

**SOLID STATE SUPRAMOLECULAR STRUCTURE OF
 (TETRAPHENYLDITHIOIMIDODIPHOSPHINATO)TRIMETHYLTIN(IV)·
 BENZENE, [Me₃Sn(SPPH₂)₂N·C₆H₆]_∞, A UNIQUE POLYMER
 CONTAINING A BRIDGING —SPR₂NPR₂S— LIGAND**

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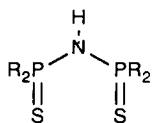
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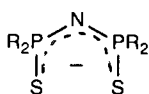
Abstract—In the solid state (tetraphenyldithioimidodiphosphinato)trimethyltin(IV) consists of Me₃Sn[SPPH₂NPPH₂S] units linked into a 1-D polymer by secondary Sn···S interactions. The coordination geometry about tin is trigonal bipyramidal *trans*-S₂SnC₃, with two sulphur atoms (belonging to different molecular units) in axial positions [Sn(1)—S(1) = 2.517(4) Å and Sn(1)···S(2') = 3.627 Å] and three methyl groups in the equatorial sites. This coordination is uncommon for organotin thio-derivatives and is now crystallographically confirmed for the first time. The compound also incorporates the first example of a bridging, rather than chelating, dithioimidodiphosphinato ligand, thus generating a supramolecular structure which acts as a host for benzene molecules aligned along the *b* axis of the crystal.

Bis-dialkyl or bis-(diarylthiophosphinyl)amines **1** can be readily deprotonated to generate anion **2**, a versatile ligand able to form either monometallic,

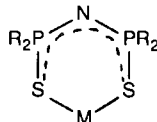
inorganic (carbon-free) metallacycles **3** (chelating ligand) or bimetallic macrocycles **4** (bridging ligand):



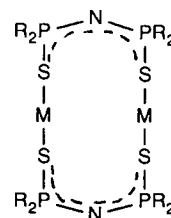
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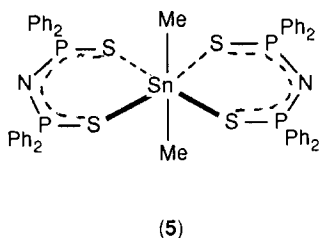


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Chelating rings (or metallocycles) **3** are formed when M is either a transition or main group metal,¹ and are inorganic analogues of the common β -diketonate derivatives. Like the β -diketonates, chelated structures are common while binuclear cyclic structures **4** are known only with $M = \text{RTe}^{1,2}$ and $\text{Au}^{1,3}$. Both classes of compound collectively underscore the strong tendency for cyclization in the interaction of **2** with a metal centre. We have previously prepared⁴ a series of organotin derivatives of **2** and a single crystal X-ray diffraction analysis of bis-(tetraphenyldithioimidodiphosphinato) dimethyltin (IV) established a symmetrical spirobicyclic structure **5**.⁵



On the other hand, a spectroscopic investigation of triorganotin derivatives, $\text{R}_3\text{Sn}(\text{SPPH}_2\text{NPPH}_2\text{S})$, raised some questions. Thus, for the trimethyltin derivative, $\text{Me}_3\text{Sn}(\text{SPPH}_2\text{NPPH}_2\text{S})$, the ^{119}Sn Mössbauer spectrum (q.s. = 3.16 mm s^{-1}) suggested five-coordinate tin in the solid state and for which IR data implied the presence of distinct P—S bonds ($601, 578 \text{ cm}^{-1}$) consistent with anisobidentate bonding to the metal. However, $^1J(\text{SnC})$ (361, 345 Hz), $^2J(\text{SnH})$ (57.5, 55.3 Hz) and the ^{119}Sn chemical shift (117.8 ppm) indicated four-coordinate tin in solution. Tribenzyltin and triphenyltin derivatives seem to be four-coordinate (tetrahedral) both in solution and in the solid state, on the basis of the analogous spectroscopic data. In addition, the ^{31}P NMR spectra suggest fluxional behaviour of triorganotin derivatives in solution.⁴ Since both monodentate and bridging behaviour for the dithioimidodiphosphinato ligand is implied by these results, both of which are unprecedented, an X-ray crystal structure determination of the trimethyltin derivative was therefore considered useful in classifying the structural nature of these compounds.

EXPERIMENTAL

The title compound has been prepared as described previously,⁴ and a crystal of approximate dimensions $0.3 \times 0.3 \times 0.2 \text{ mm}$, carefully cut from a

larger block grown from a benzene–hexane solution, used for data collection.

Crystal data: $\text{C}_{27}\text{H}_{29}\text{S}_2\text{NP}_2\text{Sn} \cdot \text{C}_6\text{H}_6$, $M = 690.4$, monoclinic, $a = 13.898(3)$, $b = 10.651(1)$, $c = 23.238(4) \text{ \AA}$, $\beta = 106.64(2)^\circ$, $U = 3295.8 \text{ \AA}^3$, space group $P2_1/n$, $Z = 4$, $D_c = 1.39 \text{ g cm}^{-3}$, $\mu (\text{Mo-K}\alpha) = 13.91 \text{ cm}^{-1}$, $F(000) = 1408$. Data were measured at room temperature on a CAD4 automatic four-circle diffractometer in the range $2 \leq \theta \leq 24^\circ$. 5718 reflections were collected of which 3701 were unique with $I \geq 2\sigma(I)$. Data were collected for Lorentz and polarization effects but not for absorption. The structure was solved by Patterson methods and refined using the SHELX^{6,7} suite of programs. In the final least-squares cycles all atoms were allowed to vibrate anisotropically. Hydrogen atoms were included at calculated positions (C—H 0.96 \AA) and refined isotropically with a common temperature factor (0.123 \AA^2). Final residuals after eight cycles of least-squares were $R = 0.0339$, $R_w = 0.0342$, for a weighting scheme of $w = 2.5096/[\sigma^2(F) + 0.000536(F)^2]$. Max. final shift/esd was 0.001. The max. and min. residual densities were 0.20 and -0.27 e \AA^{-3} respectively. Selected bond distances and angles are given in Table 1. Tables of coordinates, anisotropic temperature factors, hydrogen atom coordinates and a full listing of geometric data are available as supplementary data. The asymmetric unit is shown in Fig. 1, along with the labelling scheme used.

RESULTS AND DISCUSSION

Description of the structure

The structure of the asymmetric unit is shown in Fig. 1 along with the atom labelling scheme used, while the association of the molecular units into polymeric chains, oriented along the b axis of the crystallographic unit cell, is shown in Fig. 2. As Fig. 1 shows, the metal atom of the trimethyltin coordination centre is attached intramolecularly to only one sulphur of the ligand [$\text{Sn}(1) - \text{S}(1) = 2.517(4) \text{ \AA}$]. The trimethyltin moiety is flattened but not coplanar, with tin lying 0.40 \AA above the C_3 plane, a feature consistent with the observation of two Sn—C stretches in the infrared spectrum. In addition, the C—Sn—C bond angles are somewhat smaller than 120° [$\text{C}(25) - \text{Sn}(1) - \text{C}(26) = 114.6(4)^\circ$, $\text{C}(25) - \text{Sn}(1) - \text{C}(27) = 117.0(4)^\circ$ and $\text{C}(26) - \text{Sn}(1) - \text{C}(27) = 117.7(3)^\circ$] but significantly larger than the tetrahedral value of 109° , all of which can be ascribed to the intermolecular interaction between $\text{Sn}(1)$ and $\text{S}(2')$ of a neighbouring molecule [$\text{Sn}(1) \cdots \text{S}(2') = 3.627 \text{ \AA}$]. This interaction, though long, is markedly less than the

Table 1. Selected bond distances (Å) and angles (°) for **6**

Bond distances			
S(1)—Sn(1)	2.517(4)	C(25)—Sn(1)	2.104(7)
C(26)—Sn(1)	2.129(7)	C(27)—Sn(1)	2.103(7)
S(1)—P(1)	2.048(3)	N(1)—P(1)	1.572(5)
C(1)—P(1)	1.815(6)	C(7)—P(1)	1.810(6)
S(2)—P(2)	1.972(3)	N(1)—P(2)	1.605(5)
C(13)—P(2)	1.822(6)	C(19)—P(2)	1.813(6)
Bond angles			
C(25)—Sn(1)—S(1)	102.4(3)	C(26)—Sn(1)—S(1)	93.8(2)
C(26)—Sn(1)—C(25)	114.6(4)	C(27)—Sn(1)—S(1)	106.5(3)
C(27)—Sn(1)—C(25)	117.0(4)	C(27)—Sn(1)—C(26)	117.7(3)
N(1)—P(1)—S(1)	116.9(2)	C(1)—P(1)—S(1)	102.5(2)
C(1)—P(1)—N(1)	114.6(3)	C(7)—P(1)—S(1)	108.4(2)
C(7)—P(1)—N(1)	106.4(3)	C(7)—P(1)—C(1)	107.6(3)
N(1)—P(2)—S(2)	120.0(2)	C(13)—P(2)—S(2)	110.8(2)
C(13)—P(2)—N(1)	107.2(3)	C(19)—P(2)—S(2)	111.0(2)
C(19)—P(2)—N(1)	103.8(3)	C(19)—P(2)—C(13)	102.4(3)
P(1)—S(1)—Sn(1)	107.3(1)	P(2)—N(1)—P(1)	133.4(2)

sum of the respective van der Waals radii (*ca* 4.0 Å). If this interaction is then considered valid, the coordination geometry around tin can be described as distorted trigonal bipyramidal, with two sulphur

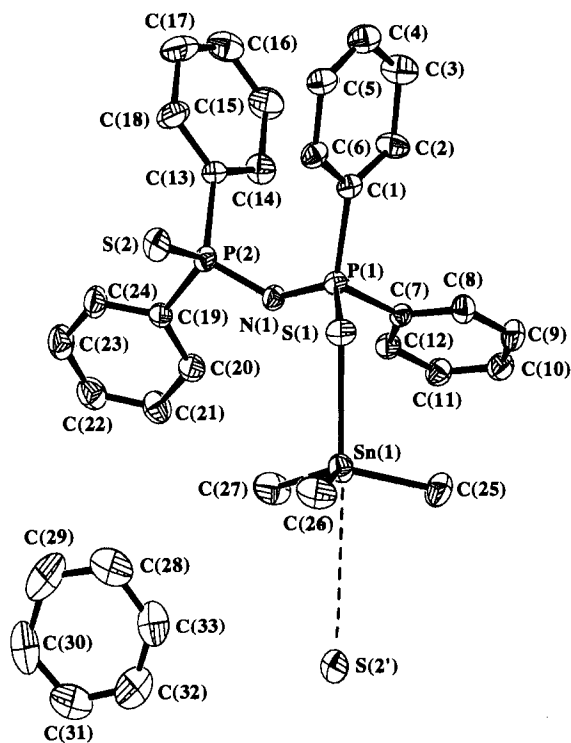


Fig. 1. The asymmetric unit of **6** showing the atomic labelling used in the text and tables. Thermal ellipsoids are at the 30% level.

atoms in axial positions and methyl groups in equatorial sites. This description is supported by the near linear S(1)—Sn(1)···S(2') moiety [174.2(4)°] and axial–equatorial dispositions approaching 90° [S(1)—Sn(1)—C(25) = 102.4(3)°, S(1)—Sn(1)—C(26) = 93.8(2)° and S(1)—Sn(1)—C(27) = 106.5(3)°]. Examples of dithio-ligands which adopt a bridging role are rare and then only with more Lewis acidic R₂Sn centres (see below). As far as we are aware the title compound is the first report of a *trans*-S₂SnC₃ arrangement, in which a dithio-ligand bridges triorganotin units. Moreover, this is the first report in which the a dithioimidodiphosphate ligand acts in a bridging mode to generate a coordination polymer.

The phosphorus–sulphur interatomic distances are slightly different, such that the P(1)—S(1) bond [2.048(3) Å] is a normal single P—S bond, while P(2)—S(2) [1.972(3) Å] is shorter and seems to retain some double bond character. The secondary interaction of S(2) with the tin atom of another molecular unit is probably the reason for some elongation of this bond, compared with the range of true P=S double bonds [1.90–1.94 Å].⁸ The P—N bonds in the ligand are also slightly different [P(1)—N(1) = 1.572(5) Å, P(2)—N(1) = 1.605(5) Å], suggesting that the π-electron delocalization within the ligand is not complete. A pattern which is consistent with observations on related organotin dithiophosphates⁹ thus emerges, which groups the short Sn—S bond with the long P—S (and short P—N bond) length and *vice versa* for the long Sn—S interaction, suggesting that **6** seems to be a fair representation of the electron distribution in

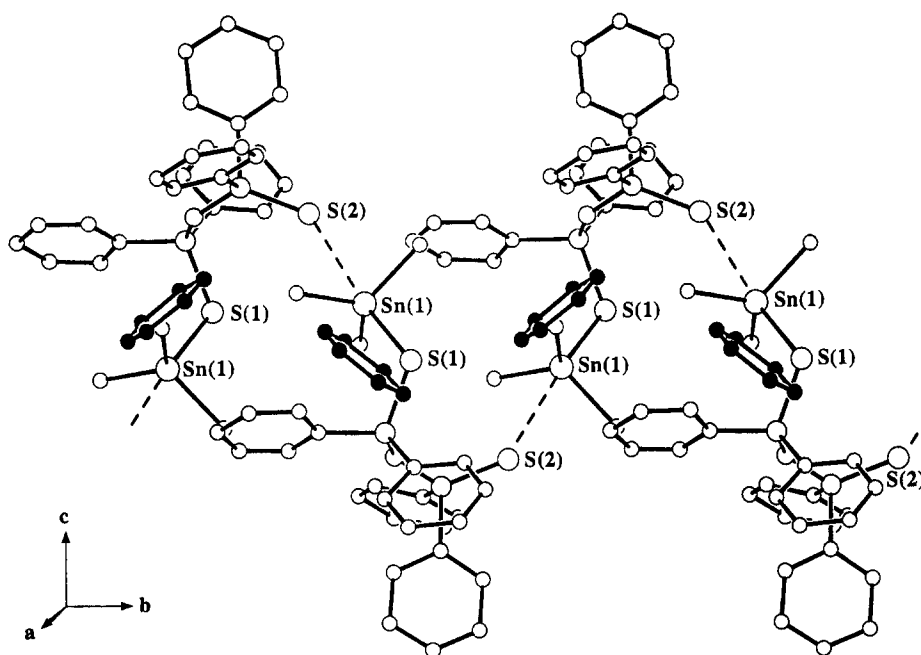
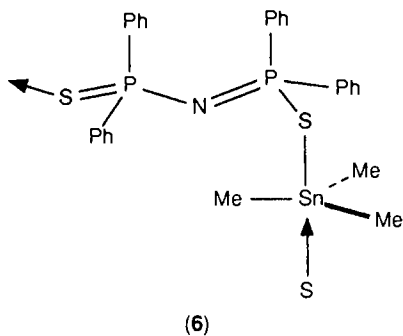


Fig. 2. The polymeric character of **6** viewed perpendicular to the *bc* plane. Primed atoms are related to their unprimed counterparts by the operator $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$. The benzene molecules which are incorporated into the lattice are highlighted. Dotted lines represent the intermolecular Sn—S' interaction.

the structure. Similar comments have been made with respect to Sn—O and C—O bonds in organotin carboxylates,¹⁰ and Sn—S, C—S bonds in organotin dithiocarbamates.¹¹



The formation of a chain, rather than a chelated, structure is remarkable, both in terms of sulphur's inherent tendency against such an arrangement^{9,11} and the fact that the ligand bite angle about tin in a chelated array, as evidenced in **5** [$97.8(1)^\circ$],⁵ would comfortably span axial-equatorial sites. Moreover, ligands such as dithiocarbamates which generate strained, four-membered chelate rings notably prefer a monomeric role about a four-coordinate triorganotin centre rather than to bridge inter-

molecularly.¹² It is tempting, therefore, to ascribe the formation of polymeric **6** to an enhanced lattice energy arising from the incorporation of benzene molecules as guests in a supramolecular polymeric host array. The packing of solvent molecules into channels formed between the "S-shaped" polymer strands is most readily appreciated from Fig. 3, looking end-on to the direction of chain propagation.

Comparison with other structures

The most interesting comparison can be made with the cyclic structure **5**, the dimethyltin derivative of the same ligand.⁵ Thus, in the cyclic compound **5** all the Sn—S bonds are identical and longer [2.737(2), 2.733(2) Å] than in polymeric **6**, and the P—N [1.582(7), 1.582(6) Å] and P—S bonds [2.009(3), 2.019(3) Å] are also equalized and are roughly the average of the values observed in **6**. Curiously, the P—N—P bond angles in the cyclic compound [$136.0(4)^\circ$] is slightly larger than in the open chain ligand [$133.4(2)^\circ$], thus showing that this angle also does not inhibit cyclization.

The intramolecular Sn—S distance observed in polymeric **6** [2.517(4) Å] is of the same order of magnitude as those observed for primary Sn—S

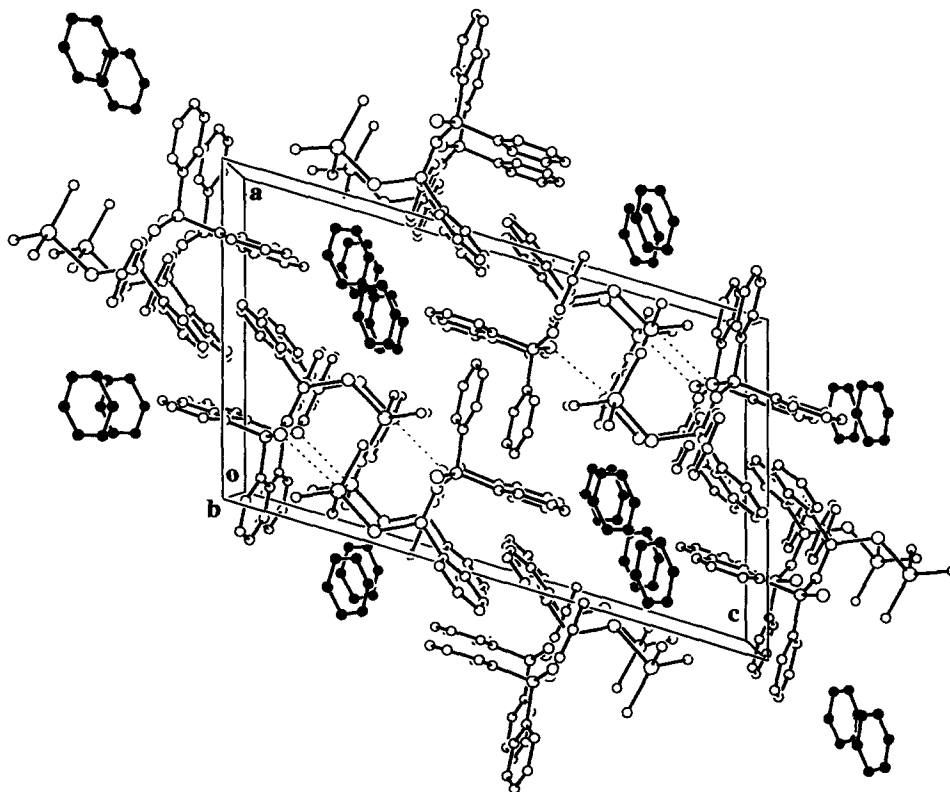
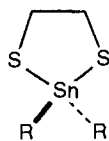
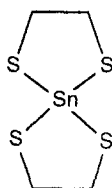


Fig. 3. Polymer propagation in **6** viewed along the direction of chain growth (the *b* axis). The benzene molecules which are incorporated into the lattice are highlighted. Dotted lines represent the intermolecular Sn—S' interaction.

bonds in organotin dithiophosphates and dithiophosphinates with monodentate or anisobidentate ligands, e.g. $\text{Ph}_3\text{SnS}_2\text{P}(\text{OEt})_2$ (2.458 Å),¹³ $\text{Ph}_2\text{Sn}[\text{S}_2\text{P}(\text{OEt})_2]_2$ (2.481 and 2.492 Å),¹⁴ $\text{Ph}_3\text{SnS}_2\text{P}(\text{OCMe}_2\text{CMe}_2\text{O})$ (2.436 Å),¹⁵ $\text{Me}_2\text{Sn}[\text{S}_2\text{P}(\text{OCMe}_2\text{CMe}_2\text{O})]_2$ (2.495 Å),¹⁶ $\text{SnI}_2(\text{S}_2\text{PETe}_2)_2$ (2.53 Å),¹⁷ $\text{Me}_2\text{Sn}(\text{S}_2\text{PMe}_2)_2$ (2.484 Å),¹⁷ and $\text{Me}_2\text{Sn}(\text{S}_2\text{PETe}_2)_2$ (2.476 Å).¹⁸ Such bonds are thus markedly shorter than in compounds with symmetrically chelating ligands such as **5**, or the symmetrical six-coordinate $\text{Ph}_2\text{Sn}[\text{S}_2\text{P}(\text{OPr}^i)_2]_2$ (2.689 and 2.678 Å) which also incorporates an isobidentate ligand.¹⁹ The intermolecular Sn...S separation in **6** (3.627 Å) is comparable with, but longer than, intramolecular (chelating) secondary bonds observed in $\text{Ph}_2\text{Sn}[\text{S}_2\text{P}(\text{OEt})_2]_2$ (3.23 Å),¹⁴ $\text{Ph}_3\text{SnS}_2\text{P}(\text{OCMe}_2\text{CMe}_2\text{O})$ (3.411 Å),¹⁵ $\text{Me}_2\text{Sn}[\text{S}_2\text{P}(\text{OCMe}_2\text{CMe}_2\text{O})]_2$ (3.13 Å),¹⁶ $\text{Me}_2\text{Sn}(\text{S}_2\text{PMe}_2)_2$ (3.334 Å),¹⁷ and $\text{Me}_2\text{Sn}(\text{S}_2\text{PETe}_2)_2$ (3.336 Å).¹⁸ Comparison of the bridging Sn—S bond in **6** with other intermolecular Sn—S interactions is made difficult by the paucity of such examples. In the 1,3,2-dithiastannolane **7a** the

ligand bridges strongly through one sulphur only to generate an unambiguously five-coordinate tin [Sn—S 2.472; Sn—S' 3.18 Å].²⁰ The related dibutyl analogue **7b** uses both sulphur atoms to bridge generating a distorted octahedral arrangement at tin, though each bridging interaction is weak [Sn—S 2.414; Sn—S' 3.69 Å]²¹ such that the resulting C—Sn—C angles in **7a** and **7b** are almost identical [121.4, 122.6°, respectively]. Spirocyclic **8** parallels **7b** structurally [Sn—S 2.388, 2.405; Sn—S' 3.764, 3.811 Å].²² In each case, lengthening the intermolecular Sn—S bond is accompanied by a shortening of the corresponding intramolecular Sn—S interaction, so it is somewhat unexpected that in **6** the intramolecular bond (2.517 Å) is weaker than would be predicted from consideration of the complimentary bridging bond (3.627 Å).

The spectroscopic properties recorded for the title compound⁴ can now be rationalized with confidence. The solid state structure with five-coordinate tin is in agreement with the Mössbauer quadrupole splitting datum, as is the infrared prediction of asymmetric P—S bonds. The weak, sec-

R = Me (**7a**)= Bu (**7b**)**(8)**

ondary bonds do not seem to survive in solution and the presence of monomeric molecules is indicated by the chemical shift of tin in its NMR spectrum. We are currently seeking to crystallographically authenticate an example of such a unidentate dithioimidodiphosphate ligand in related organotin compounds.

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