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Diorganothallium(III) diethyldithiophosphinates: crystal and molecular structures of [TlMe$_2$(S$_2$PEt$_2$)] and [TlPh$_2$(S$_2$PEt$_2$)]

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Abstract—The compounds [TlR$_2$(S$_2$PEt$_2$)] (R = Me or Ph) were synthesized by reaction of the corresponding hydroxide TlR$_2$(OH) with NaS$_2$PEt$_2$·2H$_2$O and characterized by X-ray crystallography. In both structures thallium is coordinated to the two sulfur atoms of the diethyldithiophosphinato ligand and to two carbon atoms of organyl groups. The chelate ring, TlS$_2$P, lies on a crystallographic plane of symmetry. Weak intermolecular interactions with one of the sulfur atoms of a neighbouring molecule make the coordination number of the thallium atom up to five. The vibrational and ^{1}H, ^{13}C, ^{31}P and ^{205}Tl NMR spectra of these compounds are also discussed. © 1997 Elsevier Science Ltd

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Intermolecular association in diorganothallium compounds in the solid state can involve a variety of interactions ranging from intermolecular bonds [1] to crystallographic interactions [2]. For instance, in [TlMe$_2${S(O)CNEt$_2$}] [3] the intra- and intermolecular Tl—O distances are very similar (around 2.6 Å), while in [TlMe$_2$(S$_2$CNEt$_2$)] [2] the intermolecular Tl—S distance is longer than the intramolecular distance. In solid [TlMe$_2$(S$_2$PPh$_2$)] [4], [TlPh$_2$(S$_2$PCy$_2$)] [5], [TlMe$_2$(S$_2$CPPh$_2$)]·(THF) [6] and [TlMe$_2$(S$_2$CN^{n}Pr$_2$)] [7] either one or two intermolecular Tl···S interactions are present; the intermolecular Tl—S distance is longer, the shorter the intramolecular Tl—S distance and in [TlPh$_2${(SPPh$_2$)$_2$N}], which has the shortest intramolecular Tl—S distance of all these compounds, no intermolecular interactions are observed [8].

Looking for additional data which can help to correlate inter- and intramolecular distances in diorganothallium compounds we selected [TlR$_2$(S$_2$PEt$_2$)] (R = Me or Ph). Bonati *et al.* [9] prepared the complexes [TlR$_2$(S$_2$PEt$_2$)] (R = Me or Ph), and on the basis of molecular weight measurements, deduced that they are unassociated in solution, but they provided only poor structural characterization of these compounds. Here we report the synthesis of these complexes by an alternative route, their IR and NMR spectra and their structures as determined by X-ray diffraction.

EXPERIMENTAL

TlI and TlBr (Merck) were used as received. Dimethyl- and diphenylthallium(III) hydroxide were obtained by reaction of TlMe$_2$I and TlPh$_2$Br [10] with freshly prepared aqueous suspensions of Ag$_2$O.

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Sodium diethyldithiophosphinato dihydrate was obtained by a published method [11]. The instruments used to record spectra were as mentioned elsewhere [6].

Synthesis of dimethyl(diethyldithiophosphinato)thallium(III), [$TlMe_2(S_2PEt_2)$]

Addition of a solution of $NaS_2PEt_2 \cdot 2H_2O$ (0.54 g, 2.72 mmol) in ethanol (20 mL) to $TlMe_2(OH)$ (0.69 g, 2.74 mmol) dissolved in water (*ca* 30 mL) afforded a white precipitate which, after 3 h stirring, was filtered off, washed with ethanol and vacuum dried over $CaCl_2$/KOH. M.p. 220–223°C, lit. 224–225°C [9]. Anal. Found: C, 18.6; H, 3.8%. $C_6H_{16}PS_2Tl$ requires C, 18.6; H, 4.1%. Single crystals suitable for X-ray diffraction studies were obtained by dissolution in chloroform and slow evaporation.

Synthesis of diphenyl(diethyldithiophosphinato)thallium(III), [$TlPh_2(S_2PEt_2)$]

To a solution of $TlPh_2(OH)$ (0.85 g, 2.29 mmol) in water (*ca* 30 mL) was added $NaS_2PEt_2 \cdot 2H_2O$ (0.44 g, 2.32 mmol) dissolved in ethanol (20 mL). The white precipitate formed was stirred for 3 h, filtered off, washed with ethanol and vacuum dried over $CaCl_2$/KOH. M.p. 160°C, lit. 164–162°C [9]. Anal. Found: C, 37.3; H, 3.7%. $C_{16}H_{20}PS_2Tl$ requires C, 37.5; H, 3.9%. Monocrystals suitable for X-ray analysis were obtained by recrystallization from 1 : 1 : 1 ethanol/acetone/water.

X-ray data collection, structure and refinement

Crystallographic measurements of both compounds were performed at 293 K on a CAD4 Enraf–Nonius diffractometer. Crystal data and experimental conditions are listed in Table 1. Data were corrected for polarization and Lorentz effects. Empirical absorption corrections were also applied [12].

Structure analysis was carried out by the heavy atom method for [$TlPh_2(S_2PEt_2)$] and the direct method [13] for [$TlMe_2(S_2PEt_2)$], followed in both cases by difference Fourier techniques until all non hydrogen atoms were located. All non-H atoms were anisotropically refined. The positions of H-atoms were calculated geometrically and included in the structure factor calculations in [$TlMe_2(S_2PEt_2)$]. Scattering factors for non H-atoms were taken from Cromer and Mann [14] and anomalous dispersion terms from Cromer and Liberman [15]. Most calculations were performed with the programs SHELX76 [16] and SHELXL93 [17].

RESULTS AND DISCUSSION

Structure of [$TlMe_2(S_2PEt_2)$]

Figure 1 shows a SCHAKAL [18] plot of the asymmetric unit of [$TlMe_2(S_2PEt_2)$], together with the atom numbering scheme used. The Tl, S(1), S(2) and P atoms lie in a crystallographic plane of symmetry (e position in Wyckoff notation) and each ethyl and methyl group is the reflection of the other in this plane. The chief bond distances and angles are listed in Table 2.

The thallium atom is coordinated to the carbon atoms of the two methyl groups and to the two sulfur atoms of an almost isobidentate dithiophosphinato ligand. The C—Tl distances and C—Tl—C angle are close to those found in other dimethylthallium(III) complexes with dithioligands [4,6,7,19]. The Tl—S distances are rather longer than in diorganothallium dithiocarbamate complexes [2,7], but similar to those found in dimethylthallium xanthate [$TlMe_2(S_2COMe)$] [19] and diphenyldithiophosphinate [$TlMe_2(S_2PPh_2)$] [4] (in the latter of which the ligand is rather anisobidentate). The C(1)—Tl—C(1)^i angle (169.7(6)°, $i = x, \ -y+1/2, \ z$) and the angle S(1)—Tl—S(2) (68.14(9)°) prevent the coordination polyhedron around the thallium atom being considered as a tetrahedron. Instead, since the S(1) atom of a neighbouring molecule lies closer to Tl than the sum of the Van der Waals radii (3.75 Å [20]; S(1)$\cdots$Tl^{iii} = 3.334(3) Å, $iii = x, y, z-1$, see Fig. 2), and in view of the angles S(1)—Tl—S(1)^{ii} (160.30(11)°, $ii = x, y, z+1$) and S(2)—Tl—S(1) and S(2)—Tl—C (both close to 90°; see Table 2), the polyhedron is best described as a distorted tetragonal pyramid with S(2) in apical position and S(1), C(1), C(1)^i and S(1)^{ii} in basal positions. Thus, the S(1) atom bridges between two thallium atoms by means of one strong and one weak Tl—S interaction (Fig. 2), and the weak interaction link the TlS_2P rings along the *c* axis (the Tl—S(1)$\cdots$Tl^{iii} angle is 160.34(11)°).

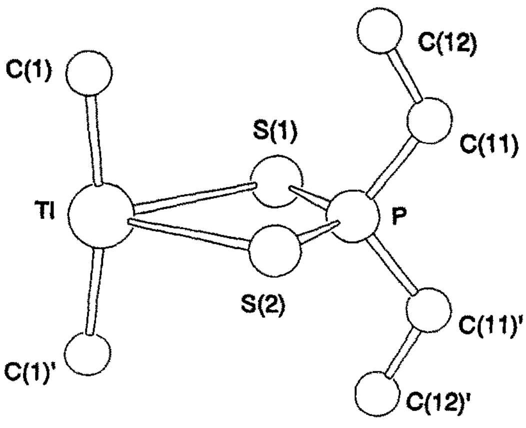

Fig. 1. Perspective view of [$TlMe_2(S_2PEt_2)$], showing the numbering scheme used (H atoms have been omitted).

Table 1. Crystallographic data of [$TlMe_2(S_2PEt_2)$] and [$TlPh_2(S_2PEt_2)$]

Formula	$C_6H_{16}PS_2Tl$	$C_{16}H_{20}PS_2Tl$
Molecular weight	388.02	511.81
Crystal class	monoclinic	orthorhombic
Space group	$P2_1/m$ (no. 11)	*Pbcm* (no. 37)
a (Å)	6.186(4)	6.152(1)
b (Å)	15.344(3)	13.088(1)
c (Å)	6.222(2)	22.138(2)
β (°)	90.76(4)	
V (Å^3)	590.6(4)	1782.6(6)
Z	2	4
D_c (g cm^{-3})	2.180	1.907
Crystal dimensions (mm)	0.10 × 0.15 × 0.20	0.26–0.13
λ (Å)	0.71073 (Mo-K_α)	1.54184 (Cu-K_α)
μ (mm^{-1})	14.10	20.33
Scan technique	$\omega/2\theta$	$\omega/2\theta$
θ (°) range	0–25	0–60
h, k, l range	−7,7 ;0,18 ;0,7	0,6 ;0,14 ;0,24
No. total of reflections measured	1194	1343
No. of reflections with $I > n\sigma(I)$, n values	1093, 2	1226, 3
Full-matrix least-squares refinement on	F^2	F
R^a	0.0349	0.067
Rw	0.0889[b]	0.070[c]

[a] $R = \Sigma\|F_0|-|F_c\|/\Sigma|F_0|$.

[b] $R_w = [\Sigma w(F_0^2-F_c^2)^2/\Sigma w(F_0^2)^2]^{1/2}$.

[c] $R_w = [\Sigma w\|F_0|-|F_c\|^2/\Sigma w|F_0|^2]^{1/2}$.

Table 2. Bond distances (Å) and angles (°) in [$TlMe_2(S_2PEt_2)$][a]

Tl—C(1)	2.128(11)	S(1)—P	2.002(4)
Tl—S(1)	2.981(3)	S(2)—P	2.005(4)
Tl—S(2)	2.991(4)	P—C(11)	1.807(10)
S(1)—Tl^{iii}	3.334(3)	C(11)—C(12)	1.51(2)

C(1)—Tl—C(1)^{i}	169.7(6)	Tl—S(1)—Tl^{iii}	160.30(11)
C(1)—Tl—S(1)	94.4(3)	P—S(2)—Tl	89.15(13)
S(1)—Tl—S(1)^{ii}	160.30(11)	C(11)^{i}—P—C(11)	105.3(6)
C(1)—Tl—S(2)	94.1(3)	C(11)—P—S(1)	109.6(3)
S(2)—Tl—S(1)^{ii}	92.15(9)	C(11)—P—S(2)	109.4(3)
S(1)—Tl—S(2)	68.14(9)	S(1)—P—S(2)	113.2(2)
P—S(1)—Tl	89.49(13)	C(12)—C(11)—P	113.7(7)
P—S(1)—Tl^{iii}	110.2(2)		

[a] Symmetry transformations relating equivalent atoms: ^{i} = x, −y + 1/2,z ; ^{ii} = x,y,z + 1 ; ^{iii} = x,y,z − 1.

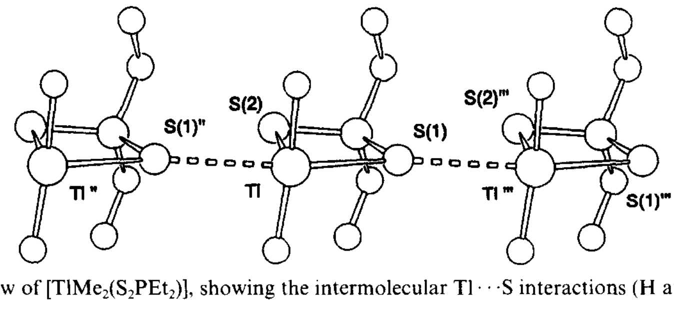

Fig. 2. A perspective view of [$TlMe_2(S_2PEt_2)$], showing the intermolecular Tl···S interactions (H atoms have been omitted).

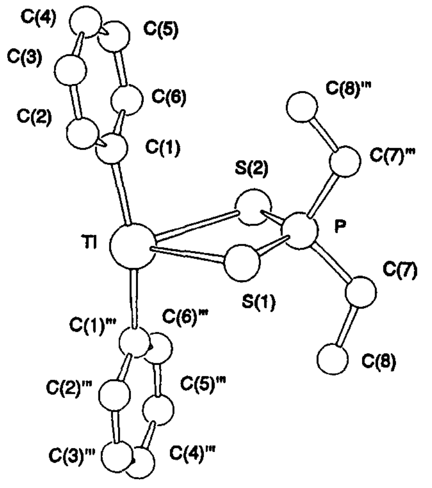

Fig. 3. Perspective view of $TlPh_2(S_2PEt_2)]$, showing the numbering scheme used (H atoms have been omitted).

Structure of $[TlPh_2(S_2PEt_2)]$

Figure 3 shows a SCHAKAL [18] plot of the structure of $[TlPh_2(S_2PEt_2)]$. Table 3 lists the main bond distances and angles.

The compound displays crystallographic Cs symmetry, with the Tl, P and S atoms lying in the special position *d* and each phenyl and ethyl group mirroring the outer in the symmetry plane.

The Tl atom is coordinated to one carbon atom of each phenyl group and to the two sulphur atoms of the dithiophosphinato ligand. Tl—C bond distances are close to those found in other diphenylthallium complexes with dithioligands [21], while the Tl—S distances are rather longer than in $[TlPh_2(S_2CNEt_2)]$ [2] and $[TlPh_2(S_2PCy_2)]$ [5]. In comparison with those of the dimethyl derivative the two Tl—S distances are both significantly shorter and differ more from each other. As in the dimethyl derivative, the C—Tl—C and S(1)—Tl—S(2) angles indicate non-tetrahedral coordination geometry (see Table 3), and an intermolecular Tl···S distance (Tl···S(2)^i = 3.321(4) Å, $i = 1+x, y, z$), is shorter than the sum of the Van der Waals radii [20] and should be considered as a weak interaction. Whether the Tl···S(1)^{ii} distance of 3.729(5) Å ($ii = 1-x, -1/2+y, 1/2-z$) should also be regarded as a weak interaction is less certain, since it is only slightly shorter than the sum of the Van der Waals radii (3.75 Å) [20]. If only Tl···S(2)^i is taken into account, the coordination polyhedron around the thallium atom should be considered as a distorted tetragonal-pyramid with S(1) in apical position. As in $[TlMe_2(S_2PEt_2)]$, the weak interaction Tl···S(2)^i links the individual molecules in chains, in this case along the *a* axis; while the very weak Tl···S(1)^{ii} interaction, if such there be, connects neighbouring chains (Fig. 4).

The structures of the title compounds appear to confirm, at least in the case of the diphenylthallium

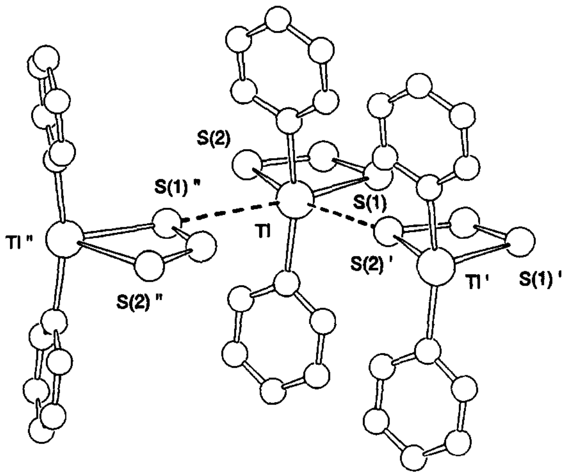

Fig. 4. A perspective view of $[TlPh_2(S_2PEt_2)]$, showing the intermolecular Tl···S interactions (H atoms and Et groups have been omitted for clarity).

Table 3. Bond distances (Å) and angles (°) in $[TlPh_2(S_2PEt_2)]^a$

Tl—S(1)	2.854(5)	Tl—S(1)^{ii}	3.729(5)
Tl—S(2)	2.933(4)	S(1)—P	1.985(6)
Tl—C(1)	2.14(1)	S(2)—P	2.019(5)
Tl—S(2)^i	3.321(4)	P—C(7)	1.82(2)
S(1)—Tl—S(2)	70.9(1)	S(2)—Tl—C(1)	92.7(3)
S(1)—Tl—S(2)^i	88.36(9)	S(2)—Tl—S(2)^i	159.28(8)
S(1)—Tl—C(1)	97.2(3)	S(2)—Tl—S(1)^{ii}	96.59(8)
S(1)—Tl—S(1)^{ii}	167.5(1)	C(1)—Tl—C(1)^{iii}	165.6(5)
S(2)—Tl—C(1)^i	89.9(3)	S(2)^i—Tl—S(1)^{ii}	104.13(8)
C(1)—Tl—S(1)^{ii}	83.0(3)	Tl—S(1)—P	89.0(2)
Tl—S(1)^{ii}—Tl^{ii}	176.4(1)	S(1)—P—S(2)	114.0(2)
Tl—S(2)—P	86.1(1)	S(2)—P—C(7)	110.4(5)
S(1)—P—C(7)	108.7(5)		

^{a}Symmetry transformations relating equivalent atoms: i) 1+x,y,z; ii) 1−x,−1/2+y,1/2−z; iii)x,1/2+y,1/2−z.

compound, the remarks in the Introduction concerning the opposite trends of inter- and intramolecular Tl—S distances in complexes of diorganothallium with dithio ligands. In [TlPh$_2$(S$_2$PEt$_2$)] the mean Tl—S and Tl···S distances, 2.894 and 3.321 Å, respectively, lie between the corresponding values for [TlPh$_2$(S$_2$PCy$_2$)] (Tl—S = 2.803 Å, Tl···S = 3.584 Å) and [TlPh$_2$(S$_2$PPh$_2$)] (Tl—S = 2.984 Å, Tl···S = 3.243 Å). In the case of the dimethylthallium complex, comparison is hindered not only by the scarcity of comparable data, but also by the possibility of interactions between Tl and other atoms in those compounds with which [TlMe$_2$(S$_2$PEt$_2$)] might otherwise be compared (specifically, with oxygen atoms in [TlMe$_2$(S$_2$CPPh$_2$)]·THF [6] and [TlMe$_2$(S$_2$COMe)] [19]).

Spectroscopic studies

The main IR and NMR data of the title compounds are listed in Table 4. Of the IR bands of ligands with PS$_2$ units those that are most sensitive to the coordination mode upon complexation are the asymmetric and symmetric vibrational modes of the PS$_2$ group itself. The gap between these stretching bands, Δν (= ν(PS)$_{as}$ − ν(PS)$_{sym}$), has been related to the degree of anisobidenticity of the ligand in the complex [4,5,21]. Hence the Δν values listed in Table 4, which are lower than that of the essentially monodentate ligand in [HgPh(S$_2$PEt$_2$)] [22], are in keeping with the X-ray results *vide supra*. With respect to the organometallic fragment, ρ(CH$_3$), ν$_{as}$(C—Tl—C) and ν$_{sym}$(C—Tl—C) have values close to those reported for similar S,S bonded systems [5,6].

The ^{1}H and ^{13}C chemical shifts for the TlMe$_2^+$ moiety are similar to those of [TlMe$_2$(S$_2$PPh$_2$)] [4] and show just slightly more deshielding than in [TlMe$_2${S(O)CNEt$_2$}] [3]; the ^1J(^{13}C—^{205}Tl) and ^2J(^{1}H—^{205}Tl) values are also very similar to those of the compounds mentioned above. These results suggest that these parameters are relatively insensitive to the substituent on the PS$_2$ group and even to the nature of the donor atoms coordinating to the thallium in this kind of compound.

As in the case of other diorganothallium dithiophosphorus complexes studied in our laboratory, the ^{31}P NMR spectra of the title compounds show no ^{31}P–^{205}Tl coupling, probably due to the lability of the ligands [23]. Moreover, δ(^{31}P) is in both cases almost the same as in organomercury derivatives [22], in spite of the very different coordination mode of the ligand in the solid state. Thus ^{31}P NMR spectroscopy would seem to be of little value for structural elucidation of this kind of complex.

Although the lack of published data for ^{205}Tl chemical shifts in CDCl$_3$ prevents extensive comparison of the values measured in this work, these values are, once temperature dependence is taken into account [24], of the same order as those reported for other Tl

Table 4. Main IR and NMR data

	IR data (KBr, cm^{-1})			NMR data in CDCl$_3$ (δ in ppm, J in Hz)[a]							
	ν(PS)[b]										
Compound	asym	sym	Δν	δ(^{13}C(C–P))	^1J(^{13}C–^{31}P)	δ(^{31}P)	δ(^{1}H(R–Tl))	^nJ(^{1}H–^{205}Tl)	δ(^{13}C(C–Tl))	^nJ(^{13}C–^{205}Tl)	δ(^{205}Tl)
[TlMe$_2$(S$_2$PEt$_2$)][c]	585vs	490s	95	35.20d	50.2	82.38s	1.49d	350.6	26.13d	2312.7	3867
[TlPh$_2$(S$_2$PEt$_2$)]	580vs	485m	95	34.35d	49.1	83.22s	H$_0$ = 7.82d	430.9	C$_i$ = 165.02d	4242.1	3512
									C$_0$ = 136.81d	334.2	
									C$_m$ = 129.48d	436.5	
									C$_p$ = 129.98d	78.3	

[a] d = doublet, s = singlet.

[b] m = medium, s = strong, vs = very strong.

[c] ρ(CH$_3$), 800 broad; ν(C—Tl—C)$_{asym}$, 535 medium and ν(C—Tl—C)$_{sym}$, 470 weak.

complexes with dithioligands, such as [TlMe$_2$(S$_2$CPPh$_2$)] [6], [TlMe$_2$(S$_2$PPh$_2$)] [4] and [TlMe$_2$(S$_2$CNEt$_2$)] [25].

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