The Crystal and Molecular Structure of Diethyldithio-phosphinatothallium (I)

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The crystal and molecular structure of diethyldithiophosphinatothallium(I), [Tl(Et$_2$PS$_2$)], has been determined from three-dimensional X-ray data collected by multiple-film technique using CuKα radiation. The crystals are orthorhombic with space group *Pcca*. The unit cell contains four formula units and has the dimensions $a = 9.026(3)$ Å, $b = 12.134(2)$ Å, and $c = 8.468(3)$ Å. The calculated density is 2.56 g/cm^3. Full matrix least squares refinement of the structure has yielded a final value of the conventional R-factor of 0.094 for 376 visually estimated reflections.

The structure is built from monomeric units linked together in two-dimensional polymeric layers parallel to the *ac*-plane. Each metal atom is coordinated by six sulfur atoms; two of these belong to the monomer, the remaining four, more distant ones, belong to four different adjacent monomers. The Tl−S distances are found to be 3.056(7) Å, 3.429(10) Å, and 3.453(7) Å.

Studies of dithiocarbamate complexes of monovalent copper, silver, gold, cesium, and thallium have revealed that these exist as polymers, both in solutions of nonpolar organic solvents [1-4] and in the solid state. [5-10] Not much is at present known with certainty about the structures of the dissolved polymers, but in most cases the degree of polymerisation obtained from solution studies agrees well with the crystal structure results. Whereas the complexes of the first three metals mentioned above are arranged as discrete low polymers, the others can be considered as interconnected dimers having very interesting structures. Dipropyldithiocarbamatothallium(I), [9] Tl(pr)$_2$-NCS$_2$, has a chain arrangement of dimeric units, whereas the dimers are linked together into

layers in diisopropyldithiocarbamatothallium-(I), [10] Tl(iso-pr)$_2$NCS$_2$, and in dibutyldithiocarbamatocesium(I), [8] Cs (bu)$_2$NCS$_2$.

The preparation of a number of metal complexes of thio- and selenophosphinic acids has been reported by Kuchen and Hertel. [11] Some of these complexes appear to be associated in nonpolar organic solvents. [11,12] The diethyldithiophosphinato complex of monovalent thallium, with which the present crystallographic study is concerned, was found to have an average degree of association in chloroform and benzene solution of 1.45 and 1.25, respectively; *i.e.*, although the molecules are associated, they are best described as built up from monomeric units. Considering the agreement between the degrees of polymerization of various dithiocarbamate metal complexes in solution and in the solid state, and the essentially dimeric crystal structure found for the diethylthioselenophosphinate analogue of thallium(I), [13] some kind of polymeric arrangement was also expected to be found in the present investigation.

EXPERIMENTAL

The crystals used in the investigation were made by Kuchen *et al.* [12] They were prepared by reduction of trivalent thallium by diethyldithiophosphinate ions:

$$Tl^{3+} + 3Et_2PS_2^- = Tl(Et_2PS_2) + (Et_2PS_2)_2$$
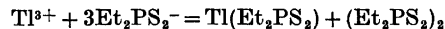
The crystals were recrystallized from chloroform solution, and were obtained as thin colourless plates elongated along the *c* axis.

Unit cell parameters were calculated from 51

high-order reflections read from NaCl-calibrated Weissenberg $0kl$ and $hk0$ films, employing $CuK\alpha$ radiation. Refinement by least squares gave final values of $a = 9.026(3)$ Å, $b = 12.134(2)$ Å and $c = 8.468(3)$ Å. There are four molecules in the cell. The calculated density is 2.56 g/cm³. From systematic absence, $0kl$ for $l = 2n + 1$, $h0l$ for $l = 2n + 1$ and $hk0$ for $h = 2n + 1$, the space group is $D_{2h}^8 - Pcca$.

Using the multiple-film technique, Weissenberg equi-inclination photographs were taken of the $hk0$, $hk1$, $hk2$, $hk3$, and $0kl$ layers, using Ni-filtered $CuK\alpha$ radiation. Reflection intensities were estimated visually. Of 507 independent reflections 376 were observed. The data were corrected for Lorentz and polarization effects to give sets of relative structure factors. During refinement they were also corrected for absorption effects ($\mu = 386$ cm⁻¹), using the Gaussian integration method as described by Coppens et al.[14] The number of grid points used along the a, b, and c axes were 14, 4, and 14, respectively, for both crystals.

The calculated structure factors were based on the atomic scattering curves given in International Tables for X-Ray Crystallography,[15] Table 3.3.1A. The curves for thallium were corrected for anomalous dispersion using the $\Delta f'$ and $\Delta f''$ values given by Cromer,[16] and taking the amplitude of f as the corrected value.

STRUCTURE DETERMINATION

In addition to the general absences, reflections hkl with $h + l = 2n + 1$ were systematically weaker than the others. This indicated that the molecules occupy fourfold special positions with the thallium and phosphorus atoms on twofold axes, i.e., the structure is probably to be interpreted in terms of monomeric molecules.

The atomic positions except those for hydrogen were determined by standard Patterson and Fourier techniques.

The refinement was carried out on an IBM 360/50H computer, using a full-matrix least squares program which minimizes the expression $r = \sum w(|F_o| - K|F_c|)$.[2] K is a scale factor and w, the relative weight assigned to a reflection, is the reciprocal of the variance, $1/\sigma^2(F)$. $\sigma^2(F)$ is equal to $(Ka_1)^2 + (a_2F_o)^2/4w_o + (a_3F_o)^6$, where w_o is a variable related to the reliability with which the intensity of a given reflection is measured, and a_1, a_2, and a_3 are constants. These were first put equal to 2.0, 1.0, and 0.0, but were on a later stage of refinement changed to 0.8, 0.15, and 0.012, respectively. Unobserved reflections were included with $|F_o|$ equal to

the observable limit, when $|F_c|$ exceeded this limit.

The difference map calculated on the basis of the thallium, sulfur, and phosphorus contributions showed a peak corresponding to about 6e⁻/Å³ and two peaks corresponding to about half this value. The largest was chosen as the methylene carbon position in the ethyl group, the two other maxima might then both correspond to the methyl carbon. Attempts to refine the structure, placing methyl carbon in either of the two positions mentioned above were not successful. It was then thought likely that the ethyl group was disordered, i.e., there are two types molecules, corresponding to two different configurations of the ethyl group statistically distributed in the crystals. Based on a 1:1 distribution of the two types of molecules, and isotropic temperature factors for all atoms, the structure refined satisfactorily, to a value of the reliability index, $R = \sum ||F_o| - |F_c||/\sum |F_o|$, of 0.180.

At this stage of refinement the data were corrected for absorption, leading to an R-value 0.122. Finally, anisotropic temperature factors were applied to the thallium, sulfur and phosphorus atoms. The R-factor converged at a value of 0.094.

A final difference electron density map showed a peak of 2.5 e⁻/Å³ near the thallium position. Similar peaks have also been found in difference maps for other thallium compounds.[13,17]

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

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

	x	y	z
Tl	0.0	0.0858(1)	0.25
S	0.1407(7)	−0.1251(5)	0.1219(12)
P	0.0	−0.2132(6)	0.25
C1	0.111(3)	−0.306(2)	0.386(4)
C21[a]	0.216(7)	−0.375(5)	0.323(10)
C22[a]	0.019(7)	−0.395(5)	0.461(12)

[a] Methyl carbon positions in the disordered ethyl group.

Table 2. Components of atomic vibration tensors, $U \times 10^3$, in Å² with standard deviations, referred to crystallographic axes. For Te, S, and P, the expression is $\exp\{-2\pi^2 \times [U_{11}(ha^{-1})^2 + U_{22}(kb^{-1})^2 + U_{33}(lc^{-1})^2 + 2U_{12}a^{-1}b^{-1}hk + 2U_{23}b^{-1}c^{-1}kl + 2U_{13}a^{-1}c^{-1}hl]\}$. For carbon atoms the expression is $\exp[-8\pi^2 U(\sin^2\theta/\lambda^2)]$.

Tl	71.1(1.1)	58.7(0.9)	71.3(1.8)	(U_{11}, U_{22}, U_{33})
	0.0	0.0	2.3(1.4)	(U_{12}, U_{23}, U_{13})
P	46.3(3.4)	49.1(3.3)	51.2(6.7)	
	0.0	0.0	−4.6(7.5)	
S	59.0(2.9)	64.3(2.8)	89.9(7.2)	
	−0.2(3.0)	−0.3(4.4)	7.2(5.3)	
Cl	65.2(6.8)			(U)
C21	82.2(17.1)			
C22	102.2(24.1)			

RESULTS AND DISCUSSION OF THE STRUCTURE

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

Table 3. Bond lengths (Å) and angles (°) in a diethyldithiophosphinatothallium(I) molecule. Standard deviations in brackets. Atoms in the other half of the molecule related to those in the asymmetric unit are denoted by primed letters.

Tl−S	3.056(7)	∠S−Tl−S′	66.2(2)
S−P	1.982(9)	Tl−S−P	89.5(3)
P−Cl	1.89(3)	S−P−S′	114.7(4)
Cl−C21	1.38(7)	S−P−Cl	108.4(8)
Cl−C22	1.50(8)	Cl−P−Cl′	107.5(12)
S−S′	3.34(1)	P−Cl−C21	119.1(36)
distance			
		P−Cl−C22	113.1(31)
		C21−Cl−C22	95.7(40)

Table 4. Intermolecular distances in Å. The left column represents distances from an atom in the original molecule (Table 2) to an atom in a molecule whose transformation from the original one is listed in the second column.

Tl−S	$\frac{1}{2}-x, -y, z$	3.453(7)
Tl−S	$x-\frac{1}{2}, -y, \frac{1}{2}-z$	3.453(7)
Tl−S	$-x, -y, -z$	3.429(10)
Tl−S	$x, -y, z+\frac{1}{2}$	3.429(10)
S−S	$\frac{1}{2}-x, -y, z$	3.621(9)
S−Cl	$\frac{1}{2}-x, y, z-\frac{1}{2}$	3.72(3)
C21−C22	$\frac{1}{2}-x, -(y+1), z$	3.86(9)
C21−C22	$-x, -(y+1), 1-z$	3.95(11)
C21−C22	$\frac{1}{2}-x, y, z-\frac{1}{2}$	3.90(12)

Bond lengths and bond angles in a diethyldithiophosphinatothallium(I) molecule are shown in Fig. 1. A view of the unit cell seen along the b-axis is shown in Fig. 2. A stereoscopic drawing showing the packing of molecules is given in Fig. 3.

The crystals of diethyldithiophosphinatothallium(I) are built from monomeric units linked together in two-dimensional polymeric layers with a thickness of two molecules parallel to the ac-plane. Each thallium atom is coordinated to six sulfur atoms situated at the corners of a distorted trigonal prism. Two of these sulfur atoms belong to the molecule proper, the remaining four more distant ones belong to four different adjacent molecules. In addition to the Tl−S intermonomer bonds, there also exist S−S, S−C, and C−C van der Waals contacts between molecules in the same layer. The only interactions between adjacent layers are of van der Waals type between the alkyl groups.
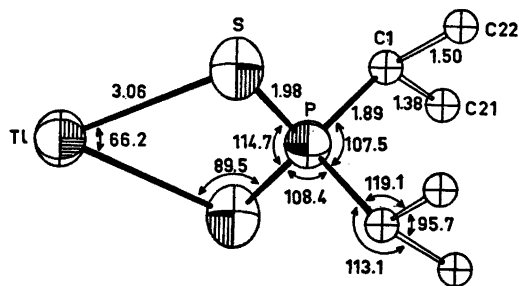

Fig. 1. The molecule with bond lengths and bond angles indicated. Both methyl carbon atoms in the disordered ethyl groups are shown.
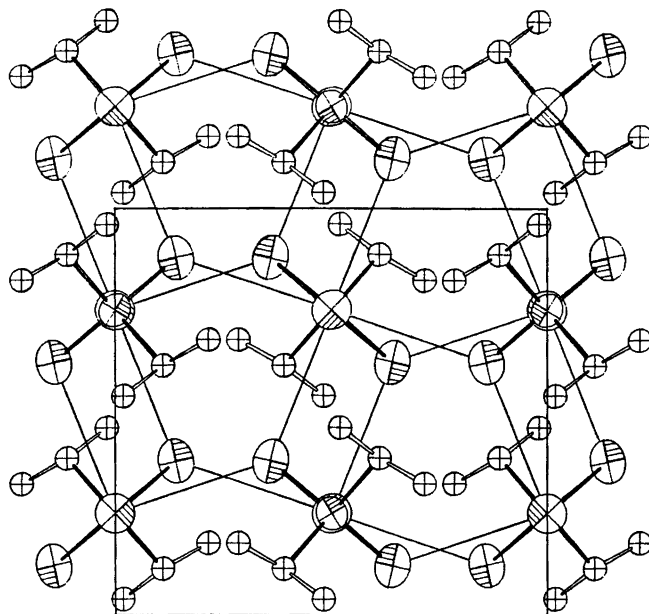
Fig. 2. A view of the unit cell as seen along the *b* axis. Intermolecular Tl − S contacts are indicated by weaker lines. The complete set of four contacts are shown only for the thallium atom in the center of the figure.

Also the structure of diethylthioselenophosphinatothallium(I) [13] and diisopropyldithiocarbamatothallium(I)[10], are built as layer arrangements. The complex described here must be regarded as consisting of monomers, in contrast to the two others which are best described as being built from dimeric units. In the other two complexes mentioned above and also in dipropyldithiocarbamatothallium(I),[9] there are four relatively short thallium-ligand bonds and two longer ones.

The intralayer Tl − Tl separations of about 4.7 Å and 5.0 Å are significantly larger than the metal-metal distances in corresponding dimeric thallium(I) complexes. In [Tl(Et₂-PSeS)],[13] [Tl(pr)₂NCS₂],[9] and [Tl(iso-pr)₂NCS₂] [10] the shortest intermetallic distances are found to be 3.86 Å, 3.98 Å, and 3.58 Å, respectively. Similar and somewhat longer distances are also found in thallium metoxide,[18] TlOCH₃, thallium cyclopentadienyl,[19] C₅H₅Tl, and thiourea complexes of thallous salts.[20] The metal-metal separations are 3.84 Å and 3.99 Å, respectively, in the former two compounds, and 4.08 Å and 4.15 Å in the thiourea compounds. Thus the Tl − Tl distances in the complex considered seem too
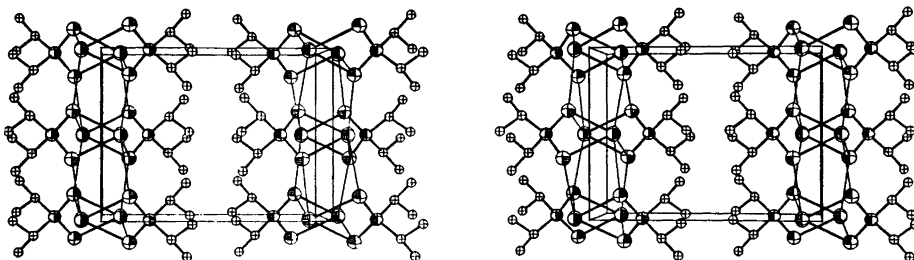

Fig. 3. A stereoscopic drawing showing the packing of molecules as seen along the *c* axis.

large to allow any metal-metal interactions.

The lone pair of electrons in this and similar compounds seems to be stereochemically active.[13,21] The four longer bonds found here are in accordance with the assumption that the lone pair occupies an sp-hybridized orbital pointing away from the shorter bonds.

The intramolecular thallium−sulfur bond lengths are 3.056(7) Å, whereas the weaker intermolecular thallium−sulfur bond distances are 3.429(10) Å and 3.453(7) Å. The former correspond to the mean value of the three short Tl−S bonds in [Tl(pr)₂NCS₂],[9] and are also close to the Tl−S intradimer coordination distances in [Tl(iso-pr)₂NCS₂].[10] In [Tl(Et₂-PSeS)],[13] on the other hand, the Tl−S bonds are 3.237(5) Å. The value of the Tl−S covalent distance is somewhat uncertain as no definite covalent radius for thallium is available in the literature. A value somewhere between 2.5 Å and 2.8 Å seems to be probable.[22,23] The thallium-sulfur bonds of the length mentioned above are, however, comparable to the sum of the atomic radii given by Slater (2.90 Å),[24] and such bonds are described as essentially covalent in a number of thallium(I) compounds.[9]

The intermolecular Tl−S coordination distances are too large for any perceptible covalent interaction. These bond lengths are, however, close to the Tl−S distances found in thiourea complexes of thallium(I) salts, as studied by Verhoef, Boeyens and Herbstein,[20,23,25] and somewhat longer than the sum of the Pauling ionic radii of Tl⁺ and S²⁻ of 3.28 Å.[26] The interaction is proposed by Verhoef *et al.* to be of ion-dipole type.

The Tl−S bonds are comparable with the Tl−S dimer-dimer interactions in [Tl(pr)₂-NCS₂],[9] and also with the Tl−Se intradimer contacts in [Tl(Et₂PSSe)],[13] as the difference in bond lengths is close to the difference in the selenium and sulfur covalent radii.

The sulfur-phosphorus bond lengths are found to be 1.982(9) Å, which seems to be normal for metal phosphinates. The length corresponds to a π-bond order of 0.50 based on Pauling's bond order−bond length relationship. The P−S single-bond length and P=S double bond length are both based on radii given by Pauling;[26] the former, corrected for bond polarity is 2.10 Å, the latter is 1.94 Å. The double-bond character of these bonds is also indicated

from IR spectra recorded by Kuchen and Hertel.[11]

The P−C and C−C bond lengths 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.

Two short interlayer contacts, C22−C22 [−x,−(y+1),1−z] of 2.66 Å and C21−C21 [½−x,−(y+1),z] of 3.10 Å, and a short intralayer intermolecular C−C distance of 3.30 Å, C21−C22 [x+½,y,1−z], are found. These distances are too short to represent real intermolecular contacts and do not exist in the true structure, but are a result of disorder in the ethyl groups. The following molecular contacts between layers, *i.e.*, across glide planes parallel to the *ac* plane at $y = \pm (n \times 0.5)$ *b*; $n = 0,1,2,\cdots$, may therefore be imagined: Pairs of molecules related by centres of symmetry lying on these glide planes must have different orientations of their methyl groups, one molecule having C21 groups only, the other C22 groups only, or *vice versa*. In this way, C22−C22 contacts (2.66 Å) across centres of symmetry are avoided. Likewise, pairs of molecules related by twofold axes lying on the same glide planes must differ in the same manner, so that the close C21−C21 contacts (3.10 Å) are avoided. However, in the *c*-direction the stacking must be based on molecules with C21 groups alternating with molecules with C22 groups, in order to maintain the symmetry. This also eliminates the short intralayer distance of 3.30 Å.

The shortest interlayer contact is thus 3.86 Å, between methyl carbons.

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