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The Crystal Structure of the Chloroform Solvate of Thallium(I) Diethyldithiocarbamate, $[TlS_2CN(C_2H_5)_2]_2.CHCl_3$

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The crystal structure of $[TlS_2CN(C_2H_5)_2]_2.CHCl_3$ has been determined at 0 °C from X-ray data collected on an automatic two-circle diffractometer. The crystals are monoclinic, space group $P2_1/c$; cell dimensions $a=13.102(2)$ Å, $b=11.734(4)$ Å, $c=16.042(3)$ Å, $\beta=112.95(2)°$, $Z=4$. The thallium atoms coordinate four sulfur atoms at distances 2.9 to 3.5 Å in dimeric, centrosymmetric molecules $[TlS_2CN(C_2H_5)_2]_2$, which are packed with the molecular centres in layers at $x=0$ and $x=0.5$. Each thallium atom also coordinates one sulfur atom in another layer, at 3.7 or 3.8 Å, and two chlorine atoms, at 3.9 to 4.5 Å, belonging to chloroform molecules situated between the layers.

The crystal structures of six dialkyldithiocarbamates of thallium(I) have been determined.[1-6] They all contain dimeric molecules with the two thallium atoms coordinated to four sulfur atoms in a plane between them. Interaction between the molecules augments the coordination number of thallium to five, six or seven. The arrangement of the intermolecular Tl–S bonds depends on the size of the alkyl groups; the highest thallium coordination number is found in the compound with the smallest alkyl group, methyl. The internal geometries of the dimers are distorted to various degrees. Large distortions are related to strong intermolecular interactions.

The chloroform solvate of thallium(I) diethyldithiocarbamate was obtained during attempts to prepare highly concentrated solutions.[7]

EXPERIMENTAL

Semitransparent crystals of $[TlS_2CN(C_2H_5)_2]_2.CHCl_3$ were obtained from a solution of $TlS_2CN(C_2H_5)_2$ in $CHCl_3$, saturated at 35 °C, by cooling to room temperature. Since the preparation was unstable in air, crystallization was performed in a thin-walled glass capillary, which was afterwards sealed with a mixture of glass powder and cyanoacrylate.

The chloroform content was determined from the loss of weight of a sample kept in air for a week at 50 °C. The density was measured by flotation in a mixture of $CHCl_3$ and $CHBr_3$.

Preliminary unit cell parameters at 25 °C were determined from small interval zero level oscillation photographs. The film radii were calibrated from α-quartz reflections. Unit cell parameters at 0 °C were determined by least squares refinement based on 73 medium or high θ-values from crystals rotated about a or b on a two-circle diffractometer. The β value remained constant at the lowered temperature, but the unit cell edges decreased by 0.99 %.

Crystal data at 0 °C. Formula unit: $[TlS_2CN(C_2H_5)_2]_2.CHCl_3$. Space group: $P2_1/c$. Unit cell parameters: $a=13.102(2)$ Å, $b=11.734(4)$ Å, $c=16.042(3)$ Å, $\beta=112.95(2)°$. $Z=4$. $D_m=2.40(1)$ g cm^{-3}. $D_x=2.412$ g cm^{-3}. $\mu(CuK\alpha)=335$ cm^{-1}. Systematic absences: $h0l$ for $l=2n+1$; $0k0$ for $k=2n+1$.

The intensities were recorded on a STOE 2-circle diffractometer using graphite monochromatized $CuK\alpha$ radiation. The intensity collection procedure was similar to that used in Ref. 8. The maximum value of $\sin\theta/\lambda$ was 0.51. Since heat development from the diffractometer's stepping motors has been observed to affect crystal volume and alignment, the temperature of the crystal was held constant at 0 °C in this experiment by a stream of dry air cooled with dry ice.[9]

Table 1. Atomic coordinates and thermal parameters. The anisotropic temperature factor is expressed as $\exp(-\beta_{11}h^2 \ldots -2\beta_{12}hk \ldots)$. The values of β_{ij} in the table have been multiplied by 10^4.

Atom	x	y	z	B/Å^2
Tl1	0.1485(3)	0.0015(3)	0.0708(2)	
Tl2	0.6541(3)	0.0215(3)	0.0728(2)	
Cl1	0.655(2)	0.499(1)	0.076(1)	
Cl2	0.733(2)	0.322(2)	0.209(1)	
Cl3	0.792(1)	0.321(1)	0.053(1)	
S11	0.008(2)	0.208(1)	0.001(1)	
S12	0.046(1)	0.053(1)	−0.128(1)	
S21	0.452(1)	0.011(1)	0.121(1)	
S22	0.426(1)	0.205(1)	0.000(1)	
N1	0.033(3)	0.283(3)	−0.148(3)	4(1)
N2	0.431(3)	0.229(3)	0.164(3)	4(1)
C	0.681(4)	0.351(4)	0.092(3)	5(1)
C10	0.036(4)	0.194(5)	−0.097(4)	5(1)
C11	0.025(5)	0.402(5)	−0.115(4)	6(1)
C12	−0.084(5)	0.443(5)	−0.150(4)	7(1)
C13	0.034(4)	0.267(4)	−0.239(3)	4(1)
C14	0.149(5)	0.274(5)	−0.234(4)	7(1)
C20	0.430(4)	0.161(4)	0.098(3)	4(1)
C21	0.417(4)	0.353(4)	0.146(3)	5(1)
C22	0.301(5)	0.395(6)	0.118(4)	8(2)
C23	0.439(4)	0.187(5)	0.256(4)	6(1)
C24	0.556(5)	0.189(5)	0.327(4)	6(1)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Tl1	98(12)	116(3)	60(2)	3(2)	25(1)	17(2)
Tl2	106(12)	79(2)	67(2)	−10(2)	21(2)	−30(2)
Cl1	194(24)	98(16)	105(13)	−11(16)	39(13)	9(13)
Cl2	183(24)	209(25)	67(11)	29(18)	47(12)	16(14)
Cl3	152(21)	128(17)	67(10)	9(14)	37(10)	0(11)
S11	270(28)	78(15)	52(9)	20(15)	77(12)	7(10)
S12	182(23)	54(13)	62(10)	−6(12)	62(11)	4(9)
S21	166(22)	67(15)	74(11)	14(12)	60(12)	12(10)
S22	147(21)	70(13)	35(8)	−19(11)	24(9)	−4(8)

Ten well-formed cylindrical crystals in sealed capillaries were used. Average cross section and length were 0.14 and 0.27 mm. Interlayer scale factors were calculated from the common reflections registered about a ($0 \leq h \leq 10$) and b ($0 \leq k \leq 1$). The intensities were corrected for Lorentz, polarization and absorption effects.

The Patterson map would fit two alternative thallium atom positions. In the successful alternative, one thallium position (0.157, 0.0, 0.071) was determined from the map. Because of the low intensities of reflections with odd h the other one was placed $a/2$ from the first one. These coordinates and isotropic temperature factors were refined by Fourier and least squares calculations. The positions of the sulfur, chlorine, nitrogen and carbon atoms were located from difference syntheses alternating with least squares refinements. Hydrogen atoms were not located. The interlayer scale factors were included and anisotropic temperature factors used for thallium, chlorine and sulfur. The final reliability index $R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$ was 0.074 which was based on 1319 observed reflections with $I_o > 1.5\sigma(I_o)$. 17 of these violating $0.5 < |F_o/F_c| < 2.0$ were excluded in the refinement. The expression minimized was $\Sigma(|F_o| - |F_c|)^2$. In the final cycle of the full matrix program refinement the shifts were less than 0.2 of the estimated standard deviations. A difference synthesis calculated with the final atomic parameters shown in Table 1 showed no spurious peaks higher than 0.08 eÅ^{-3}. Atomic scattering factors were taken from Ref. 10 (Tl, Cl, S) and Ref. 11 (N, C). Anomalous dispersion corrections [11] were applied to Tl, Cl and S. The computer programs are described in Ref. 12.

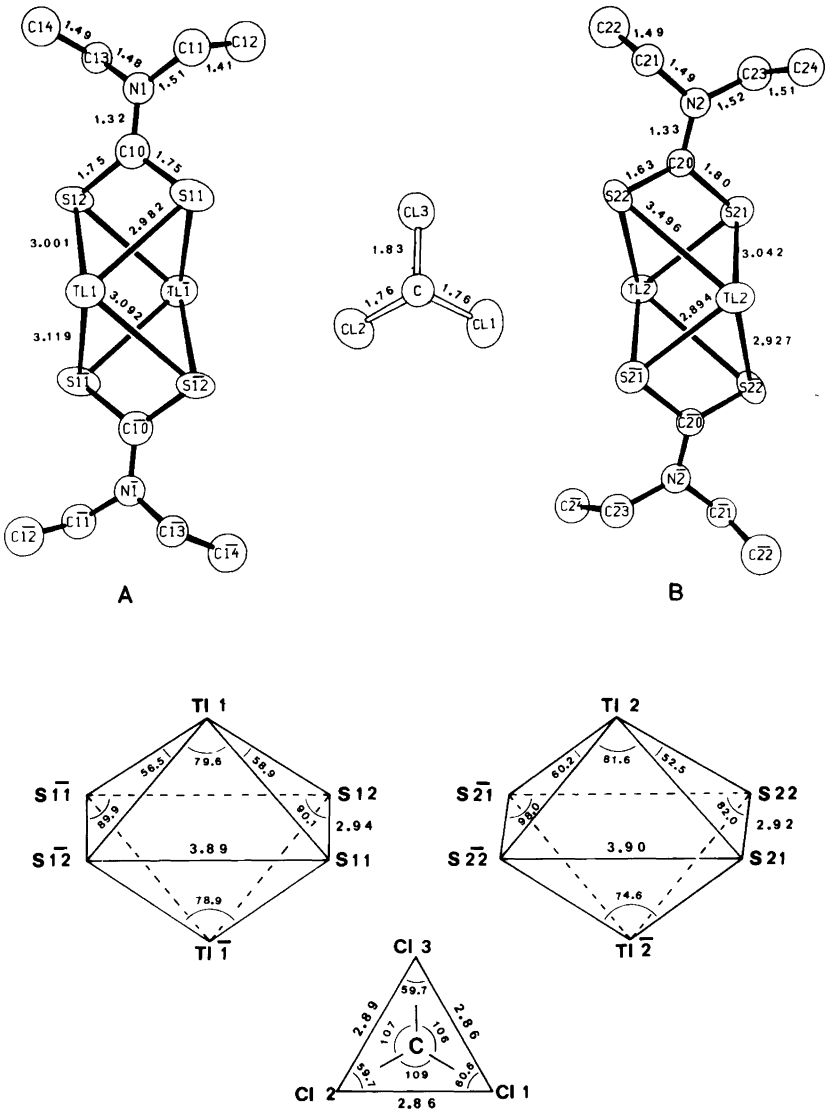

Fig. 1. Geometrical structures of the two dimeric, centrosymmetrical molecules A and B, and the chloroform molecule. The estimated standard deviations (Å) of the distances are for Tl–S 0.017, S–S 0.02, S–C 0.05, Cl–C 0.05, N–C 0.07 and C–C 0.08.

RESULTS AND DISCUSSION

The crystal contains dimeric molecules, $[TlS_2CN(C_2H_5)_2]_2$, packed so as to form a stack of layers parallel to the (*b*,*c*)-plane, with the molecular centres of symmetry at $x=0$ and $x=0.5$ and with interleaving chloroform molecules. Tl–S bonds connect the dimeric molecules from different layers to form infinite chains parallel to **a**.

The two independent dimeric molecules, A and B, Fig. 1, have the same structure as the molecules of the unsolvated compound.[5] The same type of molecule is also found in the other thallium dialkyldithiocarbamates (alkyl = methyl,[3] propyl,[1]

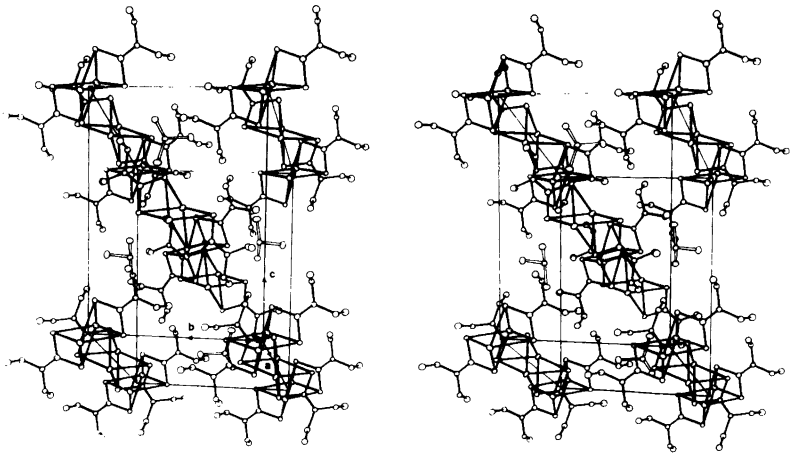

Fig. 2. Stereoscopic illustration of the stacking of the layers viewed along the normal to the (*b*,*c*)-plane. Two layers of molecules A are seen at $x=0$ and $x=1$, and one layer of molecules B at $x=0.5$. The chloroform molecules are situated between the layers.

isopropyl,[2] butyl[6] and isobutyl[4]) and in the potassium,[13] rubidium[13] and cesium[14] dibutyldithiocarbamates. Some interatomic distances are given in Fig. 1. The intramolecular Tl–Tl distances are 3.661(6) Å (A) and 3.829(7) Å (B). The S_2CNC_2 parts of the ligands are planar within experimental error. The S_4 planes of the molecules are somewhat inclined to the layers, 13.2° for A and 22.5° for the less regular B.

Molecule A is more regular than B as indicated by: (1) the smaller range of Tl–S distances, (2) the smaller angle between the Tl_2 vector and the normal to the S_4 plane (2.9° *vs.* 10.6°) and (3) the smaller angle between the S_2CNC_2 plane and the S_4 plane (9.7° *vs.* 19.6°).

The chloroform molecule has the expected structure, with average distances Cl–Cl (2.87(3) Å) and C–Cl [1.79(5) Å] agreeing with those in solid chloroform at 185 K [2.86(1) and 1.75(2) Å[15]].

The dimeric molecule may be formally obtained from that of the isopropyl compound, $[TlS_2CN(C_3H_7)_2]_2$, by replacing one methyl group in each isopropyl chain by a hydrogen atom. The molecules of the isopropyl compound form the same type of layer as the title compound, with similar dimensions. The molecules are quite regular, and the S_4 plane is inclined by only 4.3° to the layer plane. Unsolvated thallium(I) diethyldithiocarbamate, on the other hand, contains no such layers. Evidently the chloroform molecules stabilize the layers by filling the vacancies corresponding to the methyl groups replaced. Two vacancies in layer A cooperate to form one large cavity housing the Cl_3 tripod. If the glide planes were normal to the long axis, as in the isopropyl compound, the vacancies would be dispersed, producing narrow crevices which are unsuitable for accommodating the solvent molecules.

The stacking of the layers. The stacking is shown in Fig. 2. The stacking distance is longer than in the isopropyl compound, 6.03 compared to 5.55 Å, but short interatomic distances between the layers show that the layers are in contact [*e.g.* *D*(C12,C22)= 3.61(9) Å; *D*(C13,C23)= 3.89(8) Å]. The chloroform molecules are situated between the layers, the CH apices pointing towards layer B and the Cl_3 tripod towards layer A. In comparison to the isopropyl compound each solvent molecule, crystal volume[15] 104 Å^3, replaces four methylene groups, combined theoretical volume[16] 106 Å. Despite the similarities of the two values the crystal volume of one dimeric molecule + one chloroform molecule in the solvate, 568 Å^3, is actually 26 Å^3 larger than the crystal volume of one dimeric molecule in the isopropyl compound. Evidently the methylene vacancies are not perfectly located to fit the unsymmetrical solvent molecules. The Cl_3 tripod fits well into the vacancies of layer A but the CH apex is incapable of filling the vacancies in layer B.

The chains of dimeric molecules. The stacking produces chains containing alternating molecules A and B oriented crosswise, Fig. 3. The correspond-

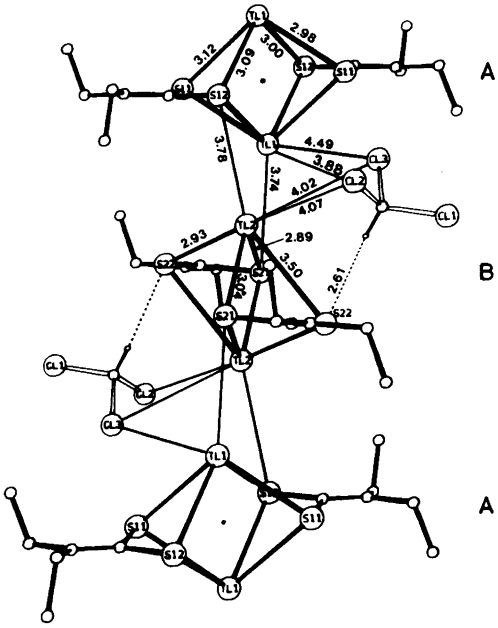

Fig. 3. Perspective illustration of the chain formed by alternating molecules A and B having their centres of symmetry along the *a*-axis which is oriented downwards. The chloroform hydrogen atom has been positioned at 2.31 Å from the three chlorine atoms.

ing chains in the isopropyl compound contain parallel molecules due to a different stacking with only one layer type and a stacking period of one layer. In the propyl compound there is one layer type but a two-layer stacking period, which again gives a crosswise orientation.

The molecules in the chain are linked by Tl–S bonds which are considerably longer than those within the dimeric molecules, D(T11,S21) = 3.74(2) Å: D(T12,S12) = 3.78(2) Å. The five sulfur atoms form a distorted rectangular pyramid about the thallium atom, the apical Tl–S bond being inclined by 25° (A) and 39° (B) to the normal of the equatorial S_4 plane.

The thallium coordination geometry is similar to that of the isopropyl compound in which the apical distance is 3.86 Å. In the unsolvated ethyl compound the coordination geometry is trigonal prismatic; apart from the four sulfur atoms in the dimeric molecule the thallium atom coordinates two extra sulfur atoms in an adjacent dimer at distances 3.7–3.9 Å.

Two chlorine atoms also appear in the vicinity of each thallium atom, D(T11,C12) = 3.88(2) Å, D(T11,C13) = 4.49(2) Å, D(T12,C12) = 4.07(2) Å, D(T12,C13) = 4.02(2) Å. Although longer than in TlCl[17] (3.27 Å) and in $TlCl_2$[18] (3.27 and 3.29 Å), the shortest of the Tl–Cl distances, 3.88 Å, is comparable to the intermolecular Tl–S distances, 3.78 and 3.74 Å. Since the van der Waals radii[19] of Cl and S are similar, 1.74 to 1.80 Å depending on the bonding conditions, Tl–Cl bonds stronger than van der Waals contacts cannot be rejected.

The chloroform carbon atom is close to one of the sulfur atoms in molecule B, D(C,S22) = 3.53(5) Å. Fig. 3 shows that the Tl–Cl and the C–H···S interactions cooperate to connect the chloroform molecule to dimer B. A hydrogen atom positioned at 2.31 Å from the three chlorine atoms, as in solid chloroform,[15] is close to the sulfur atom, D(H,S22) = 2.61 Å. This distance is less than the sum of the van der Waals radii,[19] 3.0 Å. Distances of the same kind and length were interpreted as corresponding to C–H···S hydrogen bonds in tris(morpholyldithiocarbamato)ruthenium(III). $2\frac{1}{2}$ chloroform.[16] The long Tl2–S22 bond, 3.50 Å, should then be attributed to a combination of the two interactions.

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