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Structural chemistry of organotin carboxylates

VIII *. Synthesis and spectroscopic properties of diorganotin(IV) complexes with thiophenoxyacetic acid. X-ray crystal structures of $[^nPr_2Sn(O_2CCH_2SPh)_2]$ and $\{[R_2Sn(O_2CCH_2SPh)]_2O\}_2$, R = ^{n}Pr, ^{n}Bu

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Abstract

Two types of diorganotin(IV) complexes i.e. $[R_2Sn(O_2CCH_2SPh)_2]$ (**1–5**) and $\{[R_2Sn(O_2CCH_2SPh)_2\text{-}O\}_2$ (**6–10**), R = Me, Et, ^{n}Pr, ^{n}Bu and ^{n}Oct, have been prepared in 1 : 2 and 1 : 1 molar ratios (tin:ligand) by reacting diorganotin oxide with thiophenoxyacetic acid. Characterization of the complexes was achieved using IR and ^{1}H NMR spectroscopy and in the case of the ^{n}Pr and ^{n}Bu complexes, by X-ray diffraction methods. The 1 : 2 compounds are monomeric with the Sn atoms existing in skew-trapezoidal planar geometries with asymmetrically coordinating carboxylate ligands and C–Sn–C angles of 136.7(2) and 140.7(2)° respectively. The 1 : 1 compounds adopt the familiar dicarboxylato tetraorganodistannoxane structural mode. The structures feature two bidentate bridging and two monodentate carboxylate ligands, and both Sn atoms in the centrosymmetric dimers are in distorted trigonal bipyramidal geometries.

Introduction

The major emphasis in previous papers in this series has been to determine whether the presence of an additional potential donor atom residing on the R′ group of a uninegative carboxylate ligand, has any affect on the structure adopted by organotin carboxylates [1–4]. As a general rule, when the additional donor atom is a N atom, as in 2-pyridinecarboxylate for example, the N atom invariably participates in formal coordination to the Sn atom and consequently has a direct bearing on the structure ultimately adopted by the compound [5]. In contrast, when

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* For part VII, see ref. 1.

the additional donor atom is an O or a S atom, no such interactions have been observed. Exceptions to this generalization are found, however, in the structures containing dinegative, mixed carboxylate/thiolate ligands, as in the compounds $[^nBu_2Sn(O_2CCH_2CH_2S)]_6$ [6] and $[Ph_3Sn(O_2CC_6H_4S)SnPh_3]$ in which significant Sn–S interactions are present [7].

In a recent communication [2], we reported the preparation and crystal structure of $[^nBu_2Sn(O_2CCH_2SPh)_2]$ in which the S atoms were found not to interact with the Sn atom. This paper reports full details of the preparation and characterization of this series of compounds, i.e. $[R_2Sn(O_2CCH_2SPh)_2]$ (**1–5**) and $\{[R_2Sn(O_2CCH_2SPh)]_2O\}_2$, (**6–10**) R = Me, Et, ^{n}Pr, ^{n}Bu and ^{n}Oct. In addition, the crystallographic characterization of the ^{n}Pr and ^{n}Bu compounds is reported. Original interest in these compounds arises from their biocidal activity as discussed elsewhere [8,9].

Results and discussion

Dialkyltin(IV) complexes of thiophenoxyacetic acid in 1 : 1 and 2 : 1 ratio have been prepared and characterized by elemental analysis, infrared and NMR spectroscopy, and in the case of the ^{n}Pr and ^{n}Bu derivatives, X-ray crystallography. Physical data for $[R_2Sn(O_2CCH_2SPh)_2]$ (**1–5**) and $\{[R_2Sn(O_2CCH_2SPh)]_2O\}_2$ (**6–10**) are listed in Table 1.

IR data for the free acid, its sodium salt and complexes are listed in Table 2. The free acid shows a broad O–H absorption at 3050–3500 cm^{-1} which is absent in the spectra of the ten complexes, showing the deprotonation and coordination of the carboxylate groups. IR spectral data of the complexes imply the presence of bidentate, chelating carboxylate groups, with $\Delta\nu = [\nu(COO)_{asym} - \nu(COO)_{ym}]$ greater than 200 cm^{-1}; i.e. approximately in the range observed for the sodium salt of the ligand [10]. The presence of a Sn–C absorption band in the 600–500 cm^{-1} region reveals a *trans*-configuration of the R_2Sn moiety. A band in the 510–420 cm^{-1} region is assigned to the stretching mode of the the Sn–O linkage. In the case of the 1 : 1 complexes $\{[R_2Sn(O_2CCH_2SPh)]_2O\}_2$, a strong band in the 690–630 cm^{-1} is attributed to ν(Sn–O–Sn) which indicates a Sn–O–Sn bridged structure for these complexes. The presence of two values for $\nu(COO)_{asym}$ and $\nu(COO)_{sym}$ in the

Table 1

Physical data for **1–10**

	Compound	colour	solvent [a]	% yield	m. pt. °C
1	$[Me_2Sn(O_2CCH2SPh)_2]$	white	methanol	81	123
2	$[Et_2Sn(O_2CCH_2SPh)_2]$	cream	methanol	83	98
3	$[^nPr_2Sn(O_2CCH_2SPh)_2]$	white	pet. ether [b]	80	100
4	$[^nBu_2Sn(O_2CCH_2SPh)_2]$	white	pet. ether	85	91–92
5	$[^nOct_2Sn(O_2CCH_2SPh)_2]$	white	pet. ether	82	95–97
6	$\{[Me_2Sn(O_2CCH_2SPh)]_2O\}_2$	white	methanol	80	130
7	$\{[Et_2Sn(O_2CCH_2SPh)]_2O\}_2$	cream	methanol	85	95
8	$\{[^nPr_2Sn(O_2CCH_2SPh)]_2O\}_2$	white	pet. ether	78	103
9	$\{[^nBu_2Sn(O_2CCH_2SPh)]_2O\}_2$	white	methanol/pet. ether	80	65
10	$\{[^nOct_2Sn(O_2CCH_2SPh)]_2O\}_2$	cream	– [c]	75	–

[a] Solvent of recrystallization. [b] Petroleum ether (60–80°C). [c] Liquid.

Table 2

Infrared data (200–4000 cm^{-1}) [a] for **1–10**

	Compound	$\nu(COO)_{asym}$	$\nu(COO)_{sym}$	$\Delta\nu$	ν(Sn–C)	ν(Sn–O)	ν(Sn–O–Sn)
	HO_2CCH_2SPh	1700s (C=O)	1310s (C–O)	390			
	NaO_2CCH_2SPh	1605s	1415s	190			
1	$[Me_2Sn(O_2CCH_2SPh)_2]$	1585vs, b	1350s	235	580s	500s	–
		1620vs	1385s	235	560s	455s	
2	$[Et_2Sn(O_2CCH_2SPh)_2]$	1610s, b	1375s	235	520s	495s	–
3	$[{}^{n}Pr_2Sn(O_2CCH_2SPh)_2]$	1595s	1360s	235	590s	505s	–
4	$[{}^{n}Bu_2Sn(O_2CCH_2SPh)_2]$	1585vs	1375s	210	600s	505m	–
5	$[{}^{n}Oct_2Sn(O_2CCH_2SPh)_2]$	1585s	1365s	220	590m	470w	–
					555w		
6	$\{[Me_2Sn(O_2CCH_2SPh)]_2O\}_2$	1580vs, b	1345s	235	560m	495s	630s
		1615vs	1385s	230	575sh	450sh	
7	$\{[Et_2Sn(O_2CCH_2SPh)]_2O\}_2$	1595vs	1365s	230	595s	485s	685s
		1600s	1350sh	250	550s	505s	
8	$\{[{}^{n}Pr_2Sn(O_2CCH_2SPh)]_2O\}_2$	1575s	1315s	260	590sh	450sh	640s
		1650s	1390s	260	610sh		
9	$\{[{}^{n}Bu_2Sn(O_2CCH_2SPh)]_2O\}_2$	1580s	1330s	250	565w	420sh	645s
		1635s	1345s	290	610w	450sh	
10	$\{[{}^{n}Oct_2Sn(O_2CCH_2SPh)]_2O\}_2$	1575s	1320s	255	555w		620s
		1625s	1390s	235	590m		

[a] Measured as KBr discs (neat for **10** between NaCl plates): s, strong; m, medium; w, weak; b, broad; sh, shoulder.

case of the 1 : 1 complexes indicates that the two carboxylate groups are asymmetrically bonded in these complexes.

The ^1H NMR spectra of the ligands and the complexes have been recorded in $CDCl_3$ solution (Table 3). In the spectra of the free ligand a sharp resonance is observed at δ 8.66 ppm which is absent in the spectra of the complexes, indicating replacement of the carboxylic acid proton by a diorganotin moiety on complex formation.

Table 3

^1H NMR (δ; ppm) data for **1–10** [a]

	Compound	phenyl H, m	$-CH_2-$, s	Sn–R
	HO_2CCH_2SPh [b]	6.95–7.46	3.56	–
1	$[Me_2Sn(O_2CCH_2SPh)_2]$	7.00–7.33	3.49	0.66s
2	$[Et_2Sn(O_2CCH_2SPh)_2]$	7.00–7.33	3.59	1.03–1.95m
3	$[{}^{n}Pr_2Sn(O_2CCH_2SPh)_2]$	7.06–7.23	3.59	0.72–1.62m
4	$[{}^{n}Bu_2Sn(O_2CCH_2SPh)_2]$	7.09–7.49	3.69	0.73–1.79m
5	$[{}^{n}Oct_2Sn(O_2CCH_2SPh)_2]$	7.09–7.29	3.59	0.79–1.26m
6	$\{[Me_2Sn(O_2CCH_2SPh)]_2O\}_2$	7.03–7.33	3.49	0.69s
7	$\{[Et_2Sn(O_2CCH_2SPh)]_2O\}_2$	7.00–7.23	3.59	1.00–1.85m
8	$\{[{}^{n}Pr_2Sn(O_2CCH_2SPh)]_2O\}_2$	7.06–7.29	3.66	0.75–1.62m
9	$\{[{}^{n}Bu_2Sn(O_2CCH_2SPh)]_2O\}_2$	7.06–7.29	3.59	0.75–1.66m
10	$\{[{}^{n}Oct_2Sn(O_2CCH_2SPh)]_2O\}_2$	7.06–7.29	3.52	0.82–1.49m

[a] s, singlet; m, multiplets. [b] δ COOH 8.66s ppm.

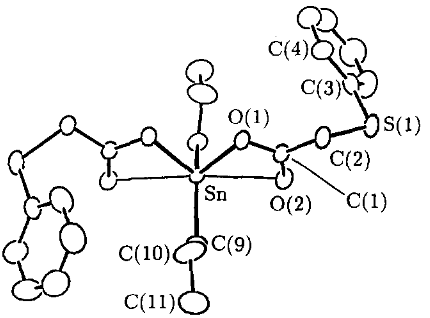

Fig. 1. Molecular structure and crystallographic numbering scheme employed for [^{n}Pr$_2$Sn(O$_2$CCH$_2$SPh)$_2$] 3.

The dimethyltin(IV) complexes show a show a single methyl resonance in the 0.66–0.69 ppm region thereby indicating a *trans*-disposition of the two methyl groups. In all other complexes a multiplet is observed in the 0.72–1.95 ppm region. It is difficult to distinguish the signals in this region but the number of protons calculated from the integration curve is equivalent to the number of protons expected from the proposed structures. Signals for the other groups, such as $-C_6H_5$, $-CH_2-$, appear at the same positions as in the free ligand.

The molecular structure of **3** is shown in Fig. 1 and selected interatomic parameters are listed in Table 4; interatomic parameters for **4** [2], which has a similar numbering scheme, are also listed in Table 4. Crystals of **3** and **4** contain

Table 4

Selected interatomic parameters for [R$_2$Sn(O$_2$CCH$_2$SPh)$_2$]

	R = ^{n}Pr	R = ^{n}Bu [2]
Sn–O(1)	2.114(3)	2.134(4)
Sn–O(2)	2.587(4)	2.559(5)
Sn–C(9)	2.098(5)	2.099(6)
C(1)–O(1)	1.291(5)	1.298(7)
C(1)–O(2)	1.211(4)	1.24(1)
C(1)–C(2)	1.512(7)	1.493(9)
C(2)–S(1)	1.796(5)	1.797(6)
S(1)–C(3)	1.758(7)	1.774(7)
O(1)–Sn–O(2)	54.1(1)	55.0(2)
O(1)–Sn–C(9)	104.5(2)	104.3(2)
O(1)–Sn–O(1′) [a]	79.5(1)	79.5(2)
O(1)–Sn–O(2′)	133.4(1)	134.5(2)
O(2)–Sn–C(9)	88.8(2)	88.4(2)
O(2)–Sn–O(2′)	172.5(1)	170.5(2)
C(9)–Sn–C(9′)	136.7(2)	140.7(2)
O(1)–C(1)–O(2)	121.0(4)	119.9(6)
O(1)–C(1)–C(2)	115.6(6)	116.8(7)
O(2)–C(1)–C(2)	123.2(6)	123.3(6)
C(1)–C(2)–S(1)	113.5(5)	114.1(5)
C(2)–S(1)–C(3)	102.7(5)	102.6(3)

[a] Primed atoms are related by crystallographic 2-fold axis.

discrete molecular units of the compounds there being no significant intermolecular interactions in either lattice. The Sn atom in **3** and **4** lies on a crystallographic 2-fold axis of symmetry implying the presence of one unique carboxylate ligand in the structure. The Sn atoms exist in skew-trapezoidal planar bipyramidal geometries with the basal plane being occupied by four O atoms derived from the symmetry related carboxylate ligands. The carboxylate ligands coordinate the Sn atom with disparate Sn–O bonds such that Δ(Sn–O) > 0.4 Å. The disparity in the Sn–O bond distances is reflected in the associated C–O bond distances with the shorter C–O bond being associated with the long Sn–O bond. The two organo groups occupy positions approximately *trans* to each other, the distortion being such that these groups lie over the Sn–O(2) (i.e. the weaker Sn–O) interactions.

There are now several crystal structures in the literature of compounds of the general formula $[R_2Sn(O_2CR')_2]$ and, to a first approximation, the interatomic parameters determined for **3** and **4** agree well with those reported for these related compounds [5]. However, meaningful comparison between the compounds is not possible owing to the fact that there is no consistency in the R and R′ groups across the series. The structure determinations of **3** and **4** provide the opportunity to compare two $[R_2Sn(O_2CR')_2]$ compounds in which the R groups have changed but the R′ groups remained constant.

As can be seen from Table 4 there are some interesting differences between some of the bond distances and angles defining the Sn atom geometries in these compounds. While individual differences between pairs of parameters may only be marginally different, when analysed as a part of a set, meaningful conclusions may be drawn. The first difference is found in the length of the Sn–O(1) bond distance, the shorter being for **3** at 2.114(3) Å compared to 2.134(4) Å for **4**. The opposite trend is found for the Sn–O(2) bond distances where the longer bond of 2.587(4) Å is found in the structure of **3** and the shorter at 2.559(5) Å being found in **4**. Perhaps more significant is the differences between the Sn–O bond distances in each structure, i.e. Δ(Sn–O) of 0.473 Å in **3** and 0.425 Å in **4**. The higher degree of asymmetry in the mode of coordination of the carboxylate ligand in **3** is reflected in a greater localization of π-electron density in the C–O bond associated with the weakly coordinating O(2) atom; i.e. Δ(C–O) is 0.080 Å for **3** and considerably less at 0.058 Å for **4**.

The cause of this disparity in the Sn–O bond distances in the two compounds, and hence asymmetry in the mode of coordination of the carboxylate ligands, is most likely electronic in origin. The $^nBu_2Sn$ moiety would be more electron deficient compared to the $^nPr_2Sn$ moiety owing to the better electron donating ability of the two n-propyl groups over the n-butyl groups. Hence one would anticipate that the $^nBu_2Sn$ moiety would be the better electron acceptor over the $^nPr_2Sn$ moiety. Given that the O(1)–Sn–O(1′) angle remains constant in the two compounds and, owing to the restricted bite distance of the carboxylate ligand, the O(1)–Sn–O(2) angles also remain constant, the net result of the increased electron accepting ability of the $^nBu_2Sn$ moiety is to bring the O(2) atoms in closer proximity to the Sn atom. A direct consequence of this is a diminished O(2)–Sn–O(2′) angle in the $[^nBu_2Sn(O_2CCH_2SPh)_2]$ compound and to relieve any additional steric strain in the molecule, the C–Sn–C angle is opened up to 140.7(2)° cf. 136.7(2)° in $[^nPr_2Sn(O_2CCH_2SPh)_2]$. It is anticipated that the n-propyl and n-butyl groups would have the same steric profile about the Sn atoms and thus it is unlikely

Table 5

Selected interatomic parameters for $\{[R_2Sn(O_2CCH_2SPh)]_2O\}_2$

$R = {}^{n}Pr$		$R = {}^{n}Bu$	
Sn(1)–O(1)	2.011(5)	Sn(1)–O(1)	2.025(4)
Sn(1)–O(2)	2.193(6)	Sn(1)–O(2)	2.164(5)
Sn(1)–O(5′) [a]	2.230(6)	Sn(1)–O(5′)	2.254(7)
Sn(1)–C(9)	2.095(9)	Sn(1)–C(9)	2.105(8)
Sn(1)–C(12)	2.12(1)	Sn(1)–C(13)	2.19(1)
Sn(1) ··· O(3)	3.044(7)	Sn(1) ··· O(3)	2.956(5)
Sn(2)–O(1)	2.062(5)	Sn(2)–O(1)	2.049(4)
Sn(2)–O(1′)	2.166(5)	Sn(2)–O(1′)	2.163(4)
Sn(2)–O(4)	2.300(6)	Sn(2)–O(4)	2.283(5)
Sn(2)–C(23)	2.129(8)	Sn(2)–C(25)	2.114(7)
Sn(2)–C(26)	2.128(8)	Sn(2)–C(29)	2.109(7)
Sn(2) ··· O(2)	2.631(8)	Sn(2) ··· O(2)	2.753(5)
Sn(2) ··· Sn(2′)	3.319(1)	Sn(2) ··· Sn(2′)	3.314(1)
C(1)–O(2)	1.30(1)	C(1)–O(2)	1.262(8)
C(1)–O(3)	1.21(1)	C(1)–O(3)	1.225(9)
C(1)–C(2)	1.51(1)	C(1)–C(2)	1.51(1)
C(2)–S(1)	1.783(9)	C(2)–S(1)	1.77(1)
S(1)–C(3)	1.766(8)	S(1)–C(3)	1.769(7)
C(15)–O(4)	1.23(1)	C(17)–O(4)	1.21(1)
C(15)–O(5)	1.25(1)	C(17)–O(5)	1.27(1)
C(15)–C(16)	1.53(1)	C(17)–C(18)	1.53(1)
C(16)–S(2)	1.81(1)	C(18)–S(2)	1.79(1)
S(2)–C(17)	1.756(8)	S(2)–C(19)	1.70(2)
O(1)–Sn(1)–O(2)	77.9(2)	O(1)–Sn(1)–O(2)	79.2(2)
O(1)–Sn(1)–O(5′)	91.4(2)	O(1)–Sn(1)–O(5′)	92.6(2)
O(1)–Sn(1)–C(9)	110.8(3)	O(1)–Sn(1)–C(9)	112.8(3)
O(1)–Sn(1)–C(12)	114.6(3)	O(1)–Sn(1)–C(13)	109.6(3)
O(2)–Sn(1)–O(5′)	168.2(2)	O(2)–Sn(1)–O(5′)	171.7(2)
O(2)–Sn(1)–C(9)	97.9(3)	O(2)–Sn(1)–C(9)	99.0(3)
O(2)–Sn(1)–C(12)	93.1(3)	O(2)–Sn(1)–C(13)	93.6(3)
O(5′)–Sn(1)–C(9)	90.5(4)	O(5′)–Sn(1)–C(9)	85.6(3)
O(5′)–Sn(1)–C(12)	86.9(4)	O(5′)–Sn(1)–C(13)	87.7(4)
C(9)–Sn(1)–C(12)	134.6(4)	C(9)–Sn(1)–C(13)	137.3(4)
O(1)–Sn(2)–O(1′)	76.6(2)	O(1)–Sn(2)–O(1′)	76.3(2)
O(1)–Sn(2)–O(4)	89.4(2)	O(1)–Sn(2)–O(4)	90.4(2)
O(1)–Sn(2)–C(23)	107.3(3)	O(1)–Sn(2)–C(25)	108.3(2)
O(1)–Sn(2)–C(26)	106.9(3)	O(1)–Sn(2)–C(29)	110.3(3)
O(1′)–Sn(2)–O(4)	165.5(2)	O(1′)–Sn(2)–O(4)	166.5(2)
O(1′)–Sn(2)–C(23)	96.6(3)	O(1′)–Sn(2)–C(25)	98.8(3)
O(1′)–Sn(2)–C(26)	98.7(3)	O(1′)–Sn(2)–C(29)	97.8(3)
O(4)–Sn(2)–C(23)	84.4(3)	O(4)–Sn(2)–C(25)	87.7(3)
O(4)–Sn(2)–C(26)	88.4(3)	O(4)–Sn(2)–C(29)	84.3(3)
C(23)–Sn(2)–C(26)	145.0(3)	C(25)–Sn(2)–C(29)	140.5(3)
Sn(1)–O(1)–Sn(2)	137.0(3)	Sn(1)–O(1)–Sn(2)	135.2(2)
Sn(1)–O(2)–C(1)	115.2(5)	Sn(1)–O(2)–C(1)	113.5(5)
O(2)–C(1)–O(3)	122.4(8)	O(2)–C(1)–O(3)	123.2(7)
O(2)–C(1)–C(2)	114.7(8)	O(2)–C(1)–C(2)	115.7(7)
O(3)–C(1)–C(2)	122.9(8)	O(3)–C(1)–C(2)	121.1(7)
C(1)–C(2)–S(1)	115.4(7)	C(1)–C(2)–S(1)	114.8(6)
C(2)–S(1)–C(3)	102.0(4)	C(2)–S(1)–C(3)	106.3(4)
Sn(1)–O(5′)–C(15′)	136.0(6)	Sn(1)–O(5′)–C(17′)	134.2(6)
Sn(2)–O(1)–Sn(2′)	103.4(1)	Sn(2)–O(1)–Sn(2′)	103.7(1)

Table 5

R = ^{n}Pr		R = ^{n}Bu	
Sn(2)-O(1′)-Sn(1′)	119.4(1)	Sn(2)-O(1′)-Sn(1′)	120.7(1)
Sn(2)-O(4)-C(15)	133.7(6)	Sn(2)-O(4)-C(17)	136.8(6)
O(4)-C(15)-O(5)	126.7(8)	O(4)-C(17)-O(5)	126.0(8)
O(4)-C(15)-C(16)	117.7(9)	O(4)-C(17)-C(18)	117.3(9)
O(5)-C(15)-C(16)	115.5(9)	O(5)-C(17)-C(18)	116.7(8)
C(15)-C(16)-S(2)	110.4(6)	C(17)-C(18)-S(2)	114.1(7)
C(16)-S(2)-C(17)	105.6(4)	C(18)-S(2)-C(19)	108.4(8)

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

that the opening of the C–Sn–C angle in the compound arises because of the increase in alkyl chain length. Although this electronic effect may be small, in the absence of any crystal packing effects (see above), this effect provides the most plausible explanation for the significantly different parameters describing the Sn atom geometries in **3** and **4**.

The molecular structures of **8** and **9** are illustrated in Figures 2 and 3, respectively and selected interatomic parameters are listed in Table 5. The compounds adopt the most common structural motif for the $\{[R_2Sn(O_2CR')]_2O\}_2$ formulation, namely that of the dicarboxylato tetraorganodistannoxanes [5]. Significantly, there are no close intra- or inter-molecular interactions between the S and Sn atoms. The structure is built up around a central, centrosymmetric (crystallographically imposed) Sn_2O_2 unit with two exocyclic R_2Sn entities being connected to the bridging O atoms. The two pairs of *exo*- and *endo*-cyclic Sn atoms are each linked by a bidentate, bridging carboxylate ligand, the two remaining carboxylate ligands coordinate the exocyclic Sn atom in the monodentate mode with the Sn(1) ··· O(3)

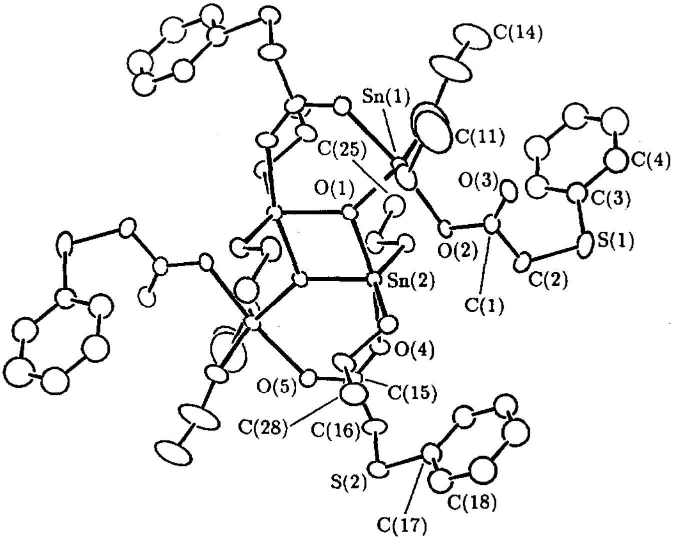

Fig. 2. Molecular structure and crystallographic numbering scheme employed for $\{[^nPr_2Sn(O_2CCH_2SPh)]_2O\}_2$ **8**.

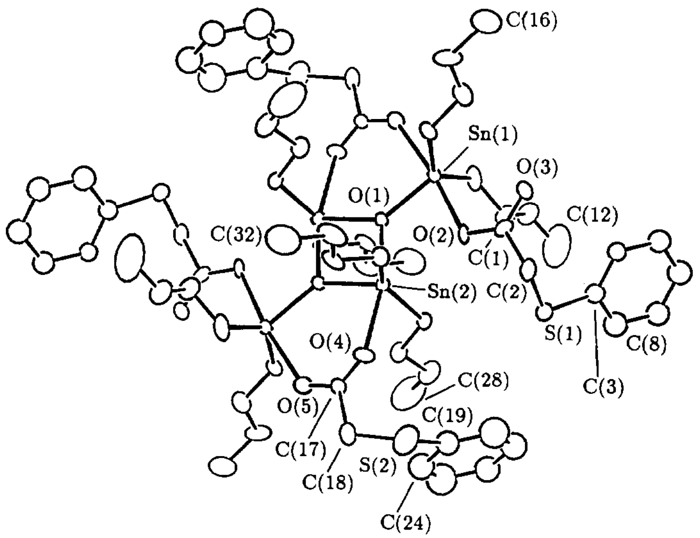

Fig. 3. Molecular structure and crystallographic numbering scheme employed for $\{[^{n}\text{Bu}_2\text{Sn}(\text{O}_2\text{CCH}_2\text{SPh})]_2\text{O}\}_2$ **9**.

separations being > 2.9 Å; neither of the O(3) atoms forms close intermolecular interactions with tin. Of interest is the close approach of the O(2) atom to the Sn(2) atom in each of **8** and **9**, however, these distances of > 2.6 Å are not indicative of significant bonding interactions. The presence of the O(2) atom does influence, to some extent, the nature of the coordination geometry about the Sn(2) atom however.

In this description both Sn atoms in both structures are five-coordinate and exist in trigonal bipyramidal geometries. The axial positions about the Sn(1) atoms are defined by two carboxylate O atoms, i.e. O(2) and O(5) with the Sn atom lying 0.021(1) Å (0.066(1) Å for **4**) out of the trigonal plane in the direction of the O(2) atom. Similarly for the Sn(2) atoms the O(1) and the carboxylate O(4) atoms occupy axial positions with the Sn atom lying 0.108(1) Å (0.106(1) Å) out of the trigonal plane in the direction of the O(1) atom. The relatively small deviations from the ideal trigonal bipyramidal geometries emphasize the fact that the close Sn(1) ··· O(3) and Sn(2) ··· O(2) interactions mentioned earlier are not indicative of substantial bonding interactions.

As for **3** and **4** above, it was hoped that the availability of two closely related structures in which only the R groups bound to the Sn atom have been varied, would have enabled a detailed comparison between the two in order to ascertain what effect the R group plays in determining the overall structure. However, while there are significant differences between the structures there are no clear trends as found for **3** and **4** above.

In the ^{n}Bu compound, **9**, the carboxylate ligand containing the O(2) and O(3) atoms coordinates the Sn(1) more symmetrically (Δ(Sn–O) 0.792 Å) than the corresponding ligand in the ^{n}Pr compound, **8** (Δ(Sn–O) is 0.851 Å). More dramatic however, is the closer approach of the O(2) atom to the Sn(2) atom in **8** compared to **9**, i.e. 2.631(8) cf. 2.753(5), a difference of 0.122 Å. The source of this disparity between the structures is far from clear, however, it is likely that the closer approach of the O(3) atom to Sn(1) in **9** is responsible for the opening of the C–Sn(1)–C angle in **9** compared to the same angle in **8** (137.3(4) cf. 134.6(4)°). Similarly the C–Sn(2)–C angle in **8** (145.0(3)°) is greater than that in **9** (140.5(3)°) owing to the close approach of the O(2) atom in **8**. A detailed analysis of other geometric parameters about the Sn atoms is precluded as the differences between comparable parameters do not exceed the normal criterion of significance.

Experimental

Preparation of compounds

Thiophenoxyacetic acid was purchased from Aldrich and used without further purification. Dimethyl-, di-n-butyl- and di-n-octyl-tin(IV) oxides were obtained from Alfa and diethyl- and di-n-propyl-tin(IV) oxides were prepared by known methods [11]. All solvents were used after purification and drying.

The complexes were prepared by refluxing thiophenoxyacetic acid and the diorganotin(IV) oxide in 1 : 1 and 1 : 2 molar ratio in a dry benzene–ethanol mixture (3/1 v/v) with azeotropic removal of water. The mixture was filtered and the solvent removed. All compounds were obtained as solids (see Table 1 for physical data) except for **10** which was obtained as a liquid.

Microanalyses (C and H) were determined by the Microanalytical service, R.S.I.C., Panjab University, Chandigarh. Tin was estimated as SnO_2. Infrared spectra were

Table 6

Crystal data and refinement details for **3**, **8** and **9**

Compound	**3**	**8**	**9**
Formula	$C_{22}H_{28}O_4S_2Sn$	$C_{56}H_{84}O_{10}S_4Sn_4$	$C_{64}H_{100}O_{10}S_4Sn_4$
Mol. wt.	539.3	1520.2	1632.4
Crystal system	monoclinic	triclinic	triclinic
Space group	$C2/c$	$P\bar{1}$	$P\bar{1}$
a, Å	31.116(3)	13.085(4)	12.591(1)
b, Å	5.160(1)	14.253(2)	13.499(2)
c, Å	18.727(2)	10.370(1)	12.237(3)
α, deg.	90	110.22(1)	104.96(2)
β, deg.	125.15(1)	108.05(2)	111.36(1)
γ, deg.	90	66.80(2)	91.05(1)
V, Å^3	2458.5	1633.9	1856.7
Z	4	1 (tetramer)	1 (tetramer)
D_c, g cm^{-3}	1.457	1.545	1.460
$F(000)$	1096	764	828
μ, cm^{-1}	11.25	15.51	13.67
Max./min trans. factors	0.835; 0.735	n/a	0.789; 0.617
No. of data collected	2414	4806	4974
No. of unique data	1606	4262	4846
No. of unique reflections used with $I \geq 2.5\sigma(I)$	1432	2707	3138
R	0.032	0.044	0.038
g	0.0041	0.0047	0.0064
R_w	0.034	0.045	0.042
Residual ρ_{max}, e Å^{-3}	0.43	1.25	0.52

recorded as KBr discs (except for **10** which was recorded neat between NaCl plates) on a Pye Unicam P321 spectrophotometer in the range 4000–200 cm^{-1}. A JEOL (JNM PMX) 60MHz spectrometer was used to record the ^1H NMR spectra in $CDCl_3$ solution with Me_4Si as the internal standard.

Crystallography

Intensity data for **3**, **8**, and **9** were measured at room temperature on an Enraf–Nonius CAD4F diffractometer fitted with graphite monochromatized Mo-K_α radiation, $\lambda = 0.7107$ Å. The ω:2θ scan technique was employed to measure data up to a maximum Bragg angle of 22.5° in each case. The data were corrected for Lorentz and polarization effects and for **3** and **9** an analytical absorption correction was applied [12]. Relevant crystal data are collected in Table 6.

The structure of **3** was solved from the interpretation of the Patterson synthesis and the structures of **8** and **9** were solved by direct methods [12]. The structures were each refined by a full-matrix least-squares procedure based on F [12]. All non-H atoms in **3** were refined with anisotropic thermal parameters and non-H, non-phenyl atoms were refined anisotropically for **8** and **9**; the phenyl rings in the latter refinements were refined as hexagonal rigid groups with individual isotropic thermal parameters. Hydrogen atoms were included in each model at their calculated positions. For **9**, the SPh group, with the S(2) and C(19)–C(24) atoms, was found to be disordered over two positions. Each group was included in the refinement with site occupancies x and $1 - x$, respectively such that the sum of x and $1 - x$ = unity; the major component (shown in Fig. 3) was found to have $x = 0.604(7)$. After the inclusion of a weighting scheme of the form, $w = k/[\sigma^2(F) + g|F|^2]$, the refinements were continued until convergence. Final refinement details are listed in Table 6. The analysis of variance showed no special features in any of the refinements indicating that appropriate weighting schemes had been applied in each case. Fractional atomic coordinates are listed in Tables 7–9 and the

Table 7

Fractional atomic coordinates ($\times 10^5$ for Sn and $\times 10^4$ for remaining atoms) for $[^{n}Pr_2Sn(O_2CCH_2SPh)_2]$ **3**

Atom	x	y	z
Sn	0(−)	10770(6)	25000(−)
S(1)	−813(1)	−1617(3)	4266(1)
O(1)	122(1)	−2073(6)	1913(2)
O(2)	292(2)	1404(5)	1459(3)
C(1)	252(2)	−932(7)	1451(3)
C(2)	−314(2)	−2680(9)	4132(3)
C(3)	−1381(3)	−1583(11)	3187(5)
C(4)	−1470(3)	−3398(16)	2571(6)
C(5)	−1932(4)	−3290(22)	1735(7)
C(6)	−2295(5)	−1488(22)	1518(8)
C(7)	−2215(5)	306(23)	2118(8)
C(8)	−1748(4)	215(19)	2968(6)
C(9)	−735(2)	2578(10)	1501(3)
C(10)	−1151(3)	687(16)	1004(6)
C(11)	−1667(3)	1748(23)	270(6)

Table 8

Fractional atomic coordinates ($\times 10^5$ for Sn and $\times 10^4$ for remaining atoms) for $\{[^n\mathrm{Pr}_2\mathrm{Sn}(\mathrm{O}_2\mathrm{CCH}_2\text{-}\mathrm{SPh})]_2\mathrm{O}\}_2$ **8**

Atom	*x*	*y*	*z*
Sn(1)	59488(5)	19309(4)	3696(6)
Sn(2)	36478(5)	7260(4)	−3539(5)
S(1)	10677(2)	163(3)	2283(3)
S(2)	2012(2)	4851(2)	1604(3)
O(1)	5257(5)	821(4)	78(6)
O(2)	7454(5)	550(4)	629(6)
O(3)	8486(6)	1501(5)	802(8)
O(4)	2904(5)	2406(5)	−668(7)
O(5)	4246(6)	3167(5)	237(8)
C(1)	8419(7)	703(7)	884(9)
C(2)	9442(7)	−192(7)	1289(10)
C(3)	10201(6)	1080(6)	3801(8)
C(4)	10805(6)	1787(6)	4550(8)
C(5)	10561(6)	2476(6)	5831(8)
C(6)	9713(6)	2459(6)	6364(8)
C(7)	9110(6)	1753(6)	5615(8)
C(8)	9354(6)	1063(6)	4334(8)
C(9)	6080(9)	2009(8)	−1551(10)
C(10)	6174(21)	3167(19)	−1438(18)
C(11)	6230(21)	3196(20)	−2618(26)
C(12)	6331(10)	2776(8)	2488(11)
C(13)	6369(20)	3816(12)	2790(17)
C(14)	6643(18)	4365(13)	4287(18)
C(15)	3240(8)	3177(7)	−209(9)
C(16)	2347(10)	4271(7)	−131(10)
C(17)	1031(7)	4299(6)	1618(6)
C(18)	724(7)	4583(6)	2909(6)
C(19)	−39(7)	4181(6)	3050(6)
C(20)	−494(7)	3494(6)	1901(6)
C(21)	−188(7)	3210(6)	611(6)
C(22)	575(7)	3613(6)	469(6)
C(23)	3144(7)	250(7)	−2576(8)
C(24)	3798(8)	460(8)	−3392(8)
C(25)	3597(9)	−186(9)	−4936(10)
C(26)	3083(8)	1353(7)	1580(9)
C(27)	3732(9)	2104(7)	2703(9)
C(28)	3350(10)	2473(9)	4087(10)

numbering schemes employed are shown in Fig. 1–3 which were drawn with ORTEP [13] at 15% probability ellipsoids. Scattering factors were as incorporated in the SHELX76 program [12] and refinement was performed on a SUN4/280 computer. Other crystallographic details (available from E.R.T.T.) comprises thermal parameters, H-atom parameters, all bond distances and angles, and tables of observed and calculated structure factors.

Table 9

Fractional atomic coordinates (×10^5 for Sn and ×10^4 for remaining atoms) for $\{[^n\mathrm{Bu}_2\mathrm{Sn}(\mathrm{O}_2\mathrm{CCH}_2\mathrm{SPh})]_2\mathrm{O}\}_2$ **9**

Atom	*x*	*y*	*z*
Sn(1)	58384(4)	50207(4)	29064(4)
Sn(2)	36239(4)	48910(3)	−2017(4)
S(1)	9724(3)	6960(3)	3588(3)
S(2)	683(4)	4378(4)	1463(5)
O(1)	5225(3)	5047(3)	1139(4)
O(2)	7425(4)	5307(4)	2666(4)
O(3)	8280(5)	5239(4)	4550(5)
O(4)	2799(5)	4944(5)	1191(6)
O(5)	4061(6)	4675(7)	2860(7)
C(1)	8313(6)	5371(6)	3608(7)
C(2)	9444(7)	5649(8)	3523(8)
C(3)	10276(6)	7660(4)	5158(6)
C(4)	10385(6)	7222(4)	6103(6)
C(5)	10863(6)	7831(4)	7317(6)
C(6)	11232(6)	8878(4)	7586(6)
C(7)	11223(6)	9316(4)	6641(6)
C(8)	10645(6)	8707(4)	5427(6)
C(9)	5893(8)	6458(7)	4130(8)
C(10)	6806(10)	7304(8)	4433(11)
C(11)	6683(12)	8285(9)	5289(12)
C(12)	7517(15)	9086(12)	5511(20)
C(13)	6114(10)	3439(8)	2991(9)
C(14)	6379(11)	3248(10)	4144(10)
C(15)	6355(12)	2113(9)	4074(14)
C(16)	6677(16)	1938(13)	5223(17)
C(17)	3058(8)	4768(7)	2168(8)
C(18)	2098(10)	4677(8)	2637(10)
C(19)	546(18)	3150(14)	573(26)
C(20)	−262(18)	2972(14)	−617(26)
C(21)	−575(18)	1971(14)	−1409(26)
C(22)	−80(18)	1147(14)	−1010(26)
C(23)	728(18)	1325(14)	181(26)
C(24)	1041(18)	2326(14)	972(26)
C(25)	2994(7)	3301(6)	−944(8)
C(26)	3616(8)	2636(6)	−129(9)
C(27)	3234(11)	1486(8)	−791(12)
C(28)	3837(16)	851(10)	−2(20)
C(29)	3060(7)	6352(6)	−207(7)
C(30)	3609(11)	7194(7)	1035(8)
C(31)	3314(13)	8243(7)	953(10)
C(32)	3897(22)	9062(11)	2208(17)

Acknowledgements

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