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The Crystal and Molecular Structure of Diethylthioselenophosphinatothallium(I)

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The crystal and molecular structure of diethylthioselenophosphinatothallium(I), [Tl(Et_2PSeS)], has been determined and refined by three-dimensional X-ray methods. The crystals are monoclinic and belong to the space group C_{2h}^3-C2/m. There are four formula units in the cell with $a=10.342(3)$ Å, $b=9.116(3)$ Å, $c=10.154(2)$ Å, and $\beta=101.98(2)°$. Calculated density is 2.88 g/cm³. For the structure analysis 997 reflection intensities above background were collected on a Siemens AED-1 single-crystal diffractometer. Full-matrix least squares refinement resulted in a conventional R-value of 0.088.

The structure can be considered as built up of dimeric units, [Tl(Et_2PSeS)]$_2$, linked together in two-dimensional polymeric layers parallel to the ab-plane. Each thallium atom is coordinated to two sulphur and two selenium atoms in the dimer and to two more distant selenium atoms belonging to different neighbour dimers. The Tl–S and Tl–Se bond lengths in the dimer are 3.237(5) Å and 3.424(4) Å, respectively, while the intermolecular Tl–Se contacts are 3.594(3) Å.

Monovalent thallium has the $(n-1)d^{10}ns^2$ configuration found also in tetravalent tellurium and selenium, trivalent arsenic, antimony, and bismuth and in divalent lead and tin. Studies of complexes of these elements have shown that the ns^2 lone pair in some compounds is stereochemically inert.[1] In other compounds it occupies either a position in the coordination polyhedron,[2–9] or it has some p-character, pointing in between some weak central atom to ligand bonds.[10] The latter type of stereochemical activity has been found in monovalent thallium compounds.[10]

In many respects the thallium(I) compounds bear a certain resemblance to the alkali and the coinage metals. Structural studies of dithiocarbamates of monovalent gold,[11] copper,[12] silver,[13] cesium [14], and thallium [15,16] have shown a tendency for these metal complexes to occur as polymers. While the complexes of the first three metals are arranged as isolated low polymers, the others can be considered as interconnected dimers having very interesting structures. Dipropyldithiocarbamatothallium(I),[15] [Tl{(n-pr)$_2$NCS$_2$}], is built as a chain arrangement of dimeric units, while in diisopropyldithiocarbamatothallium(I),[16]

[Tl{(iso-pr)$_2$NCS$_2$}], and in dibutyldithiocarbamatocesium(I),[14] [Cs{(bu)$_2$NCS$_2$}], the dimers are linked together into layers.

The present structure determination was undertaken to further investigate the polymeric nature of Tl(I) compounds and also the role of the lone pair of electrons in such compounds as mentioned above.

EXPERIMENTAL

For the present study, the thioselenophosphinate complex of monovalent thallium was prepared by Kuchen *et al.* by reaction between trivalent thallium and diethylthioselenophosphinate ions.[17]

$$Tl^{3+} + 3Et_2PSeS^- = Tl(Et_2PSeS) + (Et_2PSeS)_2$$

The crystals were recrystallized from chloroform solution as small colorless prisms elongated along the *c* axis.

Preliminary cell dimensions and the space group were determined by film methods.

For recording of data, a Siemens automatic, off-line single-crystal diffractometer (AED-1) was used. The diffractometer was operated as a three-circle instrument using Nb-filtered Mo$K\alpha$ radiation. A crystal with dimensions $0.22 \times 0.13 \times 0.09$ mm^3 was mounted with the *c* axis along the ϕ-axis of the instrument.

During exposure to X-rays, the crystal surface became slowly covered by a yellow powder. This decomposition caused the intensities of the standard reflections to decrease nearly 20 % during the data collection. The crystal orientation and unit cell dimensions were determined by measuring θ, χ, and ϕ angles for 15 reciprocal vectors. The setting angles for all reflections could then be calculated.

For determination of accurate unit cell parameters by means of least squares methods, the θ angles of 18 reflections with high θ were measured. The cell data are $a = 10.342(3)$ Å, $b = 9.116(3)$ Å, $c = 10.154(2)$ Å, and $\beta = 101.98(2)°$. There are four formula units in the cell with calculated density 2.88 g/cm^3. The systematic absences are *hkl* for $h+k=2n+1$, in the monoclinic crystal system. Thus the space group is either $C2$, Cm, or $C2/m$.

The intensity data were collected using the five-value measuring procedure and $\theta - 2\theta$ scan technique.[18] The scan speed was 2.5°/min, with automatic setting of higher speed for strong reflections. To avoid counting losses for high intensity reflections, the diffractometer inserts a proper attenuation filter into the primary beam. Each reflection was scanned between $\theta_1 = \theta - 0.5°$ and $\theta_2 = \theta + 0.5°$, where θ is the Bragg angle for the α_1-peak. The scanning was performed by going from θ to θ_1, then from θ_1 to θ_2 and finally from θ_2 to θ. The intensities for all three scans and their sum, I_t, were recorded. Likewise the background was measured for one half of the total scan time at each side of the reflection, and the respective intensities and their sum I_b were also recorded. The net count for a reflection, I_N, was put equal to $I_t - I_b$.

In order to bring the net intensities to a common scale and to check the crystal orientation, two reference reflections were measured at intervals of 50 reflections. Out of 1193 reflections attainable with $\theta \leq 28°$, 997 were found to have intensities stronger than twice the standard deviation. The remaining reflections were labelled as unobserved and each assigned an intensity equal to twice its standard deviation. This standard deviation was defined as the square root of the sum of the total intensity and the intensity of the background.

The data were corrected for Lorentz and polarization effects. During the refinement an absorption correction was applied ($\mu = 219$ cm^{-1}) using the Gaussian integration method as described by Coppens *et al.*[19] However, as both the standard deviations of the parameters and the *R*-factor increased afterwards, this data correction was omitted. The reason for this negative result may be the decomposition of the crystal as mentioned above. No extinction correction was found necessary.

The calculated structure factors were based on the atomic scattering curves given in *International Tables for X-ray Crystallography*,[20] Table 3.3.1 A. The curves for thallium were corrected for anomalous dispersion using the $\Delta f'$ and $\Delta f''$ values given by Cromer,[21] and taking the amplitude of f as the corrected value.

STRUCTURE DETERMINATION AND REFINEMENT

A three-dimensional Patterson map, calculated on the basis of the 997 observed reflections, could only be interpreted in terms of a dimeric complex. In the centric space group $C2/m$, which was the first choice, the dimers had to occupy special twofold positions with the thallium atoms on a twofold axis parallel with b and the selenium, sulphur, and phosphorus atoms lying in a mirror plane halfway between the two thallium atoms and at right angles to b. The center of the dimer, *i.e.* the intersection between the twofold axis and the mirror plane, is thus a center of symmetry.

The thallium position was taken from the Patterson map. A Fourier map with signs based on the thallium contribution then allowed the location of the selenium, sulphur, and phosphorus atoms. From the next electron density map, the positions of the carbon atoms were found.

Full-matrix least squares refinement was then carried out using a program (BDLS) which minimizes the expression $r = \sum w(|F_o| - K|F_c|)^2$. Here K is a variable scale factor and w, the relative weight assigned to a reflection, is equal to $1/\sigma^2$ (F_o). The variance of F_o is evaluated as $F_o^2\{(I_t + I_b + k^2(I_t - I_b)^2\}/4(I_t - I_b)^2$, where k may be interpreted as the relative standard deviation in the scaling curve based on the reference reflections. Non-observed reflections with $K|F_c|$ larger than the observable limit are included in the refinement with F_o put equal to the limit.

After a few cycles of refinement of coordinates and isotropic temperature factors for all atoms except hydrogen, the reliability index, $R = \sum||F_o| - |F_c||/\sum|F_o|$, reached a value of 0.109.

After introducing anisotropic temperature factors for all atoms (except hydrogen) the R-factor converged to a value of 0.088. The shifts were less than one tenth of the estimated standard deviations.

In the light of the high temperature factors of selenium related to those of sulphur ($U = 0.093$ for Se, and 0.042 for S), disorder in the positions of these atoms could be possible. Subsequent refinement based on two different configurations of the dimers, such that the selenium and sulphur atoms exchanged positions resulted in the original single configuration.

Attempts to refine the structure in the non-centric alternative space groups were not successful.

A final difference electron density map showed a maximum peak of 2.8 e/Å^3 near the thallium position. Possible explanations could be the omission of an absorption correction, termination of series errors, and the somewhat poor quality of the data due to the decomposition of the crystal. Similar peaks have also been found in difference maps for other Tl(I) compounds.[22,23]

Observed and calculated structure factors following the last refinement cycle can be obtained from the authors, upon request.

RESULTS AND DISCUSSION OF THE STRUCTURE

The final positional and thermal parameters are listed in Tables 1 and 2. Interatomic distances and angles are listed in Tables 3 and 4.

Table 1. Final atomic coordinates in fraction of cell edges with standard deviations in brackets.

	x	y	z
Tl	0.0	0.2117(2)	0.0
Se	−0.2578(4)	0.0	0.0533(5)
S	0.0551(6)	0.0	0.2616(7)
P	−0.1441(8)	0.0	0.2521(9)
C_1	−0.188(3)	0.157(4)	0.351(3)
C_2	−0.135(4)	0.298(4)	0.317(4)

Table 2. Components of atomic vibration tensors, $U \times 10^3$, in Å^2 with standard deviations, referred to crystallographic axes. For all atoms the expression is $\exp\{-2\pi^2[h^2a^{-2}U_{11}+k^2b^{-2}U_{22}+l^2c^{-2}U_{33}+2hka^{-1}c^{-1}U_{12}+2klb^{-1}c^{-1}U_{23}+2hla^{-1}c^{-1}U_{13}]\}$.

Tl	63.2(0.8)	63.6(0.9)	62.9(0.8)	(U_{11},U_{22},U_{33})
	0.0	0.0	19.1(0.6)	(U_{12},U_{23},U_{13})
Se	68.4(2.6)	118.0(3.8)	95.2(3.1)	
	0.0	0.0	11.7(2.3)	
S	20.8(2.9)	68.6(4.8)	44.3(3.7)	
	0.0	0.0	8.6(2.6)	
P	39.4(4.2)	93.3(7.0)	61.9(5.2)	
	0.0	0.0	18.5(3.7)	
C_1	78.1(17.9)	123.2(27.6)	113.3(22.7)	
	22.0(18.4)	−41.1(21.0)	38.0(16.5)	
C_2	152.4(32.0)	78.5(23.5)	178.1(38.0)	
	44.1(23.8)	22.4(24.1)	64.3(27.9)	

Table 3. Interatomic distances (Å) and angles (°) within the dimeric $[Tl(Et_2PSeS)]_2$ unit. Standard deviations in brackets. For atomic labels, see Fig. 2.

Bond lengths		Bond angles	
Tl−Se	3.424(4)	Se−Tl−S	62.9(1)
Tl−S	3.237(5)	Tl−Se−P	81.6(2)
P−Se	2.115(9)	Tl−S−P	87.5(3)
P−S	2.042(10)	Se−P−S	113.6(4)
P−C_1	1.86(4)	Se−P−C_1	111.5(9)
C_1−C_2	1.46(5)	S−P−C_1	109.3(8)
		P−C_1−C_2	113.7(25)
		C_1−P−C_1	100.7(15)
Interatomic contacts		S−Tl−S′	106.8(1)
		S−Tl−Se′	77.5(1)
Tl···Tl′	3.859(2)	Se−Tl−Se′	111.4(1)
Se···S	3.479(7)	Tl−Se−Tl′	68.6(1)
Tl···P	3.753(8)	Tl−S−Tl′	73.2(1)

Table 4. Some interatomic distances (Å) and angles (°) involving dimer-dimer interactions. Standard deviations in brackets. For atomic labels, see Fig. 2.

Tl···Se = 3.594(3)	Se(I)···Tl···Se(II)	86.0(1)
	Se(I)···Tl···Se	158.4(1)
	Se(I)···Tl···Se′	84.0(1)
	Se(I)···Tl···S	108.3(1)
	Se(I)···Tl···S′	123.9(1)
	Tl(I)···Se···Tl(II)	94.0(1)
	Tl(I)···Se···Tl	158.4(1)
	Tl(I)···Se···Tl′	96.0(1)

Some bond lengths and angles in a diethylthioselenophosphinatothallium(I) dimer are shown in Fig. 1. Views of the unit cell contents seen along the *c* and the *a* axis are shown in Fig. 2 and Fig. 3, respectively. A stereoscopic drawing showing the packing of molecules is given in Fig. 4.

The crystal structure can be regarded as built up of dimeric units, [Tl(Et$_2$PSeS)]$_2$, linked together in two-dimensional polymeric layers parallel to the *ab*-plane. Each thallium atom is bonded to two sulphur and two selenium atoms in the dimer, thallium being at the top of an approximately square pyramid with the latter atoms forming its base. However, each thallium atom also has two more distant selenium neighbours in the opposite direction, belonging to different adjacent dimers. The metal atom is thus coordinated by six atoms situated at the corners of a distorted trigonal prism. In each layer the metal atoms form a central sheet surrounded on both sides by the ligands. The only interactions between adjacent layers are of van der Waals type between the alkyl groups.

The crystal structure resembles those found for dipropyldithiocarbamatothallium(I) [15] and diisopropyldithiocarbamatothallium(I),[16] where the same type of dimers and ligand bridges are observed. In the dipropyl complex the dimers are linked into chains, while in its diisopropyl analogue the dimers are connected into layers. The similarities are even greater in dibutyldithiocarbamatocesium(I),[14] where the layer structure is essentially the same as in the

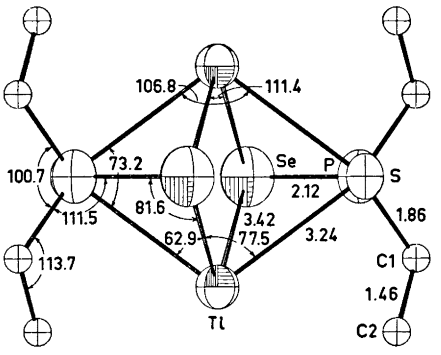

Fig. 1. The [Tl(Et$_2$PSeS)]$_2$ dimer as seen along the *c* axis with some bond lengths and bond angles indicated. The thermal ellipsoids of Tl, Se, S and P correspond to 50 % probability.

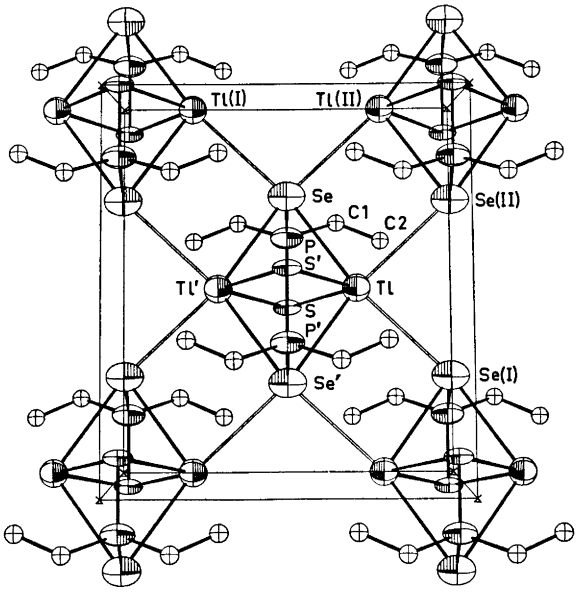

Fig. 2. A view of the unit cell as seen along the *c* axis. Unfilled bonds represent dimer-dimer contacts.

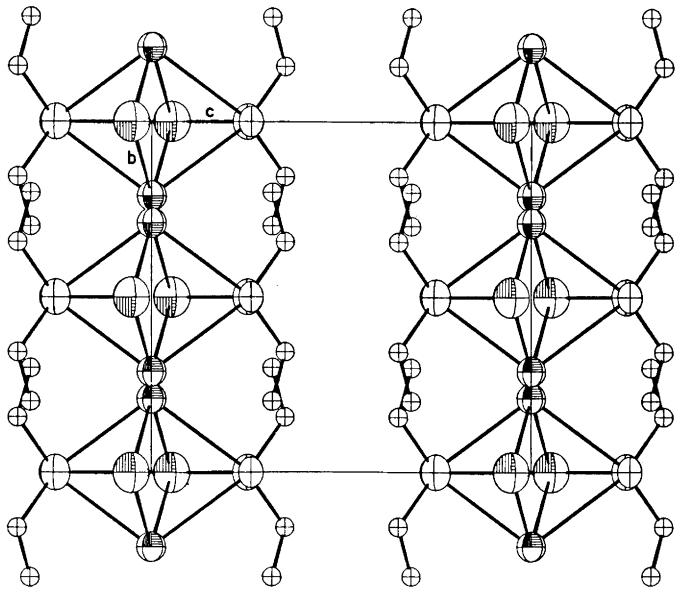

Fig. 3. A view of the unit cell as seen along the *a* axis.

present complex. A recently terminated structure investigation of diethyldithiophosphinatothallium(I),[23] [Tl(Et_2PS_2)], shows this structure to consist of monomeric units, linked together in two-dimensional polymeric layers.

The thallium-sulphur and thallium-selenium bond lengths within the dimeric unit are found to be 3.237(5) Å and 3.424(4) Å, respectively. The dimers are linked together in two-dimensional polymeric layers by thallium-selenium contacts of 3.594(3) Å. The view that the structure is built up of dimeric units is justified by the shorter thallium-selenium coordination distances within the dimer and the shorter Tl...Tl separation. In the dimer the intermetallic distance is found to be 3.859(2) Å, while the corresponding distance between adjacent dimers is 5.2 Å. Similar metal-metal distances are observed in thallium(I) methoxide,[24] $TlOCH_3$, where the intermetallic separation within the tetrameric molecules are on the average 3.84 Å. In [Tl{n-pr)$_2$NCS$_2$}] [15] the alternating interatomic distances are 3.98 Å and 4.00 Å, while in the cyclopentadienyl compound, C_5H_5Tl,[25] the metal-metal separations are all equal to 3.99 Å. In [Tl{(iso-pr)$_2$NCS$_2$}],[16] the distance between the two metal atoms in the same dimeric unit is found to be 3.584(5) Å, and this is significantly shorter than the corresponding distance in the former compounds. Whether bonding interactions between the metal atoms in all these structures occur is not clear, but according to Frasson *et al.*[25] the metal-metal distances are such as to allow the possibility of metal-metal interactions. For comparison, the shortest intermetal distances in the α-form of thallium are 3.41 Å and 3.46 Å.[26]

Similar metal-coordination as in the present investigation of diethylthioselenophosphinatothallium(I), or more correctly of bis(diethylthioselenophosphinatothallium(I)), is found in some lead salts of dithioacids. Both in diethyldithiophosphatolead(II),[27] [Pb{(EtO)$_2$PS$_2$}$_2$], and in diethyldithiocarbamatolead (II),[28] [Pb(Et_2NCS_2)$_2$], the coordination around the lead atom is a distorted tetragonal pyramid, with two distant sulphur neighbours in the opposite direction. The latter two lead-sulphur distances are, however, too large for any

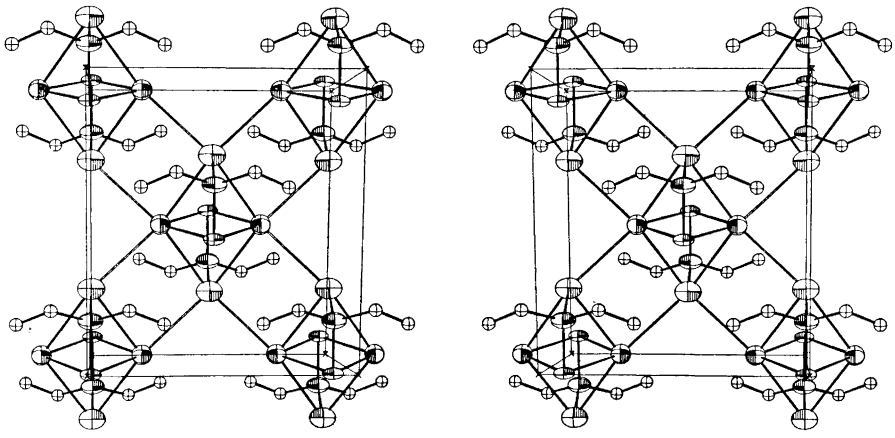

Fig. 4. A stereoscopic drawing showing the packing of molecules as seen along the *c* axis.

bonding interaction.[27,28] A somewhat similar configuration is also found in red PbO,[29,30] except that there Pb(II) has four distant neighbours as compared to the two found here for Tl(I). It is believed that in PbO the 6*s* electron pair in Pb(II) occupies a *sp* hybridized orbital pointing away from the four near neighbours and that the repulsion between this lone pair of electrons and the ligands explains the deviation from cubic symmetry.[10,29] Exactly the same structure is found for SnO.[10,29] In TlI[31] there are five near neighbours and two distant ones, with the lone pair localized between the two weaker bonds. In the present case, the *sp*-hybridized lone pair then correspondingly points away from the four near sulphur and selenium neighbours and is located in between the two weak intermolecular Tl...Se bonds.

The thallium-sulphur bond lengths of 3.237(5) Å found in the present investigation may seem large. Bond distances of the same order of magnitude are, however, found in other thallium(I) compounds. In dipropyldithiocarbamatothallium(I)[15] the Tl – S coordination distances within the dimer range from 2.88 Å to 3.29 Å, while in the diisopropyl analogue[16] the corresponding lengths show smaller variations and vary between 2.98 Å and 3.05 Å. In diethyldithiophosphinatothallium(I)[23] the intramolecular Tl – S bonds are found to be 3.056(7) Å, while the intermolecular Tl – S distances are 3.429(10) Å and 3.453(7) Å. In $Tl_2S.Tl_2S_3$, studied by Hahn and Klingler[32] where the monovalent thallium atoms are eight-coordinated the Tl(I) – S distance is determined to be 3.32 Å, a bond length in accordance with the sum of the Pauling ionic radii of Tl^+ and S^{2-} of 3.28 Å.[33] The authors also interpreted the interaction to be mainly ionic. A similar interpretation is given by Verhoef, Boeyens and Herbstein to the Tl – S coordination distances ranging from 3.38 Å to 3.45 Å found in some thiourea complexes of thallous salts.[34–36] As a larger bond distance than the sum of the ionic radii was found, the interaction was proposed to be of ion-dipole type. There does not seem to be any definite covalent radius for thallium available in the literature; however, a covalent Tl – S distance varying between 2.5 Å and 2.8 Å seems to be probable.[32,34] According to Slater the sum of the atomic radii of thallium and sulphur is 2.90 Å.[37]

The intramolecular thallium-selenium bond of 3.424(4) Å is relatively weaker than the thallium-sulphur bond, as the difference in bond lengths is larger than the difference in the selenium and sulphur covalent radii. This is, however, not surprising as only the selenium atoms are engaged in dimer-dimer interactions. This difference between sulphur and selenium is further reflected in the corresponding Se – P and S – P bond lengths of 2.115(9) Å and 2.042(10) Å, respectively. The former is just significantly larger (0.04 Å) than 2.07 Å, the sum of the P and Se double bond radii, while the latter is 0.10 Å larger than a P = S double bond.[33] For comparison the P – Se and P – S single bond lengths corrected for bond polarity are 2.24 Å and 2.10 Å, respectively. The relatively strong P – S and P – Se bonds found are not unexpected in view of the large Tl – S and Tl – Se coordination distances. The double-bond character of these bonds is also indicated from IR spectra recorded by Kuchen and Hertel.[38]

The large Tl – S and Tl – Se bond lengths in the present structure investigation are probably partly due to a high degree of ionic character and partly to the bridging nature of the sulphur and selenium atoms.

Table 5. Selected interatomic distances in some Tl(I) compounds in Å. Standard deviations in brackets.

[a]	Tl – S	Tl – Se	Tl – Tl
[Tl(Et_2PSSe)]	3.237(5)	3.424(4)	3.859(2)
[Tl{(n-pr)$_2$NCS$_2$}] [15]	2.88 – 3.29(0.015)		3.977(4)
[Tl{(iso-pr)$_2$NCS}] [16]	2.977 – 3.050(0.103)		3.584(5)
$Tl_2S.Tl_2S_3$ [32]	3.32		
[Tl(tu)$_4$]NO_3 [34]	3.43(0.015)		
[Tl(tu)$_4$]ClO_4 [34]	3.43		
	3.46		
[Tl(tu)$_4$]H_2PO_4 [35]	3.446(8)		
	3.410(8)		
[Tl(tu)$_4$]C_6H_5COO [36]	3.45(1)		
	3.38(1)		
Sum of Slater atomic radii [37]	2.90	3.05	3.80
Sum of Pauling ionic radii [33]	3.28	3.42	2.88

[a] tu = thiourea, n-pr = propyl and iso-pr = isopropyl.

The intermolecular thallium-selenium distance of 3.594(3) Å is significantly larger than the sum of the Pauling ionic radii of Tl^+ and Se^{2-} of 3.42 Å.[33] However, there is no doubt that a dimer-dimer interaction exists.

For comparison, selected interatomic distances in some Tl(I) compounds are given in Table 5.

The phosphorus-carbon and carbon-carbon bonds correspond to normal values within the error limits, and the bond angles on the phosphorus atom are in good agreement with sp^3-hybridization on this atom.

The shortest interlayer contact is found to be 3.91(5) Å, and this is the only distance shorter than 4 Å. This is between the methylene carbons in the ethyl groups. The weak interlayer contacts may perhaps be the cause of the relatively high temperature factors found for the structure.

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