The Crystal Structure of Thallium(I) Dibutyldithiocarbamate

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The crystal structure of thallium(I) dibutyldithiocarbamate, $TlS_2CN(C_4H_9)_2$, has been determined from three-dimensional X-ray data. The crystals are monoclinic, space group $P2_1/c$. Unit cell parameters: $a = 14.108(2)$ Å, $b = 10.186(2)$ Å, $c = 9.647(2)$ Å, $\beta = 104.35(2)°$, $Z = 4$. The structure is built from centrosymmetric dimeric molecules linked by thallium-sulfur coordination to form layers parallel to the bc plane. The butyl ligands cover both sides of the layer so that only van der Waals interactions exist between adjacent layers. Thallium coordinates four sulfur atoms (2.97 – 3.16 Å) within the same dimer and two more distant sulfur atoms (3.98 – 4.19 Å). The structure resembles the structure of the corresponding cesium compound. The small differences between the two structures are discussed.

A number of thallium(I) dialkyldithiocarbamates have been investigated at this Institute.[1-5] They all contain dimeric molecules of the same type but the arrangement of the dimers is different. The linkage of the dimers is strongly influenced by the size and the kind of the alkyl groups. Since the coordination number of thallium decreases with increasing length of the ligands, a delicate balance evidently exists between packing and coordination requirements.

Thallium(I) dibutyldithiocarbamate has a lower melting point[6] than the corresponding isobutyl compound (75 – 76 °C and 166 – 168 °C (decomp.), respectively) and the crystals are much softer indicating a crystal structure with lower interaction between the building stones. The structure was expected to give additional information on the interaction between metal coordination and molecular packing.

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UNIT CELL AND SYMMETRY

Formula unit: $TlS_2CN(C_4H_9)_2$

Crystal system: monoclinic

Space group: $P2_1/c$ (No. 14)

$a = 14.108(2)$ Å, $b = 10.186(2)$ Å, $c = 9.647(2)$ Å,

$\beta = 104.35(2)°$

$Z = 4$, $D_m = 2.026(3)$ g cm^{-3}, $D_c = 2.021(1)$ g cm^{-3}

EXPERIMENTAL

Crystals of thallium(I) dibutyldithiocarbamate were prepared by Åkerström.[6] They were obtained from benzene and ethanol (1:1) as pale yellow square plates.

The density was measured by flotation in an aqueous solution of K_2HgI_4. The unit cell dimensions were determined from a Guinier-Hägg powder photograph using CrKα_1 radiation with silicon ($a = 5.4305$ Å)[7] as internal standard.

489 independent reflections were recorded in the layers $0 \le k \le 8$ on equi-inclination Weissenberg photographs using CuKα radiation. The low upper θ limit, about 40°, was expected because of the low melting point and the softness of the crystals. The multiple film technique with four films was used. The crystals decomposed in the X-ray beam, so that each crystal could be used for one layer only. The relative intensities of the reflections were measured with an automatic film scanner SAAB AFS MK II,[8,9] connected on-line to an IBM 1800 processor controller. Process and integration programs by Werner[9] were used. The indexing was performed by a program of our own. The parameters for the integration procedure were the same as those used in two previous determinations.[1,5] A correction factor for the intensities of the strong reflections was applied as suggested by Werner.[10] Corrections were made for absorption as well as for Lorentz and polarization effects. Interlayer scale factors were determined from data obtained by recording the layers $hk0$ and $hk1$.

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

Atom	x	y	z	$B(Å^2)$
Tl	0.0174(3)	0.1759(7)	0.0079(5)	
S1	0.176(2)	−0.044(3)	0.087(3)	3.0(7)
S2	0.037(2)	−0.016(3)	0.272(4)	5.9(9)
C0	0.151(5)	−0.041(7)	0.255(8)	1(2)
N	0.227(8)	−0.066(11)	0.368(12)	8(3)
C11	0.329(7)	−0.068(10)	0.370(11)	4(2)
C12	0.355(5)	−0.210(13)	0.352(14)	7(3)
C13	0.468(9)	−0.222(13)	0.356(14)	8(4)
C14	0.505(11)	−0.361(15)	0.325(18)	11(5)
C21	0.211(7)	−0.071(10)	0.516(11)	4(2)
C22	0.249(7)	0.075(10)	0.605(11)	4(2)
C23	0.230(6)	0.054(9)	0.746(9)	3(2)
C24	0.263(9)	0.190(16)	0.838(15)	8(3)

	b_{11}	b_{22}	b_{33}
Tl	0.0042(3)	0.0062(30)	0.0080(6)

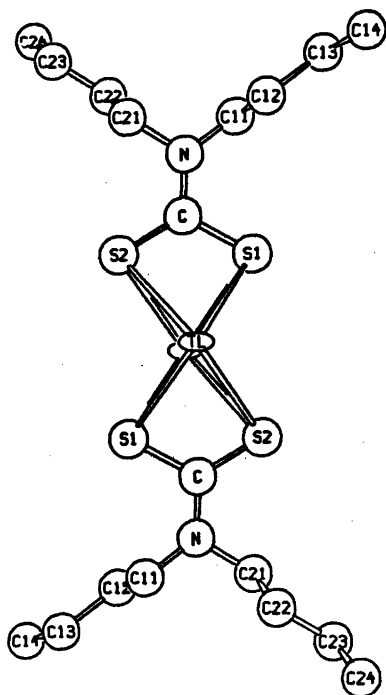|	b_{12}	b_{13}	b_{23}
Tl	0.0017(8)	−0.0013(3)	0.0038(10)

Fig. 1. The dimeric molecule in thallium(I) dibutyldithiocarbomate. The sulfur plane coincides with the paper plane.

DETERMINATION OF THE ATOMIC POSITIONS

Approximate positions of the thallium and sulfur atoms were found from a three-dimensional Patterson synthesis and adjusted by least squares calculations. Five of the carbon atoms were located from a three-dimensional difference synthesis and the temperature factor of thallium was refined anisotropically. The nitrogen atom and the remaining carbon atoms could then be located from a difference synthesis. No attempt was made to locate the hydrogen atoms.

The coordinates and isotropic temperature factors of all atoms were refined by full matrix least squares minimizing $\sum \omega(|F_o| - |F_c|)^2$. The weights, ω, were calculated according to Cruickshank[11] ($a = 90.0$, $c = 0.010$, $d = 0.0$). Atomic scattering factors were taken from Hanson *et al.*[12] The nine scale factors were included in the refinement.

The least squares calculations were continued until the shifts on the parameters were less than 10 % of the estimated standard deviations. The final discrepancy index $R = \sum(|F_o| - |F_c|)|/\sum|F_o|$, was 0.105.

The final atomic and thermal parameters are shown in Table 1. Tables of observed and

Table 2. Distances and angles in the dibutyldithiocarbamate ligand. The notation used is shown in Fig. 1. Atoms related by centrosymmetry are denoted by a bar.

Atoms	Distance (Å)	Atoms	Angle (°)	Atoms	Angle (°)
S1 − C0	1.74(8)	Tl − S1 − C0	85(3)	$\overline{\text{Tl}}$ − S1 − C0	85(3)
S2 − C0	1.67(8)	Tl − S2 − C0	85(3)	$\overline{\text{Tl}}$ − S2 − C0	83(3)
C0 − N	1.35(13)	S1 − C0 − S2	121(4)	S1 − C0 − N	116(7)
N − C11	1.44(15)	S2 − C0 − N	123(7)	C11 − N − C21	112(9)
N − C21	1.50(15)	C0 − N − C11	128(10)	C0 − N − C21	120(9)
C11 − C12	1.51(17)	N − C11 − C12	107(9)	N − C21 − C22	110(8)
C12 − C13	1.58(17)	C11 − C12 − C13	110(10)	C21 − C22 − C23	103(7)
C13 − C14	1.57(20)	C12 − C13 − C14	117(11)	C22 − C23 − C24	106(8)
C21 − C22	1.73(14)				
C22 − C23	1.47(13)				
C23 − C24	1.65(18)				
S1···S2	2.96(4)				

calculated structure amplitudes may be obtained on request from the Institute of Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala 1, Sweden.

DESCRIPTION AND DISCUSSION

The structure of thallium(I) dibutyldithiocarbamate consists of dimeric molecules [TlS$_2$CN(C$_4$H$_9$)$_2$]$_2$, Fig. 1, which also gives the atomic notation. The distances and angles are given in Table 2. There are two molecules in the unit cell.

The thallium atoms are situated on either side of a sulfur parallelogram with edges 2.96(4) and 4.03(3) Å; the shorter edges connect the sulfur atoms within the ligands. The thallium-thallium distance is 3.62(1) Å. The

SSCNCC parts of the ligands are planar with a maximum deviation of 0.1 Å from the least squares planes. The butyl groups have planar zig-zag carbon chains (maximum deviation 0.04 Å) situated on opposite sides of the central ligand plane.

A related dimeric molecule with similar shape and overall dimensions was found in the compound of cesium with the same ligand.[13] The metal-sulfur distances in the two compounds differ more than expected from metal ion radii. The intermolecular Cs − S distances, 3.53 − 3.62 Å, agree well with the sum of the ionic radii,[14] r(Cs$^+$) = 1.69 Å, r(S^{2-}) = 1.84 Å, but the corresponding distances in the thallium compound are 0.2 Å shorter than the radial sum (r(Tl$^+$) = 1.44 Å). Since thallium(I) is highly polarizable[15] it may be assumed that
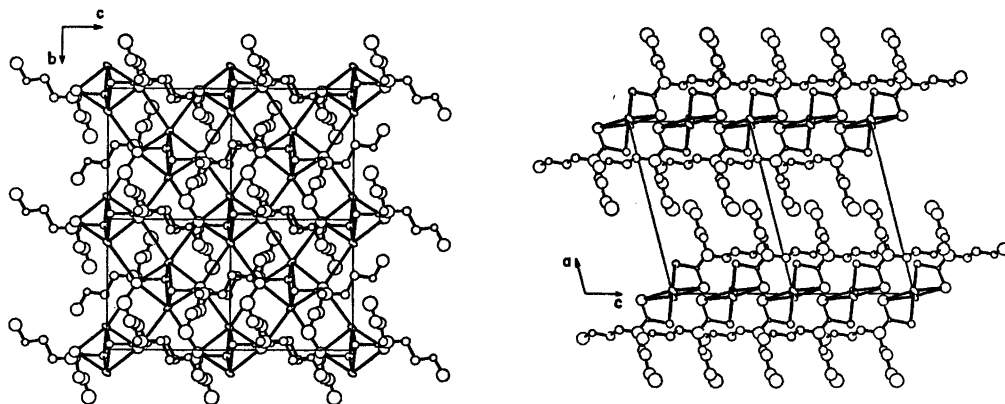

Fig. 2. The *yz* projection and the *zx* projection of two and four unit cells, respectively.

Table 3. Distances of coordination. The relationship between the coordinates of the sulfur atoms and those given in Table 2 is shown.

Atoms		Distance (Å)
Tl – S1	$-x, -y, -z$	2.97(3)
Tl – S2	$-x, -y, -z$	3.08(3)
Tl – S1	x, y, z	3.12(3)
Tl – S2	x, y, z	3.16(3)
Tl – S2	$-x, \frac{1}{2} + y, \frac{1}{2} - z$	3.98(4)
Tl – S2	$x, \frac{1}{2} - y, -\frac{1}{2} + z$	4.19(4)

such short thallium-sulfur distances require a displacement of the thallium electron clouds towards the exterior of the molecule. The dimers are linked by thallium-sulfur coordination in layers parallel to the bc plane. The butyl ligands project from both sides of this plane (Fig. 2). The layers are stacked upon one another in the a direction with only van der Waals interaction between them.

Within a sphere of radius 5 Å the thallium atom is surrounded by six sulfur atoms forming a distorted trigonal prism, Table 3 and

Table 4. Distances, D, and angles, A, in the thallium(I) dialkyldithiocarbamates listed in order of increasing D(Tl – Tl). D* refers to intermolecular distances. Values in Ångström and degrees.

Alkyl	D(Tl – Tl)	D(Tl – S)	D*(Tl – Tl)	D*(Tl – S)	Ref.
Isopropyl	3.58	2.98, 3.03, 3.04, 3.05	3.64	3.86	4
Ethyl (dimer B)	3.60	3.02, 3.05, 3.07, 3.10	3.47	3.80, 3.89	2
Ethyl (dimer A)	3.62	3.03, 3.07, 3.10, 3.12	3.54	3.71, 3.81	2
Butyl	3.62	2.97, 3.08, 3.12, 3.16	5.05	3.98, 4.19	
Isobutyl	3.68	2.97, 3.04, 3.12, 3.18	5.19	3.42	5
Methyl	3.85	2.99, 3.03, 3.28, 3.44	3.64	3.46, 3.52, 3.74	1
Propyl	3.98	2.88, 2.91, 3.02, 3.11, 3.12, 3.12, 3.29, 4.37	4.00	3.38, 3.52, 3.59, 3.69	3

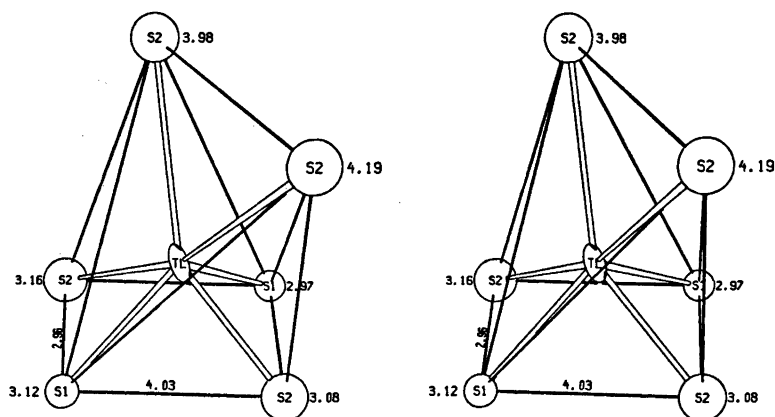| Alkyl	A(Tl$_2$ vector – S$_4$ plane normal)	A(S$_2$CNC$_2$ plane – S$_4$ plane)	D(S – S)		A(S – S – S)
Iso-propyl	0	1	2.88	3.93	89.4
Ethyl (dimer B)	1	5	2.95	3.97	89.1
Ethyl (dimer A)	1	16	2.95	4.02	88.4
Butyl	3	3	2.96	4.03	87.7
Iso-butyl	2	7	2.95	3.96	87.9
Methyl	10	30	2.98	4.13	88.0

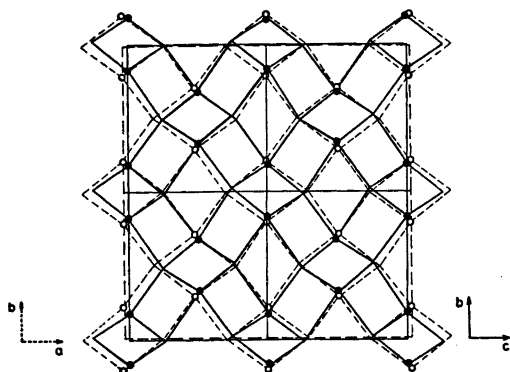*Fig. 3.* Stereoscopic view of the coordinate polyhedron.

Fig. 4. The four-connected coordination net of the thallium and sulfur atoms in thallium(I) dibutyldithiocarbamate (full lines) superimposed on the corresponding net in cesium(I) dibutyldithiocarbamate (broken lines). Only the thallium atoms (dark circles) and the cesium atoms (light circles) are indicated.

Fig. 3. The four closest sulfur atoms belong to the same dimer, the two more distant atoms S2 to two other dimers. The Tl and S2 atoms are situated close to the *bc* plane (< 0.5 Å) and the S1 atoms, which do not participate in the linkage between the molecules, are situated 2.4 Å above and below this plane. The linkage can thus be described by a slightly puckered four-connected net of metal and sulfur atoms corresponding to that found in cesium dibutyldithiocarbamate.[13]

Although the dimensions of the two nets are similar, because of the similar shape and overall dimensions of the large molecules, the metal coordination geometries are different. Whereas the cesium atom is almost equidistant from all the coordinated sulfur atoms, the thallium atom is closer to the sulfur atoms in its own dimer than to the other two. The thallium atom polarization discussed above cannot alone explain the considerable length of the thallium-sulfur bonds between the molecules, since these bonds are shorter in other thallium dialkyldithiocarbamates, Table 4.

It appears that only the larger cesium atom is capable of achieving full contact with all six sulfur atoms. This difference between thallium and cesium was also observed in the dimethyldithiocarbamates,[1,16] where cesium has eightfold and thallium sevenfold coordination.

The effect of the linkage on the molecular geometry. The symmetry of the central part

of the thallium dibutyldithiocarbamate molecule deviates only slightly from the *mmm* symmetry expected in an isolated dimer. Geometric data for the dimeric molecules in this and other thallium dialkyldithiocarbamates have been compiled in Table 4. The different degrees of distorsion from the ideal symmetry are clearly related to the interaction between the dimers in the crystal. The most regular dimers are found in the isopropyl compound, which has the lowest coordination number. Somewhat more distorted dimers occur in the butyl, isobutyl and ethyl compounds. The most distorted dimers are found in the propyl and methyl compounds which have high coordination numbers and short coordination distances between the molecules.

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