The Crystal Structure of Thallium(I)

Dipropyldithiocarbamate

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The crystal structure of thallium(I) dipropyldithiocarbamate, $(C_3H_7)_2NCS_2Tl$, has been determined from three-dimensional X-ray data. The crystals are monoclinic, space group $P2_1/a$. Unit cell parameters: $a = 9.432$ Å, $b = 17.680$ Å, $c = 13.828$ Å, $\beta = 97.70°$. There are eight formula units per elementary cell. The structure is built as a chain arrangement. In each chain the metal atoms form a nonplanar string with the alternating metal-metal distances 3.98 and 4.00 Å. The string of metal atoms is shielded by the ligands and the only interaction between adjacent chains is of van der Waals type. The chains can be considered as built of dimeric units, $[(C_3H_7)_2NCS_2Tl]_2$, linked together by thallium-sulphur coordination. The metal and sulphur atoms of a dimer form a distorted bipyramid with the metal atoms at the apices. The dimeric units are similar to those occurring in caesium(I) dibutyldithiocarbamate which, however, are linked together to form layers.

The dithiocarbamates of univalent metals belong to a group of compounds with the composition AX, which is of considerable interest in coordination chemistry. The research team to which the present authors belong is currently engaged in crystal structure studies of dithiocarbamates, mono-thiocarbamates and thiolates of monovalent copper, silver, gold, and thallium and of alkali metals. The compounds investigated occur as polymers in the solid state and these polymers usually have very interesting structures. Their formulae can be written $(AX)_n$, where $A =$ metal, $X =$ ligand and $n =$ degree of polymerisation. n has different values, mainly 2, 4, and 6. The majority of the compounds are low polymers but some of them are high polymers. Examples of low polymers are $[(C_3H_7)_2NCS_2Au]_2$,[1] $[(C_2H_5)_2NCS_2Cu]_4$,[2] and $[(C_3H_7)_2NCS_2Ag]_6$.[3]

The compounds usually form low polymers in solutions of nonpolar organic solvents as has been shown by Fredga [4] and Åkerström.[5] Little is known with certainty about the structures of the dissolved polymers but the degree of polymerisation obtained from solution studies in most instances agrees well with crystal structure results. This may serve as an indication that the

polymers in solution usually have structures which are essentially the same as in the solid state.

For the low polymers studied by Åkerström the degree of polymerisation, n, has values mainly from 2 up to 12. Among the compounds which in solution occur as dimers, $(AX)_2$, are gold(I) dipropyldithiocarbamate and thallium(I) dipropyldithiocarbamate. The structure in the solid state of the dimeric gold compound has been described by Hesse.[1] The present paper deals with the crystal structure of thallium(I) dipropyldithiocarbamate.

EXPERIMENTAL

Crystals of thallium(I) dipropyldithiocarbamate were supplied by Åkerström, who had prepared them according to his published method.[6] The crystals were obtained from ligroin as white needles with the needle-axis parallel to the [100] direction. Their density was measured by flotation using an aqueous solution of K_2HgI_4. The unit cell dimensions were determined from a Hägg-Guinier photograph using $CrK\alpha_1$ radiation ($\lambda = 2.2896$ Å) with elementary silicon ($a = 5.4305$ Å)[7] as a calibration standard.

The X-ray reflections were recorded on equi-inclination Weissenberg photographs using CuK radiation. With [100] as the rotation axis layers $0 \leq h \leq 6$ were collected. The crystals were found to decompose slowly in the X-ray beam and for that reason three crystals were used for the exposures. Details of these crystals are given below:

Crystal	Dimensions	Layers recorded	Number of reflections
1	$0.20 \times 0.04 \times 0.02$ mm	0,1,2,3	678
2	$0.30 \times 0.04 \times 0.02$ mm	4,5	277
3	$0.30 \times 0.03 \times 0.02$ mm	6	73

In all 1028 independent reflections were recorded. The relative intensities of the reflections were estimated visually with a calibrated intensity scale and using multiple film technique (six films). Corrections were made for Lorentz and polarisation effects but not for absorption and extinction. Interlayer scale factors were obtained by exposing reflections from all the layers on the same film set. These experimental scale factors proved to be satisfactory, because at the end refinement when the individual scale factors were refined only small changes were noticed (less than 4 % for the layers $0-4$, containing 80 % of all reflections).

UNIT CELL AND SYMMETRY

Formula unit: $(C_3H_7)_2NCS_2Tl$.
Crystal system: monoclinic.
Unit cell parameters: $a = 9.432 \pm 0.005$ Å; $b = 17.680 \pm 0.009$ Å; $c = 13.828 \pm 0.008$ Å; $\beta = 97.70° \pm 0.02°$.
Volume of unit cell: 2285 Å³.
Density (measured): 2.240 g cm⁻³.
Number of formula units per unit cell: 8.
Density (calculated): 2.234 g cm⁻³.
Diffraction symmetry: $2/m$.
Systematic absences: $h\,0\,l$ for $h = 2n+1$; $0\,k\,0$ for $k = 2n+1$.
Space group: $P2_1/a$.
Coordinates of equivalent positions: x, y, z; $\bar{x}, \bar{y}, \bar{z}$; $1/2+x, 1/2-y, z$; $1/2-x, 1/2+y, \bar{z}$.

DETERMINATION OF THE ATOMIC POSITIONS

Approximate positions of the thallium atoms were derived from the three-dimensional Patterson function. The coordinates of these atoms were adjusted by three-dimensional Fourier calculations using back-shift technique. The sulphur, nitrogen, and carbon atoms were located from successive three-dimensional difference syntheses. It was, however, not possible to locate the hydrogen atoms by these methods. For the structure factor calculations and the Fourier summations the programme DRF (written by A. Zalkin, Berkeley,

Table 1. Final weight analysis.

F_o interval	$\overline{\omega \ \Delta}^2$ normalized	Number of reflexions
0 — 44	0.94	102
44 — 51	1.21	103
51 — 57	1.02	103
57 — 66	1.27	103
66 — 76	0.92	103
76 — 89	1.16	102
89 — 102	1.05	103
102 — 125	0.70	103
125 — 175	0.80	103
175 — 545	0.95	103
sin θ interval		
0.00 — 0.35	1.27	204
0.35 — 0.44	1.32	183
0.44 — 0.50	0.87	170
0.50 — 0.55	1.34	135
0.55 — 0.60	1.07	118
0.60 — 0.63	1.11	86
0.63 — 0.67	1.00	60
0.67 — 0.70	1.07	32
0.70 — 0.72	0.68	18
0.72 — 0.75	0.27	11

California, U.S.A. and modified by R. Liminga & J. O. Lundgren, Uppsala) was used. The coordinates and isotropic temperature factors of all but the hydrogen atoms were refined by the method of least squares. These calculations were carried out on a CD 3600 computer with the full-matrix programme LALS.[8] In the minimized expression, $\sum \omega \ (|F_o| - |F_c|)^2$, the weights, ω, were calculated according to the equation suggested by Cruickshank *et al.*,[9] $\omega = 1/(a + |F_o| + c|F_o|^2 + d|F_o|^3)$. The constants used in the final cycles were $a = 30.0$, $c = 0.004$, and $d = 0$. The final weight analysis is given in Table 1. Atomic scattering factors for the elements were obtained from *International Tables*,[10] Vol. III, as follows: thallium (Table 3.3.1B, p. 212), sulphur, nitrogen, and carbon (Table 3.3.1A, pp. 202—203). Dispersion corrections for thallium and sulphur were introduced in the calculations.[11]

Table 2. Atomic parameters. The parameters of all atoms, with the exception of those marked by an asterisk, are taken from the final least squares refinement. The coordinates of the atoms marked by an asterisk are determined from geometrical considerations and the electron density distribution. The least squares parameters of these atoms are given in parentheses.

Atoms	x	$\sigma\,x$	y	$\sigma\,y$	z	$\sigma\,z$	B	$\sigma\,B$
Metal atoms								
Tl_1	0.3385	0.0003	0.1189	0.0001	0.1897	0.0002	8.48	0.09
Tl_2	0.0497	0.0002	0.2119	0.0001	0.3379	0.0002	6.52	0.07
Dithiocarbamate ligand I:								
S_{11}	0.3433	0.0015	0.1332	0.0007	0.3978	0.0009	6.77	0.31
S_{12}	0.1215	0.0016	0.0346	0.0008	0.2905	0.0010	7.92	0.35
C_{10}	0.236	0.004	0.052	0.002	0.393	0.003	3.4	0.8
N_1	0.248	0.004	0.005	0.002	0.467	0.003	5.5	0.8
C_{11}	0.345	0.007	0.018	0.003	0.557	0.005	10.2	1.7
C_{12}	0.267	0.005	0.060	0.002	0.637	0.004	6.7	1.2
C_{13}	0.397	0.007	0.083	0.003	0.716	0.004	8.9	1.5
C_{14}	0.156	0.005	−0.063	0.003	0.467	0.004	6.7	1.2
C_{15}	0.243	0.007	−0.129	0.003	0.433	0.004	9.9	1.7
C_{16}	0.143	0.007	−0.200	0.003	0.419	0.004	9.3	1.6
Dithiocarbamate ligand II:								
S_{21}	0.0818	0.0016	0.2287	0.0007	0.1325	0.0010	7.37	0.34
S_{22}	0.2133	0.0016	0.3483	0.0007	0.2613	0.0010	7.43	0.34
C_{20}	0.173	0.006	0.312	0.003	0.151	0.004	7.2	1.3
N_2	0.211	0.005	0.343	0.002	0.065	0.003	8.6	1.2
C_{21}*	0.136		0.330		−0.036		13	
	(0.133	0.009	0.329	0.004	−0.041	0.006	13.0	2.3)
C_{22}*	0.231		0.279		−0.090		13	
	(0.225	0.010	0.290	0.004	−0.066	0.006	13.3	2.4)
C_{23}*	0.153		0.266		−0.193		11	
	(0.150	0.008	0.264	0.004	−0.180	0.005	11.5	1.9)
C_{24}*	0.304		0.409		0.085		7	
	(0.321	0.006	0.416	0.003	0.089	0.004	7.5	1.3)
C_{25}	0.217	0.006	0.482	0.003	0.056	0.004	8.3	1.4
C_{26}*	0.313		0.550		0.077		10	
	(0.323	0.007	0.561	0.003	0.082	0.004	10.1	1.7)

The least squares calculations were continued until the shifts of the parameters were less than one tenth of the estimated standard deviations. At this stage of the refinement the discrepancy index, R, was 0.081. The atomic coordinates and isotropic temperature factors obtained from the last cycle can all be found in Table 2. For the atoms marked by an asterisk in this table the least squares values are, however, given in parentheses. The coordinates of these atoms presented without parentheses are obtained from geometrical calculations combined with considerations of the electron density distribution. The least squares values were regarded as less accurate because they gave
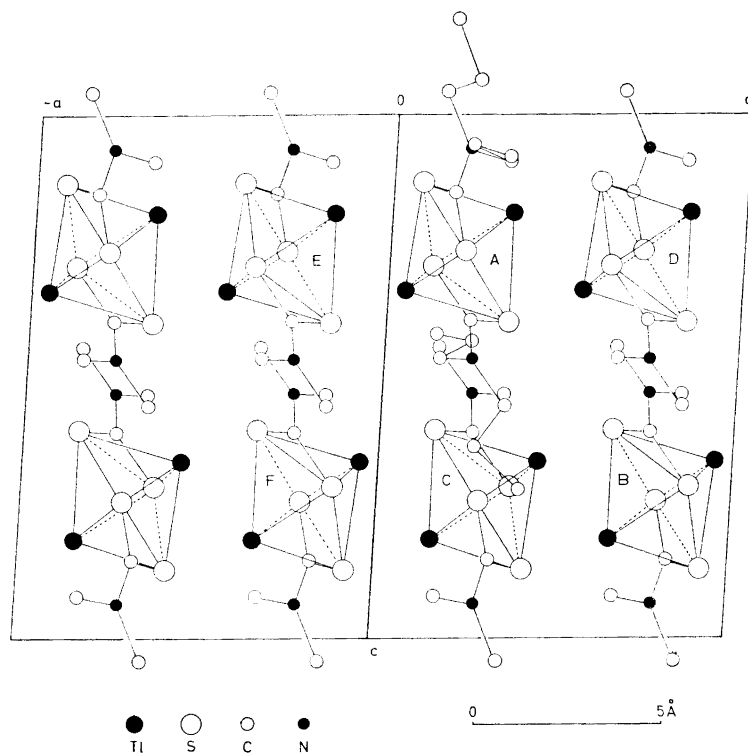
Fig. 1. The crystal structure of thallium(I) dipropyldithiocarbamate. [010]-projection.
Two elementary cells. The dimeric units are given the notations A−F (*cf.* Table 6).
Only the dimer A (coordinates in Table 2) has been completely drawn. In the other
dimers the outermost carbon atoms in the alkyl groups are omitted.

interatomic distances and angles in the propyl chains which were considered
to deviate too much from expected values (see Table 5). The discrepancy
index, R, changed to 0.083 after this operation. Interatomic distances and
angles are given in Tables 3—6. Values given in parentheses correspond to

Table 3. Metal-metal distances and angles. For the explanation of the additional notation
D, see Fig. 4 and Table 6.

Atoms	Distance (Å)	Atoms	Distance (Å)
Tl_1-Tl_2	3.977 ± 0.004	Tl_1-Tl_{2D}	4.002 ± 0.004
	Angle (°)		Angle (°)
$Tl_2-Tl_1-Tl_{2D}$	75.9 ± 0.1	$Tl_1-Tl_{2D}-Tl_{1D}$	111.9 ± 0.1

Table 4. Distances and angles of coordination. For the explanation of the additional notations D and E see Fig. 3 and Table 6.

a. *Distances*

Atoms	Distances (Å)	Atoms	Distances (Å)
Tl_1-S_{11}	2.88 ± 0.013	Tl_2-S_{21}	2.91 ± 0.014
$-S_{12}$	3.02 ± 0.015	$-S_{11}$	3.11 ± 0.014
$-S_{21}$	3.12 ± 0.014	$-S_{22}$	3.12 ± 0.014
$-S_{22D}$	3.59 ± 0.015	$-S_{12}$	3.29 ± 0.014
$-S_{21D}$	3.69 ± 0.014	$-S_{22E}$	3.38 ± 0.014
$-S_{22}$	4.37 ± 0.014	$-S_{11E}$	3.52 ± 0.013

b. *Angles*

	Angles (°)		Angles (°)
$S_{11}-Tl_1-S_{12}$	60.1 ± 0.3	$S_{11}-Tl_2-S_{12}$	54.7 ± 0.3
$-S_{21}$	96.4 ± 0.3	$-S_{21}$	95.6 ± 0.3
$-S_{22}$	70.2 ± 0.2	$-S_{22}$	88.4 ± 0.3
$-S_{21D}$	103.2 ± 0.3	$-S_{11E}$	142.2 ± 0.3
$-S_{22D}$	79.9 ± 0.3	$-S_{22E}$	135.0 ± 0.3
$S_{12}-Tl_1-S_{21}$	82.7 ± 0.3	$S_{12}-Tl_2-S_{21}$	81.2 ± 0.3
$-S_{22}$	97.6 ± 0.3	$-S_{22}$	122.9 ± 0.3
$-S_{21D}$	159.8 ± 0.3	$-S_{11E}$	157.5 ± 0.3
$-S_{22D}$	130.8 ± 0.3	$-S_{22E}$	81.6 ± 0.3
$S_{21}-Tl_1-S_{22}$	42.5 ± 0.3	$S_{21}-Tl_2-S_{22}$	58.5 ± 0.3
$-S_{21D}$	88.6 ± 0.1	$-S_{11E}$	106.3 ± 0.3
$-S_{22D}$	132.5 ± 0.3	$-S_{22E}$	86.6 ± 0.3
$S_{22}-Tl_1-S_{21D}$	64.3 ± 0.2	$S_{22}-Tl_2-S_{11E}$	77.9 ± 0.3
$-S_{22D}$	94.1 ± 0.2	$-S_{22E}$	128.7 ± 0.3
$S_{21D}-Tl_1-S_{22D}$	47.8 ± 0.2	$S_{11E}-Tl_2-S_{22E}$	77.8 ± 0.3
$C_{10}-S_{11}-Tl_1$	88.4 ± 1.2	$C_{20}-S_{21}-Tl_1$	97.4 ± 1.8
$-Tl_2$	82.4 ± 1.2	$-Tl_2$	92.7 ± 1.8
$-Tl_{2D}$	165.0 ± 1.3	$-Tl_{1E}$	69.6 ± 1.8
$C_{10}-S_{12}-Tl_1$	84.4 ± 1.3	$C_{20}-S_{22}-Tl_1$	57.8 ± 1.7
$-Tl_2$	77.3 ± 1.2	$-Tl_2$	87.4 ± 1.8
		$-Tl_{1E}$	73.2 ± 1.7
		$-Tl_{2D}$	104.7 ± 1.9
$Tl_1-S_{11}-Tl_2$	83.3 ± 0.3	$Tl_1-S_{21}-Tl_2$	82.3 ± 0.3
$-Tl_{2D}$	76.7 ± 0.3	$-Tl_{1E}$	151.4 ± 0.4
$Tl_2-S_{11}-Tl_{2D}$	95.0 ± 0.3	$Tl_2-S_{21}-Tl_{1E}$	73.4 ± 0.2
$Tl_1-S_{12}-Tl_2$	78.0 ± 0.2	$Tl_1-S_{22}-Tl_2$	61.6 ± 0.2
		$-Tl_{1E}$	112.0 ± 0.3
		$-Tl_{2D}$	60.6 ± 0.2
		$Tl_2-S_{22}-Tl_{1E}$	72.9 ± 0.3
		$-Tl_{2D}$	98.2 ± 0.3
		$Tl_{1E}-S_{22}-Tl_{2D}$	170.9 ± 0.3

coordinates given in parentheses in Table 2. For the notation of the atoms, see Fig. 2. The atomic coordinates of thallium and sulphur were also refined with anisotropic temperature factors giving $R = 0.063$. The coordinates obtained in this way did not, however, deviate significantly from those given in Table 2.
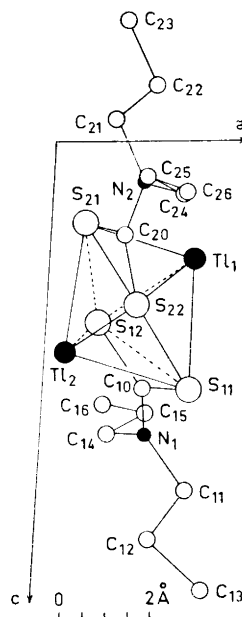

Fig. 2. The $[(C_3H_7)_2NCS_2Tl]_2$ dimer. [010]-projection. The atomic designations are indicated.

Table 5. Distances and angles in the dithiocarbamate ligands.

a. Distances

Atoms	Distances (Å)	Atoms	Distances (Å)
	Ligand I		Ligand II
$S_{11} \cdots S_{12}$	2.96 ± 0.02	$S_{21} \cdots S_{22}$	2.93 ± 0.02
$C_{10} - S_{11}$	1.74 ± 0.04	$C_{20} - S_{21}$	1.71 ± 0.05
$C_{10} - S_{12}$	1.70 ± 0.04	$C_{20} - S_{22}$	1.65 ± 0.05
$C_{10} - N_1$	1.32 ± 0.05	$C_{20} - N_2$	1.40 ± 0.07
$C_{11} - N_1$	1.46 ± 0.07	$C_{21} - N_2$	1.50 (1.58 ± 0.10)
$C_{14} - N_1$	1.48 ± 0.08	$C_{24} - N_2$	1.46 (1.66 ± 0.07)
$C_{11} - C_{12}$	1.60 ± 0.08	$C_{21} - C_{22}$	1.53 (1.19 ± 0.12)
$C_{12} - C_{13}$	1.58 ± 0.08	$C_{22} - C_{23}$	1.53 (1.71 ± 0.11)
$C_{14} - C_{15}$	1.54 ± 0.08	$C_{24} - C_{25}$	1.54 (1.55 ± 0.08)
$C_{15} - C_{16}$	1.58 ± 0.09	$C_{25} - C_{26}$	1.51 (1.72 ± 0.08)

Table 5. Continued.

b. *Angles*

Atoms	Angles (°)	Atoms	Angles (°)
	Ligand I		Ligand II
$S_{11}-C_{10}-S_{12}$	118.6 ± 2.0	$S_{21}-C_{20}-S_{22}$	121.4 ± 3.1
$-N_1$	120.7 ± 2.9	$-N_2$	113.1 ± 3.7
$S_{12}-C_{10}-N_1$	120.6 ± 2.8	$S_{22}-C_{20}-N_2$	125.5 ± 3.7
$C_{10}-N_1-C_{11}$	122.5 ± 3.8	$C_{20}-N_2-C_{21}$	126.0
			(126.1 ± 4.9)
$C_{10}-N_1-C_{14}$	122.2 ± 3.5	$C_{20}-N_2-C_{24}$	112.1
			(111.5 ± 4.0)
$C_{11}-N_1-C_{14}$	115.3 ± 3.8	$C_{21}-N_2-C_{24}$	119.4
			(120.6 ± 4.4)
$N_1-C_{11}-C_{12}$	111.4 ± 4.8	$N_2-C_{21}-C_{22}$	108.3
			(95.3 ± 6.9)
$N_1-C_{14}-C_{15}$	106.6 ± 4.1	$N_2-C_{24}-C_{25}$	109.7
			(100.1 ± 4.0)
$C_{11}-C_{12}-C_{13}$	101.7 ± 4.2	$C_{21}-C_{22}-C_{23}$	107.7
			(101.1 ± 7.3)
$C_{14}-C_{15}-C_{16}$	108.0 ± 5.0	$C_{24}-C_{25}-C_{26}$	109.5
			(103.5 ± 4.3)

Table 6. Intermolecular distances shorter than 4.0 Å.

Atoms	Distances (Å)	Atoms	Distances (Å)
$S_{11A}-C_{11B}$	3.96	$N_{1A}-C_{11B}$	3.92
$S_{11A}-C_{16C}$	3.88	$C_{11A}-C_{11B}$	3.55
$S_{12A}-C_{24E}$	3.97	$C_{13A}-C_{25G}$	3.90
$S_{21A}-N_{2E}$	3.72	$C_{13A}-C_{26G}$	3.75
$S_{21A}-C_{20E}$	3.96	$C_{13A}-C_{23H}$	3.70
$S_{21A}-C_{24E}$	3.58	$C_{14A}-C_{14F}$	3.90
$S_{22A}-C_{11C}$	4.00	$C_{16A}-C_{23J}$	3.93
$S_{22A}-C_{12C}$	3.99		

The coordinates of the atoms of the dimeric units $B-J$ are related to those of the dimer A (coordinates x,y,z in Table 2) by the following relations

Dimeric unit	Coordinates		
A	x	y	z
B	$1-x$	$-y$	$1-z$
C	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$1-z$
D	$\frac{1}{2}+x$	$\frac{1}{2}-y$	z
E	$x-\frac{1}{2}$	$\frac{1}{2}-y$	z
F	$-x$	$-y$	$1-z$
G	$\frac{1}{2}-x$	$y-\frac{1}{2}$	$1-z$
H	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$1+z$
J	$\frac{1}{2}-x$	$y-\frac{1}{2}$	$-z$

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

General features. A general view of the crystal structure of the thallium(I) dipropyldithiocarbamate is given in Fig. 1. The structure can be regarded as built from dimeric units, $[(C_3H_7)_2NCS_2Tl]_2$, (see Fig. 2). There are four such structural units per elementary cell. The dimers are linked together into unlimited chains by metal-sulphur interactions. The chains are parallel to the a-axis. The metal-ligand linkage is illustrated in Fig. 3. Metal-sulphur distances ranging from 2.88 to 3.69 Å are found within the chains. The shortest of these distances, however, appear in the dimers under consideration. The distances between neighbouring metal atoms in the chains are all equal to 4.0 Å.
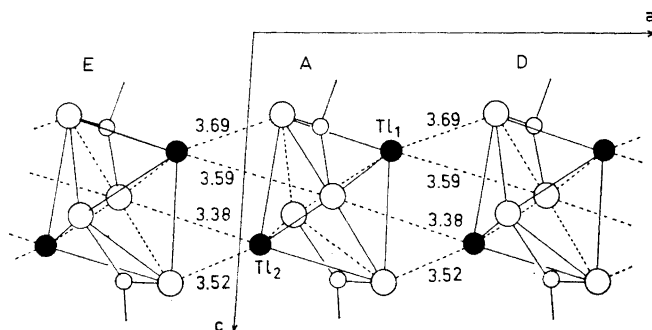
Fig. 3. The linkage of the dimeric units.

The following separations between atoms belonging to *different* chains can be noticed: thallium-thallium >9 Å, thallium-sulphur >8 Å, and sulphur-sulphur >6 Å. The metal and sulphur atoms situated in adjacent chains are accordingly well separated from each other. They are shielded from interchain interactions by the alkyl groups of the ligands and the only interactions *between* the chains are of van der Waals type.

The metal arrangement. The intermetallic distances and angles are presented in Table 3. The arrangement of the metal atoms is illustrated in Fig. 4. The metal atoms form nonplanar zigzag chains with the alternating interatomic distances 3.98 and 4.00 Å. Thus one cannot discern any distinct pairs of thallium atoms when considering the metal arrangement. Similar zigzag chains of equidistant thallium atoms have been detected in the structure of thallium(I) cyclopentadienyl, C_5H_5Tl, as reported by Frasson *et al.*[12] The intermetallic spacings in these chains are all equal to 3.99 Å and are thus almost equal to those in the present compound. According to the authors cited [12] these metal-metal distances are such as to allow the possibility of metal-metal interactions. However, the shortest intermetal distances in the α-form of metallic thallium are 3.41 and 3.46 Å.[13] These distances are considerably shorter than those in thallium(I) dipropyldithiocarbamate and thallium(I) cyclopentadienyl. In thallium(I) methoxide, $TlOCH_3$, investigated by Dahl *et al.*[14] the metal-metal distances within the tetrameric molecular aggregates are on average 3.84 Å.
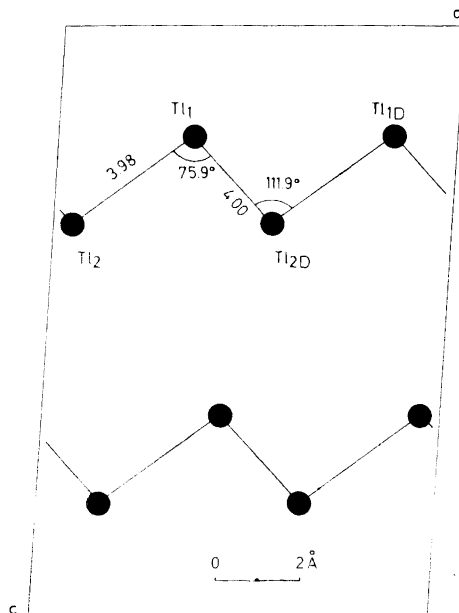
Fig. 4. The metal arrangement.

The intermetallic distances in this compound are somewhat shorter than in the high polymers mentioned above.

In the dithiocarbamates of copper(I), silver(I), and gold(I) investigated at this institute there are metal-metal distances which are comparable to those in the corresponding metallic elements. It may be mentioned that these comparatively short distances all occur in low polymers. Whether they are due to metal-metal bond interactions or can be ascribed to the metal-ligand linkage will not be discussed here.

The dimers. The dimeric unit of the structure is illustrated in Fig. 2. It comprises two thallium atoms and two dipropyldithiocarbamate ligands. The intermetallic distance in a dimer (3.98 Å) is only slightly shorter than the distance between thallium atoms belonging to adjacent dimers (4.00 Å). The consideration of the structure as built of dimers is, however, justified by the fact, that among the eleven thallium-sulphur distances ranging from 2.88 to 3.69 Å as many as seven occur within the dimer. These seven distances are all shorter than the thallium-sulphur distances *between* the dimers.

The dimer, which is rather irregular, has no symmetry. The central part of it comprising the metal and sulphur atoms has the shape of a distorted octahedron. The sulphur atoms of this octahedron form a tetragon which is not far from planar. There are two short (2.93 and 2.96 Å) and two long (4.05 and 4.34 Å) edges in this sulphur tetragon. The short edges correspond to sulphur separations within the ligands and the long ones to interligand distances. The two thallium atoms are situated on opposite sides of this sulphur

arrangement thus together with the four sulphur atoms forming a bipyramid. The four Tl_2—S distances range from 2.91 to 3.29 Å. Three of the Tl_1—S distances (2.88—3.12 Å) are short but one of them, Tl_1—S_{22} (4.37 Å), is considerably longer than the others.

The principle of the linkage of dimers to chains is very interesting and may perhaps explain the irregularities which are observed in the structure. The linkage is illustrated in Fig. 3. The thallium atoms Tl_1 and Tl_2 are linked in different ways to the sulphur atoms of the neighbouring dimers. Each of them coordinates two sulphur atoms of an adjacent dimer. The two sulphur atoms which in this way are linked to Tl_2 are situated in *different* dithiocarbamate ligands while the corresponding sulphur atoms linked to Tl_1 belong to the *same* ligand. As a consequence of this there are varying numbers of metal atoms linked to the different sulphur atoms. Thus the number of coordinated metal atoms is 2 for S_{12}, 3 for S_{11}, S_{21}, and S_{22}.

Dimeric units of a similar type have also been found in the crystal structure of caesium(I) dibutyldithiocarbamate.[15] In the $[(C_4H_9)_2NCS_2Cs]_2$ dimer the central part, comprising the two metal and four sulphur atoms, also has the shape of a bipyramid with the metal atoms situated at the apices. This dimer is, however, more regular than that in the present compound, which is probably due to the different type of linkage. As in thallium(I) dipropyldithiocarbamate there are two metal-sulphur links from each metal atom connecting the dimers to each other. In the caesium-compound, however, the two links from a metal atom go to sulphur atoms situated in *different dimeric units*. By this type of linkage a layer structure with regular features is formed.

An essentially different type of dimer is found in the crystal structure of gold(I) dipropyldithiocarbamate.[1] In this structure the metal atoms have two-fold coordination. The dimers occur as isolated units in this case and are accordingly not linked together into high polymers by metal-sulphur interactions.

According to molecular weight determinations by Åkerström [6] thallium(I) dipropyldithiocarbamate occurs as a dimer in solutions of organic solvents. It is reasonable to expect that the structure of the dimer in solution in essential features is the same as that presented here. On the other hand one cannot disregard the possibility that in some cases additional ligands from the solvent also coordinate the metal atoms. π-Complexes of thallium(I) in the solid state have been reported by Frasson *et al.*[12] The structure is probably more regular in solution than in the solid state. Dimers containing thallium(I) have also been reported from other solution studies. As an example the compound ethylthalloacetoacetate $(CH_3COCHCOOC_2H_5Tl)_2$ [16] can be mentioned.

Coordination. The distances and angles of coordination are presented in Table 4 a and b. Some details of the coordination have been given in the description of the dimers and their linkage. As has been pointed out the metal atoms have irregular coordination and act in different ways in the structure. Anyhow each of them forms chelates with two ligands. Both of them also act as bridging atoms between different ligands. The two ligands forming chelates with the metal atom Tl_1 are situated in different dimers, while those forming chelates with Tl_2 belong to the same dimer.

Except for S_{22} all of the sulphur atoms of a particular dimer are engaged in coordination with both the metal atoms of the dimer in question. S_{22} only coordinates one of them, *i.e.* Tl_2. Besides the metal-sulphur interactions within the dimer all the sulphur atoms with the exception of S_{12} are engaged in linkages between the dimers. The sulphur atoms S_{21} bridge the thallium atoms Tl_1 and in this way a non-planar zig zag chain is formed as shown in Fig. 5 a.
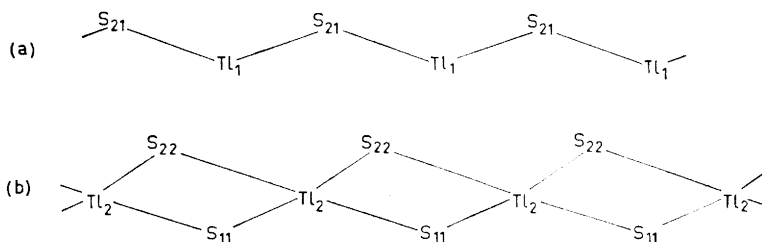

Fig. 5.

As is seen in Fig. 5 b the sulphur atoms S_{11} and S_{22} act as bridges between the atoms Tl_2. The arrangement thus formed consists of a series of almost planar tetragons with the metal atoms as common corners. Adjacent tetragons are slightly inclined to each other. The two chains illustrated in Fig. 5 are connected to each other by a number of cross-links: Tl_1-S_{11}, Tl_1-S_{22}, Tl_2-S_{21}, $Tl_1-S_{12}-Tl_2$ and $S_{21}-C_{20}-S_{22}$. With the exception of Tl_1-S_{22} all these links occur within the earlier described dimers. Tl_1-S_{22} is, however, a link between different dimeric units. The sulphur atom S_{22} is involved in coordination with one thallium atom Tl_1 and two thallium atoms Tl_2. These metal atoms are situated in three different dimers. As a result of the interaction with these three metal atoms, S_{22} is probably hindered from obtaining contact also with Tl_1 in its own dimer. In this way the metal atom Tl_1 only coordinates three sulphur atoms in the dimer of its own. Since it is also linked to two sulphur atoms in an adjacent dimer it has fivefold coordination. On the other hand the metal atom Tl_2, which is also linked to two sulphur atoms in an adjacent dimer, coordinates all the sulphur atoms in its own dimer. Accordingly this metal atom has sixfold coordination.

In the crystal structure of $Tl_2S \cdot Tl_2S_3$ studied by Hahn and Klingler [17] Tl(I) is coordinated by eight sulphur atoms whereas the coordination of Tl(III) is tetrahedral. The Tl(I)—S distance obtained is 3.32 Å. The sum of the Goldschmidt ionic radii for thallium(I) and sulphur is 3.33 Å, and the distance found in the compound mentioned above was accordingly interpreted by the authors as due to ionic interaction. A similar interpretation is given by Boeyens and Herbstein [18] to the Tl—S distances 3.43 and 3.46 Å found in the crystal structures of $TlNO_3 \cdot 4SC(NH_2)_2$ (3.43 Å) and $TlClO_4 \cdot 4SC(NH_2)_2$ (3.43 and 3.46 Å). In these thiourea compounds the coordination polyhedron formed by the sulphur atoms is a slightly distorted cube. It is inferred by the authors that the Tl—S bond distances in the thiourea complexes are due to ion-dipole interactions thus giving a somewhat longer bond distance than the sum of the ionic radii. The covalent Tl—S distance is in the discussions

by Boeyens and Herbstein taken as 2.5 or 2.7 Å.[18,19] Hahn and Klingler suggest a covalent Tl—S distance of 2.77 Å.[17]

The distances of coordination in thallium(I) dipropyldithiocarbamate (Table 4 a) have values ranging from 2.88 to 3.69 Å. According to the considerations of the previously mentioned authors,[17,18] the three shortest Tl—S distances for each thallium atom (2.88, 3.02, and 3.12 Å for Tl_1; 2.91, 3.11, and 3.12 Å for Tl_2) would correspond to essentially covalent bonds. No definitive covalent radius for thallium(I) seems, however, to be available in the literature. Still it can be mentioned that the distances are comparable to the sum (2.90 Å) of the atomic radii given by Slater.[20]

The distances mentioned above all occur within the dimer. The intermediate distance Tl_2—S_{12} (3.29 Å), which also occurs within the dimeric unit, could be regarded as an ionic distance. The two longest Tl—S distances, which are approximately equal in length for each of the metal atoms (3.59 and 3.69 Å for Tl_1; 3.38 and 3.52 Å for Tl_2), would in the same way indicate predominantly ionic interactions. These distances correspond to links between different dimers.

As mentioned earlier the atom Tl_2 and the four sulphur atoms in a dimer are arranged as a tetragonal pyramid with the metal atom at the apex. The bonds from the thallium atom to the four sulphur atoms can perhaps be described by p^3d hybrid orbitals of the metal atom as proposed by Dyatkina[21] for Ga(I) and a number of its analogues, among them Tl(I). The bonds from Tl_1 can, however, not be described in this way.

In the structures of $Tl_2S \cdot Tl_2S_3$ and the thiourea compounds mentioned above, Tl(I) is surrounded by eight sulphur atoms. It could then perhaps have been expected that the thallium atoms also in thallium(I) dipropyldithiocarbamate should have eightfold sulphur coordination. Eight sulphur atoms, situated, for example, in four dithiocarbamate ligands, could easily have been accomodated around a particular thallium atom. Since the metal atoms and ligands occur in the ratio 1:1, the sulphur atoms would then, on average coordinate four metal atoms each. Due to the unsymmetric character and the large size of the ligands, difficulties would, however, arise when each of the additional metal atoms in their turn were to coordinate eight sulphur atoms.

Table 7. Comparison of bond distances in various dialkyldithiocarbamates. Mean values of the bonds in the dithiocarbamate groups.

Dithiocarbamate	S—C (Å)	C=N (Å)	N—C (Å)	Reference
Cu(I) diethyl	1.71	1.41	1.48	2
Ag(I) dipropyl	1.71	1.38	1.50	3
Cs(I) dibutyl	1.74	1.34	1.49	15
Ni(II) diethyl	1.71	1.33	1.49	22
Cu(II) diethyl	1.72	1.34	1.47	23
Zn(II) diethyl	1.73	1.33	1.47	24
Zn(II) dimethyl	1.72	1.35	1.47	25
Ni(II) dipropyl	1.71	1.33	1.47	26
Tl(I) dipropyl	*1.70*	*1.36*	*1.48*	—

If this is the explanation the lower coordination number actually found is due to *higher order steric hindrance* as has been discussed by Hesse.[2]

The dipropyldithiocarbamate ligands. The interatomic distances and angles in the dithiocarbamate ligands are presented in Table 5 a, b. As is seen from the standard deviations and the variations of the distances and angles the accuracy is not high enough to permit any conclusions regarding the bond conditions. However, within the limits of error given, the values presented in most cases agree satisfactorily with results obtained from crystallographic investigations of other dialkyldithiocarbamates.[2,3,15,22–26] A comparison of bond distances obtained in the crystal structures of some dialkyldithio-carbamates is given in Table 7. It has, however, not been the purpose of the present investigation to obtain very accurate values of the distances and angles in the ligands.

Table 8. Deviations (in Ångström units) from least squares planes defined by the six first mentioned atoms of the dithiocarbamate ligands.

Ligand I	Dev. (Å)	Ligand II	Dev. (Å)
S_{11}	0.00	S_{21}	−0.01
S_{12}	0.00	S_{22}	0.01
C_{10}	−0.01	C_{20}	0.00
N_1	0.02	N_2	−0.02
C_{11}	0.01	C_{21}	0.48
C_{14}	−0.03	C_{24}	−0.24
C_{12}	−1.47	C_{22}	−0.61
C_{15}	1.43	C_{25}	1.19

The two ligands I and II (the Roman numerals refer to Table 2) are somewhat different. The $S_{11}S_{12}C_{10}N_1C_{11}C_{14}$ part of ligand I is practically planar with all the deviations from the least squares plane defined by these atoms less than 0.025 Å (see also Table 8). The planarity is true also for ligand II as far as the $S_{21}S_{22}C_{20}N_2$ part of it is concerned, the deviations from the least squares plane for none of these atoms exceeding 0.015 Å. However, the propyl carbons C_{21} and C_{24} are more appreciably displaced from the plane. Probably this and other irregularities in the alkyl groups of ligand II are due to the packing conditions as well as to disorder effects. Disorder phenomena have also been encountered in some other dithio- and monothiocarbamates investigated at this institute.

The two propyl chains of each ligand are situated on opposite sides of the planar part of it and are accordingly in the *trans* position relative to it. The propyl groups form with their nitrogen neighbours almost planar zigzag chains. The planes of these chains are not far from perpendicular to the corresponding $S_{11}S_{12}C_{10}N_i$ planes. The deviations of the atomic positions from the N—C—C—C planes are less than 0.12 Å and are in most cases appreciably less. This is true even for the least squares positions (given in parentheses in Table 2) of the atoms marked by an asterisk. The positions of these atoms

have been corrected by geometrical calculations in order to obtain acceptable distances and angles in the alkyl chains. By these calculations the atoms have been placed strictly into the planes of the chains. The corrected positions fall well within high regions of the electron density peaks of these atoms.

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