 ^{viii} —Tl1—Se1 ^{xiii}	110.855 (11)	Se1—Cu1—Se1 ^{xviii}	110.01 (7)
Se1 ^{xii} —Tl1—Se1 ^{xiii}	129.21 (3)	Se1—Cu1—Se2 ^{ix}	109.328 (14)
Cu1—Se1—Th1 ^{ix}	79.67 (3)	Se1 ^{xviii} —Cu1—Se2 ^{ix}	109.328 (14)
Cu1—Se1—Th1 ^{viii}	79.67 (3)	Se1—Cu1—Se2 ^{viii}	109.328 (14)
Th1 ^{ix} —Se1—Th1 ^{viii}	91.64 (2)	Se1 ^{xviii} —Cu1—Se2 ^{viii}	109.328 (14)
Cu1—Se1—Tl1 ^v	78.26 (3)	Se2 ^{ix} —Cu1—Se2 ^{viii}	109.51 (7)

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