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Synthesis and characterization of diorganotin diethylphosphorothioates. Crystal structures of $([Me_2Sn\{O(S)P(OEt)_2\}]_2O)_2$ and $[^tBu_2Sn(\mu\text{-}OH)\{O(S)P(OEt)_2\}]_2$

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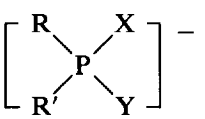
Abstract

Diorganotin diethylphosphorothioates of the types $[R_2Sn\{O(S)P(OEt)_2\}_2]$ (R = Me, Et, ^{n}Pr, ^{n}Bu or ^{t}Bu), $[Me_2SnCl\{O(S)P(OEt)_2\}]$, $([R_2Sn\{O(S)P(OEt)_2\}]_2O)_2$ (R = Me, Et, ^{n}Pr or ^{n}Bu) and $[^tBu_2Sn(\mu\text{-}OH)\{O(S)P(OEt)_2\}]_2$ have been synthesized. In the bis complexes, the ligand behaves in an anisobidentate fashion. All the complexes were characterized by elemental analyses, IR and NMR (^{1}H, ^{13}C, ^{31}P and ^{119}Sn) spectroscopy. The stereochemistry of these complexes is discussed on the basis of the NMR data. Crystal structures are reported for two representative complexes, namely $([Me_2Sn\{O(S)P(OEt)_2\}]_2O)_2$ and $[^tBu_2Sn(\mu\text{-}OH)\{O(S)P(OEt)_2\}]_2$.

Key words: Tin; Crystal structure; Thiophosphate

1. Introduction

Recently we have studied the chemistry of a number of organotin carboxylates and their isoable intermediate hydrolysis products [1]. Our interest in **I** arose because it is isoelectronic with the carboxylate moiety. A relatively large number of organotin(IV) complexes of **I** have been synthesized and characterized since their utility as biocides and as stabilizers was appreciated [2]. Subtle variations in the nature of the phosphorus-bound substituents in **I** or on the organotin moieties can be expected to lead to many structural diversites, by analogy with related carboxylate [3] and dithiolate [4] organotin complexes.



X = S or O
Y = O or S
R = alkyl, aryl or OR
R′ = alkyl, aryl or OR

(I)

A number of diorganotin(IV) complexes of **I**, where X = Y = O or S, and R = R′ = OR have been studied, both in the solid state and in solution [5–9]. However, there is a paucity of information about the stereochemistry of diorganotin(IV) complexes of **I**, where X = O and Y = S. Further, unlike organotin carboxylates, hydrolysis products of diorganotin(IV) complexes of **I**, which are expected to be formed *in vivo* when the complexes are used as biocides, have received little attention [5,10,11]. We present below the results of our investigations on diorganotin(IV) diethylphosphorothioates of the types $[R_2Sn\{O(S)P(OEt)_2\}_2]$, $[Me_2SnCl\{O(S)P(OEt)_2\}]$, $([R_2Sn\{O(S)P(OEt)_2\}]_2O)_2$, and $[^tBu_2Sn(\mu\text{-}OH)\{O(S)P(OEt)_2\}]_2$.

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2. Results and discussion

2.1. Synthesis

Diorganotin(IV) diethylthiophosphates have been synthesized by the following general routes (eqns. (1)–(5)) in quantitative yields.

$$R_2SnCl_2 + 2[NH_4][O(S)P(OEt)_2] \longrightarrow [R_2Sn\{O(S)P(OEt)_2\}_2] + 2NH_4Cl \tag{1}$$

$$[Me_2Sn\{O(S)P(OEt)_2\}_2] + Me_2SnCl_2 \longrightarrow 2[Me_2SnCl\{O(S)P(OEt)_2\}] \tag{2}$$

$$[(R_2SnCl)_2O]_2 + 4[NH_4][O(S)P(OEt)_2] \longrightarrow \{[R_2Sn\{O(S)P(OEt)_2\}]_2O\}_2 + 4NH_4Cl \tag{3}$$

$$4[R_2Sn\{O(S)P(OEt)_2\}_2] + 4NaOH \longrightarrow \{[R_2Sn\{O(S)P(OEt)_2\}]_2O\}_2 + 4NaO(S)P(OEt)_2 + 2H_2O \tag{4}$$

$$2[{}^tBu_2Sn\{O(S)P(OEt)_2\}_2] + 2NaOH \longrightarrow [{}^tBu_2Sn(\mu\text{-}OH)\{O(S)P(OEt)_2\}_2]_2 + 2NaO(S)P(OEt)_2 \tag{5}$$

The bis complexes, $[R_2Sn\{O(S)P(OEt)_2\}_2]$, are colourless oily liquids, whereas the other complexes are colourless crystalline materials. All the complexes are soluble in common organic solvents.

2.2. Infrared spectra

The IR spectra of the ammonium salt and the complexes displayed strong bands in the regions 1030–1170, 950–970, and 590–640 cm^{-1}, attributable to ν((P)–O–C), ν(P–O–(C)) and ν(P–S), respectively [12]. A medium to strong band in the region 510–580 cm^{-1}, absent from the spectrum of $[NH_4][O(S)P(OEt)_2]$, is assigned to ν(Sn–C). The absorption bands due to ν(Sn–O) and ν(Sn–S), expected in the region 300–500 cm^{-1}, have not been assigned owing to overlap with ligand vibrations. A broad absorption at 3150 cm^{-1} displayed by $[{}^tBu_2Sn(\mu\text{-}OH)\{O(S)P(OEt)_2\}]_2$ is attributed to ν(OH) stretching.

2.2. NMR spectra

2.2.1. Bis complexes

The bis complexes, $[R_2Sn\{O(S)P(OEt)_2\}_2]$, exhibited the expected integration and peak multiplicities in the ^{1}H NMR spectra (Table 1). The value of $^2J(^{119}Sn-^1H)$ for $[Me_2Sn\{O(S)P(OEt)_2\}_2]$ is in the range expected for six-coordinate dimethyltin compounds [7]. The $^{13}C\{^1H\}$ NMR spectra displayed a single set of resonances for Sn–R carbons. The ligand carbons appeared as doublets owing to $^nJ(^{31}P-^{13}C)$ couplings, the ^3J couplings being greater than the ^2J and the value of $^1J(^{119}Sn-^{13}C)$ greater than those reported for four-coordinate diorganotin(IV) complexes. The C–Sn–C angle for the dimethyltin complex has been estimated as 131.2° from the relationship $[^1J = 10.7(\langle C-Sn-C\rangle)-778]$ established in the literature [13]. The C–Sn–C angle in octahedral diorganotin(IV) complexes varies from 110 to 180° depending on the *cis*-skew to regular *trans* arrangement of the R groups on the tin atom. The estimated C–Sn–C angle for the dimethyltin complex is in good agreement with that found in dimethyl bis(1-pyrrolethiocarboxylato)tin(IV) of 132.9(3)° and $\delta(^{119}Sn)$ −80 ppm [14]. The latter complex has a slightly distorted octahedral geometry, with the ligands bonded primarily through the sulfur atoms in an anisobidentate fashion. A similar situation was reported in the structure of $[Me_2Sn(OAc)_2]$, C–Sn–C 135.9(2)° and $\delta(^{119}Sn)$ −120 ppm [15], in which the acetate groups are coordinated to the Sn atom asymmetrically. The $^{119}Sn\{^1H\}$ NMR chemical shifts (Table 2) for $[R_2Sn\{O(S)P(OEt)_2\}_2]$ resemble closely those for $[Me_2Sn(OAc)_2]$ and dimethyl bis(1-pyrrolethiocarboxylato)tin(IV), indicating that the diethylphosphorothioate complexes adopt an anisobidentate mode of ligand bonding. However, the $^{119}Sn\{^1H\}$ resonance for $[{}^tBu_2Sn\{O(S)P(OEt)_2\}_2]$, which appeared as a triplet due to coupling with two equivalent phosphorus nuclei, is shifted considerably to high field compared with that for the corresponding $^nBu_2Sn(IV)$ derivative; this shielding is in accordance with literature data [16].

The $^{31}P\{^1H\}$ NMR spectra of the complexes in $CDCl_3$ solution displayed a singlet at approximately 49 ppm, indicating that both the ligand moieties are magnetically equivalent. The coupling $^2J(^{119}Sn-^{31}P)$ could not be detected when a $CDCl_3$ solution of $[^nBu_2Sn\{O(S)P(OEt)_2\}_2]$ was cooled from room temperature to −45°C, but line broadening ($\Delta 1/2 = 6$ Hz at room temperature and 27 Hz at −45°C), with no detectable change in chemical shift, was observed. By contrast the coupling ^2J(Sn–P) was observed at room temperature in the spectrum of $[{}^tBu_2Sn\{O(S)P(OEt)_2\}_2]$. These results suggest that the n-alkyltin(IV) derivatives are fluxional in solution whereas the $^tBu_2Sn$ complexes adopt a rigid stereochemistry. Interestingly, $[Me_2Sn\{X(Y)P(O^nBu)_2\}_2]$, where X = Y = O or S, showed ^2J(Sn–P) of 36 Hz (for X = Y = S) and 202 Hz (X = Y = O) at −30 and −40°C, respectively [17].

TABLE 1. ^{1}H and $^{31}P\{^{1}H\}$ NMR data (δ, ppm) for diorganotin(IV) dialkylthiophosphates in $CDCl_3$ solution

Complex	$^{31}P\{^{1}H\}$	^{1}H NMR data [a]	
		Sn–*R*	Ligand
$[NH_4][O(S)P(OEt)_2]$	56.9	–	1.27 (t, 7 Hz, CH_3); 3.98 (m, OCH_2–); 6.00 (br, NH_4)
$[Me_2Sn\{O(S)P(OEt)_2\}_2]$	49.0	1.10 (s, $^{2}J(^{117/119}Sn–^{1}H)$ = 82 Hz	1.22 (t, 7 Hz, CH_3); 4.00 (m, OCH_2–)
$[Et_2Sn\{O(S)P(OEt)_2\}_2]$	48.4	1.12–2.25 (m, Sn–Et + $OCCH_3$)	4.00 (m, OCH_2–)
$[{}^{n}Pr_2Sn\{O(S)P(OEt)_2\}_2]$	48.6	0.95–2.00 (m, br, Sn–Pr + $OCCH_3$)	4.00 (m, OCH_2–)
$[{}^{n}Bu_2Sn\{O(S)P(OEt)_2\}_2]$	48.6	0.75–1.85 (m, br, Sn–Bu, $OCCH_3$)	4.02 (m, OCH_2–)
$[{}^{t}Bu_2Sn\{O(S)P(OEt)_2\}_2]$	48.9 $^{2}J(^{119}Sn–^{31}P)$ = 88 Hz	1.40 (s, $^{3}J(^{119}Sn–^{1}H)$ = 124 Hz)	1.25 (t, 7 Hz, CH_3); 4.00 (m, OCH_2–)
$[Me_2SnCl\{O(S)P(OEt)_2\}]$	37.6	1.24 (s, $^{2}J(^{119}Sn–^{1}H)$ = 74 Hz)	1.38 (t, 7 Hz, CH_3); 4.16 (m, OCH_2–)
$([Me_2Sn\{O(S)P(OEt)_2\}]_2O)_2$	58.7 $^{2}J(^{117/119}Sn–^{31}P)$ = 34 Hz	1.07, 1.11 (m)	1.28 (t, 7 Hz, CH_3); 4.00 (br, m, OCH_2–)
$([Et_2Sn\{O(S)P(OEt)_2\}]_2O)_2$	56.6 $^{2}J(^{117/119}Sn–^{31}P)$ = 44 Hz	1.37–1.91 (m)	1.24 (t, 7 Hz, CH_3); 3.99 (m, OCH_2–)
$([{}^{n}Pr_2Sn\{O(S)P(OEt)_2\}]_2O)_2$	56.5 $^{2}J(^{117/119}Sn–^{31}P)$ = 42 Hz	1.03 (t, Sn–$CCCH_3$) 1.50–1.84 (m, Sn–CH_2CH_2)	1.28 (t, 7 Hz, CH_3); 3.97 (m, OCH_2–)
$([{}^{n}Bu_2Sn\{O(S)P(OEt)_2\}]_2O)_2$	58.9 $^{2}J(^{117/119}Sn–^{31}P)$ = 50 Hz	0.90–1.74 (m, Sn–Bu + $OCCH_3$)	4.01 (m, OCH_2–)
$[{}^{t}Bu_2Sn(\mu\text{-}OH)\{O(S)P(OEt)_2\}]_2$	56.4 $^{2}J(^{119}Sn–^{31}P)$ = 206 Hz $^{2}J(^{117}Sn–^{31}P)$ = 197 Hz	1.40 (s, $^{3}J(^{119}Sn–^{1}H)$ = 120 Hz)	1.25 (t, 7 Hz, CH_3); 4.00 (m, OCH_2–)

[a] s, singlet; t, triplet; m, multiplet; br, broad.

TABLE 2. $^{13}C\{^{1}H\}$ and $^{119}Sn\{^{1}H\}$ NMR data (δ, ppm) for diorganotin(IV) dialkylthiophosphates in $CDCl_3$ solution

Complex	$^{119}Sn\{^{1}H\}$	^{13}C NMR data [a]	
		Sn–*R*	Ligand
$[Me_2Sn\{O(S)P(OEt)_2\}_2]$	–122	9.8, ^{1}J(Sn–C) = 626 Hz	15.8 (d, 7.8 Hz, Me); 63.4 (d, 5.7 Hz, OCH_2)
$[Et_2Sn\{O(S)P(OEt)_2\}_2]$	–137	9.2 (C-2, *J*(Sn–C) = 42 Hz); 22.0 (C-1, *J*(Sn–C) = 553 Hz);	15.7 (d, 7.8 Hz, Me); 63.3 (d, 6.0 Hz, OCH_2)
$[{}^{n}Pr_2Sn\{O(S)P(OEt)_2\}_2]$	–132	17.6 (C-3); 18.5 (C-2); 31.8 (C-1, *J*(Sn–C) = 521 Hz)	15.8 (d, 6.8 Hz, Me); 63.4 (d, 5.0 Hz, OCH_2)
$[{}^{n}Bu_2Sn\{O(S)P(OEt)_2\}_2]$	–129	13.2 (C-4); 26.0 (C-3); 26.8 (C-2); 29.1 (C-1)	15.6 (d, 7.7 Hz, Me); 63.4 (d, 5.7 Hz, OCH_2)
$[{}^{t}Bu_2Sn\{O(S)P(OEt)_2\}_2]$	–203 (t, ^{2}J(Sn–P) = 89 Hz)	29.7 (C-2); 45.3 (C-1, *J*(Sn–C) = 463 Hz)	15.8 (d, 7.8 Hz, Me); 63.6 (d, 5.4 Hz, OCH_2)
$[Me_2SnCl\{O(S)P(OEt)_2\}]$	–27 [b]	9.3 (*J*(Sn–C) = 557 Hz)	15.8 (d, 7.7 Hz, Me); 64.0 (d, 6.4 Hz, OCH_2)
$([Me_2Sn\{O(S)P(OEt)_2\}]_2O)_2$	–124 (s, br) –145 (t, ^{2}J(Sn–P) = 39 Hz)	8.13, 8.54 (*J*(Sn–C) = 664 Hz)	16.0 (d, 8.2 Hz, Me); 63.2 (d, 5.1 Hz, OCH_2)
$([Et_2Sn\{O(S)P(OEt)_2\}]_2O)_2$	–	9.4 (C-2); 20.6, 20.8 (C-1)	16.0 (d, 8.8 Hz, Me); 63.4 (br, OCH_2)
$([{}^{n}Pr_2Sn\{O(S)P(OEt)_2\}]_2O)_2$	–146 (s) –176 (t, ^{2}J(Sn–P) = 48 Hz)	18.2 (C-3); 29.3, 29.9 C-2); 30.2, 30.5 (C-1)	15.9 (d, 8.0 Hz, Me); 63.2 (br, OCH_2)
$([{}^{n}Bu_2Sn\{O(S)P(OEt)_2\}]_2O)_2$	–144 (s) –172 (t, ^{2}J(Sn–P) = 51 Hz)	13.0 (C-4); 26.3, 26.4, 27.3 (C-1 to C-3)	15.5 (d, 8.4 Hz, Me); 62.8 (d, 4.3 Hz, OCH_2)
$[{}^{t}Bu_2Sn(\mu\text{-}OH)\{O(S)P(OEt)_2\}]_2$	–289 (t, ^{2}J(Sn–P) = 201 Hz)	30.0 (C-2); 41.8 (C-1)	16.1 (d, 7.9 Hz, Me); 62.8 (d, 5.2 Hz, OCH_2)

[a] s, singlet; d, doublet; t, triplet; br, broad. [b] $\Delta 1/2 = 2346$ Hz.

2.2.2. Mono-chloro complex

The observed values of $^2J(^{119}Sn-^1H)$ (74 Hz) and $^1J(^{119}Sn-^{13}C)$ (557 Hz) for $[Me_2SnCl\{O(S)P(OEt)_2\}]$ are higher than those reported for four-coordinate dimethyltin(IV) complexes [7]. The $^{119}Sn\{^1H\}$ NMR signal (δ -27 ppm) is shifted to high field by 168 ppm from that for four-coordinate dimethyltin dichloride. The ^{119}Sn NMR resonance is broad ($\Delta 1/2 = 2346$ Hz) owing to a quadrupolar relaxation mechanism due to the chloride nucleus. The ^1H, ^{13}C and ^{119}Sn NMR data for this complex are similar to those reported for $[R_2SnCl\{S_2P(OR')\}]$, for which five-coordinate geometries have been suggested [8].

2.2.3. Hydrolysis products of $[R_2Sn\{O(S)P(OEt)_2\}_2]$

The hydrolysis of di-n-alkyltin bis(diethylphosphorothioates) with base readily gave $([R_2Sn\{O(S)P(OEt)_2\}]_2O)_2$, which can also be obtained by the reaction of $[(R_2SnCl)_2O]_2$ with the ammonium salt of the ligand. However, the hydrolysis of di-tert-butyltin(IV) complex gave a hydroxo-bridged complex $[^tBu_2Sn(\mu\text{-}OH)\{O(S)P(OEt)_2\}]_2$.

The ^1H NMR spectrum of the dimethyltin(IV) complex exhibited two Sn–Me proton signals whereas the $^tBu_2Sn(IV)$ complex showed only one resonance for the ^tBu protons. The ^{13}C NMR spectra of $([R_2Sn\{O(S)P(OEt)_2\}]_2O)_2$ displayed two signals for the C-1 carbon resonance. However, the signal from the ligand carbons appeared as doublets due to phosphorus couplings. The ^1H and ^{13}C NMR data are similar to those for the dicarboxylato tetraorganostannoxane dimers reported recently [1].

The ^{31}P NMR spectra exhibited a singlet with only one set of $^2J(Sn-P)$ couplings clearly resolved at room temperature. This indicates that all the ligand fragments are magnetically equivalent. It is noteworthy that for the $[(^nBu_2SnF)_2O]_2$ complex, two sets of $^1J(Sn-F)$, attributable to exo- and endo-cyclic tin site couplings, have been observed [18]. The $^{119}Sn\{^1H\}$ NMR spectra showed a triplet and a singlet, indicating that one tin site is coupled with two phosphorus nuclei whereas the other has little interaction with the ligand moiety. From the crystal structure of $([Me_2Sn\{O(S)P(OEt)_2\}]_2O)_2$ (see below), it is evident that the endocyclic tin centre has a weaker interaction with the ligand, and hence the singlet observed in each of the ^{119}Sn NMR spectra is attributed to this tin atom. In general, the opposite trend is observed for ^{119}Sn NMR shielding in tetraorganodistannoxanes, the endocyclic tin atom being more shielded [18] because it has either a higher coordination number or is engaged in greater interaction with a larger number of electronegative substituents than that of the exocyclic tin atom.

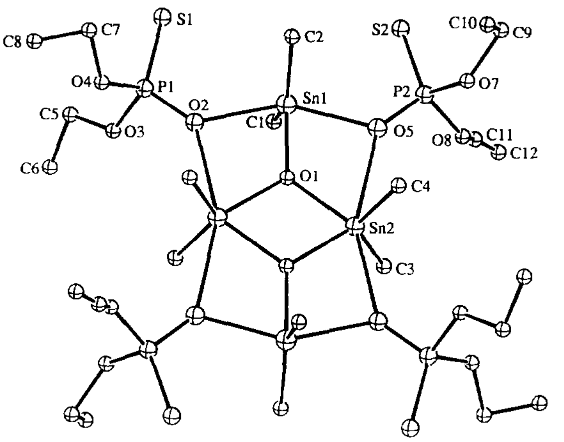

Fig. 1. Molecular structure and crystallographic numbering scheme for $([Me_2Sn\{O(S)P(OEt)_2\}]_2O)_2$.

The ^{31}P NMR spectrum of $[^tBu_2Sn(\mu\text{-}OH)\{O(S)P(OEt)_2\}]_2$ displayed a singlet at δ 56.4 ppm with a much larger $^2J(Sn-P)$ coupling than that for the corresponding n-alkyltin(IV) derivatives discussed above. The $^{119}Sn\{^1H\}$ NMR showed a doublet (δ -289 ppm) suggesting the presence of one phosphorus ligand per tin atom. Recently, a number of $[^tBu_2Sn(\mu\text{-}OH)(O_2CR')]_2$ complexes have been reported which show the ^{119}Sn NMR resonance at about δ -267 ppm [16]. Evidently in the di-tert-butyltin(IV) hydroxy-bridged complexes, the nature of the X group, *i.e.* $\{O(S)P(OEt)_2\}$ or O_2CR', has little influence on the ^{119}Sn NMR chemical shifts. The presence of the hydroxy group is indicated in the IR spectrum of the complex.

3. X-Ray structures

3.1. Molecular structure of $([Me_2Sn\{O(S)P(OEt)_2\}]_2O)_2$

The molecular structure of $([Me_2Sn\{O(S)P(OEt)_2\}]_2O)_2$ is illustrated in Fig. 1 and selected interatomic parameters are listed in Table 3. Severe disorder in the structure, primarily associated with the ethyl substituents, resulted in a less than optimal analysis, with relatively high errors associated with the derived parameters, but nevertheless the structure was determined unambiguously. The structure is comprised of discrete molecules, with no significant intermolecular interactions in the lattice; the closest non-hydrogen contact occurs between the O(7) and C(5)″ atoms, at 3.42(3) Å (symmetry operation: $-1+x,y,z$).

The molecule is centrosymmetric about a central Sn_2O_2 core with two independent tin centres, Sn(1) and Sn(2). Each of the two exocyclic Sn(2) atoms is connected to the central core *via* the oxygen atom with the result that both O(1) atoms are three-coordinate. Further links between the tin atoms are provided by

TABLE 3. Selected interatomic bond distances (Å) and angles (°) in ([$Me_2Sn\{O(S)P(OEt)_2\}]_2O)_2$

Sn(1)–O(1)	1.989(9)	Sn(1)–O(2)	2.25(1)
Sn(1)–O(5)	2.21(1)	Sn(1)–C(1)	2.10(2)
Sn(1)–C(2)	2.09(2)	Sn(2)–O(1)	2.034(9)
Sn(2)–O(1′) [a]	2.010(9)	Sn(2)–O(2′)	2.60(1)
Sn(2)–O(5)	2.77(1)	Sn(2)–C(3)	2.09(2)
Sn(2)–C(4)	2.07(1)	S(1)–P(1)	1.904(7)
S(2)–P(2)	1.898(7)	P(1)–O(2)	1.50(1)
P(1)–O(3)	1.54(2)	P(1)–O(4)	1.59(2)
P(2)–O(5)	1.48(1)	P(2)–O(7)	1.57(2)
P(2)–O(8)	1.58(2)		
O(1)–Sn(1)–O(2)	74.1(4)	O(1)–Sn(1)–O(5)	76.3(4)
O(1)–Sn(1)–C(1)	108.6(6)	O(1)–Sn(1)–C(2)	109.5(6)
O(2)–Sn(1)–O(5)	150.4(4)	O(2)–Sn(1)–C(1)	92.8(6)
O(2)–Sn(1)–C(2)	93.3(6)	O(5)–Sn(1)–C(1)	96.2(6)
O(5)–Sn(1)–C(2)	97.0(6)	C(1)–Sn(1)–C(2)	141.6(8)
O(1)–Sn(2)–O(1′)	73.6(4)	O(1)–Sn(2)–O(2′)	139.7(3)
O(1)–Sn(2)–O(5)	63.3(3)	O(1)–Sn(2)–C(3)	106.9(6)
O(1)–Sn(2)–C(4)	107.9(5)	O(1′)–Sn(2)–O(2′)	66.1(3)
O(1′)–Sn(2)–O(5)	136.9(3)	O(1′)–Sn(2)–C(3)	111.3(6)
O(1′)–Sn(2)–C(4)	109.1(6)	O(2′)–Sn(2)–O(5)	157.0(3)
O(2′)–Sn(2)–C(3)	87.4(5)	O(2′)–Sn(2)–C(4)	86.6(5)
O(5)–Sn(2)–C(3)	82.4(5)	O(5)–Sn(2)–C(4)	85.1(5)
C(3)–Sn(2)–C(4)	132.3(7)	S(1)–P(1)–O(2)	115.5(5)
S(1)–P(1)–O(3)	114.5(7)	S(1)–P(1)–O(4)	112.4(8)
O(2)–P(1)–O(3)	102.7(8)	O(2)–P(1)–O(4)	107.4(8)
O(3)–P(1)–O(4)	103 (1)	S(2)–P(2)–O(5)	115.2(5)
S(2)–P(2)–O(7)	113.7(7)	S(2)–P(2)–O(8)	113.6(8)
O(5)–P(2)–O(7)	105.8(8)	O(5)–P(2)–O(8)	106.7(9)
O(7)–P(2)–O(8)	100 (1)	Sn(1)–O(1)–Sn(2)	128.0(5)
Sn(2)–O(1)–Sn(2′)	106.4(4)	Sn(1)–O(2)–Sn(2′)	94.1(4)
Sn(1)–O(2)–P(1)	125.3(6)	Sn(2′)–O(2)–P(2)	140.2(6)
Sn(1)–O(5)–Sn(2)	92.4(4)	Sn(1)–O(5)–P(2)	124.6(6)
Sn(2)–O(5)–P(2)	142.9(6)		

[a] Primed atoms are related by centre of inversion.

bridging oxygen atoms of the diethylphosphorothioate ligands which are coordinated exclusively via their phosphorus-bound oxygen atoms, there being no significant interactions between the sulfur and tin atoms. This arrangement has the consequence that the tin atoms are in different coordination geometries, as indicated by the NMR studies.

The Sn(1) atom exists in a distorted trigonal bipyramidal geometry in which the axial positions are occupied by two bridging oxygen atoms of the diethylphosphorothioate ligand and the basal plane is defined by an oxygen atom of the Sn_2O_2 core and the two methyl substituents; the Sn(1) atom lies 0.059(1) Å out of the trigonal plane in the direction of the O(5) atom. The Sn(1) ··· S(1) and Sn(1) ··· S(2) separations of 3.637(6) and 3.548(6) Å, respectively, are not indicative of significant bonding interactions between these atoms. In contrast to the Sn(1) atom, which is five-coordinate, the endocyclic Sn(2) atom is six-coordinate. The Sn(2) atom is coordinated by the O(1) atoms, associated with the Sn_2O_2 core, two methyl groups and two oxygen atoms, each derived from a bridging oxygen atom of the diethylphosphorothioate ligand. The Sn(2)–O(1) and Sn(2)–O(1′) bond distances, of 2.034(9) and 2.010(9) Å, respectively, are significantly shorter than the Sn(2)–O(5) and Sn(2)–O(2′) distances of 2.77(1) and 2.60(1) Å, respectively. The two methyl groups define an angle of 132.3(7)° at the tin atom and hence the coordination geometry about the Sn(2) atom is best described as based on a skew-trapezoidal bipyramid, with the organic groups lying over the weaker of the Sn(2)–O interactions. In this description, the Sn(2) atom lies 0.015(1) Å out of the basal plane, which is planar to within ±0.01 Å, in the direction of the C(4) atom.

The presence of an $R_8Sn_4O_2$ framework has often been observed, in particular in the dicarboxylato tetraorganodistannoxanes [3]. In most of the crystallographically characterized examples, the carboxylate ligands employ both oxygen atoms in coordination to the tin atom and hence the structural type reported here for ([$Me_2Sn\{O(S)P(OEt)_2\}]_2O)_2$ resembles more closely that in the dichlorotetraorganodistannoxane complexes such as ([$Me_2SnCl]_2O)_2$ [19], ([$^iPr_2SnCl]_2O)_2$ [20] and ([$Ph_2SnCl]_2O)_2$ [21], the bridging chloride atoms being replaced by the bridging oxygen atoms of the diethylphosphorothioate ligands.

3.2. Molecular structure of [$^tBu_2Sn(\mu$-$OH)\{O(S)P(OEt)_2\}]_2$

The molecular structure of [$^tBu_2Sn(\mu$-OH)$\{O(S)P(OEt)_2\}]_2$ is shown in Fig. 2 and important parameters are listed in Table 4. The lattice is comprised of discrete molecular entities with the closest non-hydrogen intermolecular contact occurring between the O(3) and C(1)′ atoms of 3.66(2) Å (symmetry operation: $+x$, $0.5-y$, $0.5+z$). The structure of [$^tBu_2Sn(\mu$-OH)$\{O(S)P(OEt)_2\}]_2$ is centrosymmetric about a central $Sn_2(OH)_2$ core. The tin atom is five-coordinate, being bonded to the oxygen atoms of the central core, the carbon atoms of the tert-butyl groups, and to the

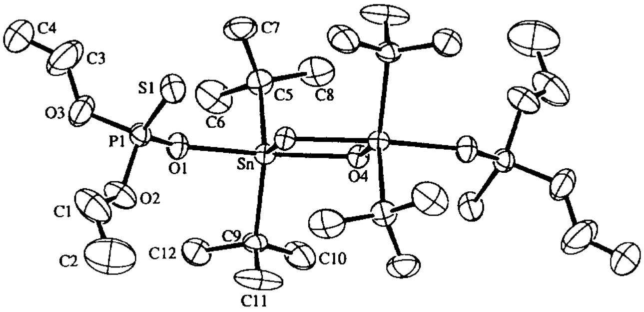

Fig. 2. Molecular structure and crystallographic numbering scheme for [$^tBu_2Sn(\mu$-OH)$\{O(S)P(OEt)_2\}]_2$.

TABLE 4. Selected interatomic bond distances (Å) and angles (°) in $[^{t}Bu_2Sn(\mu\text{-}OH)\{O(S)P(OEt)_2\}]_2$

Sn–O(1)	2.121(7)	Sn–O(4)	2.197(6)
Sn–O(4′) [a]	2.018(6)	Sn–C(5)	2.15(1)
Sn–C(9)	2.17(1)	S(1)–P(1)	1.915(4)
P(1)–O(1)	1.481(7)	P(1)–O(2)	1.541(9)
P(1)–O(3)	1.561(9)		
O(1)–Sn–O(4)	156.0(2)	O(1)–Sn–O(4′)	86.5(2)
O(1)–Sn–C(5)	92.9(4)	O(1)–Sn–C(9)	93.7(4)
O(4)–Sn–O(4′)	69.5(3)	O(4)–Sn–C(5)	99.0(4)
O(4)–Sn–C(9)	96.7(3)	O(4′)–Sn–C(5)	117.9(4)
O(4′)–Sn–C(9)	117.8(3)	C(5)–Sn–C(9)	124.1(4)
S(1)–P(1)–O(1)	116.8(3)	S(1)–P(1)–O(2)	114.2(4)
S(1)–P(1)–O(3)	113.3(4)	O(1)–P(1)–O(2)	104.2(5)
O(1)–P(1)–O(3)	106.9(5)	O(2)–P(1)–O(3)	99.7(6)
Sn–O(1)–P(1)	142.4(4)	Sn–O(4)–Sn′	110.5(3)

[a] Primed atoms are related by centre of inversion.

O(1) atom derived from a monodentate diethylphosphorothioate ligand; the Sn $\cdots$ S(1) separation of 4.110(3) Å is not indicative of a bonding interaction. In this description, the O(1) and O(4) atoms define the axial positions (O(1)–Sn–O(4) is 156.0(2)°) in a distorted trigonal bipyramidal geometry, and the Sn atom lies 0.0426(6) Å out of the trigonal plane in the direction of the O(1) atom; the C(5)–Sn–C(9) angle is 124.1(4)°. An intramolecular $OH \cdots S$ interaction of 3.105(7) Å is noted.

The structure reported here for $[^{t}Bu_2Sn(\mu\text{-}OH)\{O(S)P(OEt)_2\}]_2$ is similar to that reported previously for $[Ph_2Sn(\mu\text{-}OH)\{O(S)P(OPh)_2\}]_2$ [11]. The structure determination of $[^{t}Bu_2Sn(\mu\text{-}OH)\{O(S)P(OEt)_2\}]_2$ confirms the general observation that the dialkyl- (or diaryl-) phosphorothioate ligand coordinates to tin through the oxygen rather than the sulfur atom [11,22,23].

4. Conclusion

The size of the donor atom (O or S) and the nature of the tin-and phosphorus-bound substituents play important roles in the determination of stereochemistry of the complexes reported herein. Change in any of these variables leads to different structural forms. The hydrolysis of the di-n-alkyl derivatives gives rise to a novel structural form of tetraorganodistannoxane dimer, and the diphenyl [11] or di-tert-butyl derivatives afford a hydroxy-bridged complex.

5. Experimental details

5.1. Materials and instrumentation

Diorganotin(IV) dichloride, $(R_2SnCl)_2O$ and diethyl hydrogen phosphate [24] (δ $^{31}P\{^{1}H\} = 7.0$ ppm) were prepared by the published methods. The reaction of $(EtO)_2P(O)H$ with sulfur in the presence of triethylamine in diethyl ether gave $[Et_3NH][(EtO)_2P(O)S]$ [25], which on acidification with dilute HCl gave the free acid, $(EtO)_2P(O)SH$. The ammonium salt was prepared by bubbling anhydrous ammonia through a hexane solution of $(EtO)_2P(O)SH$, whereupon a white crystalline solid was obtained; m.p. 134–135°C.

The IR spectra were recorded either as neat liquids or Nujol mulls between CsI optics on a Perkin-Elmer spectrophotometer. The ^{1}H (80 and 200 MHz), ^{13}C (20 and 50 MHz), ^{31}P (32.203 MHz) and ^{119}Sn (29.604 and 111.82 MHz) were recorded with $CDCl_3$ solutions on Varian FT-80A, XL-300 and Bruker AC-200 NMR spectrometers. Chemical shifts are reported in ppm from the internal chloroform peak (δ 7.26 ppm for ^{1}H and δ 77.0 ppm for ^{13}C spectra), external 85% H_3PO_4 (for ^{31}P) and 33% Me_4Sn in C_6D_6 (for ^{119}Sn). Microanalyses were performed by the Analytical Chemistry Division, BARC; analytical data are listed in Table 5.

5.2. Preparations

5.2.1. Preparation of $[^{t}Bu_2Sn\{O(S)P(OEt)_2\}_2]$

To a vigorously stirred benzene suspension of $[NH_4][O(S)P(OEt)_2]$ (2.35 g, 12.55 mmol) under anhydrous conditions was added a solution of $^{t}Bu_2SnCl_2$

TABLE 5. Melting point and analytical data for diorganotin(IV) dialkylthiophosphates

Complex	m.p. (°C)	Analysis (%) [a]			
		C	H	P	S
$[Me_2Sn\{O(S)P(OEt)_2\}_2]$	Oil	24.1 (24.6)	5.0 (5.4)	12.8 (12.7)	12.9 (13.2)
$[Et_2Sn\{O(S)P(OEt)_2\}_2]$	Oil	26.8 (28.0)	5.6 (5.9)	12.0 (12.0)	12.0 (12.4)
$[^{n}Pr_2Sn\{O(S)P(OEt)_2\}_2]$	Oil	31.0 (31.0)	5.8 (6.3)	11.2 (11.4)	11.4 (11.8)
$[^{n}Bu_2Sn\{O(S)P(OEt)_2\}_2]$	Oil	33.1 (33.6)	6.4 (6.7)	11.2 (10.9)	10.8 (11.2)
$[^{t}Bu_2Sn\{O(S)P(OEt)_2\}_2]$	Oil	32.1 (33.6)	6.3 (6.7)	10.7 (10.9)	11.0 (11.2)
$[Me_2SnCl\{O(S)P(OEt)_2\}]$	85–86	20.5 (20.4)	4.6 (4.6)	9.3 (8.8)	9.4 (9.1)
$([Me_2Sn\{O(S)P(OEt)_2\}]_2O)_2$	181	22.0 (22.1)	4.9 (4.9)	9.3 (9.5)	10.0 (9.8)
$([Et_2Sn\{O(S)P(OEt)_2\}]_2O)_2$	116	27.0 (27.1)	5.6 (5.7)	9.3 (8.7)	–
$([^{n}Pr_2Sn\{O(S)P(OEt)_2\}]_2O)_2$	75	31.2 (31.4)	6.2 (6.3)	8.1 (8.1)	8.6 (8.4)
$([^{n}Bu_2Sn\{O(S)P(OEt)_2\}]_2O)_2$	119–120	34.7 (35.2)	6.9 (6.9)	7.7 (7.5)	7.5 (7.8)
$[^{t}Bu_2Sn(\mu\text{-}OH)\{O(S)P(OEt)_2\}]_2$	166	34.0 (34.4)	6.9 (7.0)	7.6 (7.4)	8.2 (7.7)

[a] Calculated values in parentheses.

(1.90 g, 6.26 mmol) in benzene (15 cm^3). Stirring was continued for 4 h at room temperature. Precipitated ammonium chloride was filtered off through a sinter, and the filtrate was concentrated *in vacuo* to leave only an oily liquid (3.35 g, yield 94 %). The other [$R_2Sn\{O(S)P(OEt)_2\}_2$] complexes were prepared similarly.

5.2.2. Preparation of [$Me_2SnCl\{O(S)P(OEt)_2\}$]

A benzene solution (15 cm^3) of dimethyltin dichloride (0.95 g, 4.32 mmol) was added to a solution of [$Me_2Sn\{O(S)P(OEt)_2\}_2$] (2.10 g, 4.31 mmol) under anhydrous conditions. The mixture was stirred at room temperature for 3 h, then the solvent was stripped off *in vacuo* to leave a white solid, which was recrystallized from a benzene/hexane mixture (1 : 1) at 0°C as colourless crystals (2.85 g, 93%).

5.2.3. Preparation of ([$Me_2Sn\{O(S)P(OEt)_2\}]_2O)_2$

An aqueous sodium hydroxide solution (12.5 cm^3, 0.51 N) was added dropwise with vigorous stirring at room temperature to an acetone solution (30 cm^3) of [$Me_2Sn\{O(S)P(OEt)_2\}_2$] (3.07 g, 6.31 mmol). Stirring was continued for 1 h and then distilled water (25 cm^3) was added to give a white precipitate, which was filtered off, washed three times with water, and dried, then recrystallized from an acetone/ethanol mixture (1 : 1) at 0°C to give colourless crystals (1.63 g, 79%). Hydrolysis of the other di-n-alkyltin complexes gave analogous complexes, which can also be made by the procedure described in Section 5.2.4.

5.2.4. Preparation of ([$^nPr_2Sn\{O(S)P(OEt)_2\}]_2O)_2$

To a benzene suspension of [NH_4][$S(O)P(OEt)_2$] (1.69 g, 9.04 mmol) was added a solution of [($^nPr_2SnCl)_2O]_2$ (2.24 g, 2.25 mmol). The mixture was stirred at room temperature for 4 h then filtered through a sinter. The filtrate was evaporated *in vacuo* to give a white solid, which was recrystallized from hexane (2.10 g, 60%). The compounds ([$^nBu_2Sn\{O(S)P(OEt)_2\}]_2O)_2$ and ([$Et_2Sn\{O(S)P(OEt)_2\}]_2O)_2$ were prepared similarly.

5.2.5. Preparation of ([$^tBu_2Sn(\mu\text{-}OH)\{O(S)P(OEt)_2\}]_2$

An aqueous sodium hydroxide solution (5.8 cm^3, 0.51 N) was added dropwise with stirring to an acetone solution (20 cm^3) of [$^tBu_2Sn\{O(S)P(OEt)_2\}_2$] (1.67 g, 2.93 mmol). The mixture was stirred for 1 h, during which a white precipitate separated. This was filtered off on a sinter, washed with water, dried, and recrystallized from an ethanol/hexane mixture (1 : 1) at 0°C.

5.3. X-Ray crystallography

Intensity data for both complexes were measured at room temperature on a Rigaku AFC6R diffractometer fitted with graphite monochromatized Mo Kα radiation, $\lambda = 0.71073$ Å, employing the ω–2θ scan technique in each case. Corrections were made for Lorentz and polarization effects [26], and for absorption by an empirical procedure [27]. Of the reflections measured those unique reflections which satisfied the $I \geq 3.0\sigma(I)$

TABLE 6. Crystal data for ([$Me_2Sn\{O(S)P(OEt)_2\}]_2O)_2$ and [$^tBu_2Sn(\mu\text{-}OH)\{O(S)P(OEt)_2\}]_2$

	([$Me_2Sn\{O(S)P(OEt)_2\}]_2O)_2$	[$^tBu_2Sn(\mu\text{-}OH)\{O(S)P(OEt)_2\}]_2$
Formula	$C_{12}H_{32}O_7P_2S_2Sn_2$	$C_{12}H_{29}O_4PSSn$
Mol. wt.	651.8	419.1
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	12.180(2)	9.307(6)
b (Å)	14.64(1)	24.47(1)
c (Å)	14.329(4)	9.408(3)
β (°)	92.16(2)	117.81(3)
V (Å^3)	2552(1)	1895(1)
Z	4 (2 dimers)	4 (2 dimers)
D_c (g cm^{-3})	1.696	1.469
F(000)	1288	856
μ (cm^{-1})	22.70	15.49
max./min. transmission coeff.	1.037, 0.946	1.093, 0.894
No. of data collected	6582	4259
No. of unique data	6300	3997
No. of unique reflections	3186	2136
R	0.058	0.034
R_w	0.083	0.051
Residual ρ_{max} (e Å^{-3})	0.79	0.40

criterion were used in the subsequent analysis. Crystal data are summarized in Table 6.

The structures were solved by direct methods [28], and each refined by a full-matrix least-squares procedure based on *F* [26]. For the refinement of ($[Me_2Sn\{O(S)P(OEt)_2\}]_2O)_2$ the non-ethyl, non-hydrogen atoms were refined with anisotropic thermal parameters. Disorder was noted in the structure, the C(8) and C(12) atoms being distributed over two positions and the C(10) atom over three positions, and so these atoms were refined isotropically and hydrogen atoms were not included in the model. For the refinement in the case of $[{}^tBu_2Sn(\mu\text{-}OH)\{O(S)P(OEt)_2\}]_2$, non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in the model in calculated positions (C–H 0.97 Å). The refinements were continued employing unit and sigma weights, respectively, until convergence; final refinement details are listed in Table 6. Fractional atomic coordinates are listed in Tables 6 and 7 and the numbering schemes are shown in Figs. 1 and 2, which were drawn with ORTEP [29] with 15 and 20% probability ellipsoids, respectively. Structure solution and refinement were performed with the TEXSAN package [26] installed on an Iris Indigo workstation. Complete lists of bond distances and bond angles, thermal parameters and H atom parameters have been deposited with the Cambridge Crystallographic Data Centre.

TABLE 7. Fractional atomic coordinates for ($[Me_2Sn\{O(S)P(OEt)_2\}]_2O)_2$

Atom	*x*	*y*	*z*
Sn(1)	0.07108(11)	0.64125(9)	0.16167(8)
Sn(2)	−0.12312(8)	0.49363(9)	0.03837(9)
S(1)	0.3383(5)	0.7499(5)	0.1944(4)
S(2)	−0.0794(5)	0.7279(5)	0.3496(5)
P(1)	0.3319(4)	0.6591(4)	0.0992(4)
P(2)	−0.1632(4)	0.6511(4)	0.2674(4)
O(1)	0.0265(6)	0.5527(7)	0.0621(7)
O(2)	0.2202(8)	0.6207(8)	0.0764(7)
O(3)	0.4005(12)	0.5728(12)	0.1218(13)
O(4)	0.3804(13)	0.6943(16)	0.0041(12)
O(5)	−0.1018(9)	0.6104(8)	0.1902(7)
O(7)	−0.2654(12)	0.6996(13)	0.2198(12)
O(8)	−0.2212(15)	0.5695(14)	0.3183(14)
C(1)	0.1398(16)	0.5687(15)	0.2757(12)
C(2)	0.0454(15)	0.7743(13)	0.1129(13)
C(3)	−0.1413(14)	0.3960(11)	0.1428(11)
C(4)	−0.2283(13)	0.5918(11)	−0.0177(11)
C(5)	0.5031(25)	0.5758(22)	0.1640(20)
C(6)	0.5448(24)	0.4793(22)	0.1731(20)
C(7)	0.3958(43)	0.7901(41)	−0.0277(35)
C(8) [a]	0.4920(54)	0.7721(50)	−0.0625(43)
C(8′) [a]	0.4618(66)	0.8340(54)	−0.0572(51)
C(9)	−0.3208(28)	0.7852(25)	0.2416(23)
C(10) [b]	−0.3380(111)	0.8286(87)	0.1479(76)
C(10′) [b]	−0.3427(85)	0.8584(66)	0.1937(73)
C(10″) [b]	−0.2856(76)	0.8231(73)	0.1778(79)
C(11)	−0.2191(42)	0.5312(35)	0.4208(37)
C(12) [a]	−0.2460(85)	0.4908(68)	0.4650(66)
C(12′) [a]	−0.3352(99)	0.5391(81)	0.4088(81)

[a] Atom has 50% site occupancy. [b] Atom has 33.3% site occupancy.

TABLE 8. Fractional atomic coordinates for $[{}^tBu_2Sn(\mu\text{-}OH)\{O(S)P(OEt)_2\}]_2$

Atom	*x*	*y*	*z*
Sn	−0.00082(8)	0.44076(3)	0.10040(8)
S(1)	0.2382(4)	0.3788(1)	−0.1373(5)
P(1)	0.1155(4)	0.3358(1)	−0.0623(4)
O(1)	0.0619(9)	0.3632(3)	0.0452(8)
O(2)	−0.0417(11)	0.3114(4)	−0.1972(11)
O(3)	0.2036(13)	0.2820(4)	0.0237(14)
O(4)	−0.0452(7)	0.5293(2)	0.0740(7)
C(1)	−0.0552(27)	0.2904(9)	−0.3424(27)
C(2)	−0.1991(32)	0.3020(13)	−0.4677(28)
C(3)	0.3567(27)	0.2726(10)	0.1221(34)
C(4)	0.4361(23)	0.2319(8)	0.1662(26)
C(5)	0.1953(14)	0.4394(5)	0.3424(11)
C(6)	0.1674(21)	0.3896(7)	0.4225(17)
C(7)	0.3560(16)	0.4316(7)	0.3429(16)
C(8)	0.1968(18)	0.4908(7)	0.4275(15)
C(9)	−0.2480(12)	0.4168(5)	0.0346(13)
C(10)	−0.3087(18)	0.4523(7)	0.1208(22)
C(11)	−0.3465(16)	0.4208(9)	−0.1418(18)
C(12)	−0.2534(17)	0.3584(6)	0.0764(22)

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