



CRYSTAL AND MOLECULAR STRUCTURE OF DIPHENYLTHALLIUM(III) TETRAPHENYLDITHIOIMIDODIPHOSPHINATE, $[\text{TIPh}_2\{(\text{SPPh}_2)_2\text{N}\}]$, CONTAINING A NEW INORGANIC (CARBON-FREE) $\text{TiS}_2\text{P}_2\text{N}$ METALLOCYCLE

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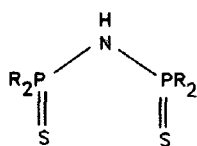
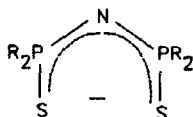
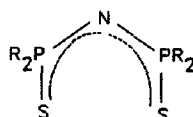
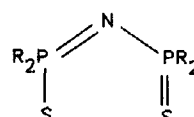
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Abstract—Reacting potassium tetraphenyldithioimidodiphosphinate (KL) with diphenylthallium(III) bromide in methanol yielded the compound $[\text{TIPh}_2(\text{L})]$, the structure of which was determined by X-ray diffraction. The unit cell contains two independent molecules with small structural differences. In both, the thallium atom is coordinated to two phenyl carbons and to two sulphurs belonging to a roughly isobidentate chelate ligand. The diphenylthallium(III) moiety bends back from the bite of the ligand (average C—Ti—C bond angle for the two molecules = 149.5°) giving, together with the narrow S—Ti—S angle (average value for the two molecules = 97.7°), a thallium environment which can be described as intermediate between tetrahedral and ψ -trigonal bipyramidal.

Bis(dialkyl[aryl]thiophosphinyl)amines, (**1**), are readily deprotonated and the resulting tetraalkyl (aryl)dithioimidodiphosphinato anions (**2**) are versatile ligands, able to form inorganic (carbon-free) chelate rings.¹ Such chelates can be formulated as

symmetric metallocycles, **3**, when the M—S bonds are (nearly) equal, or as unsymmetric chelate rings, **4**, when the M—S interatomic distances differ and bond length alternation is observed within the ring. In transition metal complexes, e.g. with

**1****2****3****4**

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M = Ni(II) (R = Me)², Fe(II) (R = Me),³ Mn(II) (R = Ph),⁴ and in the indium metallocycle [M = In(III), R = Ph]⁵ the coordination is of type 3, whereas in the bismuth complex [M = Bi(III), R = Ph] the presence of two sets of Bi—S distances [2.76(3) and 2.89(3) Å]⁶ favours formulation 4; in the lead compound [M = Pb(II), R = Ph]⁷ the Pb—S bond lengths are significantly different [2.695(4) and 2.943(4) Å] and the ring is clearly of type 4.

In the dimethyltin(IV) compound, [SnMe₂{(SPPPh₂)₂N}₂], the ring structure is very symmetrical,⁸ and in the dichlorogold(III) compound, [Au(Cl)₂{(SPPPh₂)₂N}], the Au—S bonds are also identical,⁹ in agreement with formulation 3.

In order to throw more light on the coordination of dithioimidodiphosphinato ligands with main group metals, and to extend the range of metallocycle with organometallic coordination centres, we prepared diphenylthallium(III) tetraphenyldithioimidodiphosphinate, [TlPh₂(L)], and investigated its crystal structure by X-ray diffraction.

EXPERIMENTAL

Preparation of [TlPh₂(L)]

A solution of K[(SPPPh₂)₂N] (0.490 g, 1 mmol) in 50 cm³ of methanol was added to a suspension of 0.445 g (1 mmol) of diphenylthallium(III) bromide, TlPh₂Br, in 100 cm³ of methanol, and the mixture was stirred at room temperature for 6 h. The white, microcrystalline precipitate was filtered out, washed with methanol and dried in air. Yield: 0.758 g (93.9%). Found: C, 50.1; H, 3.2; N, 1.6; C₃₆H₃₀NP₂S₂Tl requires: C, 49.6; H, 3.5; N, 1.7%; M.p. 189–90°C (dec.). ³¹P NMR (in CDCl₃, relative to 85% H₃PO₄): 34.6 ppm. IR spectrum (cm⁻¹): 516m, 569vs (PS), 695vs (PS), 721s, 748m, 745s, 995w, 1025w, 1104m, 1215vs (PN), 1432s, 1476m, 1571w.

Crystal structure determination of [TlPh₂(L)]

A colourless prismatic crystal of approximately 0.30 × 0.25 × 0.25 mm was obtained by recrystallization from chloroform and used in X-ray analysis.

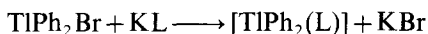
Crystallographic data. C₃₆H₃₀NP₂S₂Tl, M = 807.09, triclinic, space group P1 (No. 1), *a* = 9.5992(9), *b* = 19.839(2), *c* = 8.701(1) Å, *α* = 97.918(2), *β* = 103.171(2), *γ* = 82.885(8)°, *V* = 1589.9 Å³, *Z* = 2, *D*_{calc} = 1.947 g cm⁻³, *F*(000) = 880, *λ*(Mo-K_α) = 0.71073 Å and *μ* = 104.4 cm⁻¹.

Data for structure determination were collected at room temperature with a CAD-4 Enraf–Nonius automatic diffractometer with graphite monochromated Mo-K_α radiation. The *ω*/2*θ* scan technique was used. Of the 9468 reflections collected in the range 3–30°, 8980 with *I* > 3*σ*(*I*) were used for refinement. Absorption corrections were applied¹⁰ (max./min. corrections factors 1.126 and 0.736, respectively).

The structure was solved using direct methods and subsequent Fourier difference maps. Thallium, sulphur, phosphorus, nitrogen and the carbons of phenyl groups bonded to Tl were refined with anisotropic displacement parameters. The positions of all H atoms were calculated geometrically (C—H = 0.95 Å) and included in structure factor calculations with *B*_{iso} = 4.0 Å² fixed, but were not refined. The secondary extinction coefficient was 2.522 × 10⁻⁷. Final *R* and *R*_w values were 0.030 and 0.031 respectively for 515 parameters, and the maximum height in the final *ΔF* map was 0.804 e Å⁻³ around the Tl atoms. Most calculations were performed on a DEC MicroVAXII computer with the programs SHELXS86,¹¹ VAXSDP¹² and SCHAKAL.¹³

RESULTS AND DISCUSSION

The title compound was prepared in 94% yield by reacting diphenylthallium(III) bromide with potassium tetraphenyldithioimidodiphosphinate in methanol. It forms colourless crystals that are soluble in chloroform, hot methylene chloride and other common solvents.



The structure of [TlPh₂(L)] is built up of discrete cyclic [TlPh₂{(SPPPh₂)₂N}] molecules with no intermolecular interactions. The unit cell contains two independent molecules (hereinafter referred to as **A** and **B**); the molecular structure in the crystal is illustrated in Fig. 1 together with the atom numbering scheme. Selected bond lengths and angles are given in Table 1. Small differences between molecules **A** and **B** are as follows.

(1) The ligand is more anisobidentate in **A** than in **B**. Consequently, the Tl(1)—S(2) bond distance is longer and the S(1)—Tl(1)—S(2) bond angle narrower in **A** than the counterparts in molecule **B** [Tl(2)—S(3) and S(3)—Tl(2)—S(4)].

(2) In molecule **A**, the bond angles S(2)—P(2)—N(1) and Tl(1)—S(2)—P(2) are narrower than the corresponding bond angles in molecule **B** [S(3)—P(3)—N(2) and Tl(2)—S(3)—P(3)].

(3) The bond distance N(1)—P(2) in **A** is longer than the bond distance N(2)—P(3) in **B**.

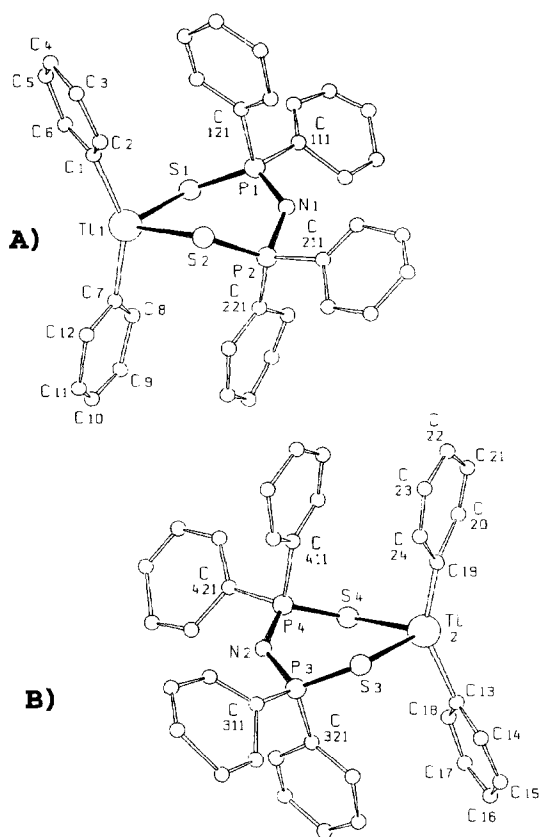


Fig. 1. Perspective view showing the atom numbering scheme and the coordination geometry about the thallium atom in molecules **A** and **B**.

(4) The Ph—Tl—Ph moiety bends back from the ligand rather more in molecule **B** (C—Tl—C bond angle $151.0(3)^\circ$ in **A** and $148.1(4)^\circ$ in **B**).

(5) The C—Tl bond distances are more unequal in molecule **A**. Nevertheless, these structural differences are not enough to prevent common discussion of the coordination features of the two molecules.

The thallium atom of the diphenylthallium moiety is bonded to two sulphur atoms of the ring-forming ligand in a geometry which can be tentatively described as intermediate between tetrahedral and Ψ -trigonal bipyramidal. The endocyclic S—Tl—S bond angle (average for the two molecules = 97.7°) is smaller than the tetrahedral value (109°) and differs widely from the angle between equatorial bonds in an ideal trigonal bipyramid (120°). The Tl—C_{Ph} bonds are nearly perpendicular to the Tl—S bonds (*ca* 100°), but the C—Tl—C bond angles (average for the two molecules = 149.5°) are *ca* 30° from colinearity, and still further from the tetrahedral value.

The six-membered $\text{TlS}_2\text{P}_2\text{N}$ ring has a folded, distorted boat conformation, as is illustrated by the values of some torsion angles (Table 2). This conformation is forced upon the ring by the very

different bond angles within it. In particular, the small bond angle at thallium is somewhat compensated by a large angle at nitrogen (average 131.3°). The bond angles at sulphur and at phosphorus (averages for the two molecules 102.7 and 118.1° respectively) contribute less to the distortion of the ring.

In spite of a slight difference, the bond lengths within the ring seem to show a symmetric structure of type **3**, suggesting a more symmetric π -electron distribution than in the $\text{PbS}_2\text{P}_2\text{N}$ ring of the lead compound $[\text{Pb}\{(\text{SPPh}_2)_2\text{N}\}_2]$,⁷ in which asymmetry is much more obvious (see Fig. 2). However, the symmetry falls short of the full symmetry of the $\text{SnS}_2\text{P}_2\text{N}$ ring $[\text{SnMe}_2\{(\text{SPPh}_2)_2\text{N}\}_2]$,⁸ which has pairs of identical bonds (see Fig. 2).

In the thallium metallocycle $\text{TlS}_2\text{P}_2\text{N}$ the P—N bonds are shorter than in the parent bis(diphenylthiophosphinyl)amine **1** ($\text{R} = \text{Ph}$, P—N *ca* $1.67 \text{ \AA}$ ¹⁴), indicating a partial double bond character. Single P—N bonds in cyclophosphazenes and related compounds (bond distances = $1.67\text{--}1.76 \text{ \AA}$ ^{15,16a,16b}) are significantly longer than in the thallium metallocycle. The P—N bond lengths in cyclophosphazenes^{17a} (e.g. in $(\text{Ph}_2\text{PN})_3$ ^{17b} and $(\text{Ph}_2\text{PN})_4$ ^{17c} $1.597 \text{ \AA}$ and $1.590 \text{ \AA}$, respectively) are similar to those observed in the $\text{TlS}_2\text{P}_2\text{N}$ ring (Fig. 2). The phosphorus–sulphur bonds in the thallium metallocycle (Fig. 2) are longer than in **1** (reported as $1.943 \text{ \AA}$,^{14a} $1.937 \text{ \AA}$ ^{14b} and $1.916 \text{ \AA}$ ^{14c}), and lie in the range for P—S single bonds.¹⁸

Proper understanding of the nature of the bonding in the $\text{MS}_2\text{P}_2\text{N}$ rings will require the determination of more structures with a variety of main group metals in both organometallic and purely inorganic (“naked”) metal coordination centres. It is quite possible that changing the peripheral organic groups attached to phosphorus may also produce structural changes, as frequently happens in the chemistry of main group metal phosphoro- and phosphinodithioates.

Comparison of the six-membered ring structure found in $[\text{TlPh}_2(\text{L})]$ with those of $[\text{TlPh}_2(\text{S}_2\text{PR}_2)]$ ($\text{R} = \text{Cy}$, Et),^{19,20} which contain four-membered TlS_2P chelate rings, is also of interest. In the latter, the molecules are associated into polymeric structures through $\text{Tl}\cdots\text{S}$ secondary bonds, and the Tl—S chelating bonds are longer [$2.789(3)$ and $2.816(3) \text{ \AA}$ in $[\text{TlPh}_2(\text{S}_2\text{PCy}_2)]$ ¹⁹ and $2.854(5)$ and $2.933(4) \text{ \AA}$ in $[\text{TlPh}_2(\text{S}_2\text{PEt}_2)]$ ²⁰] than in the six-membered $\text{TlS}_2\text{P}_2\text{N}$ ring (Fig. 2). Conversely $[\text{TlPh}_2(\text{S}_2\text{CNEt}_2)]$ ²¹ in which the intermolecular $\text{Tl}\cdots\text{S}$ interactions are weaker than in diphenylthallium(III) dithiophosphinates, has a four-membered TlS_2C ring with shorter Tl—S distances (*ca* $2.72 \text{ \AA}$) than in the six-membered $\text{TlS}_2\text{P}_2\text{N}$ ring,

Table 1. Selected bond lengths (Å) and angles (°) for [TiPh₂(L)]

Molecule A		Molecule B	
Tl(1)—S(1)	2.736(3)	Tl(2)—S(3)	2.766(2)
Tl(1)—S(2)	2.788(2)	Tl(2)—S(4)	2.740(2)
Tl(1)—C(1)	2.175(6)	Tl(2)—C(13)	2.145(7)
Tl(1)—C(7)	2.099(8)	Tl(2)—C(19)	2.204(8)
P(1)—S(1)	2.013(3)	P(3)—S(3)	2.025(3)
P(2)—S(2)	2.021(2)	P(4)—S(4)	2.010(2)
P(1)—N(1)	1.600(6)	P(3)—N(2)	1.575(5)
P(2)—N(1)	1.590(6)	P(4)—N(2)	1.596(6)
P(1)—C(111)	1.765(8)	P(3)—C(311)	1.857(6)
P(1)—C(121)	1.900(7)	P(3)—C(321)	1.715(7)
P(2)—C(211)	1.855(7)	P(4)—C(411)	1.922(8)
P(2)—C(221)	1.694(7)	P(4)—C(421)	1.785(7)
S(1)—Tl(1)—S(2)	97.21(6)	S(3)—Tl(2)—S(4)	98.19(6)
S(1)—P(1)—N(1)	118.4(3)	S(3)—P(3)—N(2)	118.2(3)
S(2)—P(2)—N(1)	116.1(2)	S(4)—P(4)—N(2)	119.7(3)
P(1)—N(1)—P(2)	131.8(5)	P(3)—N(2)—P(4)	130.7(4)
Tl(1)—S(1)—P(1)	104.44(9)	Tl(2)—S(3)—P(3)	102.27(8)
Tl(1)—S(2)—P(2)	100.64(9)	Tl(2)—S(4)—P(4)	102.44(8)
C(1)—Tl(1)—C(7)	151.0(3)	C(13)—Tl(2)—C(19)	148.1(4)
S(1)—Tl(1)—C(1)	100.6(2)	S(3)—Tl(2)—C(13)	100.5(2)
S(1)—Tl(1)—C(7)	100.3(2)	S(3)—Tl(2)—C(19)	98.2(2)
S(2)—Tl(1)—C(1)	95.3(2)	S(4)—Tl(2)—C(13)	99.3(3)
S(2)—Tl(1)—C(7)	101.6(2)	S(4)—Tl(2)—C(19)	103.4(2)
C(111)—P(1)—C(121)	102.0(3)	C(311)—P(3)—C(321)	110.0(3)
C(211)—P(2)—C(221)	109.8(3)	C(411)—P(4)—C(421)	100.7(3)

Table 2. Torsion angles (°) in [TiPh₂(L)]

Atom 1	Atom 2	Atom 3	Atom 4	Angle
S(2)	Tl(1)	S(1)	P(1)	−18.06(0.10)
S(1)	Tl(1)	S(2)	P(2)	−29.70(0.10)
S(4)	Tl(2)	S(3)	P(3)	20.34(0.10)
S(3)	Tl(2)	S(4)	P(4)	25.57(0.10)
Tl(1)	S(1)	P(1)	N(1)	57.38(0.30)
Tl(1)	S(2)	P(2)	N(1)	66.87(0.30)
Tl(2)	S(3)	P(3)	N(2)	−61.49(0.27)
Tl(2)	S(4)	P(4)	N(2)	−60.57(0.28)
S(1)	P(1)	N(1)	P(2)	−36.20(0.69)
S(2)	P(2)	N(1)	P(1)	−42.49(0.68)
S(3)	P(3)	N(2)	P(4)	45.02(0.58)
S(4)	P(4)	N(2)	P(3)	32.82(0.61)

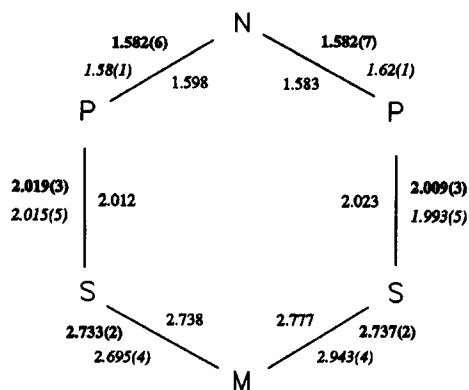


Fig. 2. Bond distances in six-membered MS₂P₂N rings: M = Tl, values inside the ring; M = Pb, italic values;⁷ M = Sn, bold face values.⁸

suggesting that the greater strain of the smaller ring has been overcome by the greater donor ability of the dithiocarbamate.

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