Crystal structure of the Tl$_4$GeSe$_4$ ternary compound

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The crystal structure of the Tl$_4$GeSe$_4$ compound was determined by X-ray single crystal diffraction. The title compound crystallizes with the Tl$_4$SiSe$_4$ structure type (space group *C2/c*). The Tl$^+$ cations are coordinated by four separate [GeSe$_4$]$^{4-}$ anions, whereas the [GeSe$_4$]$^{4-}$ anion is surrounded by nine Tl$^+$ cations. Strengthening of the cation-anion interactions was observed with respect to the Si-compound.

1. Introduction

Ternary compounds Tl$_4$XY$_4$ are known in the Tl–X–Y systems where X = Si, Ge, Sn and Y = S, Se [1-9]. The crystal structures have been investigated for all of these compounds, except for Tl$_4$GeSe$_4$. The structures are monoclinic and contain isolated [XY$_4$]$^{4-}$ tetrahedra. Tl$_4$SiS$_4$ crystallizes in space group *Cc*, with $a = 12.518(3)$, $b = 11.241(2)$, $c = 7.567(2)$ Å, and $\beta = 112.80(2)°$, $Z = 4$. The compound is isostructural with Tl$_4$GeS$_4$ and contains [SiS$_4$]$^{4-}$ anions held together by Tl$^+$ cations in irregular 6-fold coordination. Tl$_4$SiSe$_4$ crystallizes in space group *C2/c*, with $a = 11.664(9)$, $b = 7.277(4)$, $c = 24.903(12)$ Å, and $\beta = 99.93(5)°$, $Z = 8$ [6]. According to Kulieva and Babanly [3,5], Tl$_4$GeSe$_4$ exists and melts congruently at 661 K.

2. Experimental details

2.1. Synthesis

Tl$_4$GeSe$_4$ was synthesised from binary phases (Tl$_2$Se and GeSe$_2$) in evacuated quartz ampoules at 1043 K, and annealed at 703 K for 96 hours. Thallium(I) selenide and germanium diselenide were prepared from appropriate amounts of high-purity (Tl 99.997 wt.%, Ge 99.9998 wt.%, Se 99.9998 wt.%) elemental solids by encapsulating them under vacuum in quartz ampoules and melting in a flame. Tl$_2$Se obtained this way was annealed at 703 for 24 hours. GeSe$_2$ was annealed for 24 hours at 1043 K, then the

ampoule was turned and again annealed. This procedure was repeated 3-4 times. A Tl$_4$GeSe$_4$ single crystal was obtained using the Bridgman technique.

2.2. X-ray diffraction

Single-crystal X-ray diffraction data for Tl$_4$GeSe$_4$ were collected at room temperature on a four-circle diffractometer Xcalibur Oxford Diffraction equipped with a CCD detector (graphite monochromatized Mo *Kα* radiation). Scans were taken in the ω mode. The crystal structure was successfully solved by direct methods and refined using programs from the SHELX-97 package [10,11].

2.3. Chemical analysis

The weighted (0.1-0.5 g) crystal was dissolved in a 50 ml mixture of concentrated HCl and 30% H$_2$O$_2$. Germanium was extracted by CCl$_4$ and then reextracted by water from the extract. A drop of phenolphthalein was added and then NaOH was added until the solution became pink. The alkali was neutralized by 2-3 drops of 1 *N* HCl, and 2.5 ml 1 *N* HCl was added. The solution was diluted to a volume of 50 ml, 25 ml EDTA was added and the solution was heated at fuming temperature for 15 minutes. The amount of EDTA was titrated by a ZrOCl$_2$ solution using xylenol orange as indicator. Selenium was reduced to the elemental state in a stream of SO$_2$ and weighed after drying. Thallium was oxidized by KIO$_3$ in acid solution and the equivalent point was determined by potentiometric measurements. A platinum electrode was used as indicator electrode and

Table 1 Results of the chemical analysis (mass%).

Compound	Calculated			Observed		
	Tl	Ge	Se	Tl	Ge	Se
Tl$_4$GeSe$_4$	67.8	6.0	26.2	67.7(1)	5.9(1)	26.4(1)

Table 2 Crystallographic data for Tl$_4$GeSe$_4$ and experimental details of the structure determination.

Empirical formula	Tl$_4$GeSe$_4$
Structure type	*Tl$_4$SiSe$_4$*
Formula weight (g/mol)	1205.91
Space group	*C*2/*c* (15)
Pearson symbol	*mS*72
Crystal dimensions (mm^3)	0.11×0.09×0.02
Unit cell dimensions (Å, deg.)	*a* = 11.6700(2)
	b = 7.3170(1)
	c = 25.6030(10)
	β = 106.54(1)
Unit cell volume (Å^3)	2095.76(14)
Number of formula units, *Z*	8
Calculated density, D_x (g/cm^3)	7.644
Absorption coefficient, *μ* (mm^{-1})	77.955
Scan mode	ω
Theta range for data collection (deg.)	3.30 ÷ 26.37
F(000)	2032
Range in *h k l*	-13 ≤ *h* ≤ 13, -8 ≤ *k* ≤ 8, -18 ≤ *l* ≤ 32
Total number of reflections	5606
Independent reflections	2891 (R_{int} = 0.0507)
Reflections with $I > 2\sigma(I)$	2151 (R_{sigma} = 0.0214)
Weighting scheme	$1/[\sigma(F_0)^2 + (0.0386×P)^2 + 31.3272×P]$
Data/parameters	2151/84
Goodness-of-fit on F^2	0.9260
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0147
	wR_2 = 0.0551
Final *R* indices [all data]	R_1 = 0.04172
	wR_2 = 0.0789
Largest electron density peak and hole (e/Å^3)	0.573 and -0.161

a standard calomel electrode as reference electrode. The results of the chemical analysis are given in Table 1.

3. Results and discussion

The analysis of the systematic absences and the statistical test of the distribution of E-values [12] suggest that the structure of Tl$_4$GeSe$_4$ is centrosymmetric. Structure solution and refinement were also performed in the non-centrosymmetric space group *Cc*. The results clearly indicate that Tl$_4$GeSe$_4$ crystallizes in the centrosymmetric space group *C*2/*c*. Table 2 contains crystallographic data and details of the data collection and structure refinement. Atomic parameters and anisotropic displacement parameters are listed in Table 3. A projection of the structure of Tl$_4$GeSe$_4$ onto the *xz* plane is shown in Fig. 1a, emphasizing the packing of [GeSe$_4$] tetrahedra and the shortest distances between Tl$^+$ cations. Each Tl$^+$ cation in the structure is coordinated by four separate [GeSe$_4$]$^{4-}$ anions (Fig. 1b). They adopt slightly different forms of anion coordination, which may, however, all be described as strongly distorted octahedra. The [GeSe$_4$]$^{4-}$ anions are surrounded by nine Tl$^+$ cations in the shape of an irregular coordination polyhedron (Fig. 1c).

A list of interatomic distances is reported in Table 4. The Tl-Tl, Tl-Se and Ge-Se distances do not show considerable deviation from the sums of radii of the components. When we compare the Tl$_4$GeSe$_4$ compound with the Tl$_4$SiSe$_4$ prototype we notice a relative shortening of the Tl-Se distances (2.8654 Å for Tl$_4$GeSe$_4$ but 3.000 Å for Tl$_4$SiSe$_4$), which indicates strengthening of the cation-anion interaction.
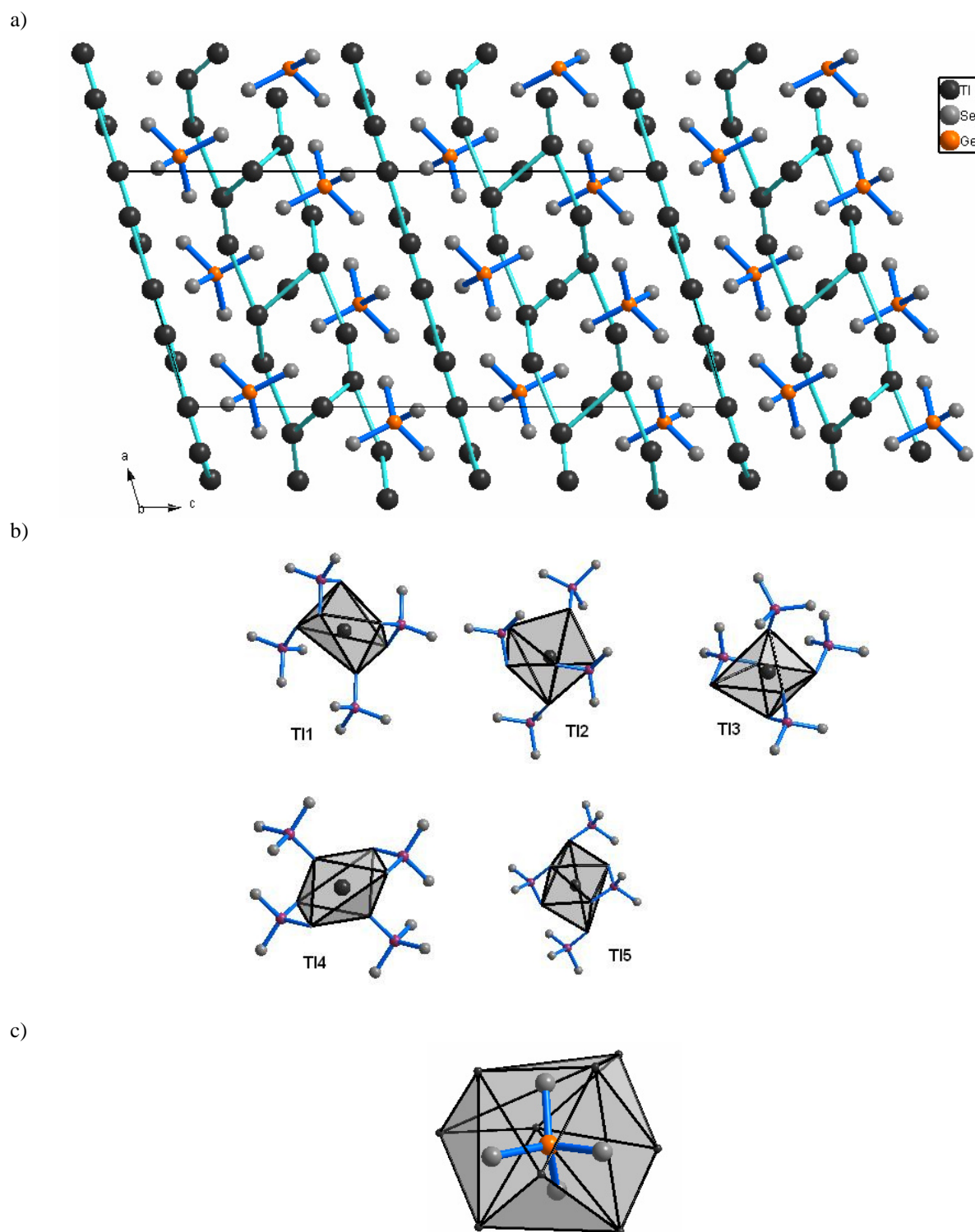
a)

b)

c)

Fig. 1 Crystal structure of Tl$_4$GeSe$_4$ projected on the *xz* plane. Packing of [GeSe$_4$] tetrahedra and Tl$^+$ split nets (a), surrounding of the Tl$^+$ ions by [GeSe$_4$] tetrahedra (b), and surrounding of the [GeSe$_4$] tetrahedra by Tl$^+$ cations (c).

Table 3 Atomic coordinates and displacement parameters (Å²) for Tl₄GeSe₄.

Atom	Wyckoff	x/a	y/b	z/c	U_{eq}
Tl1	8f	0.19374(2)	0.53903(4)	0.00248(1)	0.04637(9)
Tl2	8f	0.38974(3)	0.27749(5)	0.17946(1)	0.0591(1)
Tl3	8f	0.31210(3)	0.37192(4)	0.33578(1)	0.0538(1)
Tl4	4a	0	0	0	0.0813(2)
Tl5	4e	0	0.16948(5)	1/4	0.0496(1)
Se1	8f	0.19790(5)	0.21966(9)	0.08228(3)	0.0402(1)
Se2	8f	0.51317(5)	0.15659(7)	0.07569(2)	0.0310(1)
Se3	8f	0.10385(5)	0.19769(10)	0.38092(3)	0.0423(2)
Se4	8f	0.15477(5)	0.45964(9)	0.21225(2)	0.0379(1)
Ge	8f	0.06410(7)	0.38029(12)	0.12404(3)	0.0526(2)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Tl1	0.03733(15)	0.04239(15)	0.05897(17)	-0.0073(1)	0.01304(11)	0.00104(11)
Tl2	0.04252(16)	0.0594(2)	0.0716(2)	0.00087(13)	0.01016(14)	-0.00916(14)
Tl3	0.05127(17)	0.05009(17)	0.05178(17)	0.01150(12)	0.00125(12)	0.00351(12)
Tl4	0.0460(2)	0.0443(2)	0.1232(5)	-0.0231(2)	-0.0251(3)	0.0263(3)
Tl5	0.0651(2)	0.03818(19)	0.04411(19)	0	0.01301(17)	0
Se1	0.0356(3)	0.0404(3)	0.0417(3)	0.0128(3)	0.0059(2)	-0.0046(3)
Se2	0.0368(3)	0.0136(2)	0.0458(3)	0.01685(19)	0.0166(2)	0.00818(19)
Se3	0.0219(3)	0.0493(4)	0.0539(4)	0.0227(2)	0.0075(2)	-0.0009(3)
Se4	0.0331(3)	0.0404(3)	0.0297(3)	-0.0016(2)	-0.0084(2)	0.0006(2)
Ge	0.0402(4)	0.0526(5)	0.0592(5)	0.0021(3)	0.0045(3)	0.0165(4)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. The anisotropic displacement factor exponent takes the form $-2\pi^2[(ha^*)^2U_{11} + ... + 2klb^*c^*U_{23}]$.

Table 4 Interatomic distances (Å) for Tl₄GeSe₄.

Tl1	Se2	3.0222(6)	Se1	Ge	2.4317(12)
	Se1	3.0953(8)		Tl2	2.8654(7)
	Se2	3.3079(7)		Tl1	3.0953(8)
	Tl1	3.3715(4)		Tl4	3.0959(6)
	Se1	3.3844(8)		Tl3	3.3209(8)
	Se3	3.4386(8)		Tl1	3.3844(8)
	Se3	3.5552(8)			
	Tl4	3.6040(3)			
Tl2	Se1	2.8654(7)	Se2	Ge	2.3567(10)
	Se4	3.3631(7)		Tl1	3.0222(6)
	Tl5	3.4381(5)		Tl3	3.0243(6)
	Se3	3.4518(8)		Tl4	3.1501(5)
	Se2	3.4779(7)		Tl1	3.3079(7)
	Tl3	3.6756(5)		Tl2	3.4779(7)
Tl3	Se2	3.0243(6)	Se3	Ge	2.3454(11)
	Se3	3.2352(8)		Tl5	3.2302(8)
	Se4	3.2372(6)		Tl3	3.2352(8)
	Se1	3.3209(8)		Tl1	3.4386(8)
	Se4	3.3215(7)		Tl2	3.4518(8)
	Tl2	3.6756(5)		Tl1	3.5552(8)
Tl4	Se1	3.0959(6)	Se4	Ge	2.2796(9)
	Se1	3.0959(6)		Tl5	3.1141(7)
	Se2	3.1501(5)		Tl3	3.2372(6)
	Se2	3.1501(5)		Tl3	3.3215(7)
	Tl1	3.6040(3)		Tl2	3.3631(7)
	Tl1	3.6040(3)			
Tl5	Se4	3.1141(7)	Ge	Se4	2.2796(9)
	Se4	3.1141(7)		Se3	2.3454(11)
	Se3	3.2302(8)		Se2	2.3567(10)
	Se3	3.2302(8)		Se1	2.4317(12)
	Tl2	3.4381(5)			
	Tl2	3.4381(5)			

4. Conclusions

The Tl$_4$GeSe$_4$ compound crystallizes in space group *C*2/*c* (Tl$_4$SiSe$_4$ structure type). The structure consists of separate [GeSe$_4$] tetrahedra, which occupy voids between Tl$^+$ split nets. Strengthening of the cation-anion interactions was observed with respect to closely related compounds.

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