ACTA CHEMICA SCANDINAVICA 27 (1973) 3531–3544

The Crystal Structure of Thallium(I) Dimethyldithiocarbamate

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The crystal structure of thallium(I) dimethyldithiocarbamate, $TlS_2CN(CH_3)_2$, has been determined from 3-dimensional X-ray data. The crystals are monoclinic, space group $P2_1/a$, with unit cell dimensions: $a = 9.101$, $b = 6.673$, $c = 11.379$ Å, $\beta = 98.90°$. There are four formula units in the elementary cell.

The structure is composed of dimers, $[TlS_2CN(CH_3)_2]_2$, which are joined by thallium-sulphur coordination to form layers parallel to the (a,b)-plane. The thallium atoms are situated close to the layer plane, whereas the ligands protrude from both sides of the plane. Only van der Waals forces exist between successive layers, which are stacked in the c-direction. The thallium atoms achieve 7-coordination by using sulphur atoms from five ligands in the layer. The coordination distances are in the range 3.0 to 3.7 Å. The four closest sulphur atoms belong to the same dimer as the thallium atom. The thallium atoms within a layer form a 3-connected net with the interatomic distances 3.64 and 3.85 Å.

The dimers are related to those found in the structures of the corresponding propyl and isopropyl compounds, but in the latter the dimers are linked to form chains. The importance of packing effects and the particular coordination requirements of thallium(I) in determining the structures of these compounds are discussed.

The crystal structures of thallium(I) dipropyldithiocarbamate [1] and thallium(I) di-isopropyldithiocarbamate [2] were determined at this Institute as part of a systematic investigation of the coordination chemistry of compounds having the composition AX. The same type of dimeric molecules are found in both structures but the dimers are arranged quite differently in the two cases. In the isopropyl compound the dimers are nicely packed in layers determined by van der Waals forces. The layers are stacked in such a way that chains of dimers are formed, but only weak thallium-sulphur forces act between adjacent dimers in the chains. Similar chains are also found in the structure of the propyl compound, but the packing is quite different. No layers are formed and the dimers along the chains are connected by strong thallium-sulphur bonds. In the structure of the isopropyl compound, which appears to be de-

termined mainly by packing requirements, the symmetry of the dimer is the same as that expected for an isolated dimer. In the structure of the propyl compound, however, the dimer is considerably distorted.

The observed structural effects of changes in the ligands are related to those found in the dithiocarbamates and monothiocarbamates of copper(I) and silver(I).[3]

EXPERIMENTS

A sample of thallium(I) dimethyldithiocarbamate was kindly prepared by Dr. S. Åkerström according to his published method.[4] It consisted of pale yellow four-sided platelets. Most of the crystals were too thin for X-ray investigation, but suitable crystals could be cut from the corners of larger crystals. Their density was measured by the flotation method using an aqueous solution of K_2HgI_4. The unit cell dimensions were found from a powder photograph taken on an IRDAB XDC 700 camera using Cu$K\alpha_1$ radiation with silicon as an internal standard. Equi-inclination Weissenberg photographs were taken using Cu$K\alpha$ radiation and Ilford Industrial G film. The multiple-film technique (using four films) was used. The exposure times were approximately 50 h. For the lowest layers the strong reflexions were collected separately at exposure times of roughly 5 h. The decomposition of the crystal was comparatively slow. It was thus possible to collect the layers $0kl$ to $6kl$ using one crystal of dimensions $0.04 \times 0.13 \times 0.19$ mm^3, with the rotation axis in the plane of the crystal and bisecting one of the corners. A second crystal of dimensions $0.04 \times 0.11 \times 0.15$ mm^3 was used for the layers $7kl$ and $8kl$. This crystal was then remounted and rotated about an axis approximately normal to the plate to collect the layers $hk3$ and $hk6$. These were used for interlayer scaling.

The intensities were measured using an automatic SAAB film scanner [5] connected on-line to an IBM 1800 processor controller. Process and integration programs written by Werner were used.[6] The parameters for the integration procedure (IVRUT = IRRUT = 10, BAK = 0.85, SBAK = 0.90, MYT = 0, FK = 0.5) were chosen so that the minimum transmission point for each reflexion was at the centre of a rectangle 1.89×1.26 mm^2 corresponding to 441 measuring spots of the size 0.09×0.06 mm^2. The rectangle was large enough to include both the α_1 and α_2 reflexion. The average of the transmission values along the edges of the rectangle was taken as the background transmission T_b. All n spots within the rectangle with transmission value, T_i, less than $0.85T_b$ were used in the calculation of $I_{obs} = 10 \ln 10 \sum_{i=1}^{n} D_i$. The corrected optical density, D_i, was calculated as $D_i = D'(1 + 0.5D')$, where $D' = \log T_b/T_i$. The factor 0.5, which corrects for the negative errors in the intensities of the strong reflexions, has been suggested by Werner.[7] In this way intensities in the range 50 to 1000 were obtained corresponding to peak optical densities in the range 0.1 to 1.5. Despite the correction factor the high intensities were found to be unreliable, and only measurements in the range 50 to 450 were actually used.

During the integration procedure a number of streaks present on the films were interpreted as reflexions. In order to facilitate their elimination a program was written to produce a plot of each film on an IBM 1627 plotter. The plot showed the position in the reciprocal layer of each reported reflexion together with the position corresponding to the indices calculated for that reflexion by the integration program. From these plots it was possible to detect reflexions displaced from the crystallographic positions. Systematic mistakes in the indexing caused by errors in the alignment of the film in the film scanner were sometimes observed for the high-angle reflexions on a film. These were easily detected on the plots. After a simulated movement of the film by the program to produce a new set of indices for the reflexions, a new plot could be drawn with no such mistakes occurring.

The 786 independent reflexions were corrected for Lorentz and polarization effects, as well as for absorption ($\mu = 520$ cm^{-1}) but not for extinction. Interlayer scale factors for the layers $0kl$ to $8kl$ were obtained by comparison of the intensities of the reflexions in this data-set with the intensities of the corresponding reflexions in the two layers

*hk*3 and *hk*6. The scale factors were themselves included in the final refinement, and found to differ on average by 5 % (max. 11 %) from the experimental values.

DETERMINATION OF THE ATOMIC POSITIONS

A layer structure was suggested at an early stage by the plate-like crystal habit and by the very high intensity of the 001 line on the powder photograph; the c^*-axis was normal to the plate. The approximate position of the thallium atom was found from a 3-dimensional Patterson synthesis. The positions of the two independent sulphur atoms were then determined from a difference Fourier synthesis. After a least-squares refinement of the coordinates and isotropic temperature factors of the thallium and sulphur atoms, the positions of the remaining nitrogen and carbon atoms were found from a new difference synthesis. No attempt was made to determine the positions of the hydrogen atoms. At this point anisotropic temperature factors were introduced for the thallium and sulphur atoms and the refinement converged to an R-value of 0.130. Certain large ΔF's remained for the strong reflexions, and the errors were traced to the film factors, which had initially been calculated using conventional methods for visually estimated data. They appeared to be generally too small for the low layers and too large for the high layers. New film factors were then applied which were calculated from the reported film factor value of 2.93 for Ilford Industrial G film [8] at perpendicular incidence. A simple Lambert-Beer expression was assumed to account for the increased film thickness at higher angles of incidence. With this modification the refinement was continued and the R-value decreased to 0.105.

The scattering factors for thallium were taken from the tables provided by Cromer and Waber,[9] and for the remaining elements from Hanson *et al.*[10] Anomalous dispersion corrections were applied for thallium and sulphur.[11]

The final atomic coordinates and temperature factor coefficients are given in Table 1. A difference synthesis calculated with these parameters revealed no significant features. The observed and calculated structure amplitudes are shown in Table 2.

Table 1. Atomic coordinates and thermal parameters, listed as isotropic B or anisotropic b_{ij}. The anisotropic temperature factor is defined as $\exp(-b_{11}h^2 - 2b_{12}hk...)$. The standard deviation corresponding to the last digit is shown in parentheses.

Atom	x	y	z	B(Å^2)		
Tl	0.2087(3)	−0.0489(2)	0.0494(1)			
S1	−0.0323(8)	−0.2729(13)	−0.1530(7)			
S2	0.0149(11)	0.1571(16)	−0.2057(9)			
N	0.100(3)	−0.141(6)	−0.333(3)	4.5(6)		
C	0.033(3)	−0.095(4)	−0.237(2)	2.8(5)		
C1	0.121(4)	−0.345(7)	−0.370(3)	4.8(7)		
C2	0.172(5)	0.006(8)	−0.397(5)	6.2(9)		
Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Tl	0.0147(19)	0.0218(5)	0.0083(2)	0.0011(2)	0.0014(1)	−0.0026(2)
S1	0.0153(21)	0.0161(20)	0.0085(6)	0.0013(10)	0.0029(6)	0.0012(9)
S2	0.0202(24)	0.0168(24)	0.0120(9)	0.0031(13)	0.0045(8)	−0.0017(2)

Table 2. Observed and calculated structure factors. Reflexions marked with an asterisk were not included in the refinement.

UNIT CELL AND SYMMETRY

Formula unit: $TlS_2CN(CH_3)_2$
Crystal system: monoclinic
Unit cell parameters: $a = 9.101(2)$ Å; $b = 6.673(2)$ Å; $c = 11.379(3)$ Å; $\beta = 98.90(2)°$
Volume of unit cell: 683 Å^3
Density (measured): 3.16 g cm^{-3}
Number of formula units per unit cell: 4
Density (calculated): 3.158 g cm^{-3}
Diffraction symmetry: $2/m$
Systematic absences: $h0l$ for $h = 2n+1$; $0k0$ for $k = 2n+1$
Space group: $P2_1/a$
Coordinates of equivalent positions: $\pm(x,y,z); \pm(\frac{1}{2}+x,\frac{1}{2}-y,z)$

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

General features. The structure of thallium(I) dimethyldithiocarbamate is made up of dimers having the composition $[TlS_2CN(CH_3)_2]_2$. There are two such dimers in the unit cell with their centres at 0,0,0 and $\frac{1}{2},\frac{1}{2},0$. The dimer is illustrated in Fig. 1 which also shows the atom notation used. The dimers are linked by thallium-sulphur coordination in layers parallel to the (a,b)-plane in such a way that the thallium atoms are all situated very close to the plane; Fig. 2. The ligands project from both sides of this plane as seen in the figure. The layers are stacked upon one another in the direction of **c**, so that only carbon-carbon and carbon-nitrogen contacts are formed. The layer is shown in Fig. 3. Within the layer the metal atoms form a distorted hexagonal net

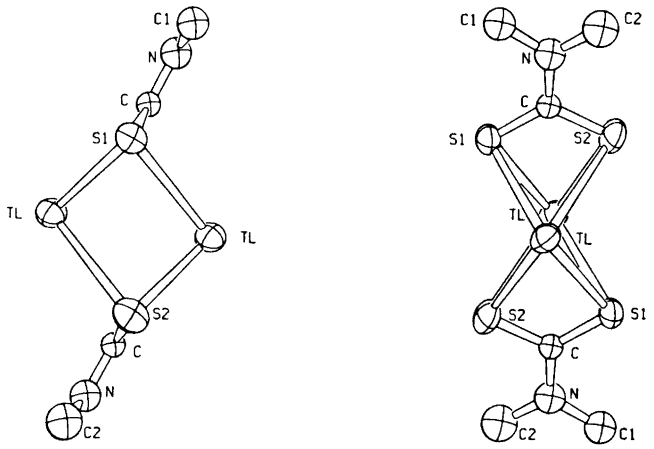

Fig. 1. The dimeric thallium(I) dimethyldithiocarbamate molecule in two orientations; left: sulphur plane normal to the plane of the paper (superimposed carbon and sulphur atoms omitted); right: sulphur plane in the plane of the paper.

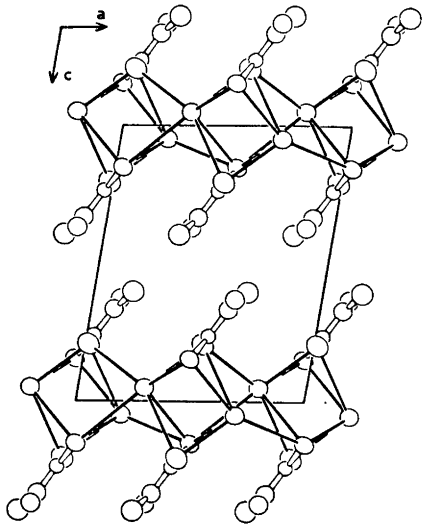

Fig. 2. Projection of the structure with the layers normal to the plane of the paper. The dimers shown have their centres at 0,0,0; ½,½,0; 1,0,0; 0,0,1; ½,½,1; 1,0,1. The thallium-sulphur coordination in the layer is indicated by thin black lines.

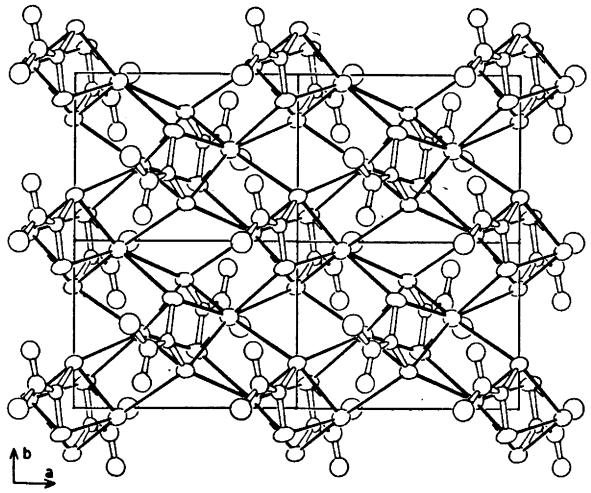

Fig. 3. View of the layer. All the dimers have their centres in the plane $z = 0$. The thallium-sulphur coordination is indicated by thin black lines. The sevenfold coordination of the thallium atoms is clearly seen although one of the bonds is almost hidden.

as shown in Fig. 4. The figure also shows how the sulphur atoms within the layer are confined to almost planar strips. The distances shorter than 4 Å between atoms in different dimeric units are listed in Table 3.

Table 3. Distances shorter than 4 Å between atoms in different dimers. If the two atoms are situated in different layers the distance is set in italics. The relationship between the coordinates of the second atom and those of Table 1 (x,y,z) is indicated.

Atoms			Distance (Å)	Atoms			Distance (Å)
Tl	S2	$\frac{1}{2}-x,-\frac{1}{2}+y,-z$	3.46(1)	N	C2	$-x,-y,-1-z$	*3.75(6)*
Tl	S1	$\frac{1}{2}-x,\frac{1}{2}+y,-z$	3.52(1)	S1	C1	$-\frac{1}{2}+x,-\frac{1}{2}-y,z$	3.78(3)
C2	C2	$-x,-y,-1-z$	*3.61(10)*	C	C1	$-\frac{1}{2}+x,-\frac{1}{2}-y,z$	3.84(4)
C1	C2	$\frac{1}{2}-x,-\frac{1}{2}+y,$ $-1-z$	*3.62(6)*	S1	C2	$-\frac{1}{2}+x,-\frac{1}{2}-y,z$	3.88(5)
Tl	Tl	$\frac{1}{2}-x,\frac{1}{2}+y,-z$	3.637(2)	S1	S2	$x,-1+y,z$	3.89(1)
Tl	Tl	$\frac{1}{2}-x,-\frac{1}{2}+y,-z$	3.637(2)	Tl	C1	$\frac{1}{2}-x,\frac{1}{2}+y,-z$	3.98(4)
S1	N	$-\frac{1}{2}+x,-\frac{1}{2}-y,z$	3.69(3)	C1	C1	$-x,-1-y,-1$ $-1-z$	*3.98(8)*
Tl	S1	$\frac{1}{2}+x,-\frac{1}{2}-y,z$	3.74(1)				

The dimer. The centrosymmetric dimeric unit is shown in Fig. 1. From consideration of the bonds within the molecule the expected point symmetry is *mmm*; but the molecule is in fact found to be somewhat distorted. The four sulphur atoms form a parallelogram which is almost rectangular, the acute angle being 88°. The edges are 2.98 Å and 4.13 Å. Ths short edges connect sulphur atoms in the same ligand. The two thallium atoms are located on each side of the sulphur plane to form a double pyramid. The thallium-thallium vector makes a small angle, 10°, to the normal of the sulphur plane. Each thallium atom is thus closer to the sulphur atoms of one ligand, 2.99 and 3.03 Å, than to those of the other, 3.28 and 3.44 Å. The double pyramid is shown in Fig. 5.

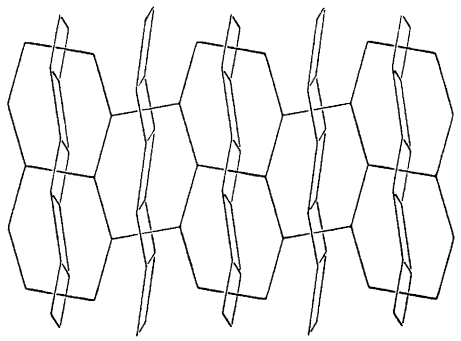

Fig. 4. Simplified drawing showing the 3-connected metal atom net and the intersecting sulphur strips. The figure has the same orientation as Fig. 3. The short thallium-thallium distances, 3.64 Å, run in the direction of **b**, the longer ones, 3.85 Å, in the direction of **a**.

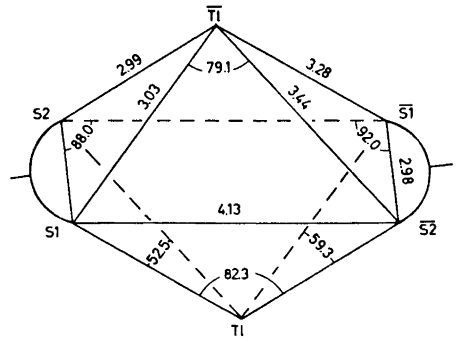

Fig. 5. Angles and distances in the central double pyramid in the dimer. Centrosymmetrically related atoms are denoted by a bar.

Table 4. Distances and angles in the dimethyldithiocarbamate ligand. The notation used is shown in Fig. 1.

Atoms	Distance(Å)	Atoms	Angle(°)
S1 – C	1.69(3)	S1 – C – S2	121(2)
S2 – C	1.74(3)	S1 – C – N	123(2)
C – N	1.36(3)	S2 – C – N	117(2)
N – C1	1.44(5)	C – N – C1	123(3)
N – C2	1.44(6)	C – N – C2	123(4)
S1...S2	2.98(1)	C1 – N – C2	114(3)

The angles and distances in the dithiocarbamate ligand are given in Table 4. They agree well with those found in other dithiocarbamates. The ligands are almost planar, except for the hydrogen atoms. The maximum deviation from the least-squares plane is 0.07 Å. The planes of the two ligands, required by symmetry to be parallel, make dihedral angles of 30° with the sulphur plane. The molecule thus acquires the shape of a paddle-wheel as seen in Fig. 1.

Although the molecule is distorted, the distances between each of the thallium atoms and the two inner carbon atoms remain the same, 3.42 and 3.43 Å, as do those between the thallium atoms and the nitrogen atoms, 4.36 and 4.37 Å. This may follow from a tendency of the thallium-sulphur-carbon angles to take up equal values. Repulsion between the thallium atoms and the carbon and nitrogen atoms may also be responsible, since there appears to be some positive charge on these atoms associated with the conjugated π-system. According to a recent calculation,[12] these charges are 0.41 and 0.34, respectively. Neither of these explanations is entirely satisfying, however. In general, it is not feasible to isolate such interactions from the other forces in the crystal which influence the geometry of the dimer. Some of these forces will be discussed later.

As mentioned above, the thallium atom is closer to the sulphur atoms of one ligand than to those of the other. The thallium atom is thus 0.74 Å from the plane of the closest ligand, see Fig. 1. Although this could suggest that the dimer may be considered as made up of two planar monomers which are slightly deformed, the compound is nonetheless known [4] to form dimers in solution. The monomeric picture would not appear then to be particularly useful in discussing the crystal structure.

Table 5. Distances of coordination. The relationship between the coordinates of the sulphur atoms to those given in Table 1 (x,y,z) is shown.

Atoms			Distance (Å)
Tl	S2	$-x,-y,-z$	2.991(10)
Tl	S1	$-x,-y,-z$	3.027(8)
Tl	S1	x,y,z	3.284(8)
Tl	S2	x,y,z	3.442(10)
Tl	S2	$\frac{1}{2}-x,-\frac{1}{2}+y,-z$	3.458(10)
Tl	S1	$\frac{1}{2}-x,\frac{1}{2}+y,-z$	3.519(8)
Tl	S1	$\frac{1}{2}+x,-\frac{1}{2}-y,z$	3.736(8)

Similar dimers have been found in thallium(I) dipropyldithiocarbamate[1] and in thallium(I) di-isopropyldithiocarbamate.[2] In the isopropyl compound the dimer is quite regular, the thallium-thallium vector being normal to the sulphur parallelogram and the least-squares plane through the S_2CNC_2 part of the ligand being coplanar with the sulphur plane. In the propyl compound, the dimer is considerably distorted. The sulphur atoms do not form a plane, and the molecule is not centrosymmetric.

The coordination. As shown in Table 5, there are seven atoms at distances ranging from 3.0 to 3.8 Å from the thallium atom. There are no other sulphur atoms closer to the thallium atom than 5 Å. The four closest sulphur atoms all belong to the same dimer as the thallium atom itself, whereas the remaining three belong to three different ligands in two other dimers; see Fig. 3. The dimeric unit is thus clearly distinguishable in the structure. The coordination polyhedron is illustrated in Fig. 6. It is most conveniently described as a tri-

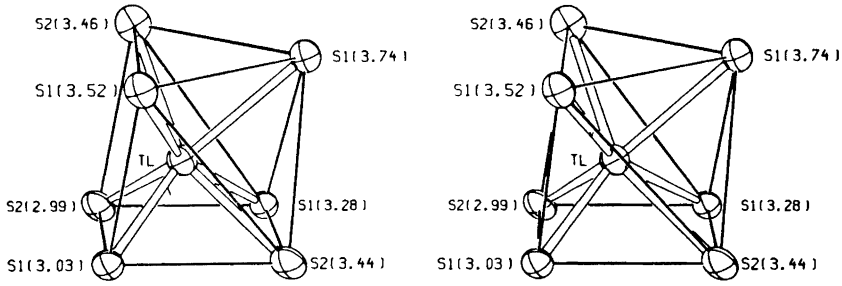

Fig. 6. Stereoscopic illustration of the coordination polyhedron. The distances of coordination are shown. See also Table 5.

gonal prism of six sulphur atoms with the seventh atom outside one of the faces of the prism. The four sulphur atoms in the dimer make up one of the faces of the prism. This face is planar and is directed downwards in the figure. The two remaining quadrangular faces are not exactly planar, but the two calculated least-squares each show a maximum deviation of 0.06 Å from the four defining points. All three faces are thus effectively planar. Furthermore, since the sum of the dihedral angles between them is 180.0° they are all parallel to a common line. The seventh atom is situated outside the largest of these three faces. The two triangular faces of the prism are not parallel.

The observed polyhedron is well known for 7-coordination; examples are found[13] in the complex ions NdF_7^{2-} and TaF_7^{2-}. 8-Coordination rather than 7-coordination appears to be the preferred arrangement for thallium(I) with respect to sulphur. In thallium sulphide,[14] TlS, one half of the thallium atoms is univalent and one half trivalent. The univalent ions are surrounded by eight sulphur atoms at the corners of a square antiprism at a distance of 3.33 Å. In this compound the sulphur atoms can easily be accomodated around the thallium atom, and can form bonds to thallium atoms in several directions. 8-Coordination also occurs in the thiourea complexes of ionic thallium(I) salts. For these compounds an idealized structure has been proposed[15] which in-

volves square antiprismatic coordination. Here the sulphur atoms belong to thiourea molecules which are uncharged so that the most favourable stoichiometry with respect to coordination may be adopted.

In the dithiocarbamates the conditions for a high coordination number and a regular coordination geometry are less favourable. Packing restrictions are imposed because the ligands are quite large and unsymmetrical. They are also charged so that the stoichiometry is determined. A lower coordination number than eight would thus be anticipated. It is interesting to note that the highest coordination number observed so far is found in the structure of the methyl compound which has the smallest ligand. In fact, the connection with the square antiprismatic coordination may be observed in the structure of this compound. The coordination polyhedron, Fig. 6, may be seen as consisting of a base parallelogram and a top triangle. The centrosymmetrically related coordination polyhedra are joined in the *a*-direction by sharing of either the base parallelograms or one edge of the top triangles. When the two triangles share an edge they form, by symmetry, a parallelogram, which is almost parallel to the base parallelogram, dihedral angle 3°. The thallium atoms are thus sandwiched between parallelograms of sulphur atoms, as may be seen in Fig. 4. They are closer to the parallelogram comprising the sulphur atoms in the dimer than to the other parallelogram, 1.90 *vs.* 2.62 Å. In the idealized structure of the thiourea complexes of the ionic thallium salts[15] a similar arrangement is found, but the parallelograms are squares and the thallium atoms are at equal distances from the two surrounding squares. As a particularly interesting aspect of this comparison it should be mentioned that this idealized structure was proposed mainly from considerations of electrostatic forces.

Deformed coordination polyhedra with various coordination numbers and ranges of bonding distances are common in thallium(I) systems. Interesting examples are given by Ohmasa and Nowacki in reports of the structures of various thallium containing minerals.[16] These are sulfosalts with the donating sulphur atoms occurring in rigid groups where all the atoms are bound by covalent bonds. It is therefore not possible for the thallium atoms to achieve a regular coordination environment. A similar case has been found in TlP_5[17] where the donating phosphorus atoms are members of a rigid phosphorus network. In these cases the conditions for a regular coordination would appear extremely unfavourable.

The same type of dimeric unit is found in the three thallium(I) dialkyldithiocarbamates which have been discussed here (propyl, isopropyl, and methyl) but the coordination numbers differ. Thus, 7-coordination is found in the methyl compound but only 5-coordination in the isopropyl compound. In the propyl compound there are two independent thallium atoms which exhibit 5- and 6-coordination. A comparison of the geometry of the dimers in the structures suggests a connection between a high coordination number and a strong deformation of the internal geometry of the dimer. Consequently, very little distorsion is observed in the iso-propyl compound. All four independent thallium-sulphur distances in the dimer are very close to 3.0 Å. The higher coordination numbers in the two other compounds are associated with considerable deformation of the geometry of the dimer. In each case a range

of distances is observed: 2.99 to 3.44 Å in the methyl and 2.88 to 4.37 Å in the propyl compound. If the thallium atom employs sulphur atoms from other dimers to increase its coordination number, the sulphur atoms must coordinate to thallium atoms outside their own dimers. These double engagements evidently disturb the bonding forces within the dimer.

Interesting features of the bonding between thallium(I) and sulphur are the variations of the bond distances, the coordination numbers and the geometries observed in different compounds, as discussed above. The structural behaviour of thallium(I) with respect to sulphur may then be summarized in the statement that *thallium(I) has weak coordination requirements*. Gold(I) may serve as an example of a species with considerably stronger coordination requirements. It is known to exhibit twofold linear coordination not only in the dithiocarbamates (propyl[18] and butyl[19]) but also in a number of other compounds.

The metal atom arrangement. The distance between the two thallium atoms in a dimer is 3.847 ± 0.006 Å, but even shorter distances, 3.637 ± 0.002 Å, exist between thallium atoms in different dimers. A thallium atom in a given dimer thus has two neighbours at 3.64 Å in different dimers as well as the neighbour at 3.85 Å in its own dimer. In this way a 3-connected net of metal atoms is formed. The net is somewhat puckered, the thallium atoms alternating between $z = \pm 0.05$, *i.e.* ± 0.57 Å. The net is illustrated in Fig. 4 together with a schematic illustration of the coordinated sulphur atoms.

The metal atom net found in the structure of thallium(I) dimethyldithiocarbamate may be compared with the metal atom chains observed in the propyl and isopropyl homologues. In these two structures the metal atoms form equidistant nonlinear chains with steps 3.6 Å in the isopropyl and 4.0 Å in the propyl compound. In the chains every second step connects metal atoms situated within one dimer. The shortest metal-metal distance between two chains is about 9 Å in both the propyl and the isopropyl compound. If the chains were to approach one another more closely, so that these distances become similar in magnitude to those within the chains, a 2-dimensional net would result. The appearance of chains in the two latter compounds is associated with the greater size of their ligands, and this evidently prevents the closer approach of the dimers.

It is interesting to note the structure of caesium(I) dibutyldithiocarbamate[20] which strongly resembles that of the present compound. It is made up of dimers arranged in layers with no caesium-sulphur interaction between the layers. However, the metal-metal distances within the dimer, 4.29 Å, are considerably shorter than those appearing between metal atoms in different dimers (minimum distance 5.03 Å). The metal atom arrangement is thus most naturally described as being made up of pairs, and the chain or net models are not particularly useful.

The linkage. It was mentioned above that thallium(I) exhibits a tendency to assume 8-coordination with respect to sulphur. Since the thallium atom in the dimethyldithiocarbamate is coordinated to only four sulphur atoms within the dimer, the higher coordination number must be associated with the linkage of the dimeric units. In the structure, each dimer is linked by thallium-sulphur coordination to four other dimers to form a layer arrange-

ment, as shown in Fig. 3. An idealized form of this linkage is illustrated in Fig. 7. Here the bonds within the dimers are heavily drawn and the sulphur parallelograms are shaded. The dimers are arranged very simply so that the sulphur atoms form planar "ladders". The metal atoms are situated between these in positions of 8-coordination. It is easily seen that each dimer is linked

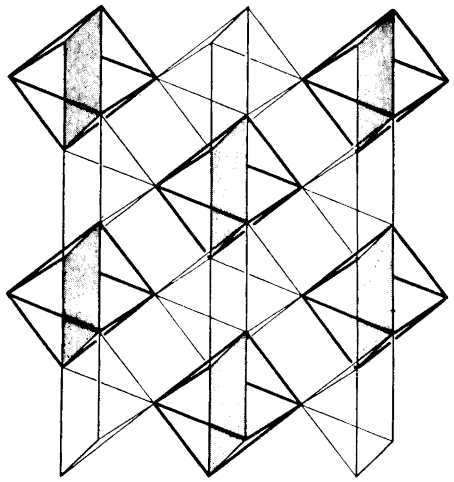

Fig. 7. Layer arrangement of the dimeric molecules giving eightfold coordination. The sulphur parallelograms of the dimers are shaded. The thallium-sulphur bonds within the dimers are heavily drawn. The outer parts of the ligands, which project upwards and downwards from the layer, have been omitted from the figure.

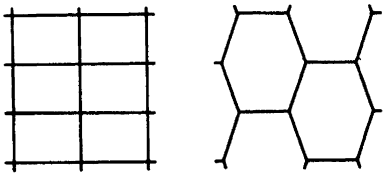

Fig. 8. The 4-connected metal atom net in the model structure (left) and the observed 3-connected hexagonal net (right).

to four others. The metal atoms form a simple 4-connected rectangular net. This "ideal" arrangement is somewhat distorted in the real structure but the nature of the distorsions can be easily understood. The steps of the ladders cannot be equal since every second step of sulphur atoms along the ladders are interconnected by sulphur-carbon-sulphur bonds. The intermediate pairs have no such connections. The former sulphur-sulphur distances are thus shorter than the latter, 2.97 *vs.* 3.89 Å. However, as the latter are very little longer than the sum of two ionic radii for S^{2-}, 3.68 Å, they also represent quite a close sulphur atom approach. The thallium atom is then stituated between two parallelograms, one small and one large. The small one belongs to the same dimer as the thallium atom; it is thus closer than the large one. In this way pairs of metal atoms are distinguishable so that the metal atom net is distorted to form the 3-connected "hexagonal" net as shown in Fig. 8. Further complications result from the necessity to pack the ligands in a favourable way both within and between the layers. The nature of the packing can be appreciated in Fig. 2. Although the structural effects of the packing

requirements are generally very difficult to analyze, it is here reasonable to assume that the ligands are responsible for the folding of the sulphur ladders to form strips. These strips are somewhat inclined, so that the metal atom net is puckered and not planar. After this distorsion the metal atom retains bonds to all four sulphur atoms in the dimer, but the bond to one of the four other atoms is lost, the corresponding distance being larger than 5 Å. The coordination number is therefore only seven.

It is to be expected that the idealized arrangement would be even further destroyed if the ligands were larger. The increased packing difficulties caused by the presence of larger alkyl groups would restrict the number of dimers to which a given dimer could be linked. In the propyl and isopropyl compounds each dimer is linked to only two other dimers, so that chains of dimers are formed instead of the layers found in the methyl compound. The coordination numbers are lower; five and six for the two non-equivalent thallium atoms in the propyl compound and five in the isopropyl compound.

On the other hand, it is expected that the destruction of the idealized arrangement would be less pronounced if the metal-sulphur distances were larger. The alkyl groups would then possess more space, so that the effects of the packing requirements would be less severe. The ligands of caesium dibutyldithiocarbamate [20] are, of course, much larger than those in thallium(I) dimethyldithiocarbamate. The similarities between the two structures can be seen as resulting from the large metal-sulphur distances in the dimer of the caesium compound, average 3.58 Å, compared to the average value of 3.18 Å in the dimer of the thallium compound. In the caesium compound each dimer is linked to four others, as in thallium(I) dimethyldithiocarbamate, but only one of the sulphur atoms in each ligand is involved in the linkage. The coordination number is then only six. The possibility of obtaining higher coordination numbers in the lower homologues of the caesium series is interesting and will be investigated further.

Acknowledgements. We thank Professor Ivar Olovsson for the facilities put at our disposal and Dr. Stig Åkerström for supply of sample. We are grateful to Dr. J.-O. Lundgren for providing programs and for instruction in the use of the film scanner. This work has been supported by a grant from the *Swedish Natural Science Research Council.*

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Received June 28, 1973.