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SYNTHESIS AND CHARACTERIZATION OF DI- AND TRIORGANOTIN(IV) DIETHYLDITHIOPHOSPHINATES. THE CRYSTAL AND MOLECULAR STRUCTURE OF BIS(DIETHYLDITHIOPHOSPHINATO)DIMETHYLTIN(IV), $Me_2Sn(S_2PEt_2)_2$

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Summary

Bis(diethyldithiophosphinato)diorganotin(IV), $R_2Sn(S_2PEt_2)_2$ (R = Me, n-Bu, CH_2Ph, Ph) and diethyldithiophosphinatotriorganotin(IV), $R_3SnS_2PEt_2$ (R = Me, cyclo-C_6H_{11}, CH_2Ph, Ph) were synthesized in nearly quantitative yield by reaction of organotin chlorides with sodium diethyldithiophosphinate. The compounds were characterized by infrared and ^1H NMR spectra and, in part, by mass and ^{119m}Sn Mössbauer spectroscopy. The probable structure of the new compounds was inferred from the spectral data. The crystal and molecular structure of $Me_2Sn(S_2PEt_2)_2$ has been determined by X-ray diffraction. The compound is monoclinic, space group $C'2/c$, with a 20.814(11), b 6.243(3), c 16.092(8) Å, β 105.42(8)°, $Z = 4$, D_x 1.500 g cm^{-3}. The molecule exhibits a distorted tetrahedral environment around tin, with angles C–Sn–C 123.7(4) and S–Sn–S 80.6(2)°. The bond distances within the dithiophosphinato ligand are P–S 1.961(2), P=S 2.054(2), P–C 1.825(10) and 1.787(8) Å. The two tin–sulfur distances Sn–S 2.476(2) and Sn ··· S 3.336(2) Å indicate the presence of two covalent bonds with additional non-bonded tin–sulfur interactions; the ligands can thus best be described as severely anisobidentate.

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Introduction

Organotin dithiophosphates, $R_nSn[S_2P(OR')_2]_{4-n}$, have been extensively investigated in recent years by spectroscopic methods and X-ray crystal structure determinations [1,2]. Some have unusual structures, made possible by the ability of tin to exhibit various geometries [3,4] and by the diversity of possible coordination patterns of dithiophosphorus ligands [5]. The related organotin dithiophosphinates, $R_nSn(S_2PR'_2)_{4-n}$, have been much less studied [6–10], and it seemed to us that a comparison of the properties and structures of compounds containing the two types of ligand would be of interest. The finding that some organotin dithiophosphinates exhibit antitumor properties [11] adds to the interest in this type of compound. (For a general survey on antitumor properties of organotins see refs. 12–14.)

We report here the synthesis and characterization by infrared and ^1H NMR spectroscopy of some organotin(IV) diethyldithiophosphinates, $R_nSn(S_2PEt_2)_{4-n}$, with R = Me, n-Bu, cyclo-C_6H_{11} (abbreviated Cy), Ph, CH_2Ph (abbreviated Bz) and $n = 2$ or 3. Some key compounds were also investigated by ^{119m}Sn Mössbauer and mass spectroscopy, and the structure of bis(diethyldithiophosphinato)dimethyltin (IV) was determined by X-ray diffraction.

Results and discussion

The organotin diethyldithiophosphinates were obtained by treating an organotin chloride with the sodium salt of diethyldithiophosphinic acid:

$$R_nSnCl_{4-n} + (4-n)NaS_2PEt_2 \cdot 2H_2O \rightarrow R_nSn(S_2PEt_2)_{4-n} + (4-n)NaCl + 2(4-n)H_2O$$

The trimethyl- and tribenzyl-tin derivatives are liquids; the other compounds are white crystalline solids, which can be recyrstallized from organic solvents (Table 1).

Infrared spectra

The infrared spectra were recorded over the range 4000–400 cm^{-1}. The P–S stretching vibrations, which can provide useful information [15], were assigned by reference to those observed for Et_2PS_2Me (585 cm^{-1} for P=S bond and 477 cm^{-1} for P–S bond) [16] and the starting materials, are listed in Table 2. The $\nu_{as}(SnC_2)$ and $\nu_{sym}(SnC_2)$ bands for $Me_2Sn(S_2PEt_2)_2$ were found at 552 and 513 cm^{-1} (medium intensity bands) respectively, suggesting a non-linear configuration for the CH_3–Sn–CH_3 fragment. The $\nu_{as}(SnC_3)$ and $\nu_{sym}(SnC_3)$ bands at 544 and 511 cm^{-1}, respectively, also indicate a non-planar arrangement of the $Sn(CH_3)_3$ groups, suggesting four-coordination at tin. In some cases the Sn–C stretching frequencies could not be assigned: for $R_nSn(S_2PEt_2)_{4-n}$ (R = n-Bu, Bz) they are masked by other strong frequencies of the organic groups and P–S bonds; for phenyltin derivatives they were not observed probably because they fall below 400 cm^{-1} [17,18].

It has been shown that the difference, Δ, between the asymmetric and symmetric P–S stretching vibrations can provide information about the coordination pattern of dithiophosphinato ligand [15]. For triorganotin diethyldithiophosphinates, the val-

TABLE 1

PREPARATION OF $R_nSn(S_2PEt_2)_{4-n}$ COMPOUNDS

Starting materials		Product $R_nSn(S_2PEt_2)_{4-n}$ (yield (%))	M.p. (°C)	Recryst. solvent	Analyses (Found (calc) (%))	
R_nSnCl_{4-n}, mol	$NaS_2PEt_2 \cdot 2H_2O$ (mol)				C	H
Me_2SnCl_2, 0.01 [a]	0.02 [a]	R = Me, $n = 2$ (89)	118–119 [b]	MeOH/EtOH (1/1)		
n-Bu_2SnCl_2, 0.0025 [c]	0.005 [c]	R = n-Bu, $n = 2$ (92)	41–43 [d]	MeOH		
Bz_2SnCl_2, 0.0025 [c]	0.005 [c]	R = Bz, $n = 2$ (97)	120–121	C_6H_6	43.19 (43.51)	5.65 (5.60)
Ph_2SnCl_2, 0.0025 [c]	0.005 [c]	R = Ph, $n = 2$ (90)	146–148 [e]	i-PrOH		
Me_3SnCl, 0.01 [c]	0.01 [c]	R = Me, $n = 3$ (94)	oil	–	26.14 (26.52)	5.83 (6.00)
Cy_3SnCl, 0.005 [c]	0.005 [c]	R = Cy, $n = 3$ (86)	84–85	Me_2CO	50.25 (50.70)	8.01 (8.26)
Bz_3SnCl, 0.005 [c]	0.005 [c]	R = Bz, $n = 3$ (92)	oil	–	54.74 (55.08)	5.42 (5.69)
Ph_3SnCl, 0.005 [f]	0.005 [f]	R = Ph, $n = 3$ (81)	92–94 [g]	MeOH		

[a] In 25 ml H_2O. [b] M.p. 115–116 °C [9]. [c] In 25 ml benzene. [d] M.p. 36–37 °C [9], 40.5 °C [7]. [e] M.p. 142–144 °C [9], 149.5 °C [7]. [f] In 30 ml EtOH. [g] M.p. 88–89 °C [6,8].

TABLE 2

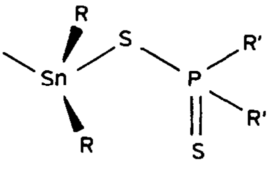
INFRARED DATA FOR $R_nSn(S_2PEt_2)_{4-n}$ (cm^{-1}) [a,b]

R	n	$\nu_{as}(PS_2)$	$\nu_{sym}(PS_2)$	Δ [d]
Me	2	590s	473s	117
n-Bu [c]	2	593s	470m	123
Bz	2	595s	472s	123
Ph	2	600s	470s	130
		586s	462s	124
Me [c]	3	597s	458s	139
			488m	
Cy	3	605s	472m	133
			497s	
Bz [c]	3	603s	488m	115
		599s	468s	131
Ph	3	593s	468s	125
			488m	

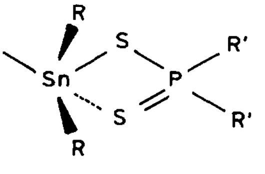
[a] m = medium, s = strong. [b] In KBr pellets. [c] In CS_2 solution. [d] $\Delta = \nu_{as}(PS_2) - \nu_{sym}(PS_2)$.

ues of Δ (Table 2) suggest monodentate coordination of the ligand to four-coordinated (tetrahedral) tin. This is also consistent with the presence of two Sn–C stretching vibrations (for R = Me, Cy) [17].

In diorganotin derivatives the dithio ligand may be either monodentate (**a**) or anisobidentate, with weak interactions between the tin atom and the sulfur atom double bonded to phosphorus (**b**) [5]. Isobidentate coordination of a dithiophosphorus ligand in an organotin compound has been observed only for the dithiophosphato derivative $Ph_2Sn[S_2P(OPr^i)_2]_2$ [19]. The Δ values observed in the infrared spectra of our compounds are consistent with both types (**a**) and (**b**) and so do not distinguish between them.



(**a**)



(**b**)

^1H NMR spectra

The ^1H NMR spectra show clear signals for the organic groups bonded to the tin and phosphorus atoms, but for the di-n-butyl- and tricyclohexyltin derivatives the

TABLE 3

^1H NMR DATA FOR $R_nSn(S_2PEt_2)_{4-n}$ [a,b]

Compound	Chemical shifts (δ, ppm) and coupling constants (J, Hz)			
	P–CH_2–CH_3	P–CH_2–CH_3	Sn–CH_3 or Sn–CH_2–C_6H_5	Sn–$C_6$$H_5$ or Sn–CH_2–$C_6$$H_5$
$Me_2Sn(S_2PEt_2)_2$ [c]	1.24dt (12H), $^3J(^{31}PCC^1H)$ 22, $^3J(^1HCC^1H)$ 6.5	1.99dq (8H), $^2J(^{31}PC^1H)$ 10.7, $^3J(^1HCC^1H)$ 6.5	1.54s (6H), $^2J(^{119}SnC^1H)$ obscd. [d] $^2J(^{117}SnC^1H)$ obscd. [d]	
$Bz_2Sn(S_2PEt_2)_2$ [e]	1.02dt (12H), $^3J(^{31}PCC^1H)$ 21.5, $^3J(^1HCC^1H)$ 6.5	1.54dq (8H), $^2J(^{31}PC^1H)$ 11, $^3J(^1HCC^1H)$ 6.5	3.51s (4H), $^2J(^{119}SnC^1H)$ 78, $^2J(^{117}SnC^1H)$ 75	7.14m (10H)
$Ph_2Sn(S_2PEt_2)_2$ [c]	1.00dt (12H), $^3J(^{31}PCC^1H)$ 21.5, $^3J(^1HCC^1H)$ 7	1.79dq (8H), $^2J(^{31}PC^1H)$ 10.7, $^3J(^1HCC^1H)$ 7		7.37m (6H), 7.53m (4H-*ortho*)
$Me_3SnS_2PEt_2$ [e]	1.32dt (6H), $^3J(^{31}PCC^1H)$ 21. $^3J(^1HCC^1H)$ 6.5	2.02dq (4H), $^2J(^{31}PC^1H)$ 11, $^3J(^1HCC^1H)$ 6.5	0.70s (9H), $^2J(^{119}SnC^1H)$ 59, $^2J(^{117}SnC^1H)$ 56	
$Bz_3SnS_2PEt_2$ [e]	1.22dt (6H), $^3J(^{31}PCC^1H)$ 21, $^3J(^1HCC^1H)$ 7	1.94dq (4H), $^2J(^{31}PC^1H)$ 10.8, $^3J(^1HCC^1H)$ 6.5	2.60s (6H), $^2J(^{119}SnC^1H)$ 67, $^2J(^{117}SnC^1H)$ 64	6.82m (15H)
$Ph_3SnS_2PEt_2$ [c]	1.02dt (6H), $^3J(^{31}PCC^1H)$ 22, $^3J(^1HCC^1H)$ 7	1.92dq (4H), $^2J(^{31}PC^1H)$ 11.5, $^3J(^1HCC^1H)$ 7		7.30m (9H), 7.63m (6H-*ortho*)

[a] TMS as internal standard. [b] s = singlet, dt = doublet of triplets, dq = doublet of quartets, m = multiplet. [c] In $CDCl_3$. [d] Obscured. [e] In CCl_4.

TABLE 4

70 eV MONOISOTOPIC MASS SPECTRA OF $R_nSn(S_2PEt_2)_{4-n}$ (m/e, (%)) [a]

	$R_2Sn(S_2PEt_2)_2$		$R_3SnS_2PEt_2$	
	R = Me	R = Ph	R = Cy	R = Ph
$R_3SnS_2PEt^+$	–	–	–	475 (0.2)
$RSn(S_2PEt_2)_2^+$	441 (0.4)	503 (13)	–	–
$Sn(S_2PEt_2)_2^+$	426 (2.5)	–	–	–
$R_2SnS_2PEt_2^+$	303 (100)	427 (100)	439 (100)	427 (100)
$R_2SnSPEt_2^+$	–	399 (1.5)	407 (2)	395 (21)
R_3SnS^+	–	–	–	383 (3)
R_3Sn^+	–	–	369 (1)	351 (22)
$SnS_2PEt_2^+$	273 (48)	273 (43)	273 (79)	273 (20)
$SnSPEt_2^+$	–	–	241 (7)	241 (17)
$RSnS^+$	–	229 (10)	–	229 (11)
RSn^+	135 (3)	197 (21)	203 (10)	197 (36)
$SPEt_2^+$	121 (32)	121 (31)	121 (22)	121 (17)
Sn^+	–	–	120 (2)	120 (14)

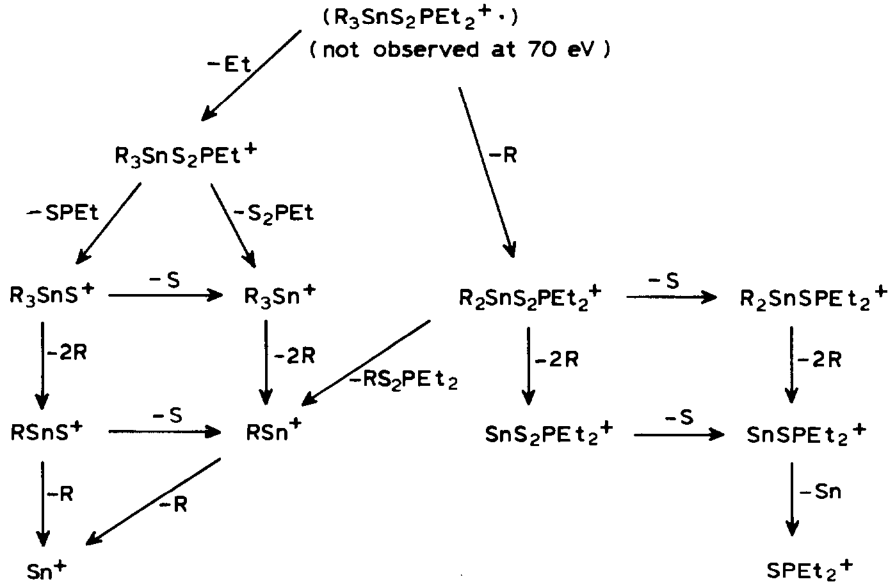
[a] The m/e values were computed according to H = 1, C = 12, P = 31, S = 32, Sn = 120.

signals cannot be unambiguously assigned because of peak overlapping. The chemical shifts and coupling constants are listed in Table 3.

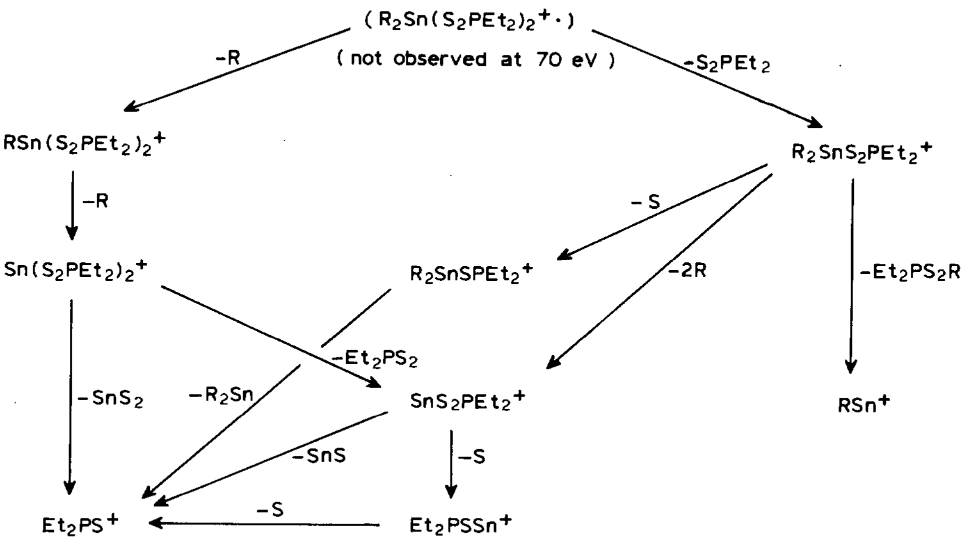
The signal of the methyl protons of the ethyl groups bonded to phosphorus appears as a doublet of triplets, while that of methylene protons of the same groups is a doublet of quartets, as expected. The $^3J(^{31}PCC^1H)$ and $^2J(^{31}PC^1H)$ coupling constants are ca. 21 and 11 Hz, respectively.

Mass spectra

The 70 eV monoisotopic mass spectra of four compounds, $R_3SnS_2PEt_2$ (R = Cy, Ph) and $R_2Sn(S_2PEt_2)_2$ (R = Me, Ph), are described in Table 4, and can be



SCHEME 1. Fragmentation pattern of $R_3SnS_2PEt_2$.



SCHEME 2. Fragmentation pattern of $R_2Sn(S_2PEt_2)_2$.

interpreted in terms of the fragmentation pattern shown in Schemes 1 and 2. Neither type of compound showed the molecular ion at 70 eV.

For the triorganotin derivatives, the presence of a $R_3SnS(S)PEt^+$ ion shows clearly that the carbon–phosphorus bond can be cleaved to give an intermediate, that can be converted into either R_3Sn^+ or R_3SnS^+. One of the ions of the first fragmentation, R_3SnS^+, could be accounted for by the loss of $Et_2P(S)$ group from the molecular ion, i.e., by the cleavage of a phosphorus–sulfur bond. The other two ions of the first fragmentation are formed by the cleavage of a tin–carbon or tin–sulfur bond, one of them, $R_2SnS(S)PEt_2{}^+$, being the base peak for both compounds studied.

When R = Cy, the Cy_3Sn^+ ion is very weak and either the fragmentation route going through Cy_3SnS^+ and $CySnS^+$ is not followed, or these ions are too unstable to be seen in the mass spectrum. The RSn^+ ion (like the R_3Sn^+ ion) is rather intense for R = Ph, but less so for R = Cy.

For both diorganotin derivatives studied, one of the expected ions of the initial fragmentation, $R_2SnS(S)PEt_2{}^+$, is again the base peak; in this case it results from cleavage of a tin–sulfur bond. The other ion formed in the initial fragmentation is much less abundant.

In the $Sn(S_2PEt_2)_2{}^+$ ion, present in low abundance in the spectrum of $Me_2Sn(S_2PEt_2)_2$, the tin has an oxidation state of III. This represents an exception to the general rule that only fragments in which tin is in oxidation state II or IV are observed in the mass spectrum of organotin compounds [20,21].

Other ions, not listed in Table 4, are also present for the dimethyltin derivative, but they are weak: viz. $C_5H_{13}P_2S_2Sn^+$ (*m/e* 319, 1%), $C_3H_8PS_4Sn^+$ (*m/e* 323, 1.5%), $C_9H_{23}P_2SSn^+$ (*m/e* 345, 1%), $C_9H_{23}S_3Sn^+$ or $C_7H_{17}P_2S_2Sn^+$ (*m/e* 347, 3%) and $C_7H_{18}PS_3Sn^+$ or $C_5H_{12}P_2S_2Sn^+$ (?) (*m/e* 348, 3%).

For the diphenyltin derivative, there are two ions which could be either Ph_3Sn^+ (*m/e* 351) and Ph_3SnS^+ (*m/e* 383) (6 and 8%, respectively), or $Et_2P(S)SSnPhH^+$

(*m/e* 351) and $Et_2P(S)SSn(SPh)H^+$ (*m/e* 383). The $Ph_3Sn_2S_2{}^+$ ion (*m/e* 535, 7%) is easily recognizable because of its isotope pattern.

The mass spectrum of the diphenyltin derivative contains an ion, $Et_2P(S)SSnPh_2S^+$ (*m/e* 459, 1.7%), which could be either $Et_2P(S)SSnPh(SPh)^+$ or $Et_2P(S)SSnPh_2S^+$; the second of these would arise from a phosphorus–sulfur bond cleavage. The first possibility is supported by the presence of the ion $Et_2P(S)SSn(SMe)_2{}^+$ (*m/e* 367, 4%) in the dimethyltin derivative spectrum, which shows that a sulfur atom can be found between tin and the organic group R.

The main features of the mass spectra of diethyldithiophosphinates are similar to those of organotin dithiophosphates [22,23].

^{119m}Sn Mössbauer spectra

Four compounds (those for which mass spectra were recorded) were studied by ^{119m}Sn Mössbauer spectroscopy. The Mössbauer data are listed in Table 5, and are consistent with the structure suggested by infrared data. The magnitudes of the isomer shift (IS) values indicate a tin(IV) oxidation state for all the compounds.

The magnitudes of the quadrupole splitting (QS) of diorganotin derivatives are indicative of a coordination greater than four, suggesting (distorted) octahedral geometry [24,25]. The C–Sn–C angles were calculated from the correlation with the magnitude of the QS values [26], given by equation:

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

where $\{R\}$ = partial quadrupole splitting for the organic groups bonded to tin (-0.95 for phenyl and -1.03 mm s^{-1} for methyl) and $\sphericalangle$C–Sn–C $(180 - 2\theta)°$. This correlation is supported, with some exceptions (e.g., $Ph_2Sn[S_2P(OPr^i)_2]_2$: calc. $\sphericalangle$C–Sn–C 162.6°; obsd. $\sphericalangle$C–Sn–C 180° [19]), by structural data for dimethyltin(IV) [10,26] and diphenyltin(IV) [23] compounds. For $Me_2Sn(S_2PEt_2)_2$ the calculated C–Sn–C angle is 127.6°, and for $Ph_2Sn(S_2PEt_2)_2$ it is 123.8°. These values are intermediate between those corresponding to tetrahedral and octahedral geometry (closer to tetrahedral), indicating a distorted structure.

The ρ values ($\rho = QS/IS$) for diorganotin derivatives are at the limit between a four-coordinated and a higher than four-coordinated configuration of the tin atom [17,25], consistent with a weak interaction with the tin atom of the sulfur atom doubly bonded to phosphorus. For the triorganotin diethyldithiophosphinates, the ρ values are consistent with a four-coordinated (tetrahedral) tin atom ($\rho < 1.6$) [25].

Crystal and molecular structure of $Me_2Sn(S_2PEt_2)_2$

Relevant bond distances and angles are listed in Table 6. Figure 1 shows the molecular structure of $Me_2Sn(S_2PEt_2)_2$ and the atom numbering scheme.

TABLE 5

^{119m}Sn MÖSSBAUER DATA FOR $R_nSn(S_2PEt_2)_{4-n}$ (at 77 K, in mm s^{-1})

Compound	$IS \pm 0.03$	$QS \pm 0.06$	$\Gamma_1 \pm 0.03$	$\Gamma_2 \pm 0.03$	$\rho = QS/IS$
$Me_2Sn(S_2PEt_2)_2$ [a]	1.49	2.96	2.52	2.23	1.99
$Ph_2Sn(S_2PEt_2)_2$ [b]	1.39	2.68	1.53	1.76	1.93
$Cy_3SnS_2PEt_3$	1.51	2.37	1.66	1.51	1.57
$Ph_3SnS_2PEt_2$	1.32	1.91	1.58	1.69	1.45

[a] lit.: IS 1.47, QS 2.89 [9]. [b] lit.: IS 1.42, QS 2.68 [9].

TABLE 6

INTERATOMIC DISTANCES (Å) AND ANGLES (°) [a]

Sn–S(1)	2.476(2)	S(1)–Sn–S(1′)	80.6(2)
Sn–S(2)	3.336(2)	S(1)–Sn–S(2)	68.1(1)
Sn–C(5)	2.122(8)	S(1)–Sn–C(5)	109.4(2)
P(1)–S(1)	2.054(2)	S(1)–Sn–C(5′)	112.8(2)
P(1)–S(2)	1.961(2)	S(2)–Sn–S(2′)	143.4(2)
P(1)–C(1)	1.787(8)	S(2)–Sn–C(5)	83.2(2)
P(1)–C(3)	1.825(10)	S(2)–Sn–C(5′)	79.7(2)
C(1)–C(2)	1.54(2)	C(5)–Sn–C(5′)	123.7(4)
C(3)–C(4)	1.55(2)		
		Sn–S(1)–P(1)	101.1(1)
		Sn–S(2)–P(1)	78.3(1)
		S(1)–P(1)–S(2)	112.2(1)
		S(1)–P(1)–C(1)	105.7(3)
		S(1)–P(1)–C(3)	109.7(3)
		S(2)–P(1)–C(1)	115.2(3)
		S(2)–P(1)–C(3)	113.9(3)
		C(1)–P(1)–C(3)	99.1(4)
		P(1)–C(3)–C(4)	116.6(8)
		P(1)–C(1)–C(2)	112.5(7)

[a] A primed atom is related to the corresponding unprimed atom by the molecular twofold symmetry axis.

The molecular structure of $Me_2Sn(S_2PEt_2)_2$ is very similar to those of the closely related compound $Me_2Sn(S_2PMe_2)_2$ [10] and $Me_2Sn(S_2AsMe_2)_2$ [27], and is consistent with the structure suggested by IR and ^{119m}Sn Mössbauer data.

As the $Me_2Sn(S_2PMe_2)_2$ and $Me_2Sn(S_2AsMe_2)_2$ molecules, the $Me_2Sn(S_2PEt_2)_2$ molecule has twofold crystallographic symmetry with the C_2 axis passing through Sn. The atoms of the $Sn(S_2P)_2$ fragment are approximately coplanar (deviations, referred to the S(1), Sn, S(1′) plane: S(2), +0.27; P(1), +0.05 Å). The molecular packing along the C_2 axis is almost identical with that observed in $Me_2Sn(S_2PMe_2)_2$ (values for this compound in parentheses): the Sn atoms lie 6.243 (6.218) Å apart, and the closest S ··· S contact is S(1) ··· S(2) at x, $y+1$, z, 3.663 (3.594) Å.

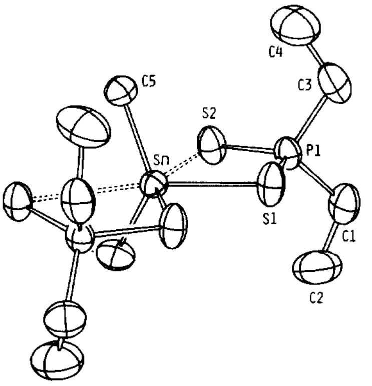


Fig. 1. The molecular structure of $Me_2Sn(S_2PEt_2)_2$.

The two phosphorus–sulfur bonds of the ligand are different, 2.054 and 1.961 Å, and may be regarded as single (long) and double (short) P–S bonds, suggesting that the diethyldithiophosphinato ligand is monodentate. In this case the coordination around tin must be regarded as severely distorted tetrahedral. This conclusion is supported by bond angles around tin: C–Sn–C 123.7(4), S(1)–Sn–C(5) 109.4(2), S(1)–Sn–C(5′) 112.8(2)°, but the bond angles S(1)–Sn ··· S(2) 68.1(1), S(1)–Sn–S(1′) 80.6(2) and S(2) ··· Sn ··· S(2′) 143.4(2)° are far from the tetrahedral value. They are similar to those observed in $Me_2Sn(S_2PMe_2)_2$ [10] and $Me_2Sn(S_2AsMe_2)_2$ [27]. Thus, in $Me_2Sn(S_2PMe_2)_2$ C–Sn–C 122.6(8), S(1)–Sn–C 109.2(5) and S(1)–Sn–S(1′) 79.9(2) and S(2)–Sn–S(2′) 142.3(1)°. In the dithioarsinate $Me_2Sn(S_2AsMe_2)_2$ C–Sn–C 121.8(5), S(1)–Sn–C 111.8(2), and S(1)–Sn–S(1′) 80.3(1)°.

The Sn–S(1) bond distances (2.476 Å) correspond to single covalent tin–sulfur bonds, but non-bonded tin–sulfur interactions are suggested by the interatomic distance Sn ··· S(2) 3.336(2) Å, which is longer than a single tin–sulfur bond but significantly shorter than the sum of Van der Waals radii (ca. 4 Å) [28]. Thus the tin atom is surrounded by two carbon atoms, two sulfur atoms at bonding distances, and two other sulfur atoms at semibonding distances, and the geometry at tin can be alternatively described as distorted octahedral, which implies that the dithiophosphinato ligands are severely anisobidentate [5].

The C–Sn–C value of 123.7° is in good agreement with that calculated from the *QS* value (127.6°), confirming again the validity of the use of *QS* values to predict the structure of diorganotin(IV) species.

Experimental

Benzyltin chlorides (from tin powder and $C_6H_5CH_2Cl$) [29] and $Et_2PS_2Na \cdot 2H_2O$ (by cleavage of $Et_2P(S)–P(S)Et_2$ with sulfur and sodium sulfide) [30] were made by published procedures. The other organotin chlorides were commercial products and were used without purification. The IR spectra were recorded on a SPECORD 75 IR Zeiss-Jena (DDR) with KBr pellets or CS_2 solutions. The ^1H NMR spectra were recorded on a TESLA B-487 spectrometer (made in Czechoslovakia) operating at 80 MHz, and mass spectra were recorded on an AEI MS-902S instrument. ^{119m}Sn Mössbauer spectra were recorded at 77 K on a Ranger Engineering constant-acceleration spectrometer with $Ca^{119m}SnO_3$ (New England Nuclear Corp.) as the source and as standard reference material for zero velocity.

Preparations of title compounds

A solution containing the organotin chloride was mixed with one containing a stoichiometric amount of sodium diethyldithiophosphinate; the solvents are shown in Table 1 (footnotes). The mixture was refluxed with stirring for 2 h, then the NaCl precipitate was filtered off and the hot filtrate was concentrated in vacuum. The white crystalline precipitate obtained was recrystallized from an organic solvent, except for trimethyltin and tribenzyltin derivatives, which were liquids. Melting points and the solvent used for recrystallization are indicated in Table 1. Yields were almost quantitative.

For $Me_2Sn(S_2PEt_2)_2$ aqueous solutions of the starting materials were used, and the deposited solid compound was filtered off from the reaction mixture and recrystallized from MeOH/EtOH (1/1).

TABLE 7

FINAL ATOMIC PARAMETERS FOR $Me_2Sn(S_2PEt_2)_2$

Atom	x	y	z	U_{eq} [a]
Sn	0.50000(0)	0.23109(8)	0.75000(0)	0.061(1)
S(1)	0.4319(1)	−0.0713(2)	0.6746(1)	0.096(1)
S(2)	0.3589(1)	0.3991(3)	0.6133(1)	0.089(1)
P(1)	0.3545(1)	0.0893(2)	0.5923(1)	0.071(1)
C(1)	0.2803(3)	−0.0385(12)	0.6029(6)	0.102(5)
C(2)	0.2658(6)	0.0097(25)	0.6899(8)	0.174(11)
C(3)	0.3498(5)	0.0155(14)	0.4811(6)	0.121(6)
C(4)	0.4055(6)	0.1247(30)	0.4489(8)	0.169(10)
C(5)	0.5448(3)	0.3915(13)	0.6635(5)	0.091(4)

[a] $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i \cdot a_j$.

X-Ray crystallography

The X-ray measurements were carried out at room temperature by use of a Philips PW 1100 single crystal diffractometer with graphite-monochromated Mo-K_α radiation (λ 0.71069 Å) and a crystal $0.2 \times 0.3 \times 0.3$ mm. Crystal data for $Me_2Sn(S_2PEt_2)_2$, $C_{10}H_{26}P_2S_4Sn$: monoclinic, space group $C2/c$, a 20.814(11), b 6.243(3), c 16.092(8) Å, β 105.42(8)°, D_x 1.500 g cm^{-3} for $Z = 4$. Intensity data (θ–2θ-mode) were collected in the range $4.5° \leq 2\theta \leq 50°$. Lp corrections, and in the later stages, an empirical absorption correction (μ 16.8 cm^{-1}) [31] were applied. Of the 1778 independent reflections, a set of 1715 with $|F_o| \geq 2\sigma(F_o)$ was used in the subsequent calculations.

The structure was solved by direct methods and refined by least squares. Hydrogen atoms were not located. The final R indices are R 0.059 and $R_w(F)$ 0.067. Atomic parameters are listed in Table 7.

The highest peak in a final difference Fourier map was 0.6 e A^{-3}. Further details of the crystal structure determination are available on request from the Fachinformationszentrum Energie-Physik-Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, by quoting the depository number CSD-52101, the names of the authors, and the journal citation.

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