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Organotin diphenylmonothiophosphinates. Crystal structure of bis(diphenylmonothiophosphinato)dimethyltin(IV), $Me_2Sn(OSPPh_2)_2$

C. Silvestru and I. Haiduc *
Facultatea de Chimie, Universitatea "Babes-Bolyai", RO-3400 Cluj-Napoca (Romania)

F. Caruso **
Consiglio Nazionale delle Ricerche, Istituto di Strutturistica Chimica "G. Giacomello", I-00016, Monterotondo Stazione, Roma (Italy)

M. Rossi
Vassar College, Chemistry Department, Poughkeepsie, NY 12601 (USA)

B. Mahieu
Université Catholique de Louvain, INAN, B-1348 Louvain-la-Neuve (Belgium)

M. Gielen
Vrije Universiteit Brussel, Pleinlaan 2, B-1050 Brussels (Belgium)

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Abstract

Organotin(IV) diphenylmonothiophosphinates, $R_nSn(OSPPh_2)_{4-n}$ (R = Me, ^{n}Bu, Bz, Ph, Cy; $n = 2$ and 3) have been synthesized in good yields by reactions of organotin halides with ammonium diphenylmonothiophosphinate. The compounds have been characterized by infrared and NMR spectra, and two representative compounds were also studied by ^{119m}Sn-Mössbauer spectroscopy. The structure of bis(diphenylmonothiophosphinato)dimethyltin(IV), $Me_2Sn(OSPPh_2)_2$, has been determined by X-ray diffraction which shows that weak Sn $\cdots$ S interactions give rise to a polymeric chain structure in which the tin atom exhibits a trigonal bipyramidal geometry. The ligand is attached primarily to tin through oxygen atoms.

1. Introduction

A large number of di- and triorganotin(IV) diorganodithiophosphinates, $R_nSn(S_2PR'_2)_{4-n}$, have been prepared and their structures investigated by various spectroscopic (IR, ^{1}H-NMR, mass and Mössbauer) and X-ray diffraction methods [1-5], but the corresponding organotin(IV) diorganomonothiophosphinates, $R_nSn(OSPR'_2)_{4-n}$, have been much less studied.

The synthesis of some diorganotin(IV) derivatives of diphenylmonothiophosphinic acid, $R_2Sn(OSPPh_2)_2$ (where R was ^{n}Bu, n-octyl, n-lauryl and Ph) and of $Ph_3SnOSPPh_2$ through the reaction between organotin(IV) chlorides and the sodium salt of the phosphorus acid, eqn. (1):

$$R_nSnCl_{4-n} + (4-n)NaOSPPh_2 \longrightarrow R_nSn(OSPPh_2)_{4-n} + (4-n)NaCl \quad (1)$$

has been mentioned only in patents concerning the possible use of such compounds as polyolefin stabilizers [6,7]. The phenyltin derivatives are white solids, while the dialkyltin monothiophosphinates are described as viscous liquids, with high boiling points.

More recently, trimethyltin(IV) diorganomonothiophosphinates have been synthesized from bis(trimethyl-

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* Correspondence to: Professor I. Haiduc.

** Corresponding author for the X-ray structure analysis.

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TABLE 1. Preparation of $R_nSn(OSPPh_2)_{4-n}$

Starting materials R_nSnCl_{4-n}, mol	NH_4OSPPh_2, mol	Product (yield, %)	M.p. (°C)	Recryst. solvent
Me_2SnCl_2, 0.0025	0.005	R = Me, $n = 2$ (91)	180–181	benzene
$^nBu_2SnCl_2$, 0.0025	0.005	R = ^{n}Bu, $n = 2$ (97)	62– 64 [a]	–
Bz_2SnCl_2, 0.001	0.002	R = Bz, $n = 2$ (75)	oil	–
Ph_2SnCl_2, 0.0025	0.005	R = Ph, $n = 2$ (82)	192–194	benzene
Me_3SnCl, 0.005	0.005	R = Me, $n = 3$ (92)	108–110	–
Cy_3SnCl, 0.0025	0.0025	R = Cy, $n = 3$ (90)	143–145	acetone
Bz_3SnCl, 0.0025	0.0025	R = Bz, $n = 3$ (89)	112–114	benzene
Ph_3SnCl, 0.0025	0.0025	R = Ph, $n = 3$ (83)	122–124	benzene

[a] Liquid in refs. 6 and 7.

tin)oxide and the corresponding diorganothiophosphorus chloride, eqn. (2) [8]:

$$(Me_3Sn)_2O + RR'P(S)Cl \longrightarrow Me_3SnOSPRR' + Me_3SnCl \quad (2)$$

(R = R' = Me, Ph; R = Me, R' = Ph)

Their structures were investigated using IR, ^{31}P-NMR and mass spectroscopy [8]. X-Ray diffraction studies on $Me_3SnOSPMe_2$ revealed a polymeric structure, with bridging monothiophosphinato ligands and planar Me_3Sn and tetrahedral $OSPC_2$ moieties [8]. A similar polymeric structure has also been established for an antimony monothiophosphinate, $Ph_2SbOSPPh_2$ [9].

We describe here the synthesis and characterization of some organotin(IV) derivatives of diphenylmonothiophosphinic acid, $R_nSn(OSPPh_2)_{4-n}$, where R = Me, ^{n}Bu, cyclo-C_6H_{11} (abbreviated Cy), $CH_2C_6H_5$ (abbreviated Bz), Ph, and $n = 2$ or 3.

2. Results and discussion

2.1. Preparation

Organotin(IV) diphenylmonothiophosphinates were prepared by reaction of the ammonium salt of the phosphorus ligand with the corresponding organotin chlorides in anhydrous benzene, eqn. (3).

$$R_nSnCl_{4-n} + (4-n)NH_4OSPPh_2 \longrightarrow R_nSn(OSPPh_2)_{4-n} + (4-n)NH_4Cl \quad (3)$$

Unlike organotin(IV) dithiophosphinates [4], the diphenylmonothiophosphinates could not be obtained

TABLE 2. Infrared spectral data for $R_nSn(OSPPh_2)_{4-n}$ and related compounds (in cm^{-1}) [a,b]

Compound	ν(P–O)	ν(P=O)	ν(P–S)	ν(P=S)	$\nu_{as}(SnC_n)$	$\nu_s(SnC_n)$	Ref.
$Ph_2P(S)OH$	892vs	–	–	633vs			[9]
Ph_2PSONH_4		1045s 1051s		628vs			[9]
$Ph_2P(S)OMe$	–	–	–	638c			[10]
$Ph_2P(O)SMe$	–	1202s	565s 568 [c]	–			[10]
$R_nSn(OSPPh_2)_{4-n}$							
R *n*							
Me 2	948s	–	–	646s 630m	576w	517w	This work
^{n}Bu 2 [d]	950s	–	–	650s	587m	–	
Bz 2 [d]	991s	–	–	645s	451w	430w	
Ph 2	993s	–	–	644s	–	–	
Me 3	1061s	–	–	632s	546m	519m	
Cy 3	1018s	–	–	631m	–	–	
Bz 3	1019s	–	–	631m	453m	433w	
Ph 3	1063s	–	–	595s	–	–	

[a] s = strong, m = medium, w = weak. [b] In KBr pellets. [c] Raman data. [d] In CS_2 solution.

by treating the corresponding organotin halides with the free acid owing to the lower acid strength.

Most of the synthesized compounds are white, crystalline solids. The dibenzyltin derivative is a high boiling liquid but the dibutyltin analogue solidified on standing. Preparation, yields, recrystallization solvents and melting points are given in Table 1.

2.2. *Spectra and structure*

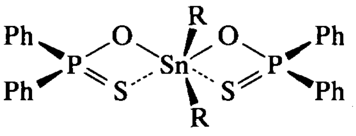
The compounds were characterized by IR spectroscopy and for some representative derivatives ^{1}H, ^{13}C and ^{119}Sn-NMR and Mössbauer spectra were also recorded. The molecular structure of $Me_2Sn(OSPPh_2)_2$ was determined by an X-ray diffraction study.

2.2.1. *Infrared spectra*

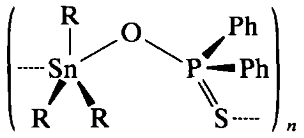
The infrared spectra of the compounds reported here are listed in Table 2. The assignments of the bands were made by comparison with the infrared spectra of the starting materials and those of the *O*- and *S*-methyl esters of the diphenylmonothiophosphinic acid.

The absence of strong intensity bands in the regions characteristic to single P–S bonds (600–500 cm^{-1}) and double P=O bonds (1250–1150 cm^{-1}), *e.g.* 565 cm^{-1} and 1202 cm^{-1} in $Ph_2P(O)SMe$ [10], along with the presence of intense vibrations in the range 650–580 cm^{-1} and 1050–950 cm^{-1}, suggested that the primary coordination of the monothiophosphinato ligand is through the oxygen atom. Additionally, weak interaction of the S atom doubly bonded to phosphorus with the metal is also possible, leading to an anisobidentate behaviour of the monothiophosphinato ligand. Such an interaction implies a shift of the ν(P=S) band to lower wave numbers, because of the delocalization of the π-electron pair. This is evident in the spectrum of $Ph_3SnOSPPh_2$, where the assigned ν(PS) is intermediate between those for a single and a double phosphorus–sulphur bond respectively.

The number and the positions of SnC_n stretching vibrations (when they appear in the frequency range studied and are not obscured by strong vibrations of the organic groups), are consistent with a non-linear orientation of the Sn–C bonds in diorganotin derivatives and non-coplanar Sn–C bonds in triorganotin derivatives. As a consequence, the structure **a**, with an *O*-bonded, anisobidentate ligand and distorted octahedral geometry around tin, is the most probable for diorganotin(IV) bis(diphenylmonothiophosphinates). For triorganotin(IV) derivatives, structure **b**, with bridging ligand and distorted trigonal bipyramidal coordination around tin, was proposed. A similar polymeric structure was revealed for $Me_3SnOSPMe_2$ by an X-ray diffraction study [8].



a



b

2.2.2. *^{1}H-NMR spectra*

Some of the organotin diphenylmonothiophosphinates were investigated by ^{1}H-NMR spectroscopy. The chemical shifts and phosphorus–hydrogen and tin–hydrogen coupling constants are listed in Table 3.

For $Me_2Sn(OSPPh_2)_2$ the observed value of the tin–proton coupling constant, $^{2}J(^{119}SnC^{1}H)$ 79.2 Hz,

TABLE 3. ^{1}H NMR data for $R_nSn(OSPPh_2)_{4-n}$ [a,b]

R	*n*	Chemical shifts and coupling constants (Hz)	Assignment
Me	2	1.28s (6H), $^{2}J(^{117}SnC^{1}H)$ 76.0, $^{2}J(^{119}SnC^{1}H)$ 79.2	$Sn-CH_3$
		7.33m (12H *meta* + *para*), 7.73dm (8H *ortho*)	$P-C_6H_5$
		$^{3}J(^{31}PCC^{1}H)$ 13.8	
Me	3	0.56 (9H), $^{2}J(^{117}SnC^{1}H)$ 57.6, $^{2}J(^{119}SnC^{1}H)$ 61.2	$Sn-CH_3$
		7.30m (6H *meta* + *para*), 7.75dm (4H *ortho*)	$P-C_6H_5$
		$^{3}J(^{31}PCC^{1}H)$ 12.9	
Cy	3	1.1–2.0m (33H)	$Sn-C_6H_{11}$
		7.27m (6H *meta* + *para*), 7.78dm (4H *ortho*)	$P-C_6H_5$
		$^{3}J(^{31}PCC^{1}H)$ 15.0	
Bz	3	2.66s (6H), $^{2}J(^{117}SnC^{1}H)$ 63.6	$Sn-CH_2-C_6H_5$
		$^{2}J(^{117}SnC^{1}H)$ 67.2	
		6.74–7.66m (25H)	$Sn-CH_2C_6H_5$, $P-C_6H_5$

[a] In $CDCl_3$ solution, and TMS as internal standard. [b] s = singlet, m = multiplet, dm = doublet of multiplets; *ortho*, *meta*, and *para* protons of phenyl groups.

TABLE 4. ^{119m}Sn-Mössbauer data for $R_2Sn(OSPPh_2)_2$ (in mm sec^{-1}, at liquid nitrogen temperature)

Compound	QS	IS	$\rho = QS/IS$
$Me_2Sn(OSPPh_2)_2$	3.62	1.34	2.70
$^nBu_2Sn(OSPPh_2)_2$	3.67	1.52	2.41

indicates a hexacoordinate environment around the tin atom [11]. Thus, anisobidentate coordination of the monothiophosphinato ligand, through oxygen and sulphur atoms, finds some support. This coupling constant was also used to estimate the magnitude of the C–Sn–C angle, using the formula [12]:

$$\measuredangle C\text{-}Sn\text{-}C = 0.0161\,|^2J\,|^2 - 1.32\,|^2J\,| + 133.4 \qquad (4)$$

The value thus obtained, *i.e.* 130°, agrees with the angular arrangement of the tin–carbon bonds suggested by the IR spectrum.

2.2.3. ^{119m}Sn-Mössbauer spectra

Mössbauer spectra were recorded for two representative diorganotin derivatives, *i.e.* $R_2Sn(OSPPh_2)_2$ (R = Me, ^{n}Bu). Mössbauer spectral parameters are listed in Table 4 and are consistent with the structure suggested by IR and ^{1}H-NMR data.

The magnitudes of the isomer shift (IS) and quadrupole splitting (QS) values are indicative of a tin(IV) oxidation state and of a *trans*-configuration of the organic groups attached to tin respectively [13]. This is in agreement with the conclusion drawn from the ratio between QS and IS values, *i.e.* $\rho = QS/IS > 2.1$, which also suggests a coordination number of more than four [14] because of weak additional interactions between tin and sulphur atoms.

For the dimethyltin(IV) derivative the C–Sn–C angle was calculated from the correlation with the magnitude of the QS values [15] given by eqn. (5):

$$|QS| = 4\{R\}[1 - 3\sin^2\theta\cos^2\theta]^{1/2} \qquad (5)$$

where $\{R\} = -1.03$ mm sec^{-1} is the partial quadrupole splitting for methyl groups bonded to tin, and the C–Sn–C angle is $(180 - 2\theta)°$. The calculated C–Sn–C angle is 147° for $Me_2Sn(OSPPh_2)_2$. The value is intermediate between those corresponding to tetrahedral and octahedral geometries, thus indicating a distorted structure, as confirmed by the X-ray diffraction study described below.

2.2.4. The molecular structure of bis(diphenylmonothiophosphinato)dimethyltin(IV), $Me_2Sn(OSPPh_2)_2$

Atomic coordinates are given in Table 5 and relevant bond distances and angles in Table 6. The asymmetric unit is shown in Fig. 1. The coordination sphere of the Sn atom involves two methyl groups (Sn–C(101)

TABLE 5. Atomic coordinates for bis(diphenylthiophosphinato)dimethyltin

	x	*y*	*z*
Sn(1)	−0.0965(1)	−0.1106(0)	−0.12083(3)
S(1)	0.0173(3)	0.2954(4)	−0.0478(2)
S(2)	−0.3703(4)	−0.1715(5)	−0.2976(2)
P(1)	0.1629(3)	0.1497(3)	−0.0722(1)
P(2)	−0.2074(3)	−0.0381(4)	−0.3073(2)
O(1)	0.1063(8)	−0.0148(8)	−0.0791(4)
O(2)	−0.0996(8)	0.0011(9)	−0.2278(4)
C(1)	0.218(1)	0.201(1)	−0.1638(7)
C(2)	0.322(1)	0.114(2)	−0.1889(8)
C(3)	0.369(2)	0.148(2)	−0.2592(9)
C(4)	0.310(2)	0.273(2)	−0.303(1)
C(5)	0.204(2)	0.361(2)	−0.2779(9)
C(6)	0.159(2)	0.329(2)	−0.2083(8)
C(7)	0.333(1)	0.141(1)	0.0049(6)
C(8)	0.453(1)	0.232(1)	0.0019(7)
C(9)	0.577(2)	0.230(2)	0.0623(8)
C(10)	0.580(2)	0.142(2)	0.1299(9)
C(11)	0.459(2)	0.054(2)	0.1336(9)
C(12)	0.335(1)	0.048(2)	0.0706(7)
C(13)	−0.272(1)	0.143(2)	−0.3508(7)
C(14)	−0.237(2)	0.269(2)	−0.307(1)
C(15)	−0.290(2)	0.404(4)	−0.335(1)
C(16)	−0.380(2)	0.416(3)	−0.414(1)
C(17)	−0.416(2)	0.290(2)	−0.457(1)
C(18)	−0.364(2)	0.150(2)	−0.425(1)
C(19)	−0.095(1)	−0.116(2)	−0.3697(7)
C(20)	0.054(2)	−0.090(3)	−0.354(1)
C(21)	0.148(3)	−0.162(3)	−0.399(1)
C(22)	0.083(3)	−0.259(4)	−0.461(2)
C(23)	−0.061(3)	−0.289(4)	−0.479(2)
C(24)	−0.152(3)	−0.217(3)	−0.430(1)
C(101)	−0.026(1)	−0.320(2)	−0.1541(8)
C(102)	−0.274(1)	0.006(1)	−0.0918(7)

TABLE 6. Selected bond distances and angles for bis(diphenylmonothiophosphinato)dimethyltin

Sn(1)–C(101)	2.10(1)	P(1)–O(1)	1.554(8)
Sn(1)–C(102)	2.09(1)	P(1)–C(1)	1.81(1)
Sn(1)–O(1)	2.041(8)	P(1)–C(7)	1.82(1)
Sn(1)–O(2)	2.081(8)	P(2)–O(2)	1.538(9)
Sn(1)–S(1)*	2.939(3)	P(2)–C(13)	1.82(1)
S(1)–P(1)	1.984(4)	P(2)–C(19)	1.79(1)
S(2)–P(2)	1.957(5)		
C(101)–Sn(1)–C(102)	144.5(5)	O(1)–P(1)–S(1)	113.7(3)
O(1)–Sn(1)–O(2)	86.5(3)	C(1)–P(1)–S(1)	110.8(4)
O(1)–Sn(1)–C(101)	98.6(4)	C(7)–P(1)–S(1)	113.2(4)
O(2)–Sn(1)–C(101)	97.5(4)	C(1)–P(1)–O(1)	109.0(5)
O(1)–Sn(1)–C(102)	114.6(4)	C(7)–P(1)–O(1)	103.8(5)
O(2)–Sn(1)–C(102)	96.6(4)	C(7)–P(1)–C(1)	105.9(5)
S(1)* –Sn(1)–O(1)	76.5(2)	O(2)–P(2)–S(2)	115.0(3)
S(1)* –Sn(1)–O(2)	162.5(2)	C(13)–P(2)–S(2)	112.5(5)
S(1)* –Sn(1)–C(101)	89.3(4)	C(19)–P(2)–S(2)	112.2(6)
S(1)* –Sn(1)–C(102)	86.8(4)	C(13)–P(2)–O(2)	104.5(6)
P(2)–O(2)–Sn(1)	123.4(5)	C(19)–P(2)–O(2)	105.5(5)
P(1)–O(1)–Sn(1)	133.6(5)	C(19)–P(2)–C(13)	106.3(7)

Note: S(1)* is in ($-x$, $1/2+y$, $-z$).

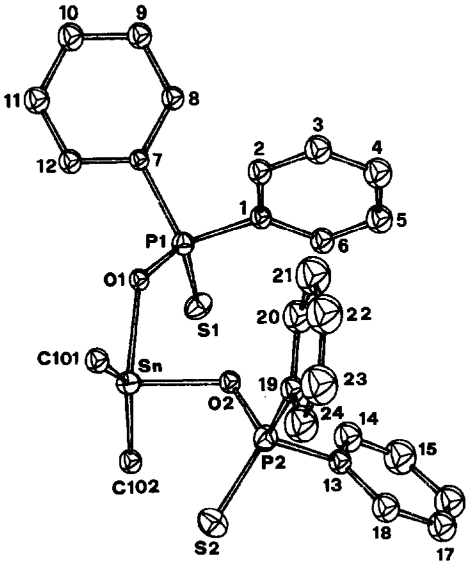


Fig. 1. Asymmetric unit for bis(diphenylthiophosphinato)dimethyltin.

= 2.10(1) Å, Sn–C(102) = 2.09(1) Å), the two O atoms belonging to the diphenylthiophosphinato ligands (Sn–O(1) = 2.041(8) Å, Sn–O(2) = 2.081(8) Å), and one S atom of another diphenylthiophosphinato ligand participating in an intermolecular bonding. This distance (Sn–S(1)* = 2.939(3) Å) is longer than the sum of the covalent radii of tin (1.40 Å) and sulphur (1.04 Å) [16], but well below the corresponding van der Waals distance (4.0 Å) [17]. The S(1)* atom belongs to the second molecule of the cell $(-x, 1/2+y, -z)$, and so the compound is a monodimensional polymer that extends through (x, y, z), $(-x, 1/2+y, -z)$, $(x, 1+y, z)$, *etc.* Figure 2 shows a view of the polymer with phenyl groups omitted. The geometry of the compound is distorted trigonal bipyramidal (TBP) with O(2) and S(1)* in axial positions (the O(2)–Sn–S(1)* bond angle is 162.5(2)°), and the methyls and O(1) in the equatorial plane. The sum of the bond angles at tin (see Table 6) in this plane is 357.7°, *i.e.* close to the expected 360°. The metal lies 0.17 Å out of the equatorial plane towards the O(2) side because the interaction of Sn with S(1)* is weaker than that with O(2). We may describe this complex as closer to a TBP than to a tetrahedral configuration (both distorted).

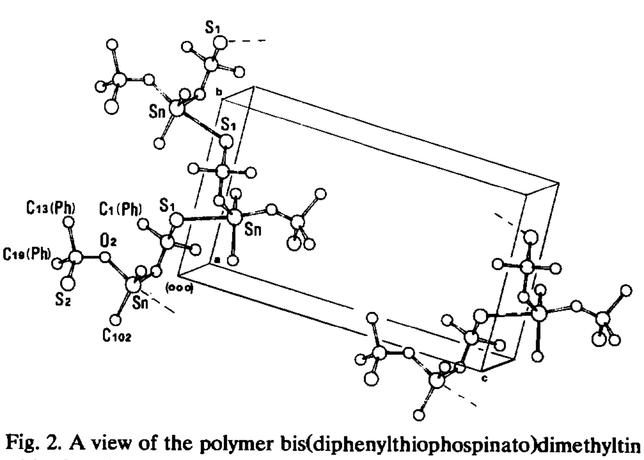


Fig. 2. A view of the polymer bis(diphenylthiophospinato)dimethyltin with phenyls omitted.

No appreciable interaction between Sn and the intramolecular S atoms is observed because these distances are long (Sn–S(1) = 3.901(3) Å, Sn–S(2) = 3.530(4) Å). In addition, these S atoms are further away from Sn than the non-bonded P atoms (Sn ··· P(1) = 3.310(3) Å, Sn ··· P(2) = 3.197(3) Å). Since intramolecular Sn–S bonds are excluded and the intermolecular Sn–S(1)* bond is weak, we can associate the thiophosphinato ester (primary) bond with the O atom, and S(2) must be regarded as doubly bonded to P(2). In complexes with ligands of the type –S–P=S the P=S bond is in the range 1.85–1.95 Å and the single P–S bond has the range 1.99–2.19 Å [18]. The phosphorus–sulphur bonds are P(1)–S(1) = 1.984(4) Å and P(2)–S(2) = 1.957(5) Å. This is in agreement with a non-involved (to tin) S(2) and a weakly bound (intermolecular) S(1) as mentioned above. This compound can be compared with (dimethylmonothiophosphinato)trimethyltin, which is also TBP [8]. The coordination is similar. Again one thiophosphinato ligand has the oxygen bound to the metal and the sulphur bound to another metal as a monodimensional polymer. Three methyls are in the equatorial plane. In other words, a methyl takes the place of O(2) in $Me_2Sn(OSPPh_2)_2$. In this complex some relevant parameters are Sn–O = 2.267(6) Å, Sn–S = 2.737(3) Å, O–Sn–S angle 172.4(3)°, C–Sn–C angles = 118.4(4)°, 120.6(4)°, 121.0(4)°. The metal lies out of the equatorial plane by 0.04 Å towards the S side. We can see in this structure that the sulphur atom is more (and the oxygen atom less) involved with the metal than in $Me_2Sn(OSPPh_2)_2$, and the axial parameter of the bipyramid (O–Sn–S angle) is closer to 180°. Also, the interbond angles at tin in the equatorial plane are closer to the ideal. The metal almost lies in this plane, indicating similar strength for the bonds to sulphur and oxygen atoms, as confirmed by the covalent nature of the Sn–S and Sn–O bonds revealed by the bond lengths. This is in contrast with the situation in $Me_2Sn(OSPPh_2)_2$, in which Sn–O bonding is favoured. From this comparison we conclude that $Me_2Sn(OSPPh_2)_2$ has a more distorted TBP configuration than the triorganotin species. Alternatively, we may describe $Me_2Sn(OSPPh_2)_2$ as having more tetrahedral character than the triorganotin compound.

The marked difference between O(1)–Sn–O(2) (86.5(3)°) and C(101)–Sn–C(102) (144.5(5)°) can be associated with the relative bulk of oxygen atoms and methyl groups. An investigation of other diorganotins with bidentate S,O ligands (–O–X–S–) shows that the Me–Sn–Me bond angles can vary appreciably. Thus, this angle is: (a) 138.9(2)° for (2-pyridinethiolato-N-oxide)$_2$SnMe$_2$ [19]; (b) 139.4(3)° for (monothioacetylacetone)$_2$SnMe$_2$ [20]; (c) 134.2(2)° for {benzoyl(thiobenzoyl)methane}$_2$SnMe$_2$ [20]; and (d) 132.9(3)° for (1-pyrrolethiocarboxylate)$_2$SnMe$_2$ [21]. All of these complexes are six-coordinate in skew trapezoide pyramidal (STP) configuration [22] (see scheme **a**), a distortion of the octahedral arrangement that is characterized by a closing of the interligand angle at tin towards the more involved donors with the metal and the organic groups accommodated on the opposite side, where more room is available. For instance, if Sn–S bonding is stronger than that of Sn–O, the S–Sn–S angle becomes smaller than the O–Sn–O angle and the methyls are accommodated on the O–Sn–O side. The four complexes mentioned above have:

(a) Sn–O = 2.356(3), 2.410(4) Å; Sn–S = 2.536(1), 2.566(1) Å.

This implies that Sn–S bonding is stronger than Sn–O bonding because the covalent distance is 2.44 Å for Sn–S and 2.06 Å for Sn–O [16].

(b) Sn–O = 2.452(6), 2.501(7) Å; Sn–S = 2.502(2), 2.528(2) Å.

This indicates a stronger Sn–S (weaker Sn–O) bonding.

(c) Sn–O = 2.489(3), 2.514(3) Å; Sn–S = 2.526(2), 2.535(2) Å.

This implies a weakening of Sn–O and Sn–S bondings.

(d) Sn–O = 2.645, 2.670 Å; Sn–S = 2.501(2), 2.505(2) Å.

Here an additional lengthening of Sn–O bonds (and a shortening of Sn–S distances) is observed.

In these four complexes the methyl groups are always accommodated on the O–Sn–O side, even in the case of (a) and (b) in which shorter Sn–O bonds than the Sn–S bonds are present. This may indicate that the arrangement in this system is mainly governed by electronic factors (reflecting weaker or stronger involvement of donors with the metal) rather than merely by the geometrical positions of these donors. In addition, a closing of the Me–Sn–Me bond angle may be associated with a progressive lengthening of the Sn–O bond distance, but a trend for Sn–S lengths is not defined. It is interesting to note that in the four complexes the primary atom of the ligand bound to tin is sulphur. In contrast, in Me$_2$Sn(OSPPh$_2$)$_2$ oxygen is the primary atom. We discuss this point later.

A structural analysis was made of bis(chelate)diorganotins [19]. Besides the STP arrangement, distorted *cis*-octahedral and *trans*-octahedral configurations were found. An interesting comparison can be made of complexes containing anions of the type –S–X–S– or –O–X–O–, where X is an atom or a group of atoms. For dithioligands a group of nine species has STP configuration (C–Sn–C bond angle range is 122–142°); one is distorted *cis*-octahedral (C–Sn–C bond angle = 101°); one is *trans*-octahedral (C–Sn–C bond angle = 180°). For dioxygen ligands five are STP (C–Sn–C bond angle range = 143.6–159.9°), six are *cis*-octahedral (C–Sn–C bond angle = 106.8–110.7°), and two are *trans*-octahedral (C–Sn–C bond angle = 180°) [19]. If X is an atom (as P in diphenylmonothiophosphinate) the bite angle (as S–Sn–O) seems to be an important factor in determining the configuration of (chelate)$_2$SnR$_2$ complexes, but the R groups and substituents on X (as phenyl in Me$_2$Sn(OSPPh$_2$)$_2$) are also important. For *trans*-octahedral complexes a bite angle range of 76–86° [19] is observed; STP configuration is found for smaller bite angles. An example of how subtle this matter can be is found in the complexes bis(O,*O*-diethyldithiophosphato)diphenyltin [23] and bis(O,*O*-diisopropyldithiophosphato)diphenyltin [24]; the former has STP geometry, a C–Sn–C bond angle of 135°, and a bite angle S(1)–Sn–S(2) of 69.7°; the latter is *trans*-octahedral, C–Sn–C = 180°, S(1)–Sn–S(2) = 76°. In this context, the configuration of Me$_2$Sn(OSPPh$_2$)$_2$, *i.e.* TBP, is unique for bis(chelate-S,O)diorganotins. However, this type of configuration has been found in one case for a bis(chelate)diorganotin, namely [(ethylenebis(dithiocarbamato)Sn(t-butyl)$_2$]$_2$ [25]. This dimer has each Sn surrounded by two t-butyls and one sulphur atom in the equatorial plane (eq) and two sulphur atoms in axial (ax) positions. Relevant parameters are Sn–S(eq) = 2.459(2) Å; Sn–S(ax) = 2.563(2) Å, 2.878(2) Å; S(ax)–Sn–S(ax) = 155.79(7)°, C–Sn–C bond angle = 119.5(3)°. No explanation was offered for this unusual structure, which has one sulphur atom non-coordinated. When we compare this structure with that of Me$_2$Sn(OSPPh$_2$)$_2$ we see that there is a similar involvement of the axial atoms to the metal in both compounds but there is a more ideal axial–Sn–axial bond angle for the TBP arrangement in our complex.

As a general conclusion we observe that bis(chelate)diorganotins can show a range of configurations, namely octahedral [19], TBP [Me$_2$Sn(OSPPh$_2$)$_2$], and tetrahedral [26]. Bidentate (S,O)-anions can extend these possibilities owing to the primary and secondary interactions of the atoms with the metal. This wide range of interactions allows several possibilities for accommodation of R groups, so that distorted STP configurations are found. It is apparent that in –S–X–O– anions, if X is a group of atoms, sulphur is more likely to be the primary coordinating atom of the ligand than oxygen (see above (a), (b), (c), (d) complexes). If X is an atom, such as phosphorus in monothiophosphinate, oxygen is more likely to be the primary coordinating atom in diorganotin complexes, but similar bond strengths are found for triorganotin complexes [8]. Thus, a wide range of structures is found. The factors determining the structures are not clear at this stage, and we are exploring this question further.

3. Experimental details

Most of the organotin chlorides, R_2SnCl_2 and R_3SnCl, were commercial products. Benzyltin chlorides were prepared from tin powder and benzyl chloride [27]. Diphenylmonothiophosphinic acid was synthesized by a published procedure [28], and its ammonium salt was obtained by bubbling dried ammonia through benzene solution of the free acid. IR spectra were recorded on a SPECORD 75 IR Carl Zeiss Jena (Germany) with KBr pellets or CS_2 solutions. The ^{1}H-NMR spectra were recorded on a VARIAN EM 360-L spectrometer operating at 60 MHz, and ^{119m}Sn-Mössbauer spectra were recorded at nitrogen liquid temperature using a $Ca^{119m}SnO_3$ source and standard material for zero velocity. Satisfactory elemental analyses (carbon and hydrogen) were obtained for all compounds prepared.

3.1. Preparation of the title compounds (Table 1)

A benzene solution containing stoichiometric amounts of organotin chlorides was added to a suspension of the ammonium diphenylmonothiophosphinate in benzene. The mixture was stirred at the reflux temperature for 2 h, and the resulting NH_4Cl was filtered off and the solution was evaporated. The white crystals obtained were recrystallized from organic solvents (see Table 1).

3.2. Collection and reduction of X-ray data

Crystals of $Me_2Sn(OSPPh_2)_2$ were obtained as described above. They are stable in air and on exposure to X-rays. Monitoring of standard reflections indicated that no decay occurred during the data collection. A Psi-scan of some suitable reflections, (0, 2, 0), (0, 3, −1) showed absorption phenomena, with minimum transmission of 30% for both reflections. The appropriate correction was applied along with that for Lorenz and polarization effects. A summary of crystal and intensity data is given in Table 7.

3.3. Solution and refinement of the structure

The structure was determined using three-dimensional Patterson functions to locate the position of the heavy atom (Sn) and Fourier maps to find the other non-hydrogen atoms. Refinement by least-square was subsequently applied. The quantity minimized was $\Sigma w(|F_o| - |F_c|)$, with weights of the type $w = (a + F_o + cF_o^2)$ where a and c are of the order of $2F_o$(min) and $2/F_o$ (max), respectively [29]. In the final cycles of least-square the hydrogen atoms were included at fixed positions (d(C–H) = 0.96 Å, C–C–H angle = 120°, H–C–H angle = 109.5° (methyls)). The structure was solved with the CAOS program [30], which was run on an Eclipse MV/8000II Data General computer.

TABLE 7. Summary of crystal data for bis(diphenylmonothiophosphinato)dimethyltin, $Me_2Sn(OSPPh_2)_2$

Formula	$C_{26}H_{52}O_2P_2S_2Sn$
Fw	641.46
a (Å)	9.254(3)
b (Å)	8.924(3)
o (Å)	17.134(6)
α (°)	90
β (°)	102.90(3)
γ (°)	90
V (Å^3)	1379(1)
Z	2
Density (calc.)	1.545
Space group	$P2_1$
Crystal dimension (mm)	0.25 × 0.10 × 0.05
μ (cm^{-1})	102.41
Radiation	CuKα
Diffractometer	Syntex $P2_1$
Scan mode	$2\theta - \theta$
Scan range	0.8
Background counts	1/4 of scan time at the end of scan
2θ limits (°)	3140
Reflections collected no.	3055
No. unique data	2657
Final no. of variables	158
Final R, R_w	0.052, 0.073

The absolute configuration of $Me_2Sn(OSPPh_2)_2$ was determined after convergence of the refinement process on one enantiomer that had $R_f = 0.061$, $R_w = 0.083$. At that stage the inverted configuration was refined, resulting in $R_f = 0.052$, $R_w = 0.073$, showing that the original configuration was not correct. As a consequence the helicity of the polymer along the y axis was changed. It is noteworthy that the original configuration showed significantly different Sn–methyl bond lengths (Sn–C(101) = 2.21(1) Å, Sn–C(102) = 2.03(1) Å). In contrast, the correct configuration has these bonds equivalent, as normally found in diorganotins.

Atomic scattering factors and anomalous dispersion terms were taken from ref. 31. A list of displacement parameters and observed and calculated structure factors are available from the authors.

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