The Crystal Structure of a New Thiosilicate of Thallium, $TlInSiS_4$

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The crystal structure of a new synthetic compound with the composition of $TlInSiS_4$ has been determined. The crystal is orthorhombic, and the space group is *Pbnm* with $Z=8$. The cell dimensions are $a=11.74(1)$, $b=17.038(7)$, and $c=7.285(3)$ Å. The structure was solved by the Patterson method and refined to a final R-value of 0.074 for all the observed reflections. The structure is characterized by a sheet structure built up from alternating infinite $(InS_3)_n$ chains and dimeric Si_2S_6 groups. The Si_2S_6 groups consist of two SiS_4 tetrahedra sharing an edge. The thallium atoms are situated between the sheets and are surrounded by nine sulfur atoms at distances between 3.293 and 3.957 Å.

Studies of ternary and quaternary chalcogenides containing 4B elements in the periodic table have been extensively carried out during the last two decades. Numerous phases have been found, and the determinations of their crystal structures have provided evidence for the existence of various anionic groups formed by arrangements of thioanions. For example, it is well known that there are SiS_4^{4-},1) GeS_4^{4-}1—3), and SnS_4^{4-}4) (isolated tetrahedral anions), $Ge_2S_7^{6-}$5) and $Sn_2S_7^{6-}$5) (dimeric anions consisting of two tetrahedra sharing one corner), $Ge_2S_6^{4-}$6,7), and $Sn_2S_6^{4-}$7) (dimeric isolated anions consisting of edge-sharing tetrahedra), $Si_4S_{10}^{4-}$8) and $Ge_4S_{10}^{4-}$8—10) (adamantane-like anions), and $(GeS_3)_n^{2n-}$11,12) (infinite chains).

In order to elucidate systematically the crystal chemistry of those chalcogenides, we have undertaken the preparation of Tl–III–IV–S_4 type compounds with III=Al, Ga, In; IV=Si, Ge by the conventional evacuated-silica-tube method. This study produced single crystals of five new compounds with a quaternary composition.13) The crystal structure of $TlInSiS_4$ is described in the present paper.

Experimental

A tabular crystal with approximate dimensions of 0.050×0.175×0.125 mm was used for the X-ray investigations. The rotation and Weissenberg photographs with Cu *Kα* radiation showed an orthorhombic symmetry with systematic absences of $h+l=2n+1$ for $(h0l)$ reflections and of $k=2n+1$ for $(0kl)$ reflections, so that possible space groups are non-centrosymmetric $Pbn2_1$ and centrosymmetric *Pbnm*; the latter was subsequently established by the crystal-structure analysis.

The lattice parameters were determined by a least-squares refinement using the 2θ values of 22 reflections in the range of 21—34° centered automatically on a Rigaku AFC-5 four-circle diffractometer with Mo *Kα* radiation ($\lambda=0.71068$ Å); they led to these orthorhombic cell constants: $a=11.74(1)$, $b=17.038(6)$, and $c=7.285(3)$ Å.

The chemical composition was determined by means of electron-probe X-ray microanalysis (JEOL JXA-50A X-ray microanalyzer automated by the ELIONIX ACPS-XR control system at the Chemical Analysis Center of the University of Tsukuba). The result of analysis gave the following values: Tl=41.1(42.98), In=25.1(24.15), Si=5.7(5.90), S=27.1(26.97), $\sum$ 99.0(100.00) wt%, The theoretical values for $TlInSiS_4$ are given in brackets. The density calculated for $TlInSiS_4$, $D_x=4.34\ \mathrm{g\cdot cm^{-3}}$ for eight formula units in the unit cell, agrees well with the measured density of $4.37\ \mathrm{g\cdot cm^{-3}}$. Table 1 summarizes the crystallographic data of $TlInSiS_4$.

Table 1. Crystallographic data

Formula	$TlInSiS_4$
Formula weight	475.52
Decomposition point	300 °C
Crystal system	Orthorhombic
Space group	*Pbnm*
a	11.74(1) Å
b	17.038(7) Å
c	7.285(3) Å
V	1457(2) Å^3
Z	8
D_m	4.37 g·cm^{-3}
D_x	4.34 g·cm^{-3}
μ(Mo *Kα*)	266.72 cm^{-1}

The intensity data were collected on a Rigaku Rotaflex four-circle diffractometer operated at 50 kV and 160 mA with graphite monochromated Mo *Kα* radiation, 2θ-ω scan technique, and a scan speed of 2° per minute. The scanning widths and offset values were determined by the following formulae; $\Delta\omega=1.0+0.5\times tan\theta$ and $\delta=0.5\times\Delta\omega$ respectively. The intensity measurements were repeated up to two times for each reflection until $\sigma(|Fo|)/|Fo|$ became less than 0.05. The intensities of three standard reflections, (122), (0, 10, 0) and (004), were measured every 50 reflections. No significant fluctuation in the intensities could be observed during the data collection. A total of 2383 independent reflections below $2\theta=61°$ were measured, of which 940 reflections with $|Fo|\geqq3\sigma(|Fo|)$ were considered as observed and used for the structure determination. The intensity data were corrected for Lorentz, polarization, and absorption factors (μ(Mo *Kα*)=266.72 cm^{-1}). The absorption corrections were made by the use of the computer program ACACA.14) The transmission factors varied from 0.079 to 0.278.

Determination and Refinement of the Structure

The positions of one independent thallium atom and the indium atom were determined from the Patterson maps. The positions of the other thallium atom, six sulfur atoms, and two silicon atoms were determined by successive Fourier and difference Fourier syntheses. The full-matrix least-squares refinements, including all atoms with isotropic temperature factors using RFINE-2,15) yielded the $R(=\sum||Fo|-|Fc||/\sum|Fo|)$ value of 0.234 and $R_w(=\{\sum w(|Fo|-|Fc|)^2/\sum w|Fo|^2\}^{1\ 2}$, where $w=1/\sigma^2(|Fo|)$) of 0.241 for all observed reflections. The difference Fourier synthesis at this stage indicated that the assumed silicon sites with high positive residual peaks seemed to be partly occupied by indium atoms. In a similar way, the indium site showed a negative residual peak, suggesting that the site is partly replaced by the silicon atoms. Then, the site occupancies were refined with the program RFINE-2 on the basis of the assumption that the total occupancy of the site is 1. The occupancies of the silicon atoms at the Si(1) and Si(2) sites were 0.42 and 0.91 respectively, and the partial occupancy of the indium atom at the In site could be determined to be 0.67. Further refinement with anisotropic temperature factors and anomalous dispersion correction reduced the R-value to 0.074 and the R_w-value to 0.059 for all the observed reflections. The maximum shift of the atomic parameters in the last cycle was less than 0.01 times the corresponding standard deviations. A difference Fourier synthesis using the final atomic parameters showed no significant residual peaks. The scattering factors for neutral atoms tabulated by Cromer and Mann[16] were used in the calculations. The anomalous dispersion correction factors were taken from the International Tables for X-ray Crystallography.[17] The computations were performed on a FACOM M-200 computer at the Information Center of the University of Tsukuba.

The final atomic coordinates and thermal parameters are given in Table 2, while Table 3 shows the site occupancies of the indium and silicon atoms. Lists of the anisotropic temperature factors and the observed and calculated structure factors are deposited as Document No. 8419 at the Chemical Society of Japan.

TABLE 2. ATOMIC COORDINATES AND ISOTROPIC THERMAL PARAMETERS[a)]

Atom	x	y	z	$B_{eq}/Å^2$
Tl(1)	0.0578(2)	0.1555(1)	0.25	7.3
Tl(2)	0.3817(2)	0.0572(1)	0.25	6.6
In	0.7395(2)	0.1538(1)	−0.0021(3)	2.9
Si(1)	0.8076(3)	0.3229(2)	0.25	2.8
Si(2)	0.6899(6)	0.4831(4)	0.25	2.8
S(1)	0.8591(6)	0.0411(4)	0.0064(9)	4.5
S(2)	0.8626(7)	0.2622(5)	−0.0064(11)	5.8
S(3)	0.1190(9)	0.3511(6)	0.25	4.9
S(4)	0.6177(9)	0.1618(5)	0.25	4.4
S(5)	0.6177(8)	0.3693(5)	0.25	4.1
S(6)	0.8719(9)	0.4543(6)	0.25	4.9

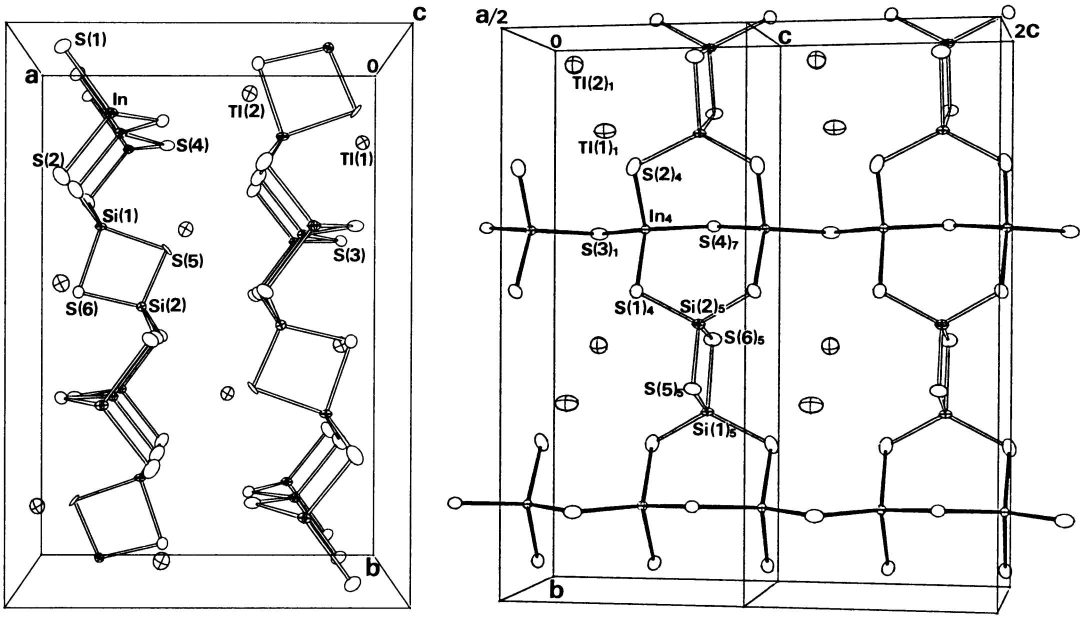
a) Estimated standard deviations are shown in parentheses.

Description and Discussion of the Structure

The crystal structure of $TlInSiS_4$ is presented in Fig. 1-(a) (projected along the c axis) and Fig. 1-(b) (projected on to the (100) plane). In the structure, In, S(1), and S(2) are located in the general positions at nearly $z=0$, while all the remaining atoms are in the special positions at $z=0.25$.

TABLE 3. SITE OCCUPANCIES OF INDIUM AND SILICON ATOMS

Site	In	Si	Position
In	0.67	0.33	8 d
Si(1)	0.58	0.42	4 c
Si(2)	0.09	0.91	4 c



(a) (b)

Fig. 1. Structure of $TlInSiS_4$ with the numbering scheme of atoms. (a) Projection along the c axis. (b) Projection along the a axis.

The two silicon atoms, Si(1) and Si(2), are essentially four-coordinated by sulfur atoms forming the SiS_4 tetrahedra. The two tetrahedra share an edge to form dimeric Si_2S_6 groups. Similarly, the indium atom is tetrahedrally coordinated by four sulfur atoms. The InS_4 tetrahedra are linked together to form an infinite chain by sharing one vertex along the *c* axis, as is shown in Fig. 1-(b). The chains are connected with the dimeric Si_2S_6 groups by sharing two sulfur atoms at the apexes to form an infinite two-dimensional sheet. The sheet extends parallel to the (100) plane. Individual layers are held together by the electrostatic forces of the thallium ions lying between them. It may be worth mentioning that the temperature factors of all the atoms in the structure have unusually large values in comparison with those of any compound including these atoms.

The interatomic distances and bond angles are listed in Tables 4 and 5 respectively. The atomic configuration of the Si_2S_6 group is illustrated in Fig. 2, along with the calculated bond lengths. The Si_2S_6 groups consist of two tetrahedra joined by a common edge, where two silicon atoms, Si(1) and Si(2), and two sulfur atoms, S(5) and S(6), in the four-membered ring lie on the same plane. The S(1) and S(2) atoms in the Si_2S_6 group seem to imply some terminal character due to comparatively weak bonding with indium atoms. Such atoms will be called "terminal" in the present paper. The terminal Si–S bond distances are shorter than the bridging Si–S bond distances. This feature is especially remarkable in the configuration of sulfur atoms bonded with Si(1). In the dimer, the mean Si(1)–S bond distance is longer than the mean Si(2)–S bond distance. This difference can be ascribed to the partial substitution of indium atoms for silicon atoms. The Si(1)–S distances for distorted $Si(1)S_4$ tetrahedron range from 2.230 to 2.365 Å, with an average of 2.297 Å, which is close to the value for the sum of the covalent radii, 2.30 Å, estimated by considering the occupancies of silicon and indium atoms at the Si(1) site. The terminal bonds have a definite π-content, while the bridging Si(1)–S bonds correspond approximately to single bonds. On the other

TABLE 4. BOND DISTANCES (l/Å), WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES, AN ASTERISK (*) INDICATES AN ATOM RELATED BY THE TWO-FOLD SYMMETRY

Si(1)-S(2)$_1$	2.230(8)	In-S(3)$_7$	2.296(7)
Si(1)-S(2)$_6$	2.230(8)	In-S(4)$_1$	2.331(7)
Si(1)-S(6)$_1$	2.362(10)	In-S(2)$_1$	2.346(9)
Si(1)-S(5)$_1$	2.365(10)	In-S(1)$_1$	2.379(7)
Mean:	2.297	Mean:	2.338
Si(2)-S(1)$_3$	2.111(7)		
Si(2)-S(1)$_8$	2.111(7)		
Si(2)-S(5)$_1$	2.117(11)		
Si(2)-S(6)$_1$	2.191(13)		
Mean:	2.133		
Tl(1)-S(3)$_1$	3.410(10)	Tl(2)-S(4)$_1$	3.293(11)
Tl(1)-S(2)$_1$*	3.471(9)	Tl(2)-S(6)$_3$*	3.382(11)
Tl(1)-S(2)$_6$*	3.471(9)	Tl(2)-S(3)$_3$*	3.512(10)
Tl(1)-S(1)$_1$*	3.519(7)	Tl(2)-S(2)$_4$	3.559(8)
Tl(1)-S(1)$_6$*	3.519(7)	Tl(2)-S(2)$_7$	3.559(8)
Tl(1)-S(5)$_7$	3.734(3)	Tl(2)-S(6)$_7$	3.650(2)
Tl(1)-S(5)$_7$*	3.734(3)	Tl(2)-S(6)$_7$*	3.650(2)
Tl(1)-S(1)$_2$*	3.957(7)	Tl(2)-S(1)$_2$*	3.780(7)
Tl(1)-S(1)$_5$*	3.957(7)	Tl(2)-S(1)$_5$*	3.780(7)
Mean:	3.641	Mean:	3.574

Code	Symmetry operator			Code	Symmetry operator		
1	x,	y,	z	5	$-x$,	$-y$,	$1/2+z$
2	$-x$,	$-y$,	$-z$	6	x,	y,	$1/2-z$
3	$1/2-x$,	$1/2+y$,	$1/2-z$	7	$1/2+x$,	$1/2-y$,	$-z$
4	$1/2+x$,	$1/2-y$,	$1/2+z$	8	$1/2-x$,	$1/2+y$,	z

TABLE 5. BOND ANGLES (ϕ/°) FOR SILICON AND INDIUM ATOMS, WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

S(2)$_1$-Si(1)-S(2)$_6$	113.8(4)
S(2)$_1$-Si(1)-S(5)$_1$	115.3(3)
S(2)$_1$-Si(1)-S(6)$_1$	110.3(3)
S(2)$_6$-Si(1)-S(5)$_1$	115.3(3)
S(2)$_6$-Si(1)-S(6)$_1$	110.3(3)
S(5)$_1$-Si(1)-S(6)$_1$	89.1(3)
Mean:	109.0
S(1)$_3$-Si(2)-S(1)$_8$	114.4(5)
S(1)$_3$-Si(2)-S(5)$_1$	108.7(3)
S(1)$_3$-Si(2)-S(6)$_1$	111.8(3)
S(1)$_8$-Si(2)-S(5)$_1$	108.7(3)
S(1)$_8$-Si(2)-S(6)$_1$	111.8(3)
S(5)$_1$-Si(2)-S(6)$_1$	100.6(5)
Mean:	109.3
Si(1)$_1$-S(5)-Si(2)$_1$	85.9(4)
Si(1)$_1$-S(6)-Si(2)$_1$	84.4(4)
S(1)$_1$-In-S(2)$_1$	105.8(3)
S(1)$_1$-In-S(3)$_7$	110.8(3)
S(1)$_1$-In-S(4)$_1$	112.9(3)
S(2)$_1$-In-S(3)$_7$	113.4(3)
S(2)$_1$-In-S(4)$_1$	110.0(3)
S(3)$_7$-In-S(4)$_1$	104.1(3)
Mean:	109.5
In$_4$-S(3)-In$_7$	103.8(4)
In$_1$-S(4)-In$_6$	104.0(4)

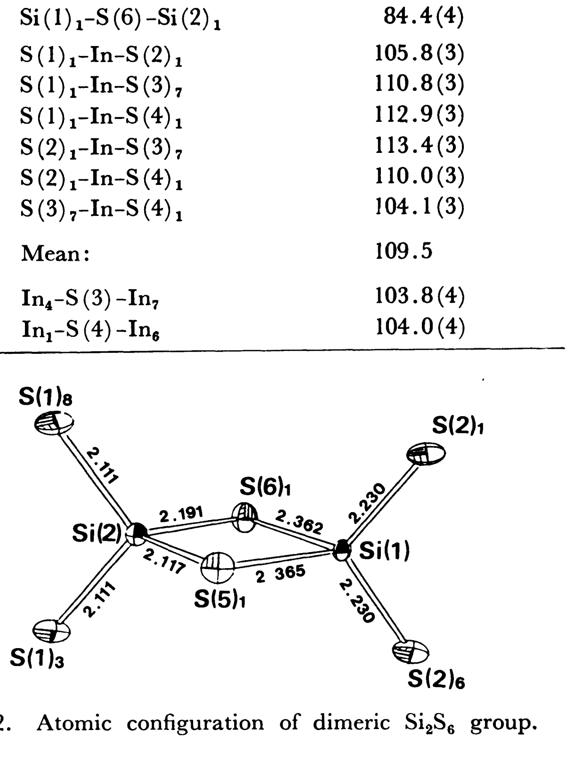


Fig. 2. Atomic configuration of dimeric Si_2S_6 group.

hand, in the distorted $Si(2)S_4$ tetrahedron, the partial substitution of the indium atom for the Si(2) site seems to have no influence on the Si(2)–S bond lengths, which range from 2.111 to 2.191 Å. The mean Si(2)–S bond length of 2.133 Å is closely related to the mean bond lengths observed in other thiosilicates, e.g., Fe_2SiS_4 (2.130 Å),[18] Ba_2SiS_4 (2.17 Å),[1] $Na_4Si_4S_{10}$ (2.107 Å; bridge, 2.144 Å; terminal, 2.035 Å),[8] and SiS_2 (2.13 Å).[19] The S(terminal)–Si–S(bridge) bond angles are in the 108.7—115.3° range; also, the S(terminal)–Si–S(terminal) bond angles are 113.8° for Si(1) and 114.4° for Si(2). These bond angles are larger than the regular tetrahedral angle of 109.28′. On the other hand, the S(bridge)–Si–S(bridge) bond angles within the four-membered ring, 89.1° for Si(1) and 100.6° for Si(2), are significantly smaller than those in the regular tetrahedron. The distortion from the regular tetrahedral angle must be due to the repulsion between the two positively charged silicon atoms. The formation of such dimers is, therefore, attributable to the tendency of the configuration of the four-membered ring to minimize repulsions by electrostatic force: the repulsions between the two positively charged silicon atoms and those between the two negatively charged sulfur atoms. This unexpected atomic configuration of the Si_2S_6 group, which is novel for thio- and oxo-anions, is similar to the structure of Al_2Cl_6 (in the gas phase) and Al_2Br_6, and is very similar to configurations of. *e.g.*, the $Ge_2S_6^{4-}$ anions in $Tl_4Ge_2S_6$[6] and $Na_4Ge_2S_6 \cdot 14H_2O$,[7] the $Ge_2Se_6^{4-}$ anion in $Na_4Ge_2Se_6 \cdot 16H_2O$,[20] and the $Sn_2S_6^{4-}$ anion in $Na_4Sn_2S_6 \cdot 14H_2O$.[7] On the contrary, taking into account the substitution of the indium atom for the Si(1) site, it appears that the SiS_4 tetrahedron combines with the InS_4 tetrahedron by means of a common edge to form a dimeric (SiS_3–InS_3) group. This is the first example of a dimer composed of both silicon and indium tetrahedra.

The indium atom is bonded to the four nearest sulfur atoms, thus forming an almost regular tetrahedron, as is shown in Fig. 3. The S–In–S bond angles range from 104.1 to 113.4°, with an average value of 109.5°. These values are in agreement with the regular tetrahedral angle of 109°28′. The In–S bond lengths in the range from 2.296 to 2.379 Å are significantly less than the values found in β-In_2S_3 (tetrahedron: 2.44—2.48 Å; octahedron: 2.54—2.68 Å).[21] These values are in accord with the value for the sum of the covalent radii, 2.32 Å, calculated on the basis of the occupancies of the indium atom and the silicon atom in the In site. The sharing of two sulfur atoms for each InS_4 tetrahedron may result in simple infinite chains with the formula of $(InS_3)_n$, as is shown in Fig. 1-(b). The In–S(1) and In–S(2) bond lengths, 2.346 and 2.379 Å, are somewhat longer than the In–S(3) and In–S(4) bond lengths, 2.296 and 2.331 Å. The dimeric Si_2S_6 groups hold the parallel chains by sharing two edges to form a two-dimensional sheet-like network (see Fig. 1).

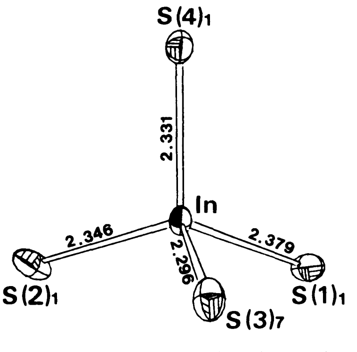


Fig. 3. Atomic arrangement in the InS_4 tetrahedron.

Two thallium atoms which are nonequivalent in the cell are located between these sheets, bonded weakly to their nearest neighbours. One of them, Tl(1), forms a 7+2 irregular coordination polyhedron (Fig. 4). Seven sulfur atoms are closer to the thallium atom at distances from 3.410 to 3.734 Å, while two sulfur atoms are further away, at distances of 3.957 Å. The average Tl–S distance for Tl(1) is 3.641 Å in the nine-fold coordination polyhedron. The arrangement of sulfur atoms around the other thallium atom, Tl(2), shows no systematic coordination geometry (Fig. 5), with nine Tl(2)–S contacts ranging from 3.293 to 3.780 Å, with the mean of 3.574 Å.

The mean Tl–S bond distances for the Tl(1) and Tl(2) atoms in the nine-fold coordination polyhedron are considerably longer than the mean bond distances for the similar coordination polyhedra found in $Tl_4Ge_4S_{10}$ (Tl–S: 3.43 Å)[10] and in thallium sulfosalts, *e.g.*, simo-

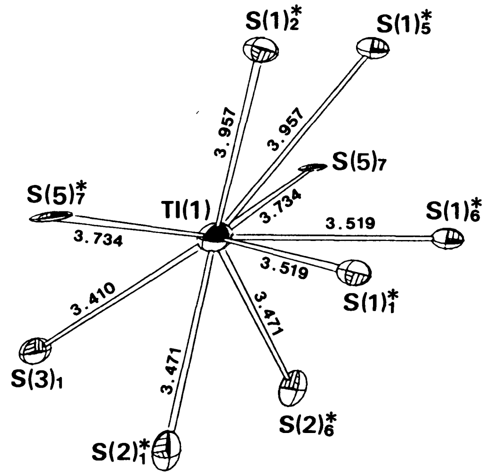


Fig. 4. Coordination of the sulfur atoms about the Tl(1) atom.

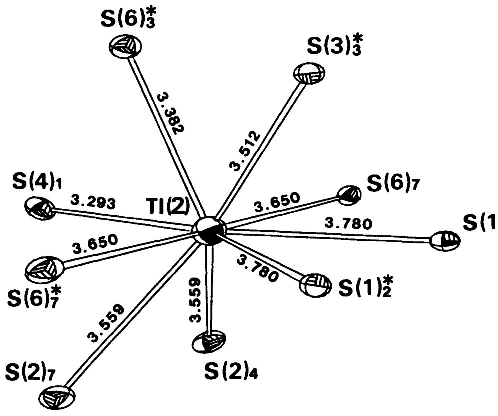


Fig. 5. Coordination polyhedron of the Tl(2) atom.

nite, $TlHgAs_3S_6$ (Tl–S: 3.43 Å)22) and synthetic parapierrotite, $TlSb_5S_8$ (Tl–S: 3.39 Å).23) Because those long bond distances represent relatively weak bonding interactions, such substances might be expected to cleave most readily in directions parallel to the sheets, as is observed in micas. In fact, this expectation is confirmed in a series of quaternary chalcogenides having the formulae of $TlInSiS_4$, $TlInGeS_4$, $TlGaSiS_4$, $TlGaGeS_4$, and $TlAlGeS_4$.13)

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