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Crystallographic and Structural Data of Three Thallium(I) Compounds

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The crystal structures of diethylthiosele-nophosphinatothallium(I), $[\text{Tl}(\text{Et}_2\text{PSeS})]$, and diethyldithiophosphinatothallium(I), $[\text{Tl}(\text{Et}_2\text{PS}_2)]$, have been determined by three-dimensional X-ray methods. Space group and unit cell have further been determined for diethyldiselenophosphinatothallium(I), $[\text{Tl}(\text{Et}_2\text{PSe}_2)]$.

The crystals of $[\text{Tl}(\text{Et}_2\text{PSeS})]$ (I) are colourless prisms elongated along the c axis. The structure is monoclinic with cell dimensions $a = 10.342(3)$ Å, $b = 9.116(3)$ Å, $c = 10.154(2)$ Å, $\beta = 101.98(2)^\circ$, and $Z = 4$. Possible space groups were $C2$, Cm , and $C2/m$.

The intensity data of 997 reflections greater than background were recorded by means of a Siemens AED-1 single crystal diffractometer, using $\text{MoK}\alpha$ -radiation. The crystal structure was solved by a three-dimensional Patterson synthesis. The map could only be interpreted in terms of a dimeric complex. In the centric space group, $C2/m$, which was the first choice and which proved to be the correct one, the dimers occupy special twofold positions with the Tl atoms on a twofold axis parallel to b and the Se, S, and P atoms

lying in a mirror plane halfway between the two Tl atoms at right angles to b . The structure was refined by full-matrix least squares methods to an R -value of 0.088. Attempts to refine the structure in the non-centric alternative space groups were not successful.

The crystals of $[\text{Tl}(\text{Et}_2\text{PS}_2)]$ (II) are thin colourless plates with $a = 9.026(3)$ Å, $b = 12.134(2)$ Å, $c = 8.468(3)$ Å, and $Z = 4$. The crystals are orthorhombic with the space group $Pcca$, which requires that the molecules occupy fourfold special positions.

Intensities were estimated visually from Weissenberg photographs taken with Ni-filtered $\text{CuK}\alpha$ -radiation using the multiple film technique. 376 out of 507 independent reflections from the five layers $hk0-hk3$ and $0kl$ were observed and measured. The structure was solved by three-dimensional Patterson and Fourier syntheses. The Tl and P atoms lie on a twofold axis. The atomic parameters were refined by least squares methods to an R -value of 0.094.

The crystals of $[\text{Tl}(\text{Et}_2\text{PSe}_2)]$ form extremely thin colourless monoclinic prisms extended along the b axis, with $a = 11.731(7)$ Å, $b = 6.741(3)$ Å, $c = 13.091(4)$ Å, $\beta = 111.71(3)^\circ$, and $Z = 4$. The space group is $P2_1/c$. During exposure to X-rays, the crystal surface became gradually covered by a yellow powder. This happened also to the two former complexes, but to a lesser degree. This effect together with the crystal size made a structure solution difficult.

Thallium (I) compounds have a tendency to occur as polymers in the solid state.

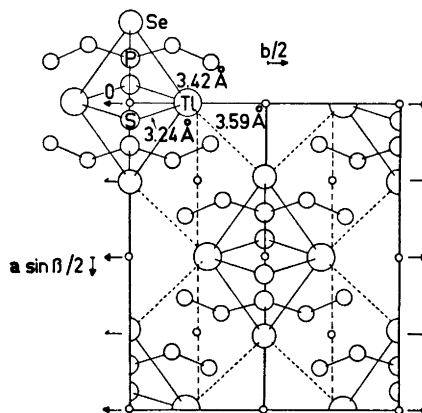


Fig. 1. The arrangement of the $[\text{Tl}(\text{Et}_2\text{PSeS})]_2$ dimers in the unit cell as seen along the c axis.

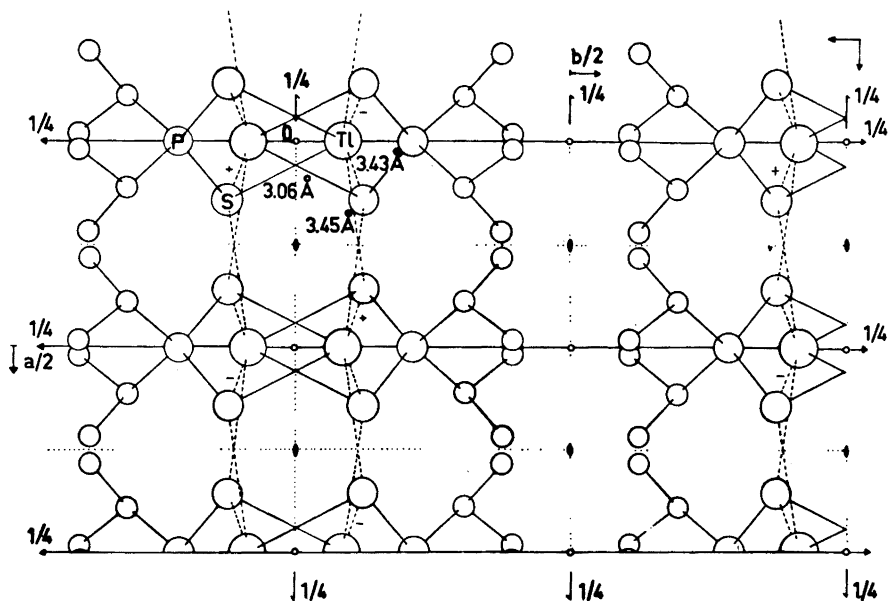


Fig. 2. The arrangement of the $[\text{Tl}(\text{Et}_2\text{PS}_2)]$ molecules in the unit cell as seen along the c axis. Tl-S bonds labelled plus or minus represent bonds to sulphur atoms one unit cell above or beneath the original one, respectively.

From Fig. 1 it is seen that complex I can be regarded as built up from dimeric units, $[\text{Tl}(\text{Et}_2\text{PSeS})_2]$. In this dimer, both ligands are shared equally between the two thallium atoms, so that each sulphur and selenium atom in addition to being bonded to phosphorus also is bonded to both metal atoms. The resulting planar Tl_2S_2 and Tl_2Se_2 parallelograms are nearly at right angles to each other. The dimers are knit together into two-dimensional layers parallel to the ab -plane, through weak intermolecular Tl-Se bonds.

Each thallium atom is bonded to two sulphur and two selenium atoms in the dimer and to two more distant selenium atoms belonging to different neighbour dimers. The coordination is best described as a distorted trigonal prism. Analogous configurations are found in dipropyldithiocarbamatohallium(I)¹ and in dibutyldithiocarbamatocaesium(I).²

A schematic view of the crystal structure of $[\text{Tl}(\text{Et}_2\text{PS}_2)]$ is shown in Fig. 2. The structure is best described as monomers linked together in two-dimensional polymeric layers parallel to the ac -plane. Each

metal atom is coordinated by six sulphur atoms situated at the corners of a distorted trigonal prism. Two of these sulphur atoms belong to the molecule proper, the remaining four more distant ones belong to four different adjacent molecules.

A general feature of the two complexes is the large Tl-S and Tl-Se bond lengths. This is not surprising in view of the bridging nature of the sulphur and selenium atoms, and the largely ionic bonding.^{1,3} The intramolecular Tl-S bond lengths of 3.237(5) Å and 3.056(7) Å found in I and II, respectively, and the weak intermolecular Tl-S bonds of 3.429(10) Å and 3.453(7) Å found in II are of the same order of magnitude as those found in other complex Tl(I) compounds.^{1,3-7} The Tl-Se bond in I of 3.424(4) Å is relatively weaker than Tl-S bond in I, as the difference in bond length is larger than the difference in the selenium and sulphur covalent radii. This is not unexpected as only selenium atoms are engaged in dimer-dimer interactions. The weak intermolecular Te-Se bond is found to be 3.594(3) Å.

Coordinates with standard deviations in