

During our chemical investigations, by heating and by precipitation from solutions of different concentrations, we have obtained crystalline iron phosphates with less water (Meisel *et al.*, 1986). The structure of such materials remains to be investigated.

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Structures of Tetrathallium(I) Tetrathiosilicate(IV) and Tetrathallium(I) Tetraselosilicate(IV)

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Abstract. $\text{Tl}_4[\text{SiS}_4]$, $M_r = 973.8$, monoclinic, Cc , $a = 12.518$ (3), $b = 11.241$ (2), $c = 7.567$ (2) Å, $\beta = 112.80$ (2)°, $V = 981.4$ (4) Å³, $Z = 4$, $D_x = 6.59$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 668$ cm⁻¹, $F(000) = 1608$, room temperature, final $R = 0.066$ for 883 observed unique reflections. $\text{Tl}_4[\text{SiSe}_4]$, $M_r = 1161.4$, monoclinic, $C2/c$, $a = 11.664$ (9), $b = 7.277$ (4), $c = 24.903$ (12) Å, $\beta = 99.93$ (5)°, $V = 2082$ (2) Å³, $Z = 8$, $D_x = 7.41$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 772$ cm⁻¹, $F(000) = 3792$, room temperature, final $R = 0.064$ for 866 observed unique reflections. $\text{Tl}_4[\text{SiS}_4]$ is isostructural with $\text{Tl}_4[\text{GeS}_4]$ and contains $[\text{SiS}_4]^{4-}$ anions held together by Tl^+ cations in irregular sixfold coordination. The relations between the structures of $\text{Tl}_4[\text{SiS}_4]$, tetragonal $\text{Na}_4[\text{SnS}_4]$, and $\text{Tl}_4[\text{SnS}_4]$ are discussed. $\text{Tl}_4[\text{SiSe}_4]$ is built up from slabs parallel to (001) which consist of almost planar 3⁶ nets of Tl^+ cations enclosed between two parallel layers of

$[\text{SiSe}_4]^{4-}$ tetrahedra. Further Tl^+ cations are located in voids between the $[\text{SiSe}_4]^{4-}$ tetrahedra of each layer and between the slabs. The Tl atoms in three general and two special positions are coordinated to essentially six, five, and four Se atoms. The lone pairs of 6s electrons of univalent thallium exhibit strong stereochemical effects with two of the Tl atoms. The pseudohexagonal properties of the structure are described by means of a group-subgroup relation to a hypothetical hexagonal aristotype.

Introduction. In the Tl–Si–S and Tl–Si–Se systems, the phases $\text{Tl}_4[\text{Si}_2\text{S}_6]$ and $\text{Tl}_4[\text{Si}_2\text{Se}_6]$ have been prepared and structurally characterized (Eulenberger, 1982). The two compounds adopt the $\text{Tl}_4[\text{Ge}_2\text{S}_6]$ structure (Eulenberger, 1978). Further investigations on the same systems led to the synthesis of $\text{Tl}_4[\text{SiS}_4]$ and $\text{Tl}_4[\text{SiSe}_4]$ (Eulenberger, 1984a). It appeared to be of interest to

compare the structures of the new compounds with those of other ternary chalcogenides, particularly thallium(I) chalcogenides such as $\text{Tl}_4[\text{GeS}_4]$ (Eulenberger, 1977) and $\text{Tl}_4[\text{SnS}_4]$ (Klepp & Eulenberger, 1984). Therefore single-crystal X-ray studies of the new compounds were carried out.

Lazarev, Peresh & Starosta (1983) studied phase equilibria in the $\text{Tl}_2\text{S}-\text{SiS}_2$ and $\text{Tl}_2\text{Se}-\text{SiSe}_2$ systems and observed the compounds $\text{Tl}_4[\text{SiS}_4]$ and $\text{Tl}_4[\text{SiSe}_4]$ as well. No structural data of these phases, however, have been reported.

Experimental. $\text{Tl}_4[\text{SiS}_4]$ was prepared from the elements which were sealed in an evacuated quartz-glass ampoule in quantities according to the stoichiometry of the compound. The temperature of the ampoule was gradually raised in an electric tube furnace to 770 K, and then held at 680 K for 83 days. The major part of the reaction product formed a yellow crystalline regulus containing a small amount of a dark glassy material.

$\text{Tl}_4[\text{SiSe}_4]$ was synthesized in an analogous way. In this case, the reaction temperature was raised to 970 K within eight days to achieve complete reaction of silicon. The ampoule was then cooled to 570 K and the solidified reaction product annealed at this temperature for one week. A crystalline gray regulus of metallic appearance was obtained. The two materials are stable on exposure to the atmosphere.

Irregularly shaped single crystals of the compounds suitable for X-ray diffraction were isolated from the fractured reguli. Buerger precession and De Jong-Bouman photographs were taken on an Explorer camera (Stoe). As the photographs of reciprocal-lattice planes of the $\text{Tl}_4[\text{SiS}_4]$ crystal were almost identical with those of the corresponding ones of $\text{Tl}_4[\text{GeS}_4]$, the further work was based on the assumption that $\text{Tl}_4[\text{SiS}_4]$ is isostructural with $\text{Tl}_4[\text{GeS}_4]$ in the space group Cc . For $\text{Tl}_4[\text{SiSe}_4]$, a larger monoclinic cell with the space group Cc or $C2/c$ was found ($hkl: h+k=2n, h0l: h,l=2n$). Preliminary lattice parameters were determined from the X-ray photographs.

Crystal size: $\text{Tl}_4[\text{SiS}_4]$, $0.16 \times 0.05 \times 0.03$ mm ($\text{Tl}_4[\text{SiSe}_4]$, $0.16 \times 0.09 \times 0.05$ mm). Automatic four-circle diffractometer (Syntex $P2_1$), graphite-monochromated $\text{Mo } K\alpha$ radiation. Refinement of lattice parameters by least squares from 25 centred reflections with $26 \leq 2\theta \leq 39^\circ$ ($20 \leq 2\theta \leq 36^\circ$). Experimental absorption correction: ψ scans of seven suitable reflections (six reflections); transmission factors ranging from 1 to 0.43 (1 to 0.14). Intensity measurement: ω scan, $2 \leq 2\theta \leq 55^\circ$ ($1 \leq 2\theta \leq 45^\circ$), $-16 \leq h \leq 16$, $-14 \leq k \leq 14$, $0 \leq l \leq 9$ ($0 \leq h \leq 12$, $0 \leq k \leq 7$, $-26 \leq l \leq 26$), three standard reflections measured after every 97 reflections, variations less than 3σ . 1220 (1373) unique reflections measured, 337 (507) reflections unobserved with $I \leq 1.96\sigma(I)$. Structure solution:

Table 1. Fractional atomic coordinates and equivalent isotropic temperature factors (\AA^2) for $\text{Tl}_4[\text{SiS}_4]$ and $\text{Tl}_4[\text{SiSe}_4]$

The e.s.d.'s are given in parentheses.

$$B_{\text{eq}} = \frac{4}{3} \sum_i \sum_j \beta_{ij} (a_i, a_j).$$

	x	y	z	B_{eq}
$\text{Tl}_4[\text{SiS}_4]$				
Tl(1)	0.4863	0.1113 (2)	0.5064	3.0 (1)
Tl(2)	0.1200 (3)	0.8751 (2)	0.4132 (4)	3.5 (1)
Tl(3)	0.1935 (3)	0.2096 (2)	0.4378 (4)	2.7 (1)
Tl(4)	0.2834 (2)	0.4999 (3)	0.4133 (4)	2.4 (1)
Si	0.4106 (12)	0.7887 (14)	0.4781 (20)	1.4 (4)
S(1)	0.3283 (13)	0.2784 (12)	0.1539 (21)	2.4 (4)
S(2)	0.0781 (14)	0.6474 (14)	0.1620 (23)	3.1 (5)
S(3)	0.3140 (14)	0.9332 (14)	0.3029 (21)	2.9 (5)
S(4)	0.4300 (12)	0.6516 (12)	0.3012 (23)	2.5 (4)
$\text{Tl}_4[\text{SiSe}_4]$				
Tl(1)	0.1911 (2)	0.4621 (3)	0.0008 (1)	2.65 (8)
Tl(2)	0.3887 (2)	0.2757 (4)	0.6793 (1)	3.32 (8)
Tl(3)	0.3110 (3)	0.3705 (3)	0.8350 (1)	3.04 (8)
Tl(4)*	0	0	0	5.14 (16)
Tl(5)†	0	0.1674 (4)	0.75	3.25 (13)
Si	0.0655 (13)	0.3766 (21)	0.6243 (6)	1.08 (40)
Se(1)	0.3060 (5)	0.2754 (8)	0.4169 (2)	1.86 (16)
Se(2)	0.0175 (5)	0.3528 (7)	0.0772 (2)	1.76 (17)
Se(3)	0.4014 (5)	0.2969 (8)	0.1194 (3)	2.40 (18)
Se(4)	0.3521 (6)	0.0442 (8)	0.2905 (2)	2.21 (18)

* Special Wyckoff position 4(a).

† Special Wyckoff position 4(e).

positional parameters from $\text{Tl}_4[\text{GeS}_4]$ [Tl and most Se positions by 'centrosymmetric direct methods' of *SHELX76* (Sheldrick, 1976), further positions from difference Fourier maps]. $\sum w|\Delta F|^2$ minimized in full-matrix refinement, $w=1/\sigma^2(F)$, 81 (84) refined parameters: all atoms anisotropic, one scale factor, for $\text{Tl}_4[\text{SiS}_4]$ x and z parameters of Tl(1) fixed. $R=0.066$ (0.064), $wR=0.048$ (0.048), $S=1.88$ (2.13). Max. ratio of least-squares shift/e.s.d.: 0.74 (0.02). Max. and min. heights in final difference Fourier map 2.7 and -1.9 e \AA^{-3} (1.1 and -1.6 e \AA^{-3}). Atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). Final calculations: *XTL* system of programs (Syntex, 1976) on a Nova computer.

Discussion. Atomic parameters are given in Table 1 and the interatomic distances and bond angles in Table 2.*

$\text{Tl}_4[\text{SiS}_4]$ adopts the $\text{Tl}_4[\text{GeS}_4]$ structure (Eulenberger, 1977) which, as recently has been demonstrated (Klepp & Eulenberger, 1984), can be considered as built from pseudotetragonal layers parallel to (001) (Fig. 1). Similar layers are found in the structure of

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42710 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

tetragonal Na₄[SnS₄] (Jumas, Philippot, Vermot-Gaud-Daniel, Ribes & Maurin, 1975) as well as in that of Ti₄[SnS₄] (*P2₁/c*) (Klepp & Eulenberger, 1984) where the layers are also distorted but not as strongly as in Ti₄[GeS₄] and Ti₄[SiS₄]. A group-subgroup relation (Bärnighausen, 1975; *International Tables for Crystallography*, 1983) between the structures of Na₄[SnS₄] and Ti₄[GeS₄]/Ti₄[SiS₄] is presented (Fig. 2). While in the latter compounds there are two layers in the repeat unit in the direction of the *c* axis, in Ti₄[SnS₄] four analogous pseudotetragonal layers are stacked in a different way.

Table 2. *Interatomic distances (Å) and bond angles (°) for Ti₄[SiS₄] and Ti₄[SiSe₄]*

The e.s.d.'s are given in parentheses.

Ti ₄ [SiS ₄]			
Coordination of the Ti atoms (distances Ti—X ≤ 4.1 Å)			
Ti(1)—S(3 ^{vi})	2.91 (2)	Ti(2)—S(3)	2.93 (2)
Ti(1)—S(2 ^v)	3.18 (2)	Ti(2)—S(1 ⁱ)	3.07 (2)
Ti(1)—S(1)	3.24 (2)	Ti(2)—S(2)	3.11 (2)
Ti(1)—S(2 ⁱⁱ)	3.26 (2)	Ti(2)—S(1 ^{vi})	3.58 (2)
Ti(1)—S(3 ⁱ)	3.70 (2)	Ti(2)—S(3 ^{viii})	3.70 (2)
Ti(1)—S(4 ⁱ)	3.72 (2)	Ti(2)—S(4 ^{vii})	3.81 (2)
Ti(1)—Ti(2 ⁱⁱ)	3.607 (4)	Ti(2)—Ti(1 ⁱⁱⁱ)	3.607 (4)
Ti(1)—Ti(3)	3.667 (5)	Ti(2)—Ti(3 ⁱ)	3.831 (4)
Ti(1)—Ti(3 ^v)	3.857 (4)	Ti(2)—Ti(3 ^{ix})	3.859 (4)
Ti(1)—Ti(4 ^v)	4.000 (4)		
$\bar{d}(\text{Ti—S}) = 3.335 (8) \pm 0.313^*$		$\bar{d}(\text{Ti—S}) = 3.367 (8) \pm 0.374$	
Ti(3)—S(3 ⁱ)	3.04 (2)	Ti(4)—S(4)	2.86 (2)
Ti(3)—S(2 ⁱ)	3.07 (2)	Ti(4)—S(1 ⁱ)	3.01 (1)
Ti(3)—S(4 ^v)	3.12 (2)	Ti(4)—S(2)	3.03 (2)
Ti(3)—S(1)	3.30 (2)	Ti(4)—S(4 ⁱ)	3.27 (2)
Ti(3)—S(4 ⁱ)	3.53 (2)	Ti(4)—S(1)	3.35 (2)
Ti(3)—S(3 ^{vi})	3.76 (2)	Ti(4)—S(2 ⁱ)	4.08 (2)
Ti(3)—Ti(4)	3.480 (4)	Ti(4)—Ti(3)	3.480 (4)
Ti(3)—Ti(1)	3.667 (5)	Ti(4)—Ti(4 ⁱ)	3.783 (4)
Ti(3)—Ti(2 ^{vi})	3.831 (4)	Ti(4)—Ti(4 ⁱⁱ)	3.783 (4)
Ti(3)—Ti(1 ⁱⁱⁱ)	3.857 (4)	Ti(4)—Ti(1 ⁱⁱⁱ)	4.000 (4)
Ti(3)—Ti(2 ^{vii})	3.859 (4)		
$\bar{d}(\text{Ti—S}) = 3.303 (8) \pm 0.289$		$\bar{d}(\text{Ti—S}) = 3.267 (8) \pm 0.346$	
SiS ₄ tetrahedron			
Si—S(1 ⁱ)	2.11 (2)		
Si—S(2 ⁱⁱⁱ)	2.14 (2)		
Si—S(3)	2.15 (2)		
Si—S(4)	2.12 (2)		
$\bar{d}(\text{Si—S}) = 2.130 (10) \pm 0.018$			
S(1 ⁱ)—Si—S(2 ⁱⁱⁱ)	107.7 (9)	S(1 ⁱ)—S(2 ⁱⁱⁱ)	3.44 (3)
S(1 ⁱ)—Si—S(3)	111.3 (9)	S(1 ⁱ)—S(3)	3.52 (2)
S(1 ⁱ)—Si—S(4)	110.0 (9)	S(1 ⁱ)—S(4)	3.46 (2)
S(2 ⁱⁱⁱ)—Si—S(3)	108.8 (9)	S(2 ⁱⁱⁱ)—S(3)	3.49 (2)
S(2 ⁱⁱⁱ)—Si—S(4)	109.4 (9)	S(2 ⁱⁱⁱ)—S(4)	3.48 (2)
S(3)—Si—S(4)	109.6 (9)	S(3)—S(4)	3.49 (2)

Symmetry code for Ti₄[SiS₄]: no superscript *x, y, z*; (i) *x, 1-y, 0.5+z*; (ii) *0.5+x, -0.5+y, z*; (iii) *0.5+x, 1.5-y, 0.5+z*; (iv) *0.5+x, 0.5-y, 0.5+z*; (v) *x, y-1, z*; (vi) *-0.5+x, 0.5+y, z*; (vii) *x, 2-y, 0.5+z*; (ix) *x, 1+y, z*; (x) *-0.5+x, -0.5+y, z*; (xi) *x, 1-y, -0.5+z*; (xii) *-0.5+x, 0.5-y, -0.5+z*.

* $\bar{d}(\sigma \times 10^3) \pm s$: where $\bar{d} = (\sum_i d_i)/n$, $\sigma = (\sqrt{\sum_i \sigma_i^2})/n$, and $s = \sqrt{(\sum_i (d_i - \bar{d})^2)/(n-1)}$.

Table 2 (cont.)

Ti ₄ [SiSe ₄]			
Coordination of the Ti atoms (distances Ti—X ≤ 4.2 Å)			
Ti(1)—Se(1 ^{xv})	3.061 (6)	Ti(2)—Se(1 ^{xx})	3.027 (6)
Ti(1)—Se(2)	3.110 (6)	Ti(2)—Se(4 ^{xx})	3.302 (6)
Ti(1)—Se(2 ^v)	3.143 (6)	Ti(2)—Se(2 ^{xvii})	3.304 (6)
Ti(1)—Se(1 ⁱ)	3.283 (6)	Ti(2)—Se(3 ^{xii})	3.464 (7)
Ti(1)—Se(3 ^{xvix})	3.545 (7)	Ti(2)—Se(4 ^{ix})	3.698 (6)
Ti(1)—Se(3)	3.699 (7)	Ti(2)—Se(4 ^{vii})	3.787 (7)
Ti(1)—Ti(1 ^{xix})	3.382 (3)	Ti(2)—Ti(5 ^{xii})	3.482 (4)
Ti(1)—Ti(4 ^{xii})	3.617 (3)	Ti(2)—Ti(3 ⁱⁱ)	3.647 (4)
		Ti(2)—Ti(3 ^{xviii})	3.736 (4)
		Ti(2)—Ti(2 ⁱⁱ)	3.999 (4)
$\bar{d}(\text{Ti—Se}) = 3.307 (3) \pm 0.260$		$\bar{d}(\text{Ti—Se}) = 3.430 (3) \pm 0.281$	
Ti(3)—Se(3 ^{xv})	3.144 (7)	Ti(4)—Se(2,2 ^{ix})	3.192 (6) × 2
Ti(3)—Se(2 ^{xv})	3.150 (6)	Ti(4)—Se(1 ^{xvii, xviii})	3.234 (6) × 2
Ti(3)—Se(4 ^{ix})	3.278 (6)	Ti(4)—Se(3 ^{xiv, xvix})	3.678 (6) × 2
Ti(3)—Se(1 ^{xi})	3.295 (6)		
Ti(3)—Se(4 ^{xv})	3.422 (6)		
Ti(3)—Se(3 ^{vii})†	4.134 (7)		
Ti(3)—Ti(2 ⁱⁱ)	3.647 (4)	Ti(4)—Ti(1 ^{xiv, xvix})	3.617 (3) × 2
Ti(3)—Ti(2 ^{xv})	3.736 (4)	Ti(4)—Ti(1,1 ^{ix})	4.032 (2) × 2
Ti(3)—Ti(5 ^{xii})	3.952 (3)		
$\bar{d}(\text{Ti—Se}) = 3.404 (3) \pm 0.372$		$\bar{d}(\text{Ti—Se}) = 3.368 (3) \pm 0.269$	
		excluding that marked with a dagger	3.258 (3) ± 0.108
Ti(5)—Se(4 ^{xx, xxiii})	3.000 (6) × 2		
Ti(5)—Se(3 ^{xx, xxiii})	3.268 (6) × 2		
Ti(5)—Ti(2 ^{xiv, xviii})	3.482 (4) × 2		
Ti(5)—Ti(3 ^{xiv, xviii})	3.951 (3) × 2		
$\bar{d}(\text{Ti—Se}) = 3.134 (4) \pm 0.190$			
SiSe ₄ tetrahedron			
Si—Se(1 ^{xx})	2.249 (16)		
Si—Se(2 ^{xii})	2.312 (16)		
Si—Se(3 ^{xxiii})	2.278 (16)		
Si—Se(4 ^{xx})	2.248 (15)		
$\bar{d}(\text{Si—Se}) = 2.272 (8) \pm 0.030$			
Se(1 ^{xx})—Si—Se(2 ^{xii})	108.0 (6)	Se(1 ^{xx})—Se(2 ^{xii})	3.689 (8)
Se(1 ^{xx})—Si—Se(3 ^{xxiii})	108.8 (6)	Se(1 ^{xx})—Se(3 ^{xxiii})	3.682 (9)
Se(1 ^{xx})—Si—Se(4 ^{ix})	110.3 (7)	Se(1 ^{xx})—Se(4 ^{ix})	3.690 (8)
Se(2 ^{xii})—Si—Se(3 ^{xxiii})	108.5 (6)	Se(2 ^{xii})—Se(3 ^{xxiii})	3.725 (8)
Se(2 ^{xii})—Si—Se(4 ^{ix})	106.7 (6)	Se(2 ^{xii})—Se(4 ^{ix})	3.659 (8)
Se(3 ^{xxiii})—Si—Se(4 ^{ix})	114.3 (7)	Se(3 ^{xxiii})—Se(4 ^{ix})	3.802 (9)

Symmetry code for Ti₄[SiSe₄]: no superscript *x, y, z*; (i) *-x, y, 0.5-z*; (ii) *1-x, y, 1.5-z*; (iii) *-x, y, 1.5-z*; (iv) *-x, -y, -z*; (v) *-x, 1-y, -z*; (vi) *1-x, -y, 1-z*; (vii) *1-x, 1-y, 1-z*; (viii) *x, -y, -0.5+z*; (ix) *x, -y, 0.5+z*; (x) *x, 1-y, -0.5+z*; (xi) *x, 1-y, 0.5+z*; (xii) *0.5+x, 0.5+y, z*; (xiii) *0.5+x, -0.5+y, z*; (xiv) *-0.5+x, -0.5+y, z*; (xv) *0.5-x, 0.5+y, 0.5-z*; (xvi) *0.5-x, 0.5+y, 1.5-z*; (xvii) *0.5-x, -0.5+y, 0.5-z*; (xviii) *0.5-x, -0.5+y, 1.5-z*; (xix) *0.5-x, 0.5-y, -z*; (xx) *0.5-x, 0.5-y, 1-z*; (xxi) *0.5+x, 0.5-y, 0.5+z*; (xxii) *-0.5+x, 0.5-y, -0.5+z*; (xxiii) *-0.5+x, 0.5-y, 0.5+z*.

An essential component of the pseudotetragonal layers is formed by an arrangement of four Ti atoms situated at the corners of a distorted square (Figs. 1 and 3). Three of the edges of this configuration are associated with the shortest Ti—Ti distances of the structure [3.480 (4), 3.607 (4) and 3.667 (5) Å] while the fourth edge is elongated to 4.442 (5) Å (Table 2). All Ti atoms are coordinated to six S atoms forming a highly irregular arrangement; several of the S atoms bridge two, three, and four Ti atoms, respectively (Fig. 3). The general coordination pattern is surprisingly

similar to that occurring in the pseudotetragonal layers of $Tl_4[SnS_4]$ (Klepp & Eulenberger, 1984) despite the different stacking of these layers. However, the 'square' is remarkably less distorted in the latter case, the opening of the fourth edge of the 'square' being limited to 3.776 (4) Å. Thus, a more densely packed octahedral arrangement of four Tl and two S atoms is attained in the thioannate and the coordination number of the Tl atom corresponding to Tl(2) is raised to seven. The anisotropic directional distribution of the Tl–S bond lengths in $Tl_4[SiS_4]$ clearly indicates varying degrees of stereoactivity of the lone pairs of 6s electrons on the univalent Tl atoms.

Furthermore, it is an interesting feature of the $Tl_4[SiS_4]$ structure that the Tl(4) atoms are situated in

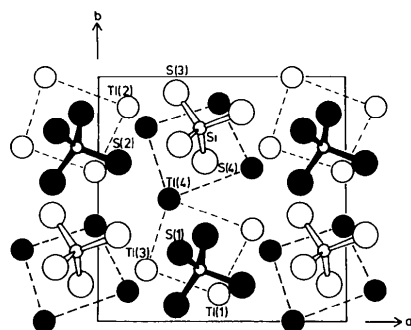


Fig. 1. Projection of the structure of $Tl_4[SiS_4]$ down [001]. The Tl and S atoms of the upper pseudotetragonal layer are depicted by filled circles, those of the lower layer by open circles. The broken lines indicate the 'squares' of Tl atoms.

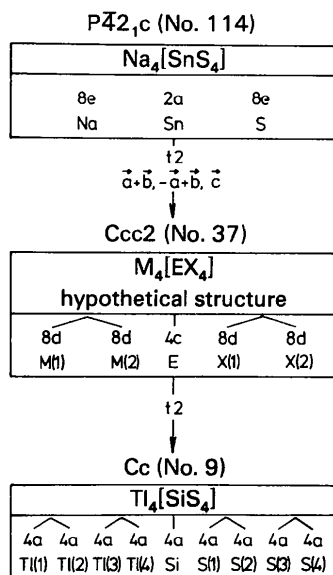


Fig. 2. The group–subgroup relations between the structures of $Na_4[SnS_4]$ and $Tl_4[SiS_4]$.

equidistant positions along straight lines extending in the [001] direction, the Tl(4)–Tl(4) distance being 3.783 (4) Å. If the idea of weak attractive interactions between Tl atoms at distances comparable with those in the Tl metal (3.41 and 3.46 Å) is valid (Fleet, 1973; Eulenberger, 1984b), the formation of the Tl sublattice described above might significantly contribute to the stability of the structure.

The Tl–S distances ranging from 2.86 (2) to 4.08 (2) Å (Table 2) [$\bar{d}(Tl-S) = 3.318$ (4) Å] are very similar to those in $Tl_4[GeS_4]$ and $Tl_4[SnS_4]$. The mean Si–S distance in the SiS_4 tetrahedra, 2.130 (10) Å, is very close to the mean value from numerous thiosilicates, 2.123 Å (Shannon, 1981).

The structure of $Tl_4[SiSe_4]$ (Table 1, Fig. 4) is dominated by $SiSe_4$ tetrahedra isolated from each other as the major structural units. Chemically, the $SiSe_4$ tetrahedra have to be interpreted as $[SiSe_4]^{4-}$ anions held together by Tl^+ cations. Thus $Tl_4[SiSe_4]$ is characterized as tetrathallium(I) tetraselenosilicate(IV).

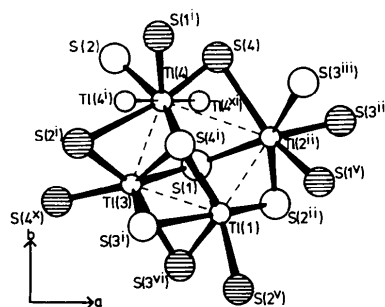


Fig. 3. Coordination of the Tl atoms in $Tl_4[SiS_4]$. Orthogonal projection on (001). The hatched circles represent S atoms which belong to SiS_4 tetrahedra situated in the same layer as the 'square' of Tl atoms indicated by broken lines (compare with Fig. 1).

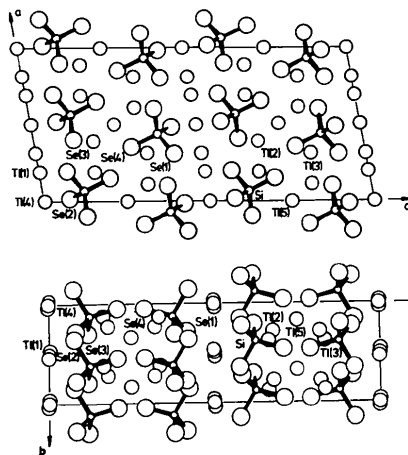


Fig. 4. Projection of the structure of $Tl_4[SiSe_4]$ down [010] (top) and down [100] (bottom).

A high density of Tl⁺ cations is observed in the $xy0$ and $xy\frac{1}{2}$ planes which are occupied by the Tl(1) atoms in a general position and by the Tl(4) atoms situated at centres of symmetry. The Tl(1) sites are slightly shifted out of the planes for a distance of only 0.02 Å. On each side of the plane of Tl⁺ cations a layer of parallel-oriented [SiSe₄]⁴⁻ tetrahedra is located in such a way that tetrahedral faces are directed toward the central plane (Fig. 4). Thus, centrosymmetric structural slabs are formed which consist of two layers of SiSe₄ tetrahedra enclosing a plane of Tl atoms. Owing to the *c* glide planes two symmetrically equivalent slabs occur within the repeat unit in the [001] direction. Further Tl atoms [Tl(2) and Tl(3)] are found in general positions within the layers of SiSe₄ tetrahedra in voids situated between these tetrahedra. The Tl(5) atoms occupy sites on twofold axes in the $xy\frac{1}{4}$ and $xy\frac{3}{4}$ planes which separate the slabs described above from each other. As a consequence of the formation of Se—Tl bonds within the SiSe₄ layers to the Tl(2) and Tl(3) atoms, between the SiSe₄ layers belonging to the same slab to the Tl(1) and Tl(4) atoms in the central plane, and also between adjacent slabs to the Tl(5) atoms, a three-dimensional framework structure results. A layered structure exists only from a purely geometrical viewpoint.

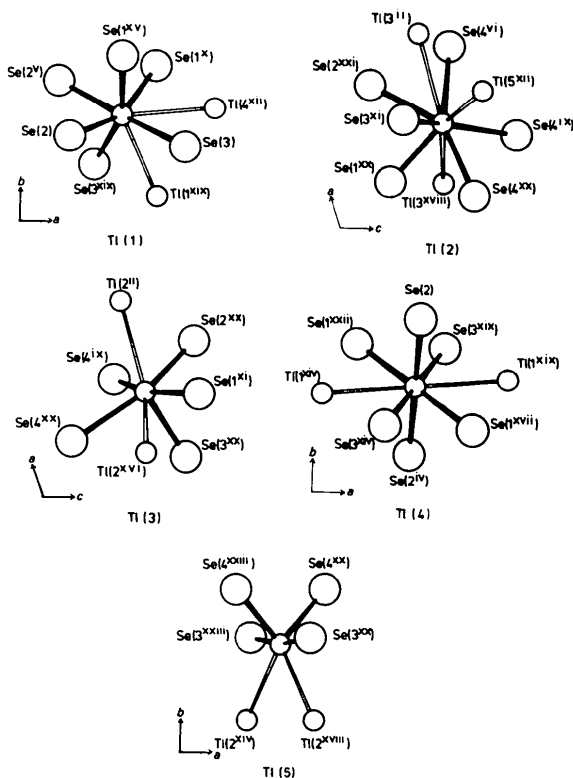


Fig. 5. Coordination of the Tl atoms in Tl₄[SiSe₄] viewed along the [010] or [001] directions.

The five different positions occupied by the Tl atoms are associated with different coordination patterns (Table 2, Fig. 5). Tl(1) is coordinated to six Se atoms in a strongly distorted octahedral arrangement at a mean distance of 3.307 (3) Å. The six Se atoms surrounding Tl(2) form a highly asymmetrical configuration with $\bar{d}(\text{Tl—Se}) = 3.430$ (3) Å. The influence of the lone pairs of 6s electrons on the configurations around Tl(1) and Tl(2) is not well defined. Tl(3) is essentially five-coordinated to Se in a distorted pseudooctahedral environment with $\bar{d}(\text{Tl—Se}) = 3.258$ (3) Å and to a sixth Se atom at a distance of 4.134 (7) Å. In this case, a high degree of lone-pair stereoactivity is indicated, the 6s electron pair apparently occupying an orbital directed toward the distant Se atom. The thermal parameters of Tl(4) and Tl(5) exhibit more pronounced anisotropy than those of the remaining Tl atoms: $B_{33} = 7.4$ (3) Å² for Tl(4) and $B_{11} = 5.9$ (3) Å² for Tl(5). Tl(4) in the 4(*a*) position is clearly six-coordinated to the Se atoms [$\bar{d}(\text{Tl—Se}) = 3.368$ (3) Å]; in this case the coordination polyhedron is a centrosymmetric distorted octahedron. Tl(5) in the 4(*e*) position situated on twofold axes is surrounded by four Se atoms which are located at the corners of a distorted octahedron from which two corners in the *cis* position are removed [$\bar{d}(\text{Tl—Se}) = 3.134$ (4) Å]. The unilateral spatial distribution of the Se ligands around the Tl(5) atoms indicates a strong stereochemical activity of the lone pair of electrons. Two Tl(2) atoms approach the Tl(5) atom from that side where the electron density of the lone pair is to be expected, and complete the coordination polyhedron to a strongly distorted octahedron [$\bar{d}[\text{Tl(5)—Tl(2)}] = 3.482$ (4) Å].

Further short Tl—Tl distances, 3.617 (3) and 3.382 (3) Å, occur in zigzag chains of Tl atoms with the sequence —Tl(4)—Tl(1)—Tl(1)— in the repeat unit (Table 2, Fig. 6). This observation lends further support for the idea of weak Tl—Tl interactions contributing to the stability of thallium chalcogenide structures.

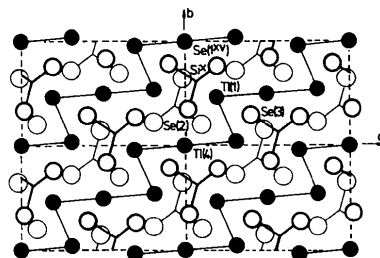


Fig. 6. Pseudo-hexagonal layers in Tl₄[SiSe₄] viewed along [001]. The Tl atoms at height 0 are represented by filled circles joined by solid lines corresponding to the shortest Tl—Tl distances. The layer of the Se atoms above (below) the Tl layer is indicated by heavy (light) open circles. The Si—Se bonds are shown by light and heavy lines respectively; the Se(4) atoms are omitted.

Projections of slabs of the $\text{Tl}_4[\text{SiSe}_4]$ structure along the c axis show distorted hexagonal nets of atoms (Fig. 6). The pseudo-hexagonal properties of the structure can be rationalized by taking into account the fact that the hexagonal space group $P\bar{3}c1$ is a minimal supergroup of $C2/c$ (*International Tables for Crystallography*, 1983). In this space group an idealized hexagonal structure can be described which represents a hypothetical 'aristotype' $M_4[EX_4]$ (Megaw, 1973) of the $\text{Tl}_4[\text{SiSe}_4]$ structure (Figs. 7 and 8). This idealized structure contains equivalent 3^6 nets consisting of $M(1)$ and $M(4)$ atoms in the $z = 0$ and $z = \frac{1}{2}$ planes, respectively, that are enclosed by parallel 3^6 nets of $X(1)$ atoms. From a topological standpoint, these M and X atoms form a cubic closest packing. The structure is completed by additional strongly corrugated nets consisting of $M(5)$ and $X(2)$ atoms around $z = \frac{1}{4}$ and $z = \frac{3}{4}$, respectively, the E position in the tetrahedral holes, and the $M(2)$ and $M(3)$ positions in elongated trigonal-pyramidal holes between these nets and those composed of the $X(1)$ atoms.

On the transition from the space group $P\bar{3}c1$ to $C2/c$ considerable distortions are necessary to meet the spatial and directional bonding requirements of the Tl atoms, particularly those of the Tl(2) and Tl(3) atoms.

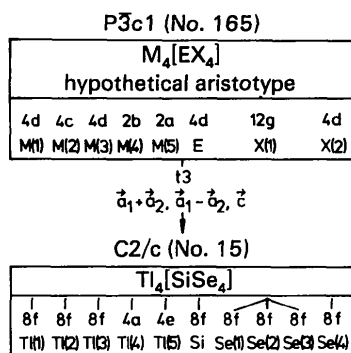


Fig. 7. The group-subgroup relation between $\text{Tl}_4[\text{SiSe}_4]$ and the hypothetical hexagonal aristotype $M_4[EX_4]$.

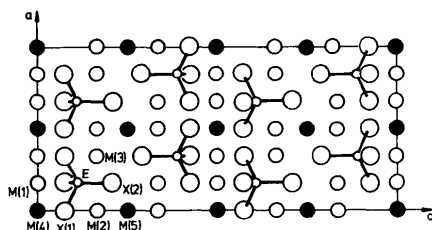


Fig. 8. Schematic topological diagram of the hypothetical hexagonal aristotype $M_4[EX_4]$ related to $\text{Tl}_4[\text{SiSe}_4]$. C -centred cell projected on (010) (compare with Fig. 7). The filled circles are M atoms equivalent to $M(4)$ with $z = 0$ or $\frac{1}{2}$ and $M(5)$ with $z = \frac{1}{4}$ or $\frac{3}{4}$.

Besides the increase of the β angle from 90 to 99.93 (5)°, the most significant distortion of the aristotype structure is the tilt of the SiSe_4 tetrahedra approximately parallel to $[1\bar{1}0]$. While the sites of the Se(4) atoms at one of the vertices of each tetrahedron remain almost identical with the $X(2)$ sites, the tetrahedral faces situated opposite to these vertices are displaced with respect to the planes of Tl atoms (Figs. 4, 6 and 8). A strongly distorted c.c.p. arrangement of the Tl atoms [Tl(1) and Tl(4)] and the Se atoms of the tetrahedral faces [Se(1), Se(2) and Se(3)] is formed. The positions $M(2)$ and $M(3)$ follow the displacement of the $X(1)$ atoms to make possible the accommodation of the large Tl^+ cations [Tl(2) and Tl(3)] particularly by increasing the distances from the $M(5)$ and $X(2)$ sites, respectively, of their originally trigonal-pyramidal environments. The original $M(5)$ position finally occupied by Tl(5) is displaced along the twofold axes apparently due to the stereoactivity of the lone pair of electrons of the Tl^+ cations (Fig. 4). The 3^6 nets formed by the Tl(1) and Tl(4) atoms show a comparatively small degree of deviation from the hexagonal symmetry. The distortion is accompanied by the formation of the above-mentioned zigzag chains of Tl atoms.

The Tl—Se distances vary from 3.000 (6) to 4.134 (7) Å (Table 2). The mean value $\bar{d}(\text{Tl—Se})$ seems compatible with the corresponding values for other ternary thallium selenides, if their dependence on the mean coordination numbers of the Tl atoms is taken into account: $\text{Tl}_4[\text{Ge}_4\text{Se}_{10}]$, 3.538 (1) Å (CN = 9) (Eulenberger, 1981); $\text{Tl}_4[\text{Ge}_2\text{Se}_6]$, 3.461 (1) Å, $\text{Tl}_4[\text{Si}_2\text{Se}_6]$, 3.456 (1) Å (mean CN = 7.5) (Eulenberger, 1982); $\text{Tl}_4[\text{TiSe}_4]$, 3.418 (2) Å (mean CN = 6.25) (Klepp & Eulenberger, 1984); $\text{Tl}_4[\text{SiSe}_4]$, 3.343 (1) Å (mean CN = 5.75).

The mean deformation of the SiSe_4 tetrahedron is significantly greater than that of the SiSe_4 tetrahedron in $\text{Tl}_4[\text{SiSe}_4]$ (Table 2). The mean distance $\bar{d}(\text{Si—Se})$ for $\text{Tl}_4[\text{SiSe}_4]$ [2.272 (8) Å] is almost identical with those for $\text{Tl}_4[\text{Si}_2\text{Se}_6]$ [2.271 (5) Å], SiSe_2 [2.275 (1) Å] (Peters, Mandt, Meyrin & Krebs, 1981), and $\text{Pb}_2[\text{SiSe}_4]$ [2.270 (5) Å] (Iglesias & Steinfink, 1973). The sum of the tetrahedral bonding radii (Pauling, 1960) is 2.31 Å.

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Structure of the Antitumour Active Compound Tetrachloro(2,2-dimethyl-1,3-propanediamine)platinum(IV)

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Abstract. [PtCl₄(C₅H₁₄N₂)], *M_r* = 439.08, monoclinic, *P*2₁/*m*, *a* = 7.5618 (6), *b* = 9.1686 (10), *c* = 8.6113 (8) Å, β = 107.92 (7)°, *V* = 568.07 Å³, *Z* = 2, *D_x* = 2.57 g cm⁻³, λ(Mo *K*α) = 0.71073 Å, μ = 134 cm⁻¹, *F*(000) = 404.3, *T* = 295 K, *R* = 0.022 for 2365 significant reflections. Molecular symmetry *m* (*C_s*). An alternative refinement in *P*2₁ shows high correlations. The octahedral coordination around Pt shows no unusual bond lengths or angles [Pt–Cl 2.304 (1), 2.309 (1), 2.318 (1) Å, Pt–N 2.062 (2) Å; all angles within 3° of 90 or 180°]. The six-membered Pt–diamine ring adopts a chair-like conformation which is somewhat flattened at the Pt–N₂ end. The molecular geometry is compared with that of analogous compounds.

Introduction. A number of square-planar Pt^{II} and octahedral Pt^{IV} compounds with *cis*-coordinated neutral primary (or secondary) amines and moderately strongly bound anions, such as chloride, appear to possess antitumour activity (Marcelis & Reedijk, 1983; Lippard, 1982; Lippert & Beck, 1983).

Until recently, most attention was given to the structure and kinetics of the Pt^{II} drugs, whereas the kinetically inert Pt^{IV} drugs (Mason, 1972) were barely studied. Recently, molecular structures of a few Pt^{IV}–amine compounds (Vollano, Blatter & Dabrowiak, 1984; Kuroda, Ismail & Sadler, 1984) as well as some mechanistic studies (Blatter, Vollano, Krishnan & Dabrowiak, 1984; van der Veer, Peters & Reedijk, 1985) have been reported, including the very promising

second-generation drug CHIP, [PtCl₂(OH)₂{HC–(CH₃)₂–NH₂}₂] (Harrap, 1984). Here we report the structure of the compound [Pt^{IV}Cl₄(dmdap)] (dmdap = 2,2-dimethyl-1,3-propanediamine). The synthesis of this compound has been published elsewhere (Van Kralingen, Reedijk & Spek, 1980).

Experimental. Crystal size approximately 0.17 × 0.21 × 0.15 mm. Cell constants from setting angles of 24 reflections (10 < θ < 12°) centred on an Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo *K*α radiation, ω/θ scan, 2 < θ < 36°, *h*–12→12, *k* 0→15, *l*–15→15. Reflections corrected for Lorentz, polarization, absorption (de Graaff, 1973) and extinction effects (transmission coefficients 0.094–0.264). Three standard reflections, 3.1% intensity variation. 5640 reflections measured, 2828 independent, *R*_{int} = 0.075; 2365 reflections with *I* > 2σ(*I*) taken as observed.

Position of Pt derived from Patterson synthesis, other atoms from subsequent Fourier maps. *F* used in least-squares refinement. *R* = 0.0221, *wR* = 0.0266, *w* = 1/σ²(*F*), *S* = 1.053, Δ_{max}/σ < 0.01. Max. and min. Δρ excursions in final difference map 1.2 and –1.4 e Å⁻³ (close to Pt). Least-squares refinement; anisotropic thermal parameters for non-H atoms; H positions could be located in the difference-Fourier maps; however, H positions calculated (C–H: 0.96 Å) and only isotropic temperature factors refined. Scattering factors and anomalous-dispersion corrections taken from *International Tables for X-ray Crystallography* (1974). Leiden University Computer (Amdahl V7B); programs written or modified by Mrs E. W. Rutten-Ceulemans and Dr R. A. G. de Graaff.

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