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The Crystal Structure of Thallium(I) Diisopropyldithiocarbamate

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The crystal structure of thallium(I) diisopropyldithiocarbamate, $Tl(I)S_2CN(C_3H_7)_2$, has been determined from three-dimensional X-ray data. The crystal is monoclinic, space group $P2_1/n$. Unit cell parameters: $a = 10.279$ Å, $b = 16.704$ Å, $c = 6.315$ Å, $\beta = 92.86°$. There are four formula units per elementary cell.

The structure may be regarded as consisting of dimers with the composition $[TlS_2CN(C_3H_7)_2]_2$ packed in layers which are then stacked upon one another. It may also be seen as being built around almost planar, zig-zag chains of thallium atoms. The string of metal atoms is shielded by the ligands and the metal-metal distances along the chain alternate between 3.58 and 3.64 Å. The thallium-sulphur coordination is fivefold with the sulphur atoms approximately at the corners of a tetragonal pyramid. The structure of the title compound is more regular than its propyl analogue and the dimers closely resemble those found in Cs(I) dibutyldithiocarbamate.

A number of *N*,*N*-dialkyldithiocarbamates of thallium(I) have been prepared by Åkerström.[1] With the exception of the isopropyl compound these dithiocarbamates are quite soluble in a number of organic solvents. From measurements of colligative properties Åkerström concluded that they are present as dimers in these solvents.

The crystal structure of thallium(I) dipropyldithiocarbamate was studied by Nilson and Hesse [2] as part of a systematic investigation of the coordination chemistry of compounds with the composition AX. They found that the structure may be considered as being composed of dimers, possibly of the type present in solution. The dimers are, however, distorted by interactions with their neighbours. Since the low solubility of the isopropyl compound may be caused by a different type of arrangement in the solid state, an investigation of its structure has been undertaken.

EXPERIMENTS AND COMPUTER PROGRAMMES

A sample of thallium(I) diisopropyldithiocarbamate was kindly prepared by Dr. S. Åkerström. It consisted of aggregates of white needles. Good single crystals could,

however, be cut from these aggregates. The density of the crystals was determined by the flotation method using an aqueous solution of K_2HgI_4. The unit cell dimensions were found from a Guinier-Hägg powder photograph using $CrK\alpha_1$ radiation ($\lambda = 2.2896$ Å) [3] with silicon ($a = 5.4305$ Å) [4] as internal standard. Equi-inclination Weissenberg photographs were taken with the crystal rotating about the needle axis, which corresponds to the [001]-direction. The multiple-film technique with four films was used. Preliminary experiments showed that the intensities of the reflections declined quite rapidly with increasing $\sin\theta$ and that the crystal slowly decomposed in the X-ray beam. A new crystal was therefore mounted after every two layers and each layer was collected using two exposure times *ca.* 50 h for weak reflections and 5 h for strong reflections. The crystal sizes were *ca.* $0.02 \times 0.02 \times 0.12$ mm^3. In all, six layers with 732 independent reflections were recorded. The intensities were estimated visually by comparison with a calibrated intensity-scale and corrected for Lorentz and polarization effects as well as absorption.

Inter-layer scale factors were estimated by exposing reflections from different layers on the same film. Due to the small number of strong reflections for the higher values of l, it was not possible to record strips of all layers on the same film. Therefore three "inter-layer films" were needed and the zero layer was exposed on each film and used as an internal standard. These experimental scale factors changed by less than 20 % when the individual scale factors were refined at the end of the least squares treatment of the data.

The following computer programmes were used.

Programmes	Authors
Least squares refinement of unit cell dimensions	J. Tegenfeldt, Uppsala, Sweden
Lorentz, polarization, and absorption corrections	P. Coppens, L. Leiserowitz and D. Rabinovich, Rehovoth, Israel, modified by O. Olofsson and M. Elfström, Uppsala, Sweden
Fourier summations and structure factor calculations	A. Zalkin, Berkeley, U.S.A. modified by R. Liminga and J.-O. Lundgren, Uppsala, Sweden
Least squares refinement of positional parameters and temperature factors	P. K. Gantzel, R. A. Sparks and K. N. Trueblood, Los Angeles, U.S.A., modified by C.-I. Brändén, R. Liminga and J.-O. Lundgren, Uppsala, Sweden
Interatomic distances and angles	A. Zalkin, Berkeley, U.S.A.
Least squares planes	C.-I. Brändén, Uppsala, Sweden
Perspective illustrations	C. K. Johnson, Oak Ridge, U.S.A.

UNIT CELL AND SYMMETRY

Formula unit: $Tl(I)S_2CN(C_3H_7)_2$.

Diffraction symmetry: $2/m$.

Crystal system: monoclinic.

Unit cell parameters: $a = 10.279 \pm 0.004$ Å; $b = 16.704 \pm 0.008$ Å; $c = 6.315 \pm 0.002$ Å; $\beta = 92.86° \pm 0.03°$; $V = 1083$ Å^3.

Density (measured): 2.34 g cm^{-3}. Number of formula units: 4. Density (calculated): 2.330 g cm^{-3}.

Systematic absences: $0k0$ for $k = 2n+1$, $h0l$ for $h+l = 2n+1$.

Space group: $P2_1/n$.

Coordinates of equivalent positions: $\pm(x, y, z; 1/2-x, 1/2+y, 1/2-z)$.

DETERMINATION OF THE ATOMIC POSITIONS

The approximate position of the thallium atom in the asymmetric unit was found from three-dimensional Patterson syntheses. The y-coordinate was found to be 0.00. This value would require the peak height ratios 2:1:1, as observed, instead of the ratios 2:2:1 demanded by a general y-coordinate. It may also be noted that this y-value places the thallium atoms on two interpenetrating body-centered lattices in agreement with the observation that reflections with $h+k+l=2n$ are generally much stronger than reflections with $h+k+l=2n+1$. Of the two sulphur positions one could be unequivocally determined. This atom was also found to have $y=0.00$. For the other sulphur atom there was a choice between two symmetry-related positions.

Three-dimensional electron density maps were then calculated using the thallium and sulphur atoms for sign determination and improved positional parameters were found for these atoms. Two possible sets of coordinates were obtained for one of the sulphur atoms. When the refined positions were used to calculate F_c-values, it became evident that these were systematically too small for reflections with odd values of $h+k+l$. It was therefore concluded that the y-value 0.00 found for thallium from the Patterson function was caused by the overlap of two peaks situated close to the plane $v=1/2$. From the width of the peak the y-coordinate was estimated to lie in the range $0.015>|y|>0$.

F_o-syntheses were then computed where only the thallium atoms were used to sign the F_o's. Calculations were performed with $y=0.015$, 0.010, and 0.005. The electron density maps, which were almost identical, were used to find the coordinates of the sulphur atoms and to improve the thallium position ($y=0.007$). A new Fourier synthesis was calculated, from which the coordinates of the remaining atoms (except the hydrogens) could be determined.

The coordinates and isotropic temperature factors of all but the hydrogen atoms were refined by the method of least squares. The function $\sum\omega(|F_o|-|F_c|)^2$, where the weight, ω, was calculated according to Cruickshank, was minimized using a full-matrix program. Atomic scattering factors were taken from Hanson *et al.*[5] The real parts of the dispersion corrections for thallium and sulphur were introduced.[6] These calculations rapidly converged, but the R-value ceased to fall beyond the disturbingly high value of 0.22. Despite this, the structure was considered to be essentially correct since the model gave interatomic distances and angles for the dithiocarbamate ligand in good agreement with the values found for this ligand in similar structures.

An anisotropic temperature factor for the thallium atom was then applied. After four more cycles the shifts were less than one fifth of the estimated standard deviations and the R-value had decreased to 0.126. The parameters obtained from the last cycle are shown in Table 1. The greatest change in the thallium and sulphur parameters on introduction of the anisotropic temperature factor for thallium was 0.0015.

When anisotropic temperature factors were used also for the two sulphur atoms, the R-value decreased to 0.112. No significant changes in the coordinates

Table 1. Atomic parameters and standard deviations from the final least squares refinement.

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B(Å^2)	$\sigma(B)$
Tl	0.0845	0.0002	0.0065	0.0002	−0.2408	0.0004		
S1	0.2092	0.0012	−0.0075	0.0009	0.1932	0.0020	5.8	0.3
S2	0.0667	0.0015	0.1371	0.0009	0.0896	0.0024	7.2	0.3
N	0.2980	0.0030	0.1369	0.0020	0.2982	0.0047	4.1	0.6
C1	0.207	0.005	0.095	0.003	0.211	0.007	6.3	1.1
C2	0.411	0.005	0.094	0.003	0.414	0.007	5.7	1.0
C3	0.309	0.005	0.226	0.003	0.300	0.008	6.8	1.2
C21	0.432	0.005	0.114	0.003	0.630	0.008	6.3	1.1
C22	0.536	0.006	0.107	0.003	0.276	0.008	7.6	1.3
C31	0.315	0.006	0.271	0.004	0.114	0.010	8.9	1.5
C32	0.212	0.006	0.268	0.004	0.446	0.009	8.7	1.5

Coefficients of the anisotropic temperature factor for the thallium atom defined as $\exp(-b_{11}hh - b_{12}hk \ldots)$.

ij	b_{ij}	$\sigma(b_{ij})$	ij	b_{ij}	$\sigma(b_{ij})$
11	0.0130	0.0003	22	0.0114	0.0002
33	0.0405	0.0010	12	−0.0077	0.0004
13	−0.0023	0.0006	23	−0.0069	0.0006

were observed. Introduction of the imaginary part of the dispersion correction for thallium gave no improvement in the R-value. As a test of the absorption correction the coordinates from the Fourier synthesis were also refined using data not corrected for absorption. This refinement gave a higher R-value. Possible contributions from extinction was investigated by excluding from the refinement the reflections with the largest observed structure amplitudes. As no significant changes in the coordinates were observed and the R-value for the remaining reflections decreased only by a small fraction, corrections for extinction were considered unnecessary.

Since the anisotropic character of the thallium atom could be an indication of deviations from the assumed space group, attempts were made to refine the coordinates of the thallium and sulphur atoms in the two noncentrosymmetric space groups $P2_1$ and Pn. The final coordinates (Table 1) and their centrosymmetric counterparts – with small shifts applied to the latter group in order to avoid a singular matrix – were used as input. No convergence was obtained in these refinements and thus no evidence was found for deviation from the assumed symmetry, $P2_1/n$. The assumed symmetry was also tested by replacing the thallium atom with two isotropic atoms with half the scattering factor of thallium. The two atoms were placed at equal distances (0.7 Å) from the position of the thallium atom along the largest principal axis of its thermal vibration ellipsoid. The distance between these atoms decreased during the refinement and no improvement in the R-value was

obtained. Thus the anisotropic thallium atom is better represented by one ellipsoid than by two spherical atoms.

The difference synthesis calculated with the final coordinates and temperature factors revealed no significant features.

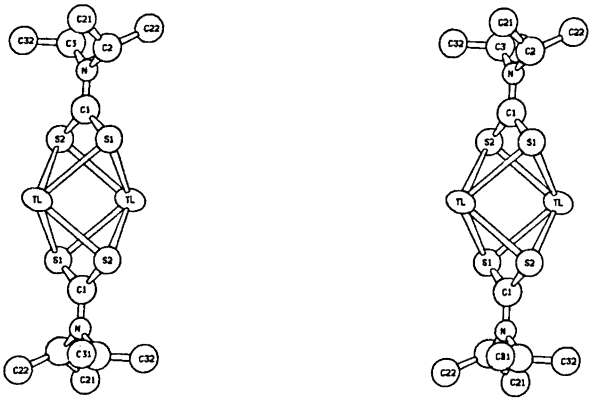


Fig. 1. A stereoscopic pair showing the $[TlS_2CN(C_3H_7)_2]_2$ dimer with the N – C1 – C1 – N axis in the plane of the paper.

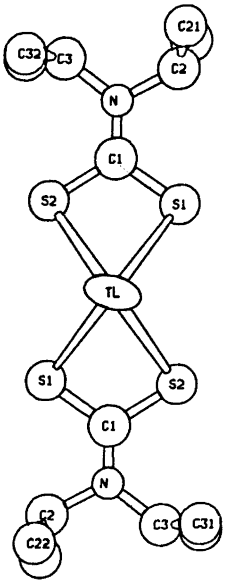


Fig. 2. The $[TlS_2CN(C_3H_7)_2]_2$ dimer with the Tl – Tl vector perpendicular to the plane of the paper.

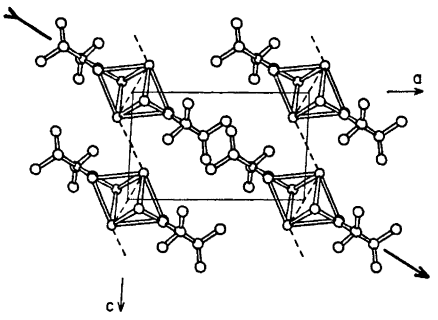


Fig. 3. Projection of the structure along the *b*-axis. Only dimers with their centres at 0,0,0 are shown. The dimers with their centres at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ are seen in Fig. 4. The thallium chains are indicated by broken lines. The trace of the plane shown in Fig. 4 is indicated by an arrow.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

General features. The crystal structure of thallium(I) diisopropyldithiocarbamate is made up of centrosymmetric, dimeric units, $[TlS_2CN(C_3H_7)_2]_2$. The unit is shown in Figs. 1 and 2 and the arrangement of the units in Figs. 3 and 4. Some distances and angles are given in Table 2. There are two such

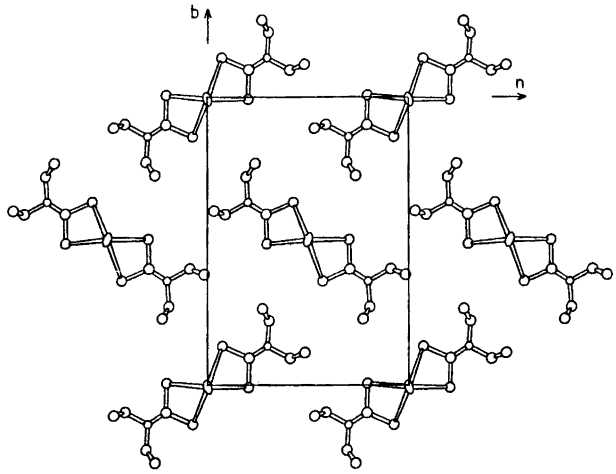


Fig. 4. (101) section of the crystal structure. The *n* glide is in the plane of the paper. The trace of this plane is indicated by an arrow in Fig. 3. Superimposed atoms have been omitted.

dimers in the elementary cell with their centres at 0,0,0 and 1/2,1/2,1/2. The four metal-sulphur distances within the dimer are in the range 3.0 to 3.1 Å and the corresponding distances between the dimers are 3.9 Å. The dimeric units can be described as linked together by thallium-sulphur coordination to form chains in the *c*-direction. One sulphur atom in each dithiocarbamate ligand takes part in this linkage. The distances between neighbouring metal atoms in the chain are all 3.6 Å. The interactions between dimers belonging

Table 2. Distances and angles in the centrosymmetric, dimeric unit. Atoms related by symmetry are denoted by an asterisk.

Atoms	Dist.(Å)	σ	Atoms	Angle (°)	σ
Tl – Tl*	3.584	0.005	S1 – Tl – S1*	107.0	0.3
Tl – S1	2.977	0.013	S2 – Tl – S2*	107.6	0.4
Tl – S1*	3.050	0.013	S1 – Tl – S2	57.3	0.4
Tl – S2	3.030	0.016	S1* – Tl – S2*	56.5	0.4
Tl – S2*	3.038	0.016	S1 – Tl – S2*	81.5	0.4
			S1* – Tl – S2	80.5	0.4

to different chains are of van der Waals type with the alkyl groups acting as shields between the active centres of the dimeric units. Distances less than 4 Å between atoms in different dimers are given in Table 3. The shortest distance between thallium atoms in different chains is 8.9 Å. No thallium atom is less than 7.3 Å from a sulphur atom in another chain.

Table 3. Intermolecular distances shorter than 4 Å. The relationship of the positions of the atoms in the second column to those given in Table 1 is expressed by a combination of one of the following symbols corresponding to a symmetry operation
01: x, y, z
02: $-x, -y, -z$ (centre of symmetry)
03: $1/2-x, 1/2+y, 1/2-z$ (screw axis)
04: $1/2+x, 1/2-y, 1/2+z$ (glide plane)
with one or more of the symbols $\pm\mathbf{a}$, $\pm\mathbf{b}$, $\pm\mathbf{c}$ corresponding to unit translations along the axes of the unit cell.

Atoms		Dist.(Å)	Atoms		Dist.(Å)
C22	C32(04 − c)	3.52	S2	C3(04 − a − c)	3.89
Tl	Tl (02 − c)	3.64	S1	C31(03 − b)	3.90
C21	C22(02 + a + c)	3.75	C2	C22(02 + a + c)	3.91
C2	C2(02 + a + c)	3.77	C21	C32(04)	3.94
C2	C21(02 + a + c)	3.85	S1	C32(03 − b)	3.95
Tl	S1(01 − c)	3.86			

Fig. 4 shows molecules having their centres on the plane through 0,0,0 and parallel to (101). The largest deviation of an atom in the central parts (SSCNCC) of the ligands from this plane is 0.12 Å. Similar arrangements are found in the structures of several molecular crystals, *e.g.* I_2, in which the molecules have roughly the same exterior shape as the dimer. It thus appears that the arrangement in the layer shown is governed by simple packing considerations. The thallium-thallium distance in the dimer (3.58 Å) represents the thickness of the layer and they are stacked as shown in Fig. 3.

The stacking has been studied by calculating the interlayer atomic distance for different relative positions of two successive layers – referred to in the following as the top- and bottom-layer, respectively – using the program PACK written for this purpose. The two layers are moved relative to one another by translations of the top layer. One translational direction is normal to the plane of the layers and defined by the vector $\mathbf{d}_0$, where $|\mathbf{d}_0|$ is the perpendicular distance between the layers. The other movement translates the top-layer in a plane parallel to the bottom-layer. This translation is defined by the two coordinates x' and y'. These are the coordinates of the perpendicular projection onto the bottom-layer of the origin in the top-layer. In the present structure, the origin in the bottom-layer coincides with the origin of the unit cell. The x'-axis has been chosen parallel to the vector $\mathbf{a}+\mathbf{c}$, (indicated by an arrow in Fig. 3) and the y'-axis parallel to $\mathbf{b}$. The coordinates are expressed as fractions of the lengths of these vectors. For each translation interlayer atomic distances are calculated. If these distances all exceed a certain

minimum value then this particular translation of the layers is considered to be permitted and thus constitutes one of the possible ways of stacking the layers. The output from the program is a "stacking map" in which x' and y' are the axes. In the map, allowed translations are denoted by 0 and unallowed by 1; see Fig. 5.

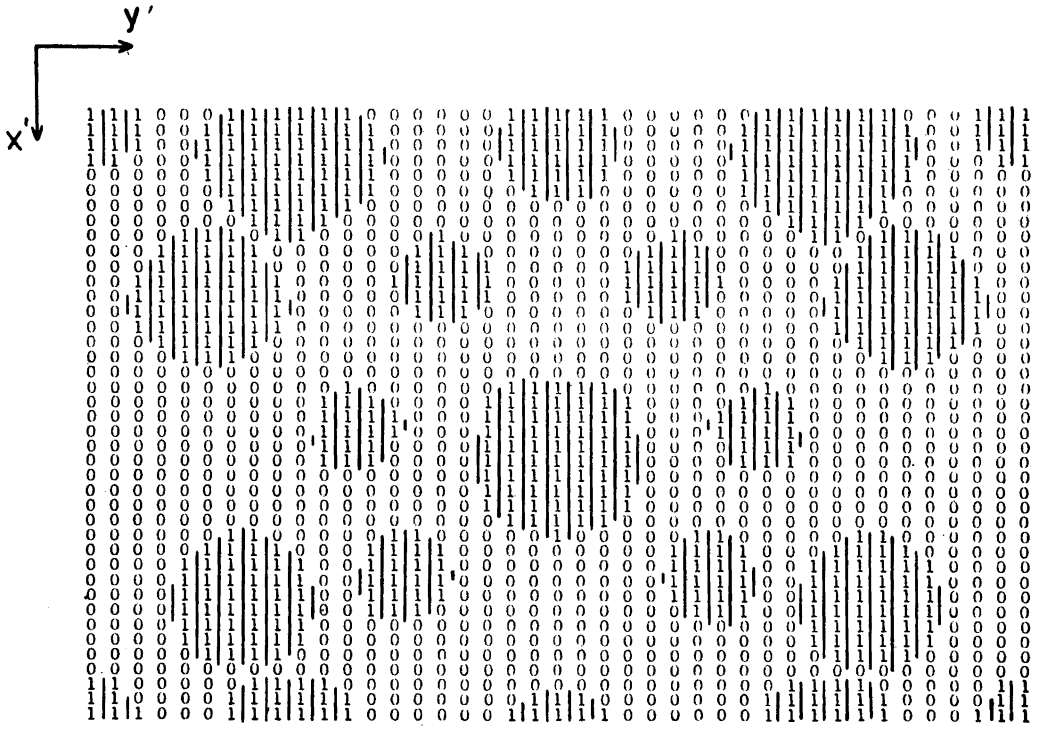


Fig. 5. Stacking map output from the program PACK. Translations (defined by the coordinates x' and y') which are allowed are marked with 0 and unallowed with 1. For clarity, the unallowed regions have also been indicated by vertical lines.

The calculations have been done using $|\mathbf{d}_o| = 5.497$ Å, which is the interlayer distance required by the observed density. Fig. 6 shows the result when the minimum interlayer atomic distance is 3.50 and 3.40 Å, respectively. These values are estimates of the lower limit of this distance and the dotted areas in the figure give the ranges of the coordinates (x' and y') of the permissible relative translations of the layers. The ranges for which the interlayer thallium-sulphur distance is less than 4.0 Å are indicated by unshaded areas in the figure.

For a primitive monoclinic cell ($y' = 0$) the ranges of x' are quite restricted. The translational coordinates ($x' = 0.264$, $y' = 0.000$) of the proposed structure are indicated in the figure. The other translation ($x' = -0.264$) compatible

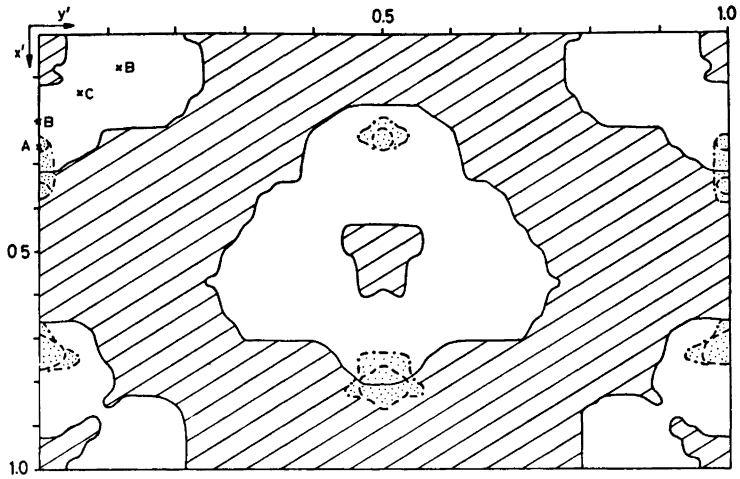


Fig. 6. Stacking map. Dotted areas within boundaries – – – – and –.–.–.– show permissible range of x' and y' for interatomic distances less than 3.50 and 3.40 Å, respectively. Unshaded area, Tl – S distance less than 4.0 Å. Positions × show x' and y' for A: actual structure, B: regular 5-fold and C: regular 6-fold Tl – S coordination.

with the observed monoclinic angle is also within a permitted area. In this position the shortest intermolecular Tl – S distance is 3.68 Å, which accordingly is somewhat less than the value 3.86 Å in the proposed structure. A least-squares refinement of the diffraction data with this stacking gave $R = 0.17$. One would therefore conclude that thallium-sulphur interaction is not the dominant factor in determining the stacking of the layers. In both positions thallium coordinates a sulphur S1 atom. These two sulphur atoms are related by a centre of symmetry. The shortest Tl – S1 vectors would occur for a regular pyramidal coordination. The lengths of these vectors would then be 3.80 Å and 3.62 Å, respectively. However, neither this coordination nor a regular sixfold prismatic coordination can be achieved in the permitted area. The required translations are indicated in the figure.

The dimer. The dimeric unit illustrated in Figs. 1 and 2 is centro-symmetric and approaches very closely the symmetry $2/m$ with the rotation axis containing the two thallium atoms (Fig. 2). The Tl – Tl vector is perpendicular (within 2°) to the least squares plane calculated from the positions of the six central atoms (SSCNCC) in the two ligands. Due to the centrosymmetric arrangement this plane passes through the centre of the dimeric unit. The deviations of the atoms from this plane are given in Table 4. The central part of the dimer is close to *mmm* symmetry but the outer carbon atoms destroy this high symmetry. The relative orientation of the two isopropyl groups, which can be seen in Fig. 1, is probably caused by steric effects within the molecule.

The two thallium and four sulphur atoms in the central part of the dimeric unit form a somewhat distorted octahedron. The distances and angles in this

Table 4. Distances of the atoms from the least squares plane calculated from the positions of the atoms S1, S2, C1, N, C2, and C3 and their centrosymmetric equivalents in the dimer.

Atom	Dist. (Å)	Atom	Dist. (Å)	Atom	Dist. (Å)
S1	0.043	S2	−0.081	C1	−0.023
N	−0.002	C2	−0.058	C3	0.086
Tl	1.79	C21	−1.14	C22	1.38
C31	1.17	C32	−1.23		

unit are presented in Table 2 and in Fig. 7. The four sulphur atoms form a plane passing through the centre of the molecule. The Tl−Tl vector is perpendicular (within 1°) to and the central parts of the ligands coplanar (within 3°) with this plane.

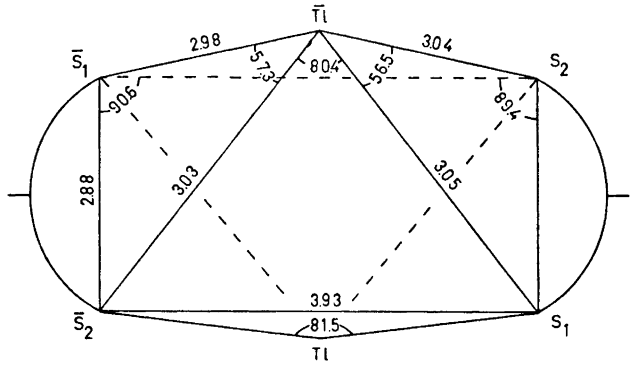


Fig. 7. The central part of the centrosymmetric dimeric unit showing the two thallium and the four sulphur atoms. Atoms related by symmetry are denoted by a bar. The angles and distances are given in degrees and Ångströms.

The metal atom arrangement. The distance between the two metal atoms in the same dimeric unit is 3.584 ± 0.005 Å and the corresponding distance between thallium atoms in different dimers is 3.635 ± 0.005 Å. The Tl−Tl−Tl angles are all equal to 122.0 ± 0.1°. The intermetallic distances in the thallium chain thus alternate between two almost equal values, so that no distinct pairs of thallium atoms can be discerned in the metal arrangement. Similar chains with equal distances (4.0 Å) were also found in thallium(I) dipropyldithiocarbamate. Equidistant chains (4.0 Å) are also present in thallium(I)-cyclopentadienyl,[7] but in this compound there are no chemical bridges between thallium atoms in the same chain. The distances between the thallium atoms in the present compound are shorter than those in the thallium(I) compounds mentioned above but longer than the shortest interatomic distance, 3.408 Å, found in the hexagonal modification of the metal stable at ordinary tempera-

tures.[8] Whether bonding interactions between the metal atoms occur in the structure is not clear. It is possible, however, that the short distance found between the metal atoms in the same dimer may be the result of the two metal atoms being attached to the same two dithiocarbamate ligands by thallium-sulphur bonds of a certain length. Thus the thallium atoms may be held at "contact" distance by the bridging sulphur atoms with no bonding interactions between the metal atoms. The longer distance, 3.98 Å, found between the thallium atoms in the similar dimer occurring in the structure of thallium(I) dipropyldithiocarbamate may be quoted as evidence against this idea. It must, however, be remembered that this dimer is quite distorted so that one of the thallium atoms is attached to only three of the sulphur atoms in the dimer. The distance to the fourth sulphur atom is 4.4 Å. The two thallium atoms are thus less rigidly held together than in thallium(I) diisopropyldithiocarbamate.

This line of reasoning can be placed on a more quantitative basis if it is assumed that the Tl – S distance and the ligand bite, S1 – S2, have fixed values. With the given geometry and symmetry of the dimer, the Tl – Tl distance would then be determined by the length of the longest edge of the base plane in Fig. 7, *i.e.* the distance between two sulphur atoms in different ligands. The Tl – S bond length is given the value 3.0 Å which is the value found in this structure and also close to the mean value of the three short Tl – S distances in the propyl analogue. The bite is given the value 2.90 Å, which is an intermediate value for the two structures. On these assumptions the following corresponding values (in Å) of the S – S and Tl – Tl distances are obtained: 3.40, 4.02; 3.60, 3.84; 3.80, 3.64; 4.00, 3.42. The van der Waals radius of sulphur is *ca.* 1.85 Å.[9] Hence the relevant S – S distance would be at least 3.70 Å and, to judge from the figures just given, the short Tl – Tl distance (3.58 Å) could, at least in part, be the result of the geometrical arrangement of the sulphur and thallium atoms in the complex.

In the two thallium(I) dithiocarbamates, the distances between adjacent metal atoms in different dimers are very similar to the intermetallic distances within the dimers. This may be surprising since the chemical bridges are quite different. Thus, in the present structure, there are four Tl – S – Tl bridges between metal atoms belonging to the same dimer but only two between thallium atoms in different dimers. There does not appear to be an obvious explanation for this. The situation may, however, be accidental and merely the geometrical result of the molecular packing discussed earlier.

The coordination and linkage of the thallium atom. The distances and angles of the coordination around the thallium atom are shown in Tables 2 and 3. There are five sulphur atoms at reasonable bonding distances from each thallium atom. Four of these belong to the same dimeric unit as the thallium atom and the fifth to an adjacent unit; see Fig. 3. Thus there are four short coordination distances (2.98 – 3.05 Å) and one long (3.86 Å). Another sulphur atom in the adjacent unit is situated at 4.75 Å from the thallium atom, but no bonding interactions are expected at such a distance. There are no further sulphur atoms closer to the metal atom than 6 Å. The five coordinated sulphur atoms form a pyramid with the distant sulphur atom at the apex and the

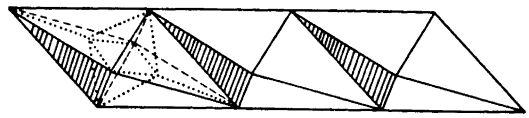


Fig. 8. The arrangement of the coordination pyramids. A transparent view of one pyramid is shown with the metal-sulphur coordination indicated by dotted lines. The sulphur atom S1 occupies the shared corners in the arrangement.

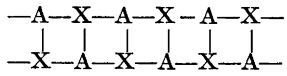
others forming the base plane. This pyramid can be seen in Fig. 8. The base plane is almost rectangular with the corner angle 89.4°. The apex of the pyramid is not situated directly above the centre of the base plane. The line from this centre to the apex makes the angle 7.3° with the normal to the base plane. This could be connected with one of the four edges from the apex being shared with another pyramid, so that there are two S – Tl – S bridges along this edge. The distortion can, however, also be seen as the result of the packing requirements discussed above.

Within the dimer the thallium-sulphur bonds are *ca.* 3.0 Å with small variations. Bonds of this length are described as covalent in a number of studies on thallium(I) compounds with sulphur-containing ligands.[2] The much longer bonds (3.86 Å) between the dimers are obviously not covalent and are also considerably longer than the sum of the Goldschmidt ionic radii (3.33 Å). The interaction is thus considered to be weak and of long-range character.

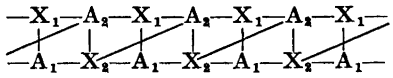
The two coordination pyramids associated with the two thallium atoms in a dimer have a common base plane and thus form a bipyramid. This bipyramid shares two opposite and parallel edges with two other bipyramids, so that a chain of bipyramids is formed as shown in Fig. 8. A similar situation occurs in cesium(I) dibutyldithiocarbamate,[10] where the coordination figure of the two metal atoms in a dimer is a double prism, which shares six edges with six other double prisms to form a plane layer.

The structure of the title compound is a representative of the large number of structures of the class AX, where A stands for a metal atom and X for an anionic group. This class contains such familiar structures as those of the alkali halides. In a topological treatment there is not more than one link between a specific A object and a specific X object, irrespective of the number of bonds between them. The link number of an A object is the number of X objects with which it forms links, and *vice versa* for the link number of the X object.

In thallium(I) diisopropyldithiocarbamate each thallium atom, A, is linked to three dithiocarbamate groups, X, two within its own dimer and one in an adjacent dimer. Each dithiocarbamate group is also linked to three thallium atoms. The link number is thus three for all A and X objects. This is also the case in a number of mono- and dithiocarbamates of Cu(I) and Ag(I), which form hexamers or tetramers.[11–13] The Tl(I) compound is, however, a high polymer with the simple linkage scheme shown below



In thallium(I) dipropyldithiocarbamate,[2] which is also a high polymer, the linkage is somewhat more complicated. In this compound one half of the A objects and one half of the X objects have link number three. They are denoted by A_1 and X_1, respectively. The other half of the A and X objects, A_2 and X_2, have link number four.



In the isopropyl compound the linkage pattern of the isolated dimeric unit, the finite arrangement, can be represented by the following figure

Such figures placed side by side give the infinite arrangement shown above. It is then not surprising to find that the chains in the structure consist of individual dimeric units related by simple translations.

The finite arrangement of the propyl compound is the same as for the isopropyl compound and thus the same scheme is obtained by placing the finite arrangements side by side. In this case, however, the infinite arrangement requires the introduction of the diagonal $A_2 - X_2$ links. It is easy to understand that the structure, which is the spatial representation of this linkage pattern, is more complicated for this compound. The dimeric units in the chains thus have two orientations, related by a glide plane, and they are not centrosymmetric.

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