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The Crystal Structure of Hexathallium(I) Hexatellurodigermanate(III), $Tl_6[Ge_2Te_6]$

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The new compound $Tl_6[Ge_2Te_6]$ was prepared by thermal synthesis from the elements. The material is triclinic, space group $P\bar{1}$, with $a = 9.471(2)$, $b = 9.714(2)$, $c = 10.389(2)$ Å, $\alpha = 89.39(1)$, $\beta = 97.27(1)$, $\gamma = 100.79(1)°$, and $Z = 2$. The crystal structure was determined from single-crystal intensity data measured by means of an automated four-circle diffractometer and refined to an R value of 0.053 for 1831 observed reflections. $Tl_6[Ge_2Te_6]$ is characterized by Ge_2Te_6 units with Ge–Ge bonds which are linked into a three-dimensional structure by Tl atoms coordinated to essentially six Te atoms. The most important mean distances are $\bar{d}$(Ge–Ge) = 2.456 Å, $\bar{d}$(Ge–Te) = 2.573 Å, and $\bar{d}$(Tl–Te) = 3.515 Å. The lone 6*s* electron pairs of the thallium(I) atoms exhibit significant stereochemical activity. $Tl_6[Ge_2Te_6]$ represents a new structure type.

Introduction

The occurrence of the ternary phases Tl_2GeTe_3 (*1*), $TlGeTe_2$ (*1*), Tl_8GeTe_5 (*2*), and Tl_2GeTe_2 (*2*) in the Tl–Ge–Te system has been reported. Recently, Kulieva *et al.* (*3*, *4*) studied phase equilibria and thermodynamic properties in the same system and confirmed the ternary phases mentioned above. However, no structural data for the Tl–Ge–Te phases except for the lattice parameters of Tl_8GeTe_5 (*3*) have been published so far. After examining the crystal structures of several compounds in the Tl–Ge–S and Tl–Ge–Se systems (*5*), we began studying the structural principles of corresponding tellurium compounds. The structure analysis of the hitherto unknown compound $Tl_6[Ge_2Te_6]$ revealed anionic $[Ge_2Te_6]^{6-}$ groups, identical with those previously described by Dittmar (*6*) for $K_6[Ge_2Te_6]$, as features of the new phase.

The Ge atoms in the anion $[Ge_2Te_6]^{6-}$ are formally trivalent; one of the four bonds formed by these atoms is a Ge–Ge bond, the remaining ones being Ge–Te bonds. Taking into account the well-known similarity between Tl^+ and alkali-metal cations such as K^+ and Rb^+, it appeared to be of considerable interest to compare the structure of $Tl_6[Ge_2Te_6]$ with that of $K_6[Ge_2Te_6]$.

Experimental and Structure Determination

The compound $Tl_6[Ge_2Te_6]$ was prepared from the elements which were sealed in stoichiometric quantities in an evacuated quartz glass ampoule. The ampoule was kept at a temperature of 500°C for several days to obtain a homogeneous melt. On cooling to 300°C the material solidified; after holding the temperature at this value for 2 days the ampoule was cooled to room temperature within 1 day. The homogene-

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ous reaction product had a gray metallic appearance and was stable in the atmosphere. From a fractured regulus of the material it was possible to isolate irregularly shaped single crystals suitable for X-ray diffraction experiments. Buerger precession and De Jong–Bouman photographs taken on an Explorer camera (STOE) with Mo*Kα* radiation showed the unit cell of $Tl_6[Ge_2Te_6]$ to be triclinic. Preliminary lattice parameters were determined.

A single crystal of the material with the approximate dimensions 0.25 × 0.25 × 0.33 mm was transferred to a Syntex $P2_1$ four-circle single crystal diffractometer. After centering 25 strong reflections with 2θ values ranging from 21.5 to 33.5° using Mo*Kα* radiation, least-squares refinement gave the lattice parameters in Table I.

The intensities of 2618 reflections with $2\theta \leqq 45°$ and $h \geqq 0$ were measured using the ω scan mode (scanning width $\Delta\omega = 2°$, graphite monochromator, Mo*Kα* radiation). An experimental absorption correction based on the ψ scan data of eight suitable reflections was applied using the program TAPER of the XTL system of programs. After applying the Lorentz- and polarization corrections and averaging symmetry-related intensities, 2437 unique structure amplitudes were obtained.

The statistical evaluation of the normalized structure factors indicated a center of symmetry; as a consequence the space group $P\bar{1}$ was selected for further calculations. The crystal structure was solved by means of a direct method ("centrosymmetric direct methods" of the program system SHEL-X) and successive difference Fourier syntheses. The final least-squares refinement (programs FMLS and BLOCK of the XTL system) with anisotropic temperature factors converged to R (conventional) = 0.053 and R (weighted) = 0.051 [$w = 1/\sigma^2(F), |F_{obs}| \geqq 3.92\sigma(F)$, 1831 observed reflections]. The coefficients for the analytical approximation to the atomic scattering factors and the corrections for anomalous dispersion were taken from the International Tables of X-ray Crystallography (*7*).

TABLE I

CRYSTAL DATA OF $Tl_6[Ge_2Te_6]$

Triclinic, space group $P\bar{1}$	
$a = 9.4706(17)$ Å	$Z = 2$
$b = 9.7140(15)$	$V = 931.2$ Å^3
$c = 10.3890(16)$	$M_r = 2137.0$
$\alpha = 89.387(12)°$	$D_x = 7.62$ g cm^{-3}
$\beta = 97.270(13)$	$\mu(MoK\alpha) = 649.5$ cm^{-1}
$\gamma = 100.789(14)$	

The calculations were in part performed using the SHEL-X 76 system (*8*) implemented on an ICL 2906 computer, in part using the XTL system of programs (Syntex Analytical Instruments, Inc., Cupertino, Calif.) on a NOVA computer. The final structural parameters are summarized in Table II. A list of observed and calculated structure factors can be obtained from the author upon request.

It deserves attention that $Tl_6[Ge_2Te_6]$ is not contained in the phase diagram of that Tl–Ge–Te system as published by Kulieva *et al.* (*3, 4*). The available data do not permit a convincing resolution of this discrepancy and further work on the phase equilibria in this system appears to be necessary. However, at the present it cannot be excluded that the compound referred to as "Tl_2GeTe_2" by Kulieva *et al.* is identical with $Tl_6[Ge_2Te_6]$ described in this work.

Structure Description and Discussion

The crystal structure of $Tl_6[Ge_2Te_6]$ is characterized by centrosymmetric anionic groups $[Ge_2Te_6]^{6-}$ which contain pairs of Ge atoms forming a Ge–Ge bond. Each Ge atom is further bonded to three Te atoms, thus attaining tetrahedral coordination (Fig. 1). The Ge_2Te_6 group has staggered conformation with respect to rotation about the Ge–Ge axis. Hence the geometrical configuration of the Ge_2Te_6 group (point group $\bar{1}$)

TABLE II

STRUCTURAL PARAMETERS OF $Tl_6[Ge_2Te_6]$

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Tl(1)	3649(2)	2261(2)	9121(2)	2.81(10)	3.63(10)	1.63(9)	0.91(8)	0.24(8)	0.54(7)
Tl(2)	985(2)	4351(2)	6518(2)	2.14(9)	2.76(9)	1.54(8)	0.83(7)	0.30(7)	−0.05(7)
Tl(3)	936(2)	450(2)	3519(2)	4.58(12)	3.19(11)	3.71(11)	1.32(9)	−2.00(10)	−1.14(9)
Tl(4)	4912(2)	3813(2)	3531(2)	2.70(10)	2.29(9)	3.28(10)	0.44(8)	0.98(8)	0.29(8)
Tl(5)	6883(2)	2841(2)	7581(2)	1.92(9)	2.30(9)	2.04(8)	−0.36(7)	0.19(7)	−0.60(7)
Tl(6)	8002(2)	1447(2)	1480(2)	3.51(11)	2.89(10)	2.98(10)	0.61(8)	1.15(8)	0.89(8)
Ge(1)	936(4)	4275(4)	171(4)	0.53(18)	1.25(18)	1.34(20)	−0.03(15)	0.21(15)	−0.14(15)
Ge(2)	5782(5)	151(4)	4131(4)	1.09(19)	1.00(18)	1.15(19)	0.18(15)	0.33(15)	0.09(15)
Te(1)	4184(3)	679(3)	2065(3)	1.84(14)	1.98(13)	1.06(13)	−0.08(11)	−0.19(11)	0.37(10)
Te(2)	3167(3)	2113(3)	5903(3)	1.95(13)	1.62(13)	1.18(13)	0.69(11)	0.49(11)	−0.17(10)
Te(3)	24(3)	1970(3)	8917(3)	1.54(14)	1.53(13)	1.92(14)	−0.27(11)	0.51(11)	−0.63(10)
Te(4)	6853(3)	4360(3)	802(3)	0.82(13)	2.11(13)	1.69(14)	−0.28(11)	0.43(11)	0.20(10)
Te(5)	1342(3)	3845(3)	2628(3)	1.67(13)	2.03(13)	0.99(13)	0.68(11)	0.24(10)	0.55(10)
Te(6)	7886(3)	2246(3)	4718(3)	1.55(13)	1.56(13)	1.15(13)	−0.41(11)	0.17(11)	0.14(10)

Note. Positional parameters $\times 10^4$. The anisotropic thermal parameters B_{ij} [Å]^2 are defined for: $\exp[-\frac{1}{4}(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$. Standard deviations in parenthesis in units of the last decimal.

can be derived by a moderate distortion from an octahedral arrangement of the Te atoms which is centered by a pair of Ge atoms with its axis parallel to a threefold rotation axis of the octahedron. The crystal structure contains two sets of crystallographically independent Ge_2Te_6 groups. The Te octahedra centered by Ge(1) atom pairs are situated at the special position 1(c): 0, ½, 0; the octahedra containing the Ge(2) pairs at 1(f): ½, 0, ½. The axes of the Ge(1) atom pairs are oriented approximately parallel to $[1\bar{1}0]$, those of the Ge(2) atom pairs to $[10\bar{1}]$ (Fig. 1).

The cationic Tl atoms occupy holes of the packing of the octahedral Ge_2Te_6 groups. The six closest Te atoms surrounding each Tl atom form strongly distorted octahedral coordination polyhedra sharing corners, edges, and faces with the Ge_2Te_6

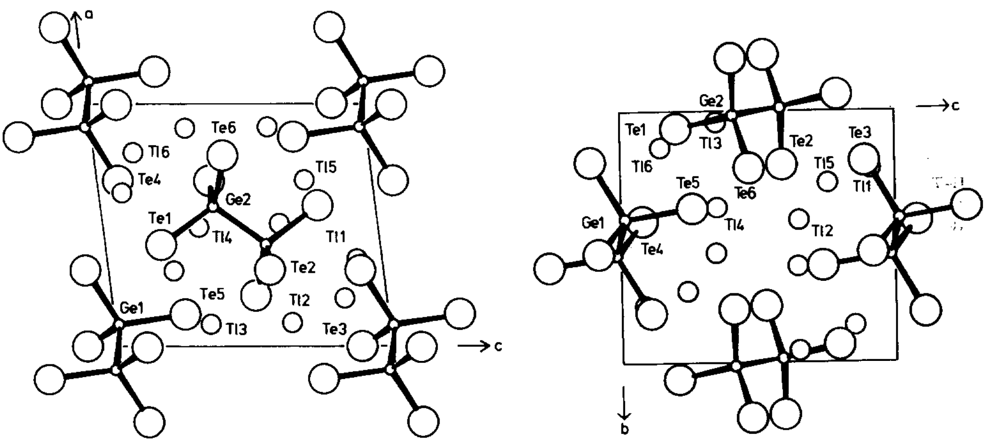

FIG. 1. Projections of the crystal structure of $Tl_6[Ge_2Te_6]$ along [010] (left) and [100] (right).

octahedra. In this way, the various crystallographically different Tl atoms link two, three, or four Ge_2Te_6 octahedra in a three-dimensional framework.

So far, the Ge_2Te_6 group described above has only been reported in $K_6[Ge_2Te_6]$ (*6*). In this structure, the Ge_2Te_6 octahedra are arranged in layers with parallel orientation of the Ge–Ge axes. The K atoms are accommodated in octahedral and trigonal prismatic holes within and between the Ge_2Te_6 layers.

In $Tl_6[Ge_2Te_6]$, the Tl–Te distances range from 3.270 to 4.152 Å, if only the six closest Te atoms around each Tl atom are taken into account (Table III). With the atoms Tl(1), Tl(4), and Tl(5), these six closest Te ligands are separated from more distant Te atoms by a fairly large distance gap; in these cases, the coordination number six appears to be well established. With Tl(2), one of the faces of the strongly deformed octahedron formed by the six closest Te neighbors is capped by a Te atom at 4.140 Å (Fig. 2). Thus, a (6 + 1)-coordination is established. The additional Te atoms with distances of 4.312 and 4.330 Å in the environments of Tl(3) and Tl(6) make the assignment of a definite coordination number in these cases more difficult.

The distortion of the Te octahedra in the environments of the Tl atoms follows a general pattern stressing a polarity of the octahedron from Te(e) to Te(f) (Table III, Fig. 2): While the distance Tl–Te(e) is among the short Tl–Te distances, Te(f) is the most distant Te atom or only slightly closer as in the case of Tl(5). Almost all angles between

TABLE III

LENGTHS AND ANGLES OF INTERATOMIC DISTANCE VECTORS ORIGINATING FROM THE Tl ATOMS IN $Tl_6[Ge_2Te_6]$[a]

1. Distances [Å]

	Tl(1)		Tl(2)		Tl(3)		Tl(4)		Tl(5)		Tl(6)	
Tl–Te(a)[b]	Te(2)	3.317(3)	Te(5^{xi})	3.270(4)	Te(5)	3.381(3)	Te(2)	3.385(3)	Te(6)	3.322(3)	Te(3^{v})	3.452(4)
Tl–Te(b)	Te(3)	3.371(4)	Te(3)	3.471(3)	Te(2)	3.270(4)	Te(5)	3.399(4)	Te(5^{xii})	3.360(3)	Te(1)	3.679(4)
Tl–Te(c)	Te(1^{ii})	3.431(3)	Te(2)	3.383(4)	Te(6^{x})	3.455(4)	Te(4)	3.553(4)	Te(4^{ii})	3.677(3)	Te(6)	3.481(3)
Tl–Te(d)	Te(4^{ii})	3.582(3)	Te(6^{xii})	3.557(3)	Te(3^{viii})	3.391(4)	Te(6)	3.529(4)	Te(1^{x})	3.409(3)	Te(5^{i})	3.633(4)
Tl–Te(e)	Te(4^{xii})	3.407(3)	Te(4^{xii})	3.345(3)	Te(1)	3.564(4)	Te(1)	3.333(3)	Te(3^{i})	3.370(4)	Te(4)	3.256(4)
Tl–Te(f)	Te(1^{x})	4.099(4)	Te(6^{iii})	3.568(3)	Te(6^{iii})	3.973(4)	Te(2^{xii})	4.050(3)	Te(2)	3.670(4)	Te(3^{x})	4.152(4)
			Te(5)	4.140(3)	Te(2^{viii})	4.312(4)					Te(1^{vi})	4.330(4)
											Te(2^{x})	4.339(3)
	Tl(5)	3.583(3)	Tl(2^{xi})	3.784(3)	Tl(6^{iii})	3.553(3)	Tl(4^{xii})	3.813(3)	Tl(1)	3.583(3)	Tl(3^{i})	3.553(3)
	Tl(6^{x})	3.675(3)	Tl(4^{xii})	3.967(3)	Tl(3^{viii})	3.757(3)	Tl(2^{xii})	3.967(3)	Tl(4^{xii})	4.035(3)	Tl(1^{x})	3.675(3)
			Tl(5^{iii})	4.169(3)			Tl(5^{xii})	4.035(3)	Tl(2^{i})	4.169(3)		
$\bar{d}$(Tl–Te)[c]		3.535		3.432		3.506		3.542		3.468		3.609

2. Angles [°]

Angle	Tl(1)	Tl(2)	Tl(3)	Tl(4)	Tl(5)	Tl(6)
Te(a)–Tl–Te(c)	150.55(10)	171.74(9)	151.59(10)	159.64(9)	161.39(9)	145.47(10)
Te(b)–Tl–Te(d)	138.65(9)	154.62(9)	153.52(11)	154.54(9)	167.61(9)	139.23(9)
Te(e)–Tl–Te(f)	150.10(9)	155.62(9)	150.49(9)	156.00(9)	154.60(9)	159.75(9)
Te(a)–Tl–Te(e)	92.89(8)	86.79(8)	81.51(8)	84.39(8)	86.78(8)	89.80(9)
Te(b)–Tl–Te(e)	75.96(8)	75.44(8)	82.52(9)	84.72(8)	88.56(8)	75.78(8)
Te(c)–Tl–Te(e)	116.44(9)	92.82(8)	84.92(8)	76.63(8)	84.35(8)	86.39(8)
Te(d)–Tl–Te(e)	71.65(8)	83.84(8)	76.91(8)	75.96(8)	79.34(8)	82.36(8)

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[a] The transformations of the positional parameters are designated as (i) $x + 1, y, z$ (ii) $x, y, z + 1$ (iii) $x - 1, y, z$ (iv) $x, y, z - 1$ (v) $x + 1, y, z - 1$ (vi) $-x + 1, -y, -z$ (vii) $-x, -y + 1, -z$ (viii) $-x, -y, -z + 1$ (ix) $-x + 1, -y + 1, -z$ (x) $-x + 1, -y, -z + 1$ (xi) $-x, -y + 1, -z + 1$ (xii) $-x + 1, -y + 1, -z + 1$.

[b] The letters a, b, c, d, e, and f refer to different positions at the corners of the distorted octahedron of Te atoms around the Tl atoms: (e) close axial position, (f) distant axial position; (a, b, c, d) equatorial positions.

[c] Mean value of the distances Tl–Te(a) to Tl–Te(f).

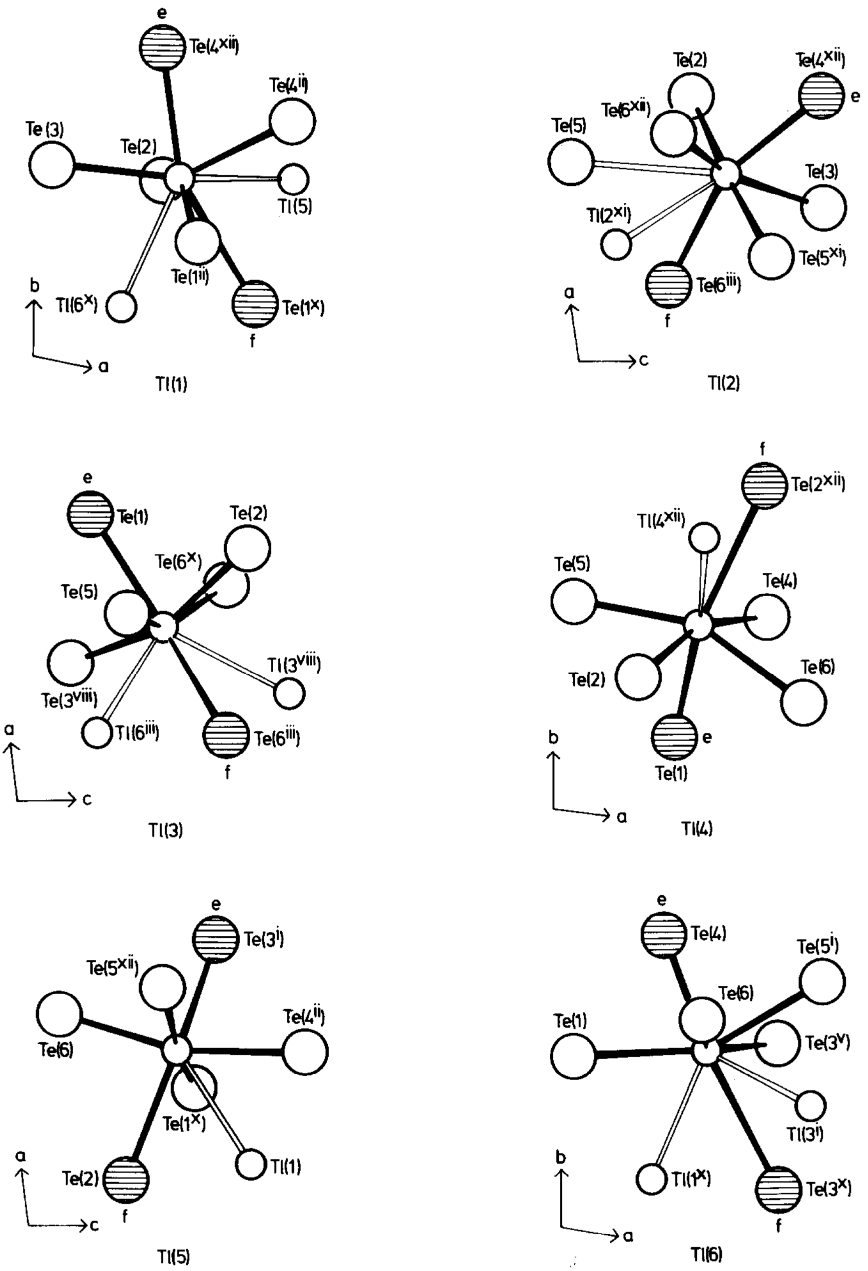

FIG. 2. Coordination polyhedra around the Tl atoms projected along [010] or [001]. Only Te and Tl atoms at distances smaller than 4.2 and 3.9 Å, respectively, are depicted. Te(e) and Te(f) atoms hatched.

the axial Tl–Te(e) distance vector and the four equatorial Tl–Te distance vectors are smaller than 90°; thus the central Tl atoms with their Te ligands except for Te(f) represent umbrella-like configurations. (Exceptionally, the angle Te(1^{ii})–Tl(1)–Te(4^{xii}) is

TABLE IV

INTERATOMIC DISTANCES [Å] AND BOND ANGLES [°] OF THE Ge$_2$Te$_6$ GROUPS IN Tl$_6$[Ge$_2$Te$_6$][a]

Ge(1)–Ge(1$^{\mathrm{vii}}$)	2.454(6)	Ge(2)–Ge(2$^{\mathrm{x}}$)	2.457(6)
Ge(1)–Te(3$^{\mathrm{iv}}$)	2.552(5)	Ge(2)–Te(1)	2.570(5)
Ge(1)–Te(4$^{\mathrm{ix}}$)	2.575(4)	Ge(2)–Te(2$^{\mathrm{x}}$)	2.581(5)
Ge(1)–Te(5)	2.574(5)	Ge(2)–Te(6)	2.586(5)
Ge(1$^{\mathrm{vii}}$)–Ge(1)–Te(3$^{\mathrm{iv}}$)	108.77(20)	Ge(2$^{\mathrm{x}}$)–Ge(2)–Te(1)	106.23(20)
Ge(1$^{\mathrm{vii}}$)–Ge(1)–Te(4$^{\mathrm{ix}}$)	106.07(20)	Ge(2$^{\mathrm{x}}$)–Ge(2)–Te(2$^{\mathrm{x}}$)	105.79(19)
Ge(1$^{\mathrm{vii}}$)–Ge(1)–Te(5)	106.44(20)	Ge(2$^{\mathrm{x}}$)–Ge(2)–Te(6)	109.09(20)
Te(3$^{\mathrm{iv}}$) –Ge(1)–Te(4$^{\mathrm{ix}}$)	108.89(18)	Te(1) –Ge(2)–Te(2$^{\mathrm{x}}$)	116.53(18)
Te(3$^{\mathrm{iv}}$) –Ge(1)–Te(5)	110.90(18)	Te(1) –Ge(2)–Te(6)	110.07(18)
Te(4$^{\mathrm{ix}}$) –Ge(1)–Te(5)	115.46(18)	Te(2$^{\mathrm{x}}$)–Ge(2)–Te(6)	108.84(18)
Te(3$^{\mathrm{iv}}$)–Te(4$^{\mathrm{ix}}$)	4.171(4)	Te(1) –Te(2$^{\mathrm{x}}$)	4.381(4)
Te(3$^{\mathrm{iv}}$)–Te(5)	4.222(4)	Te(1) –Te(6)	4.225(4)
Te(4$^{\mathrm{ix}}$)–Te(5)	4.354(4)	Te(2$^{\mathrm{x}}$)–Te(6)	4.202(4)
Te(3$^{\mathrm{iv}}$)–Te(4$^{\mathrm{iii}}$)	4.737(4)	Te(1) –Te(2)	4.512(4)
Te(3$^{\mathrm{iv}}$)–Te(5$^{\mathrm{vii}}$)	4.699(4)	Te(1) –Te(6$^{\mathrm{x}}$)	4.739(4)
Te(4$^{\mathrm{ix}}$)–Te(5$^{\mathrm{vii}}$)	4.545(4)	Te(2$^{\mathrm{x}}$)–Te(6$^{\mathrm{x}}$)	4.762(4)

[a] The transformations of the positional coordinates are identical with those of Table III.

considerably larger than 90°). The similarity of this configuration with the AB_5E coordination according to Gillespie (*9*) appears to justify the assumption that the lone pair of 6*s* electrons on the Tl$^+$ cations exhibits significant stereochemical activity. Hence some accumulation of the lone-pair electron density is to be expected on the side of the Tl atom opposite to Te(e).

The mean Tl–Te distance in Tl$_6$[Ge$_2$Te$_6$] based on the six closest neighbors of each Tl atom is 3.515 Å in good agreement with the mean Tl–Te distance in TlTe (*10*, *11*) of 3.52 Å. In this compound, the Tl atom is asymmetrically coordinated to seven Te atoms at distances ranging from 3.40 to 3.67 Å with one close Tl atom at 3.54 Å. In Tl[GaTe$_2$] and Tl[InTe$_2$] (*12*) crystallizing in the TlSe type the Te atoms form a tetragonal antiprismatic arrangement centered by the Tl atom. Due to the eight-coordination of the Tl atom the Tl–Te distances of 3.569 and 3.595 Å for Tl[GaTe$_2$] and Tl[InTe$_2$], respectively, are somewhat longer than those for Tl$_6$[Ge$_2$Te$_6$] and TlTe.

The mean distance K–Te of 3.65 Å in K$_6$[Ge$_2$Te$_6$] (*6*) is considerably longer than the corresponding distance of 3.515 Å in the Tl compound. This is in obvious contradiction to the ionic "crystal radii" for six-coordination in oxides and fluorides of K$^+$ (1.52 Å) and Tl$^+$ (1.64 Å) (*13*). Shannon's newer crystal radii for sulfides (*14*) ($^{\mathrm{vi}}r_{\mathrm{K}^+}$ = 1.52 Å, $^{\mathrm{vi}}r_{\mathrm{Tl}^+}$ = 1.45 Å) appear to be better suited to obtain agreement between observed and calculated *M*-Te distances (with $r_{\mathrm{Te}^{2-}}$ = 2.07 Å: *d*(K–Te) = 3.59 Å, *d*(Tl–Te) = 3.52 Å). In the Tl(I) halides Tl*X*, a contraction of the Tl$^+$ crystal radius is observed as the atom *X* changes from F to I. This effect is attributed to the increasing covalence of the Tl–*X* bond due to the decreasing electronegativity of the *X* atom (*15*). Obviously, the same explanation is valid for the remarkable contraction of the Tl$^+$ crystal radius in sulfides as compared to that in oxides and fluorides. Due to the comparatively small electronegativity difference between sulfur and tellurium a similar or even smaller crystal radius of Tl$^+$ in tellurides is to be expected.

The Ge–Ge bond length in K$_6$[Ge$_2$Te$_6$] and the mean Ge–Ge bond length in Tl$_6$[Ge$_2$Te$_6$] (Table IV) are 2.492 and 2.456 Å, respectively, somewhat longer than the Ge–Ge bond length calculated from Pauling's tetrahedral radius (*16*) [$d(\mathrm{Ge–Ge})_{\mathrm{calc}}$ = 2.44 Å, identical with *d*(Ge–Ge) in the element]. The almost identical mean Ge–Te bond lengths in K$_6$[Ge$_2$Te$_6$] and Tl$_6$[Ge$_2$Te$_6$] of 2.579 and 2.573 Å, respectively, are also slightly expanded if compared to the sum of the corresponding tetrahedral radii: $d(\mathrm{Ge–Te})_{\mathrm{calc}}$ = 2.54 Å.

The shortest Te–Te distance is 4.093 Å between Te atoms belonging to different Ge(1) octahedra, that between Te atoms belonging to the same octahedron is 4.171 Å. Essentially, these distances correspond to van der Waals' contacts between the Te atoms (*6*).

In binary and ternary thallium chalcogenides, frequently "short" Tl(I)–Tl(I) distances are encountered which are similar to or somewhat longer than the Tl–Tl distances in thallium metal [3.41 and 3.46 Å (*17*)]. Weak bonding interactions have been assumed to be associated with such short Tl–Tl distances, particularly by Fleet in the case of the ternary thallium sulfide lorandite, $Tl_2As_2S_4$ (*18*). Short Tl–Tl distances occur in all known binary thallium tellurides, the shortest Tl–Tl contacts being: Tl_5Te_3: 3.48 Å (*19*); TlTe: 3.54 Å (*11*); and Tl_2Te_3: 3.40 Å (*19*). Some evidence for Tl–Tl interaction and limited participation of the 6*s* electrons in bonds was supplied by the XPS measurements of Porte and Tranquard on Tl_5Te_3, TlTe, and Tl_2Te_3 (*20*). The structures of $Tl[GaTe_2]$ and $Tl[InTe_2]$ contain linear chains of Tl(I) atoms with Tl–Tl distances of 3.423 and 3.590 Å, respectively (*12*).

While in $K_6[Ge_2Te_6]$ (*6*) the shortest distances between K atoms are 3.872 and 4.083 Å as to be expected for cations with repulsive electrostatic interaction, several significantly shorter Tl–Tl distances are encountered in $Tl_6[Ge_2Te_6]$ (Table III). Eight Tl atoms separated by distances ranging from 3.553 to 3.757 Å form a strongly folded centrosymmetric chain ($\sphericalangle$Tl(5)–Tl(1)–Tl(6^x) = 105.88°, $\sphericalangle$Tl(1)–Tl(6^x)–Tl(3^{viii}) = 90.10°, and $\sphericalangle$Tl(6^x)–Tl(3^{viii})–Tl(3) = 98.24°], possibly indicating weak attractive interactions between the Tl atoms with participation of the 6*s* electrons. In all cases, the closest Tl neighbors approach the central Tl atom from that side where the lone pair electron density is assumed to be located (Fig. 2).

The comparison of the crystal structures of $K_6[Ge_2Te_6]$ and $Tl_6[Ge_2Te_6]$ shows that the replacement of K atoms by Tl atoms leads to a new less-symmetrical structure type, the symmetry of the structure being reduced from space group *C*2/*c* to $P\bar{1}$. The reduction of symmetry is also apparent in the wider variability of the Tl–Te distances (Table III) as compared with that of the K–Te distances (*6*). In addition, the deviations of the bond angles at the Ge atoms (Table IV) from the ideal tetrahedral values are significantly larger in the Tl compound. As the space requirements of the K and the Tl atoms in the ternary tellurides are approximately comparable, the structural change must primarily be attributed to the increased covalence of the Tl–Te bonds associated with the stereochemical activity of the "lone" electron pair of Tl(I) in contrast to the predominantly ionic K–Te interaction and the spherical symmetry of the Ar configuration of the K^+ ion.

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