

## Crystal Structures of Diethyldithiocarbamatodiphenylthallium(III) and Diphenyltropolonatothallium(III) †

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The crystal structures of the title complexes, (1) and (2) respectively, are reported. Complex (1) crystallises in the orthorhombic space group  $Pca2_1$  with  $a = 20.399(5)$ ,  $b = 8.177(6)$ , and  $c = 10.699(4)$  Å. Crystals of the complex (2) are triclinic, space group  $P\bar{1}$ , with  $a = 10.219(3)$ ,  $b = 10.436(3)$ ,  $c = 8.452(2)$  Å,  $\alpha = 91.83(3)^\circ$ ,  $\beta = 111.28(4)^\circ$ , and  $\gamma = 101.30(3)^\circ$ . Full-matrix least-squares refinement has given an  $R$  of 0.050 for 475 reflections for (1) and of 0.051 for 2 564 reflections for (2). Complex (1) is monomeric with four-co-ordinate thallium and a C-Tl-C angle of  $148^\circ$ ; (2) is dimeric with bridging oxygen atoms giving five-co-ordination around the thallium atom and a C-Tl-C angle of  $163^\circ$ . Factors determining the degree of polymerization for this class of thallium compounds are discussed, and  $^{13}\text{C}$  n.m.r. spectra of (1) and (2) are reported.

RECENT X-ray crystallographic studies of dialkylthallium(III) complexes have shown that the C-Tl-C unit has a tendency to remain nearly linear, even in situations where a reduction of the C-Tl-C angle would produce a much more symmetrical overall arrangement of the ligands. Thus C-Tl-C angles for four- and five-co-ordinate thallium in dimeric derivatives<sup>1</sup> are within the same range ( $163$ – $180^\circ$ ) as those found for essentially six-co-ordinate thallium in polymeric derivatives.<sup>2,3</sup> The unusual cluster anion ( $\eta^4$ -decaborato)dimethylthallate(III) shows a low C-Tl-C angle of  $134.1^\circ$ ,<sup>4</sup> which is close to the values reported for the pentafluorophenyl complexes  $[\text{Tl}(\text{C}_6\text{F}_5)_2(\text{OH})]$  ( $139^\circ$ ),<sup>5</sup>  $[\text{Tl}(\text{C}_6\text{F}_5)_2(2,2'$ -dipyridylamido)] ( $127^\circ$ ),<sup>6</sup> and for  $[\text{TlBr}(\text{C}_6\text{HF}_4)_2]$  ( $149.9$ ,  $144.2^\circ$ ).<sup>7</sup> In order to investigate whether the tendency of the C-Tl-C unit to remain nearly linear is present in the diphenyl derivatives, we have determined the crystal structures of  $NN'$ -diethyldithiocarbamatodiphenylthallium(III), (1), and diphenyltropolonatothallium(III), (2). These two structures are the first such determinations for diphenylthallium(III) species. The  $^{205}\text{Tl}$ - $^{13}\text{C}$  and  $^{205}\text{Tl}$ - $^1\text{H}$  spin-spin coupling constants have also been determined for (1) and (2) to investigate possible relationships<sup>1a</sup> between structural and n.m.r. parameters.

### EXPERIMENTAL

**Physical Measurements.**—Carbon-13 n.m.r. spectra were obtained at 22.63 and 45.28 MHz on Bruker HX-90E and WH180 spectrometers respectively,  $^1\text{H}$  n.m.r. spectra at 60 MHz in lock mode on a Perkin-Elmer R12B spectrometer.

**Preparations.**—*Diethyldithiocarbamatodiphenylthallium*(III), (1). This was prepared from the reaction of chlorodiphenylthallium(III)<sup>8</sup> and sodium diethyldithiocarbamate as previously reported.<sup>9</sup> Colourless rectangular crystals suitable for X-ray analysis were obtained from light petroleum (b.p.  $40$ – $60^\circ\text{C}$ ). Proton n.m.r. spectrum in  $\text{S}(\text{CD}_3)_2\text{O}$ : phenyl resonances  $\delta$   $7.91 \pm 0.05$  [ $^3J(\text{Tl-H})$   $437.8 \pm 2.4$ ],  $7.38 \pm 0.03$  [ $^4J(\text{Tl-H})$   $130.8 \pm 1.5$ ], and  $7.21 \pm 0.03$  [ $^5J(\text{Tl-H})$   $49.8 \pm 1.5$  Hz].

*Acetatodiphenylthallium*(III). A mixture of chlorodiphenylthallium(III)<sup>8</sup> (3.8 mmol) and silver(I) acetate (3.7 mmol) in water ( $80 \text{ cm}^3$ ) was shaken vigorously for 20 min.

† Di-*u*-2-hydroxycyclohepta-2,4,6-trien-1-onato-bis[diphenylthallium(III)].

Filtration of the reaction mixture through french chalk and evaporation of the filtrate to dryness gave the compound as a white crystalline solid.

*Diphenyltropolonatothallium*(III), (2). Tropolone (1.3 mmol) and acetatodiphenylthallium(III) (0.6 mmol) were dissolved in methanol ( $25 \text{ cm}^3$ ). The reaction mixture was stirred for 10 min and the product was precipitated by addition of water ( $50 \text{ cm}^3$ ). Crystallization of this material from methanol-chloroform (1:1) solution gave crystals suitable for X-ray analysis. Proton n.m.r. spectrum in  $\text{S}(\text{CD}_3)_2\text{O}$ : phenyl resonances,  $\delta$   $7.62 \pm 0.06$  [ $^3J(\text{Tl-H})$

TABLE I  
Summary of crystal data

Compound	(1)	(2)
Formula	$\text{C}_{17}\text{H}_{20}\text{NS}_2\text{Tl}$	$\text{C}_{10}\text{H}_{15}\text{O}_2\text{Tl}$
$M$	506.8	479.7
Space group	$Pca2_1$	$P\bar{1}$ *
$a/\text{Å}$	20.399(5)	10.219(3)
$b/\text{Å}$	8.177(6)	10.436(3)
$c/\text{Å}$	10.699(4)	8.452(2)
$\alpha/^\circ$	(90)	91.83(3)
$\beta/^\circ$	(90)	111.28(4)
$\gamma/^\circ$	(90)	101.30(3)
$U/\text{Å}^3$	1 784	810
$Z$	4	2
$D_c/\text{g cm}^{-3}$	1.88	1.96
$F(000)$	968	452
$\mu(\text{Mo-K}\alpha)/\text{cm}^{-1}$	89	95.7
Crystal size/mm	$0.10 \times 0.06 \times 0.12$	$0.08 \times 0.08 \times 0.10$
Reflections with $I \geq 3\sigma(I)$	475	2 564
$R$	0.050	0.051

\* The structure of (2) was refined in the space group  $C\bar{1}$  with cell constants  $a = 9.536(3)$ ,  $b = 16.736(3)$ ,  $c = 10.436(2)$  Å,  $\alpha = 91.63(3)^\circ$ ,  $\beta = 102.94(4)^\circ$ , and  $\gamma = 86.89(3)^\circ$ . The atomic fractional co-ordinates listed in Table 3 for this structure are given in the  $C\bar{1}$  unit cell.

$453.2 \pm 4.0$ ],  $7.40 \pm 0.06$  [ $^4J(\text{Tl-H})$   $136.0 \pm 4.0$  Hz]; the *para*-H signals were obscured by the tropolonate resonances. The  $^1\text{H}$  n.m.r. parameters for (1) and (2) are in good agreement with the corresponding values reported for other diphenylthallium(III) compounds.<sup>10</sup>

**Crystal Data.**—Weissenberg photographs indicated orthorhombic symmetry for (1), with systematic absences  $h0l$  where  $h = 2n + 1$  and  $0kl$  where  $l = 2n + 1$ , and the possible space groups  $Pca2_1$  or  $Pcam$ . The non-centric space group  $Pca2_1$  was confirmed by satisfactory refinement. Crystals of complex (2) are triclinic, space group  $P\bar{1}$ , but the data were collected and refined in the non-standard  $C$ -face-

centred space group  $C\bar{1}$ . Table 1 summarizes the pertinent crystal information and details of data collection for both complexes.

The unit-cell parameters for each sample were calculated by a least-squares fit of the angular parameters for 25 reflections with  $2\theta$  ca.  $20^\circ$  using a Philips PW1100 automatic four-circle diffractometer and graphite-monochromatised Mo- $K_\alpha$  radiation ( $\lambda$  0.710 7 Å). A  $\theta$ — $2\theta$  scan mode was used for data collection and reflections with  $3.0 \leq \theta \leq 30.0^\circ$  were examined. Weak reflections which gave  $I_t - 2(I_t)^{1/2} < I_b$  on the first scan were not further examined ( $I_t$  being the count rate at the top of the reflection peak,  $I_b$  the mean count rate of two preliminary 5-s background measurements on either side of the peak). Of the remaining reflections, those for which the total intensity recorded in the first scan of the peak ( $I_i$ ) was  $< 500$  counts were scanned twice to increase their accuracy. A constant scan speed of  $0.05^\circ \text{ s}^{-1}$  and scan width of  $0.85^\circ$  were used for both samples,

TABLE 2

Atomic fractional co-ordinates ( $\times 10^4$  for Tl,  $\times 10^3$  for others) for complex (1) \*

Atom	$x$	$y$	$z$
Tl	2 287(1)	426(2)	2 500
S(1)	292(1)	-249(2)	272(3)
S(2)	309(1)	-32(2)	55(1)
N	367(1)	-326(7)	81(5)
C(1)	324(3)	-213(7)	135(6)
C(2)	404(2)	-289(7)	-32(5)
C(3)	386(3)	-396(7)	-141(6)
C(4)	385(3)	-482(6)	141(4)
C(5)	450(3)	-458(6)	220(7)
C(6)	132(1)	-22(5)	186(3)
C(7)	125(1)	-129(5)	86(3)
C(8)	62(1)	-171(5)	43(3)
C(9)	7(1)	-105(5)	101(3)
C(10)	14(1)	2(5)	201(3)
C(11)	76(1)	44(5)	244(3)
C(12)	290(1)	199(4)	363(3)
C(13)	258(1)	314(4)	438(3)
C(14)	295(1)	411(4)	520(3)
C(15)	363(1)	394(4)	526(3)
C(16)	394(1)	279(4)	451(3)
C(17)	358(1)	182(4)	369(3)

\* In this and subsequent Tables, estimated standard deviations are given in parentheses.

with a background measuring time proportional to  $I_b/I_i$ . Three standard reflections were measured every 4 h during data collection and showed no significant variations in intensity for either sample.

The reflection intensities were calculated using a program written for the PW1100 diffractometer.<sup>11</sup> The variance of the intensity,  $I$ , was calculated as the sum of the variance due to counting statistics and  $(0.04I)^2$ , where the term in  $I^2$  was introduced to allow for other sources of error.<sup>12</sup>  $I$  and  $\sigma(I)$  were corrected for Lorentz and polarization factors and gave 475 (1) and 2 564 (2) reflections having  $I \geq 3\sigma(I)$ . No absorption corrections were applied. Although crystals of (1) showed only poor diffraction, it was decided to continue with the analysis because attempts to obtain suitable crystals of other [TlPh<sub>2</sub>X] derivatives (*e.g.* X = Cl or O<sub>2</sub>CMe) were unsuccessful.

**Structure Solution and Refinement.**—The Tl atom in each case was located from a Patterson map. For each complex a subsequent difference-Fourier synthesis revealed the positions of all the non-hydrogen atoms. Both structures were refined by full-matrix least squares. The H atoms were included at calculated positions in the refinement, riding on

TABLE 3

Atomic fractional co-ordinates ( $\times 10^4$ ) for complex (2)

Atom	$x$	$y$	$z$
Tl	6 657(1)	5 790(1)	361(1)
O(1)	4 692(9)	5 308(5)	1 197(9)
O(2)	6 337(11)	6 468(6)	2 364(10)
C(1)	4 533(13)	5 552(7)	2 338(13)
C(2)	5 447(15)	6 233(8)	3 007(14)
C(3)	5 307(17)	6 619(10)	4 190(16)
C(4)	4 504(19)	6 474(11)	5 100(18)
C(5)	3 534(17)	5 866(10)	5 057(16)
C(6)	3 152(17)	5 290(9)	4 108(15)
C(7)	3 549(15)	5 176(8)	2 918(14)
C(8)	8 276(9)	4 934(5)	1 286(8)
C(9)	8 664(9)	4 892(5)	2 654(8)
C(10)	9 643(9)	4 290(5)	3 251(8)
C(11)	10 235(9)	3 731(5)	2 479(8)
C(12)	9 847(9)	3 773(5)	1 111(8)
C(13)	8 868(9)	4 375(5)	515(8)
C(14)	5 542(9)	6 730(5)	-850(8)
C(15)	6 260(9)	7 254(5)	-1 465(8)
C(16)	5 491(9)	7 881(5)	-2 209(8)
C(17)	4 005(9)	7 982(5)	-2 338(8)
C(18)	3 287(9)	7 458(5)	-1 722(8)
C(19)	4 055(9)	6 831(5)	-979(8)

the respective C atoms with C-H of 1.08 Å. For both structures the phenyl rings were refined as rigid bodies with C-C 1.395 Å, and for the final stages of refinement the Tl atom in each case was assigned anisotropic thermal parameters as were the S atoms in (1). For (1),  $R$  was 0.050 and  $R' = 0.047$  and for (2)  $R = 0.051$  and  $R' = 0.055$ ;  $R' = (\sum w||F_o| - |F_c||^2 / \sum w|F_o|^2)^{1/2}$  where  $w = m(\sigma^2|F_o| + n|F_o|^2)^{-1}$ ,  $m = 1.142 8$  and  $n = 5.4 \times 10^{-5}$  for (1), and  $m = 1.0$  and  $n = 5.91 \times 10^{-3}$  for (2). Neutral-atom scattering factors were used,<sup>13</sup> those for Tl and S being corrected for anomalous-dispersion effects.<sup>14</sup> In each case a final difference map revealed some residual electron density around the Tl atom,

TABLE 4

Interatomic distances (Å) and angles ( $^\circ$ ) for complex (1)

(a) Intramolecular distances			
Tl-C(6)	2.160(29)	C(1)-N	1.403(68)
Tl-C(12)	2.158(32)	N-C(2)	1.458(71)
Tl-S(1)	2.717(16)	N-C(4)	1.471(72)
Tl-S(2)	2.722(16)	C(2)-C(3)	1.506(73)
S(1)-C(1)	1.626(70)	C(4)-C(5)	1.593(73)
S(2)-C(1)	1.732(61)		
(b) Angles			
C(6)-Tl-C(12)	148.4(1.6)	S(2)-C(1)-N	117.7(5.3)
C(6)-Tl-S(1)	104.3(1.2)	C(1)-N-C(2)	122.3(5.7)
C(6)-Tl-S(2)	104.9(1.2)	C(1)-N-C(4)	122.8(6.1)
C(12)-Tl-S(1)	101.5(1.3)	N-C(2)-C(3)	113.1(5.0)
C(12)-Tl-S(2)	102.2(1.2)	N-C(4)-C(5)	109.2(4.7)
S(1)-Tl-S(2)	65.3(0.8)	C(1)-S(1)-Tl	87.5(2.4)
S(1)-C(1)-S(2)	121.8(4.0)	C(1)-S(2)-Tl	85.3(2.3)
S(1)-C(1)-N	120.4(5.1)	C(2)-N-C(4)	114.5(5.6)
(c) Intermolecular contacts *			
Tl...S(2 <sup>I</sup> )	3.413	H(13)...S(2 <sup>I</sup> )	3.23
S(1)...H(3b <sup>I</sup> )	3.01	H(5b)...H(8 <sup>I</sup> )	2.32
S(1)...H(7 <sup>I</sup> )	3.06	H(10)...H(17 <sup>II</sup> )	2.28
C(6)...H(3a <sup>I</sup> )	2.85	H(2b)...H(16 <sup>III</sup> )	2.04
C(7)...H(3a <sup>I</sup> )	2.95	C(16)...C(5 <sup>IV</sup> )	3.47
C(11)...H(2a <sup>I</sup> )	2.78	C(16)...H(5a <sup>IV</sup> )	2.66
C(11)...H(3a <sup>I</sup> )	2.95	C(17)...H(4a <sup>IV</sup> )	3.04
C(12)...S(2 <sup>I</sup> )	3.45	C(17)...H(5a <sup>IV</sup> )	3.08
C(13)...S(2 <sup>I</sup> )	3.39	H(16)...H(5a <sup>IV</sup> )	2.42
C(17)...C(7 <sup>I</sup> )	3.46		

\* Superscripts refer to the atoms at the following equivalent positions relative to the first atom at  $x, y, z$ : I  $0.5 - x, y, 0.5 + z$ ; II  $-0.5 + x, -y, z$ ; III  $1.0 - x, -y, -0.5 + z$ ; IV  $x, 1.0 + y, z$ . Contacts are less than the appropriate sums of the following radii: C 1.75, H 1.25, N 1.70, S 1.90, and Tl 2.0 Å.

but was otherwise featureless. The SHELX<sup>15</sup> and ORTEP<sup>16</sup> programs were used. The refined atomic positional parameters and bond lengths and angles for (1) and (2) are presented in Tables 2 and 3 and 4 and 5 res-

TABLE 5  
Interatomic distances (Å) and angles (°) for the centrosymmetric dimer (2)

(a) Intramolecular distances			
Tl-O(1)	2.421(9)	C(1)-C(2)	1.529(19)
Tl-O(1')	2.612(9)	C(1)-C(7)	1.407(18)
Tl-O(2)	2.422(10)	C(2)-C(3)	1.406(20)
Tl-C(8)	2.131(6)	C(3)-C(4)	1.381(22)
Tl-C(14)	2.129(6)	C(4)-C(5)	1.405(22)
Tl...Tl'	4.156	C(5)-C(6)	1.366(21)
O(1)-C(1)	1.286(15)	C(6)-C(7)	1.383(20)
O(2)-C(2)	1.278(16)		
(b) Angles			
Tl-C(8)-C(9)	120.3(2)	C(1)-O(1)-Tl	118.9(9)
Tl-C(8)-C(13)	119.5(2)	C(2)-O(2)-Tl	121.4(9)
Tl-C(14)-C(15)	122.0(2)	O(2)-C(2)-C(1)	114.3(12)
Tl-C(14)-C(19)	118.0(2)	O(2)-C(2)-C(3)	120.7(14)
O(1)-Tl-O(2)	66.5(3)	C(2)-C(1)-C(7)	123.2(12)
O(1)-Tl-O(1')	68.7(3)	C(1)-C(2)-C(3)	125.0(13)
O(2)-Tl-O(1')	135.1(3)	C(2)-C(3)-C(4)	133.0(16)
O(1)-Tl-C(8)	97.3(3)	C(3)-C(4)-C(5)	127.6(17)
O(1)-Tl-C(14)	99.9(3)	C(4)-C(5)-C(6)	128.4(16)
O(2)-Tl-C(8)	96.3(3)	C(5)-C(6)-C(7)	129.6(15)
O(2)-Tl-C(14)	93.0(4)	C(6)-C(7)-C(1)	132.7(14)
C(8)-Tl-C(14)	162.6(3)	O(1)-C(1)-C(7)	118.9(12)
Tl-O(1)-Tl'	111.3(2)	O(1)-C(1)-C(2)	117.9(15)
(c) Intermolecular contact distances *			
Tl...H(16 <sup>I</sup> )	3.29	C(10)...H(6 <sup>IV</sup> )	2.89
O(2)...C(16 <sup>I</sup> )	3.31	C(12)...H(15 <sup>V</sup> )	2.95
O(2)...H(15 <sup>I</sup> )	2.94	C(13)...C(13 <sup>V</sup> )	3.44
O(2)...H(16 <sup>II</sup> )	2.50	C(15)...H(4 <sup>VI</sup> )	2.92
C(5)...H(17 <sup>II</sup> )	2.78	C(15)...H(12 <sup>VII</sup> )	2.97
C(6)...H(17 <sup>III</sup> )	2.66	C(16)...H(4 <sup>VI</sup> )	2.56
C(7)...H(17 <sup>III</sup> )	2.86	C(16)...H(12 <sup>VII</sup> )	2.96
C(9)...H(5 <sup>III</sup> )	2.81	C(17)...H(4 <sup>VI</sup> )	2.66
C(10)...H(5 <sup>III</sup> )	2.87	H(12)...H(15 <sup>V</sup> )	2.29

\* Superscripts refer to the atom at the following equivalent positions relative to the first atom at  $x, y, z$ : I  $1.5 - x, 1.5 - y, -z$ ; II  $0.5 - x, 1.5 - y, -z$ ; III  $1.0 - x, 1.0 - y, 1.0 - z$ ; IV  $1.0 + x, y, z$ ; V  $2.0 - x, 1.0 - y, -z$ ; VI  $x, y, -1.0 + z$ ; VII  $-0.5 + x, 0.5 - y, z$ . Contacts less than the appropriate sums of the following radii: C 1.75, H 1.25, O 1.80, and Tl 2.10 Å.

pectively. Atomic thermal parameters, hydrogen positional parameters, equations of least-squares planes, and observed and calculated structure factors are to be found in Supplementary Publication No. SUP 22808 (26 pp.).\* The

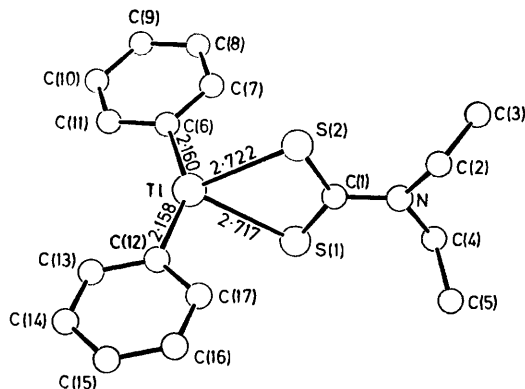


FIGURE 1 Structure of (1) showing important bond lengths (Å) and the atom-numbering scheme

structures of (1) and (2) are shown in Figures 1 and 2 respectively together with the atom-labelling schemes.

## RESULTS AND DISCUSSION

The molecule of (1) exists as a discrete monomer (Figure 1). The shortest intermolecular contact in-

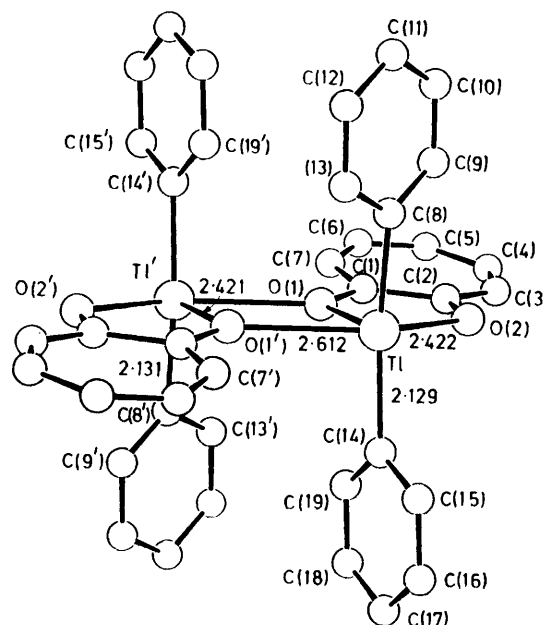


FIGURE 2 Structure of the centrosymmetric dimer (2) showing important bond lengths (Å) and the atom-numbering scheme

volving Tl is Tl...S 3.41 Å (Figure 3). Although this is less than the sum of the reported van der Waals radii for Tl (1.96 Å)<sup>17</sup> and S (1.85 Å),<sup>18</sup> the interaction must be

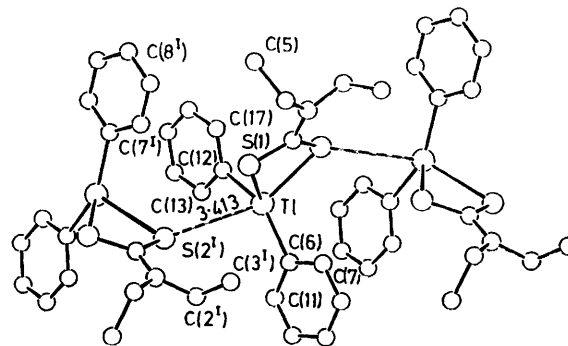


FIGURE 3 Arrangement of the monomeric units of (1). The shortest intermolecular contact involving thallium is Tl...S(2') 3.413 Å [Table 4(c)]

weak. This distance is considerably greater than that found for the long bridging Tl-S bonds (2.99 Å) in the dimeric complex dimethylthallium(III) thiophenoxide.<sup>1a</sup> This structure appears to be the first reported for a neutral diorganothallium(III) species where the TlR<sub>2</sub>X unit is not oligomerized.<sup>1-3,5-7</sup>

The co-ordination geometry around Tl in (1) can be

\* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

considered as a highly distorted tetrahedron with a C-Tl-C angle of  $148^\circ$  and an S-Tl-S angle ( $65^\circ$ ) that is dictated by the size of the four-membered chelate ring. The complex tris(*NN'*-dimethyldithiocarbamato)thallium(III) monohydrate<sup>19</sup> has similar S-Tl-S angles (mean  $68.2^\circ$ ) and shows Tl-S bond lengths of 2.613–2.677 Å.

The complex (2) exists as a centrosymmetric dimer with five-co-ordination at the Tl atom (Figure 2) and there is no suggestion of further association in the solid state, in contrast to the structure of (3), the dimethylthallium(III) analogue,<sup>2b</sup> where polymerization increases the co-ordination of the Tl atom to six [Figure 4(a)]. The

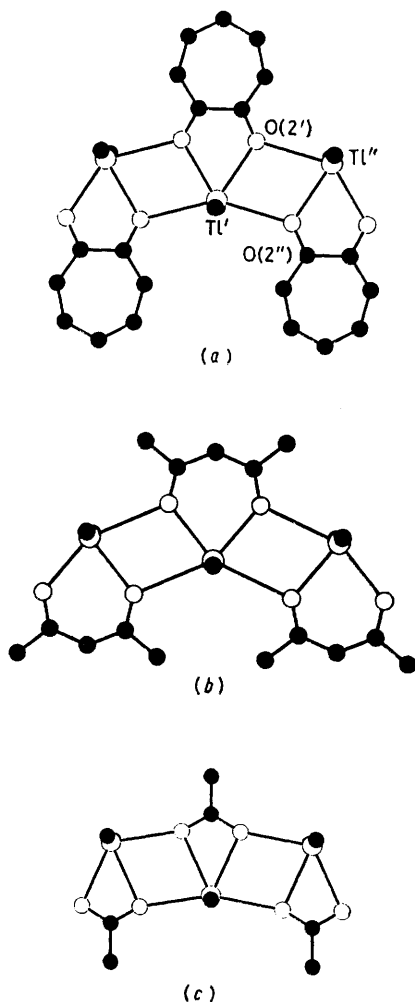


FIGURE 4. Reported structures [ref. 2(b)] of dimethylthallium(III) complexes with bidentate oxygen donors: (a) tropolonate, (3); (b) acetylacetonate; and (c) acetate

only intermolecular contact less than 3.9 Å involving thallium is a  $\text{Tl} \cdots \text{H}$  distance of 3.29 Å [Table 5(c)].

The co-ordination geometry round the Tl atom in (2) may be envisaged as derived from a slightly distorted pentagonal bipyramid with two vacant equatorial sites (Figures 2 and 5). The phenyl groups are in the axial positions with a nearly linear C-Tl-C angle of  $162.6^\circ$  which is slightly smaller than that of  $166.9^\circ$  in the poly-

meric dimethylthallium(III) analogue (3) and the mean Tl-C bond length of 2.130 Å is equal to that in (3).<sup>2b</sup> The average Tl-O distance of 2.42(1) Å in the chelate ring of (2) is significantly shorter than the corresponding distance of 2.47(1) Å in (3); the bridging Tl-O distance of 2.61 Å in (2) is similarly shorter than that of 2.74 Å in (3). The differences between these equatorial bond lengths in (2) and (3) are expected on the basis of the

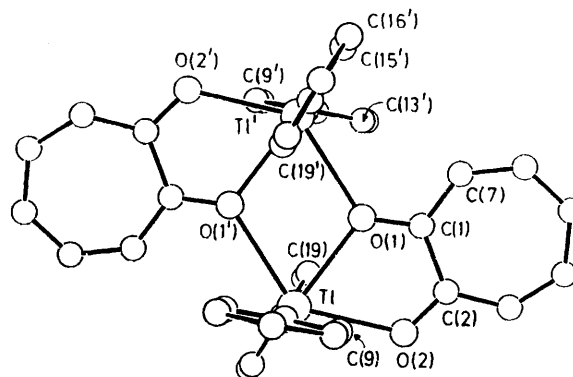


FIGURE 5. Dimeric structure of (2) viewed perpendicular to the  $\text{TlOTl'O'}$  bridge to show the relative orientation of the phenyl rings. The shortest intra-dimer contact is  $\text{H}(7) \cdots \text{H}(13')$  2.56 Å

different thallium co-ordination numbers, *i.e.* five in the dimeric structure of (2) and six in the polymeric structure of (3). The tropolonato-ligand is planar to within 0.08 Å and the Tl atom is 0.28 Å out of the plane.

Steric factors do not appear to be of major importance in determining the C-Tl-C angle in diorganothallium(III) complexes. The C-Tl-C angle ( $163^\circ$ ) in the five-co-ordinate complex (2) is close to that found in the six-co-ordinate polymeric  $[\text{TlMe}_2(\text{O}_2\text{C}_7\text{H}_5)]$  ( $167^\circ$ ).<sup>2b</sup> The corresponding angle in the four-co-ordinate complex (1) ( $148^\circ$ ) is close to the value found in the five-co-ordinate polymeric  $[\text{Tl}(\text{C}_6\text{F}_5)_2(\text{OH})]$  ( $139^\circ$ ).<sup>5</sup> This suggests that there is no correlation between the C-Tl-C angles and the co-ordination number of thallium. It may be concluded that electronic factors are dominant in determining the tendency of the  $\text{R}_2\text{Tl}$  unit to remain near linear. Interestingly, the arrangement of the phenyl rings in (1) and (2) is quite different. In (1) the phenyl rings are nearly coplanar with an angle of  $8.2^\circ$  between their respective planes, but in (2) the conformation is nearer orthogonal with an angle of  $69.5^\circ$  between the planes of the rings. These arrangements are the reverse of what would be expected if steric factors controlled the size of the C-Tl-C angle.

The extent of oligomerization in diorganothallium(III) derivatives,  $[\text{TlR}_2\text{X}]$ , seems to be largely controlled by the nature and size of the anionic ligand  $\text{X}^-$ . Unidentate ligands appear to give polymers only if  $\text{X}^-$  is very small; the hydroxide,<sup>5</sup> chloride,<sup>3b,7</sup> and bromide<sup>7</sup> derivatives for which structures have been reported are all polymeric, whereas for larger anionic ligands  $\text{OPh}^-$ ,  $\text{SPh}^-$ ,  $\text{OC}_6\text{H}_4\text{Cl-}o^-$ , and  $[\text{Al}(\text{CH}_3)_3(\text{NCS})]^-$  association is limited to dimer formation.<sup>1a,c</sup> Where  $\text{X}^-$  is a bidentate

oxygen donor, polymeric chain structures (with bridging systems similar to those shown in Figure 4) have previously been found in all cases<sup>2b,3c</sup> except that of  $\beta$ -hydroxychalconatodimethylthallium(III)<sup>2b</sup> which is dimeric. The lack of oligomerization in this case is directly attributable<sup>2b</sup> to steric factors as replacement of the acetylacetonato-methyl groups by phenyl groups in the structure shown in Figure 4(b) is clearly impossible.

At first sight it seemed possible that oligomerization in (2) was limited to dimer formation by steric factors caused by the replacement of methyl groups, present in the polymeric structure of (3) [Figure 4(a)], by the bulkier phenyl groups. The phenyl groups in (2) are staggered relative to each other so that they are aligned along the Tl-O chelate bonds (Figure 5) with O(1)  $\cdots$  H(19) 2.64 and O(2)  $\cdots$  H(9) 2.59 Å. One phenyl ring points towards the second half of the dimer giving the shortest intradimer contacts, H(7)  $\cdots$  H(13') 2.56 and C(7)  $\cdots$  H(13') 2.90 Å. If polymer formation of the type found in (3) [Figure 4(a)] were to occur a second dimeric unit would be linked to Tl' and O(2') through O(2'') and Tl''. The highly symmetrical nature of this type of chain makes it possible to see that this would involve similar close non-bonded contacts to those already present in the dimer. Furthermore, there is nothing to prevent these contact distances being lengthened by a rotation of the phenyl rings towards an eclipsed orientation, *i.e.* bisecting the chelate angle O(1)-Tl-O(2) in the view shown in Figure 5. We can only conclude that, in spite of the marked preference for polymeric structures in molecules of this type, it is not steric factors that prevent oligomerization beyond the dimer stage in diphenyltropolonatohallium(III).

Three structures have been previously reported for diorganothallium(III) compounds with anionic ligands in which sulphur atoms are the only donors,<sup>1a,c,3d</sup> and all have thallium atoms linked by sulphur bridges (Tl-S 2.75–3.19 Å). In (1) (Figure 3) adjacent monomeric molecules approach most closely in the direction of the *c* glide [*i.e.* of the Tl  $\cdots$  S(2') contact] as can be seen from the large number of short contacts with superscript I in

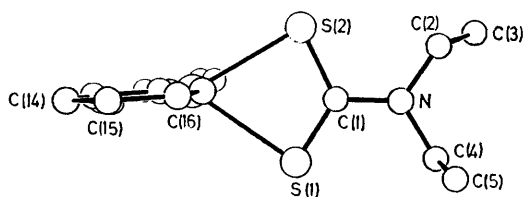


FIGURE 6 Structure of (1) viewed perpendicular to the chelate ring to show the relative orientations of the phenyl rings

Table 4. Thus steric factors do not allow any reduction in the Tl  $\cdots$  S(2') distance and prevent polymerization of the molecules of (1) in their present relative orientations. However, it might be envisaged that the monomeric units (Figure 6) could reorganize to form a polymeric structure similar to that of acetatodimethylthallium(III) [Figure 4(c)]. Models indicate that in spite of the bulky ethyl groups this is sterically possible provided

that the phenyl rings adopt a staggered orientation similar to that in (2) (Figure 5). Such a structure has not so far been observed for any diorganothallium(III) compound with sulphur ligands. This is possibly related to the observation that for  $[\{\text{Tl}(\text{CH}_3)_2(\text{OPh})\}_2]$  the bonds around the bridging oxygen have the approximately planar arrangement<sup>1a</sup> required by structures of the type shown in Figure 4, whereas in  $[\{\text{Tl}(\text{CH}_3)_2(\text{SPh})\}_2]$  the sulphur atom has pyramidal co-ordination geometry.<sup>1a</sup>

<sup>13</sup>C N.M.R. Spectra.—The <sup>13</sup>C n.m.r. spectra for (1) and (2) are given in Table 6. Assignment of the spectra was

TABLE 6

Carbon-13 n.m.r. parameters for complexes (1) and (2)<sup>a</sup>

Complex	C <sup>1</sup>	C <sup>2</sup>	C <sup>3</sup>	C <sup>4</sup>	Other
(1)	165.3 (4 996) <sup>e</sup>	136.9 (319)	128.4 (453)	127.7 (83)	12.0, <sup>b</sup> 47.3, <sup>c</sup> 204.7 <sup>d</sup>
(2)	165.6 (5 359) <sup>d</sup>	136.2 (317)	128.3 (469)	127.9 (87)	121.0, 181.5, <sup>f</sup> 124.8, 136.1 <sup>g</sup>

<sup>a</sup> Carbon atoms of C<sub>6</sub>H<sub>5</sub> groups are labelled C<sup>1</sup> to C<sup>4</sup>. Solvent: S(CD<sub>3</sub>)<sub>2</sub>O.  $\delta$  in p.p.m. from internal SiMe<sub>4</sub>. Errors:  $\pm 0.2$  p.p.m. Values of  $|J(\text{Tl}-\text{C})|$  are given in parentheses (Hz). Errors:  $\pm 6$  Hz. Separate coupling to <sup>205</sup>Tl and <sup>203</sup>Tl was unresolved unless otherwise noted. <sup>b</sup> CH<sub>3</sub>. <sup>c</sup> CH<sub>2</sub>. <sup>d</sup> S<sub>2</sub>CN. <sup>e</sup>  $|J(^{205}\text{Tl}-^{13}\text{C})|$ . <sup>f</sup> C<sup>1</sup> and C<sup>4</sup> of tropolonate respectively. <sup>g</sup> C<sup>2</sup>, C<sup>3</sup> of tropolonate.

facilitated by comparison of spectra obtained at 22.63 and 45.28 MHz for (1). There appear to be no previous reports of <sup>13</sup>C n.m.r. spectra of diphenylthallium(III) derivatives despite considerable interest in the spectra of monophenylthallium(III) compounds.<sup>20–23</sup> In both types of complex, <sup>1</sup>J(Tl-C) is the most sensitive <sup>13</sup>C n.m.r. parameter to changes in the environment of thallium; <sup>1</sup>J(Tl-C) changes by 363 Hz between (1) and (2) in S(CH<sub>3</sub>)<sub>2</sub>O solution, and by 816 Hz between [TlPh(OCOCF<sub>3</sub>)<sub>2</sub>] in S(CH<sub>3</sub>)<sub>2</sub>O and tetrahydrofuran solution.<sup>20,23</sup> The magnitudes of  $J(\text{Tl}-\text{C})$  for [TlPh<sub>2</sub>X] are approximately half those<sup>20–23</sup> of corresponding couplings in monophenylthallium(III) derivatives  $\{e.g. \text{ for } [\text{TlPh}(\text{OCOCF}_3)_2], {}^nJ(\text{Tl}-\text{C}) = 10\,718 \text{ (} n = 1), 527 \text{ (} n = 2), 1\,047 \text{ (} n = 3), \text{ and } 202 \text{ Hz (} n = 4) \}^{20}$ . This could be accounted for on the assumption that the couplings are dominated by the Fermi-contact mechanism and largely dependent on the *s* character of the thallium hybrid orbitals involved in bonding to the phenyl rings.<sup>24</sup> No conclusion can be drawn concerning a correlation between <sup>1</sup>J(Tl-C) and the C-Tl-C angle in (1) and (2). Although in the solid state there are no intermolecular interactions which appear to be constraining the C-Tl-C angles observed, it is uncertain whether these angles would be preserved in solution in a highly co-ordinating solvent such as dimethyl sulphoxide. It was not possible to obtain the spectra in less strongly co-ordinating solvents.

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