Crystal and molecular structures of 1,2;3,4-Di-μ-o-methyl/o-chlorobenzoato-OO'-1,3 bis(o-methyl/o-chlorobenzoato-O)-1,2,4;2,3,4-di-μ₃-oxo tetrakis[di-n-butyltin(IV)] and molecular structure of 1,2;3,4-Di-μ-o-hydroxybenzoato-OO'-1,3 bis(o-hydroxybenzoato-O)-1,2,4;2,3,4-di-μ₃-oxo tetrakis[di-n-butyltin(IV)] compounds

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Abstract

The title distannoxanes [(n-Bu₂SnO₂CC₆H₄-o-CH₃)₂O]₂(1), [(n-Bu₂SnO₂CC₆H₄-o-Cl)₂O]₂ (2) and [(n-Bu₂SnO₂CC₆H₄-o-OH)₂O]₂ (3) were obtained by azeotropic dehydration from a mixture of n-Bu₂SnO and the appropriate substituted benzoic acids. Single-crystal X-ray diffraction studies revealed that both 1 and 2 have tetranuclear centrosymmetric dimeric structures. The structurally significant bond lengths and bond angles (for 1: Sn(1)–O(3), 2.992 Å; Sn(2)–O(2), 2.929 Å; C(1)–Sn(1)–C(5), 134.8(4)°, C(9)–Sn(2)–C(13), 137.7(5)°) (for 2: Sn(1)–O(3), 3.012 Å, Sn(2)–O(2), 2.975 Å; C(1)–Sn(1)–C(5), 135.4(5)°; and C(9)–Sn(2)–C(13), 136.3(7)°) reveal the least distorted trigonal bipyramidal structures at exocyclic and endocyclic tin atoms observed to date. Multinuclei (¹H, ¹³C and ¹¹⁹Sn) NMR, Mössbauer and IR spectra are in agreement with the X-ray data. Compound 3 is extremely insoluble in organic solvents. Its IR spectra reveal extensive hydrogen bonding, the extent of which is reduced at higher temperatures (30–60°C). Its ¹¹⁹Sn NMR spectra in solution at these temperatures show signals usually assigned to five- and six-coordinate organotin species; such species probably arise by breakdown of the structure of 3 found in the solid state. A comparison with the structures of known $ortho$-substituted distannoxane is presented.

Keywords: Tin; Carboxylate; Crystal structure

1. Introduction

Information on the structures of organotin carboxylates continues to accumulate, and at the same time new applications of such compounds are being discovered in industry, ecology and medicine [1–4]. Recently substituted benzoato-tetraalkyl-distannoxanes [5,6] have shown positive tests against human tumor cells as well as other catalytic activity.

Among the di-carboxylato-tetraalkyl distannoxanes that have been structurally analyzed by X-ray crystallography [6–8], the majority have a tetranuclear centrosymmetric structure with a planar four-membered Sn–O–Sn–O ring.

A close scrutiny of the structural data reveals varying intramolecular or intermolecular Sn ← O coordinate bond distances in distannoxane molecules. For example, Sn(1)–O(3) and Sn(2)–O(2) distances vary between

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2.736(7)–3.164(7) Å and 2.66(2)–2.975(8) Å (including the present data) respectively (see Table 7 later). These linkages have often been regarded as weak, insignificant or even non-bonding interactions [7]. Although it has been difficult to demonstrate actual contribution by such interactions to the coordination geometry of Sn(1) and Sn(2) atoms, the ideal structure is likely to show no such interactions (distance, greater than 3.67 Å) and possess trigonal bipyramidal geometry around both exocyclic and endocyclic tin atoms; there is, however, no example of this in the literature either for the solid or solution state. The structures of [(n-Bu$_2$SnO$_2$CC$_6$H$_4$-o-X)$_2$O]$_2$ (where X = CH$_3$ or Cl) described here are again not of the regular trigonal bipyramidal configuration but do contain the least distortion from such structures so far reported.

2. Experimental details

Benzene, dichloromethane, light petroleum and chloroform were dried by standard procedures [9]. Di-n-butyltin oxide (Aldrich) was used as purchased. o-Methylbenzoic, o-chlorobenzoic and o-hydroxybenzoic acids (Aldrich) were purified by crystallization from a 2 : 1 mixture of dichloromethane and light petroleum ether (boiling point (b.p.), 40–60°C). Microanalyses (C and H) were carried out with a Perkin–Elmer (model 2400) CHN analyzer. Analysis for tin was by a gravimetric method [10]. IR spectra of solids were recorded as KBr pellets and the solution spectra in CHCl$_3$ in NaCl or KBr cells with a Perkin–Elmer 621 spectrophotometer. ^{119}Sn Mossbauer spectra were obtained at 77 K on a Harwell spectrophotometer equipped with a 356-multichannel analyzer and Ba^{119m}SnO$_3$ source; the least-squares method was used for data reduction of the lorentzian line shape. The ^{1}H, ^{13}C and ^{119}Sn NMR spectra were recorded on a Varian EM-390 or Bruker AMX-500 spectometer with tetramethylsilane (for ^{1}H and ^{13}C) and tetramethyltin (for ^{119}Sn) as references.

3. Synthesis

3.1. Preparation of [(n-Bu$_2$SnO$_2$CC$_6$H$_4$-o-CH$_3$)O]$_2$ (1)

To a suspension of di-n-butyltin oxide (2.49 g, 10 mmol) in dry benzene (80 ml) was added o-methylbenzoic acid (1.36 g, 10 mmol). The mixture was heated under reflux for 5–6 h in a Dean–Stark apparatus for azeotropic removal of the water formed in the reaction. The resulting solution was concentrated to 20 ml under vacuum and light petroleum (b.p., 40–60°C) (70 ml) was added to precipitate a white solid, which was recrystallized from a mixture of dichloromethane and

light petroleum (yield, 3.19 g (85%); melting point (m.p.), 104°C). Found: C, 50.9; H, 6.9; Sn, 31.2.C$_{32}$H$_{50}$O$_5$Sn$_2$ Calc.: C, 51.1; H, 7.0; Sn, 31.6%, ^{1}H NMR (CDCl$_3$): δ 7.7–7.2 (m, 4H, C$_6$H$_4$), 2.6 (s, 3H, ring-CH$_3$), 1.8–1.3 (m, 12H, Sn(CH$_2$)$_3$, 0.9 (t, 6H, CH$_3$) ppm. ^{13}C NMR (CDCl$_3$): δ 174.6 (CO$_2$), 131.4–125.5 (ring carbons), 28.2, 27.6, 27.4, 26.9, 26.3 (SnCH$_2$CH$_2$CH$_2$), 13.6 (CH$_3$) ppm. ^{119}Sn NMR (CDCl$_3$): δ −212.9, −213.4 ppm. IR (KBr pellet): ν(CO$_2$) 1620, 1610, 1578 cm^{-1}.

3.2. Preparation of [(n-Bu$_2$SnO$_2$CC$_6$H$_4$-o-Cl)$_2$O]$_2$ (2)

This was prepared from di-n-butyltin oxide (2.49 g, 10 mmol) and o-chlorobenzoic acid (1.56 g, 10 mmol) by a procedure similar to that described for 1 (yield, 3.65 g (90%); m.p., 86°C). Found: C, 45.3; H, 5.3; Sn, 29.6.C$_{30}$H$_{44}$Sn$_2$O$_5$Cl$_2$. Calc.: C, 45.4; H, 5.6; Sn, 29.9%. ^{1}H NMR (CDCl$_3$): δ 7.6–7.2 (m, 4H, C$_6$H$_4$), 1.8–1.3 (m, 12H, SnCH$_2$CH$_2$CH$_2$), 0.8 (t, 6H, CH$_3$) ppm. ^{13}C NMR (CDCl$_3$): δ 172.2 (CO$_2$), 131.1–126.3 (ring carbons) 28.2, 27.5, 26.8, 26.3 (SnCH$_2$CH$_2$CH$_2$), 13.6 (CH$_3$) ppm. ^{119}Sn NMR (CDCl$_3$): δ −203.6, −201.2 ppm. IR (KBr pellet): ν(CO$_2$) 1635 1620, 1580 cm^{-1}.

3.3. Preparation of [(n-Bu$_2$SnO$_2$CC$_6$H$_4$-o-OH)$_2$O]$_2$ (3)

This compound was prepared from di-n-butyltin oxide (2.49 g, 10 mmol) and o-hydroxybenzoic acid (1.38 g, 10 mmol) by a procedure similar to that described for 1 (yield, 3.14 g (83%); m.p., 200°C). Found: C, 47.4; H, 6.0; Sn, 31.2. C$_{30}$H$_{46}$Sn$_2$O$_7$ Calc.: C, 47.6; H, 6.1; Sn, 31.4%. ^{1}H NMR (CDCl$_3$): δ 11.4 (s, 1H, OH), 7.9–6.9
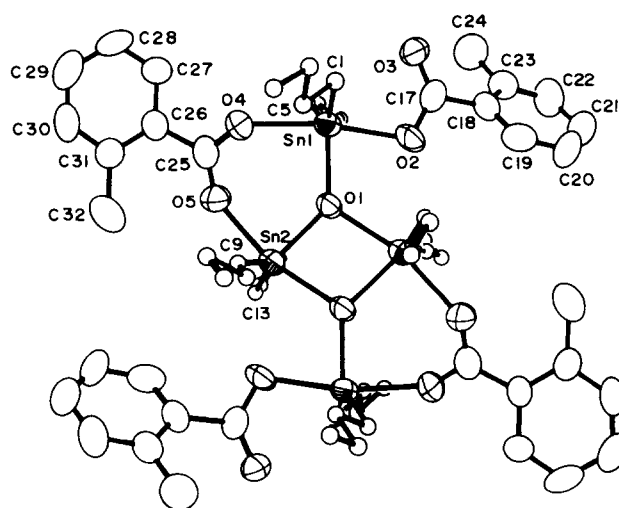
Fig. 1. ORTEP plot of [(n-Bu$_2$SnO$_2$CC$_6$H$_4$-o-CH$_3$)$_2$O] (1) (thermal ellipsoids at 30% probability level) showing the atomic numbering scheme. Hydrogen atoms are omitted for clarity.

(m, 4H, C_6H_4), 1.8–1.3 (m, 12H, $SnCH_2CH_2CH_2$), 0.8 (t, 6H, CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ 174.4 (CO_2) 160.7–114.3 (ring carbons), 26.4, 25.9, 25.8, 25.4 ($SnCH_2CH_2CH_2$), 12.8 (CH_3) ppm. ^{119}Sn ($CDCl_3$): δ −205.1, −199.7, −188.9, −172.4, −157.5 ppm. IR (KBr pellet): $\nu(CO_2)$ 1628, 1605, 1560; $\nu(OH)$ 3450, 3190 cm^{-1}.

3.4. X-ray crystallography

X-ray crystallographic data for 1 and 2 were collected on an Rigaku AFC 6S diffractometer using Mo Kα radiations ($\lambda = 0.71073$ Å) and highly oriented graphite monochromator at 296 K. Unit-cell parameters and standard deviations were obtained by least-squares fit to 25 reflections, $15° < 2\theta < 30°$, for 1 and 15 reflections, $20° < 2\theta < 40°$, for 2.

The data were corrected for Lorentz and polarization effects and a ψ-dependent absorption correction was applied. There were no systematic absences in the data so the space group $P\bar{1}$ was assumed and later confirmed by successful refinement of the structure. The structure was solved by Patterson synthesis method using SHELXS. A subsequent difference Fourier map revealed the posi-

Table 1
Summary of crystal data, data collection and structural refinement for 1

Crystal data	
Unit-cell parameters	
a (Å)	11.763(4)
b (Å)	12.183(2)
c (Å)	13.380(2)
α (°)	84.39(2)
β (°)	81.65(2)
γ (°)	65.00(2)
Volume (Å^3)	1710.8(7)
Crystal system	Triclinic
Space group	$P\bar{1}$ (No. 2)
Empirical formula	$C_{32}H_{50}O_5Sn_2$
Formula weight	752.1
Z; $F(000)$	2; 764
Density (calculated) (Mg m^{-3})	1.460
Absorption coefficient (μ) (mm^{-1})	1.498
Absorption correction	Transmission factors, 0.81–1.28
Data collection	
Radiation	Mo Kα ($\lambda = 0.71073$ Å)
Monochromator	Highly oriented graphite crystal
Temperature (K)	296
2θ range (°)	4.0–45.0
Scan type	2θ–θ
Scan speed (° min^{-1})	Constant 8.00 in ω (for details see text)
Scan width	1.785 + 0.350 tan θ
Scan time : background time	2 : 1
Index ranges	$0 \leqslant h \leqslant 12, -11 \leqslant k \leqslant 13, -14 \leqslant l \leqslant 14$
Total number of reflections collected	4857
Number of independent reflections	4509 ($R_{int} = 2.30\%$)
Number m of unique data used	3321 ($F > 4.0\sigma(F)$)
Solution and refinement	
Number n of parameters refined	345
Data-to-parameter ratio m/n	9.6 : 1
Final R indices (observed data)	3.99
R (%)	3.99
wR (%)	6.67
Goodness of fit S	0.93
Largest shift/error Δ/σ	0.010
Largest difference peak Δp_{max}	0.56 (electrons Å^{-3})
Largest difference hole	−1.17 (electrons Å^{-3})

$R = (\Sigma \| \| F_o \| - \| F_c \| \| / \Sigma \| F_o \|)$; $wR = (\Sigma w(\| F_o \| - \| F_c \|)^2 / \Sigma w \| F_o \|^2)^{1/2}$; $S = (\Sigma w(\| F_o \| - \| F_c \|)^2 / (m - n))^{1/2}$.

tion of all other non-hydrogen atoms. Since compounds 1 and 2 have similar cell dimensions and space groups, as a starting point the C, Sn and O coordinates for 1 were used for 2 and positions of the Cl atoms were obtained from a difference Fourier map. All non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method. In the case of 2 one phenyl ring (C(18)–C(23) was found to be unstable during refinement and was treated as a rigid group of D_{6h} symmetry with a C–C distance of 1.395 Å and a C–C–C angle of 120°. Two carbon atoms C(10) and C(11) in 1 and one butyl group C(9)–C(12) in 2 were

found to be disordered. Consequently, two separate positions with structure occupany factors of 0.5 were refined for each of these carbon atoms. The function minimized was $\Sigma w(\| F_o \| - \| F_c \|)^2$. Hydrogen atoms were included in the ideal positions with a fixed isotropic U value of 0.08 Å². A weighting scheme of form $w = 1/[\sigma^2(F) + gF^2]$ with $g = 0.001$ was used. There was no evidence of secondary extinction. The refinement converged to R indices given in Tables 1 and 2 which also includes Δ/σ and $\Delta\rho(\text{max})$ in the last cycles of refinement.

The final difference map for 1 was devoid of signifi-

Table 2
Atomic coordinates and equivalent isotropic displacement coefficients for 1

	x $(\times 10^{-4})$	y $(\times 10^{-4})$	z $(\times 10^{-4})$	U_{eq} [a] $(\times 10^{-3}\,\text{Å}^{-2})$
Sn(1)	5014(1)	2248(1)	5301(1)	48(1)
Sn(2)	5787(1)	4736(1)	5997(1)	48(1)
O(1)	5128(4)	3877(4)	5135(4)	52(2)
O(2)	4443(5)	2806(5)	3790(4)	62(2)
O(3)	4547(6)	948(5)	3730(4)	71(3)
O(4)	5514(5)	2051(5)	6918(4)	65(3)
O(5)	6825(5)	2947(5)	6815(4)	72(3)
C(1)	3238(7)	2295(8)	5985(6)	61(4)
C(2)	2606(9)	3083(8)	6885(7)	72(4)
C(3)	1378(9)	3032(11)	7334(8)	96(6)
C(4)	770(13)	3771(15)	8243(11)	159(11)
C(5)	6844(8)	857(8)	4965(7)	78(4)
C(6)	7524(10)	903(10)	3983(9)	93(5)
C(7)	8827(11)	−154(14)	3829(12)	134(8)
C(8)	9510(15)	−147(18)	2977(18)	284(20)
C(9)	4410(13)	5341(14)	7263(9)	126(8)
C(10A) [a]	3400(22)	6047(21)	7481(18)	89(6)
C(10B)	4406(24)	5287(25)	8102(21)	111(7)
C(11A) [a]	2508(27)	6017(25)	8605(19)	103(7)
C(11B)	3138(28)	6078(27)	8890(21)	118(8)
C(12)	1635(28)	6792(29)	8625(20)	242(12)
C(13)	7665(7)	4590(8)	5522(6)	65(4)
C(14)	8505(8)	3582(8)	4876(7)	73(4)
C(15)	9782(8)	3553(10)	4530(8)	96(6)
C(16)	10592(12)	2613(14)	3779(9)	139(8)
C(17)	4404(7)	1927(8)	3340(5)	57(4)
C(18)	4219(8)	2213(8)	2226(5)	57(4)
C(19)	3320(10)	3325(8)	1950(8)	82(5)
C(20)	3106(11)	3648(10)	965(7)	91(5)
C(21)	3801(12)	2851(11)	222(8)	98(7)
C(22)	4735(10)	1728(10)	485(6)	85(5)
C(23)	4930(8)	1396(8)	1456(6)	64(4)
C(24)	5917(10)	148(9)	1719(7)	86(5)
C(25)	6450(8)	2143(8)	7208(6)	59(4)
C(26)	7127(7)	1268(7)	8006(5)	54(3)
C(27)	7156(8)	114(8)	8017(7)	68(4)
C(28)	7774(10)	−763(8)	8697(8)	81(5)
C(29)	8389(9)	−491(10)	9376(7)	82(5)
C(30)	8358(9)	635(10)	9349(7)	83(5)
C(31)	7761(8)	1548(8)	8670(7)	69(4)
C(32)	7790(13)	2801(10)	8636(10)	129(8)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor, i.e. $U_{eq} = \frac{1}{3}\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* a_i a_j$.

cant features while that for **2** showed a peak of height 2.26 electrons A^{-3} near Sn(1); we suspect that this is due to inadequate absorption correction.

For **1**, calculations were carried out on an IBM compatible PC using the programs TEXSAN [11] (data reduction) SHELXS86 [12] (structure solution) SHELXS [13] (refinement) and ORTEP [14] (plotting). For **2**, calculations were carried on an silicon graphics personal Iris d/35 and IBM compatible PC using the programs TEXSAN [15] (data reduction) and SHELXTL [16] (refinement and plotting).

4. Results and discussion

The compounds $[(n\text{-}Bu_2SnO_2CC_6H_4\text{-}o\text{-}X)_2O]_2$ (X = CH_3 (1), Cl (2) or OH (3)) are white crystalline solids, obtained by azeotropic removal of water generated in reactions between di-*n*-butyltin oxide and the relevant substituted benzoic acid in 1:1 molar ratio in benzene. Compounds **1** and **2** are soluble in common organic solvents, whereas **3** is insoluble.

5. Solid state structure

The atom-labeling schemes for **1** and **2** are shown in the ORTEP plots in Figs. 1 and 2 respectively. Crystal data, atomic coordinates, and selected bond lengths and angles for **1** are given in Tables 1, 2 and 3 respectively, and corresponding information for **2** in Tables 4, 5 and 6 respectively. Both these compounds crystalize in the space group P$\bar{1}$ and possess tetranuclear centrosymmetric dimeric structures with a four-membered planar Sn–O–Sn–O ring (for **1**: (Sn(2)–O(1)–Sn(2A), 103.6(2)°; O(1)–Sn(2)–O(1A), 76.4(2)°) (for **2**: Sn(2)–O(1)–Sn(2′), 104.2(3)°, O(1)–Sn(2)–O(1′), 75.8(3)°). The four tin atoms are linked by two bridging carboxyl groups, while the remaining two carboxyl groups are attached to each of the exocyclic tin atoms. For the exocyclic tin atoms, covalent Sn(1)–O distances range between 2.034(6) and 2.288(6) Å (for O(2), O(4) and O(1) atoms). The O–C–O bond angles for bridging and non-bridging carboxyl groups are 121.2(7)° and 125.0(7)° for **1**, and 122.4(9)° and 124.7(9)° for **2**. The bond angles in these pairs correspond to an almost monodentate character for the carboxy ligands.
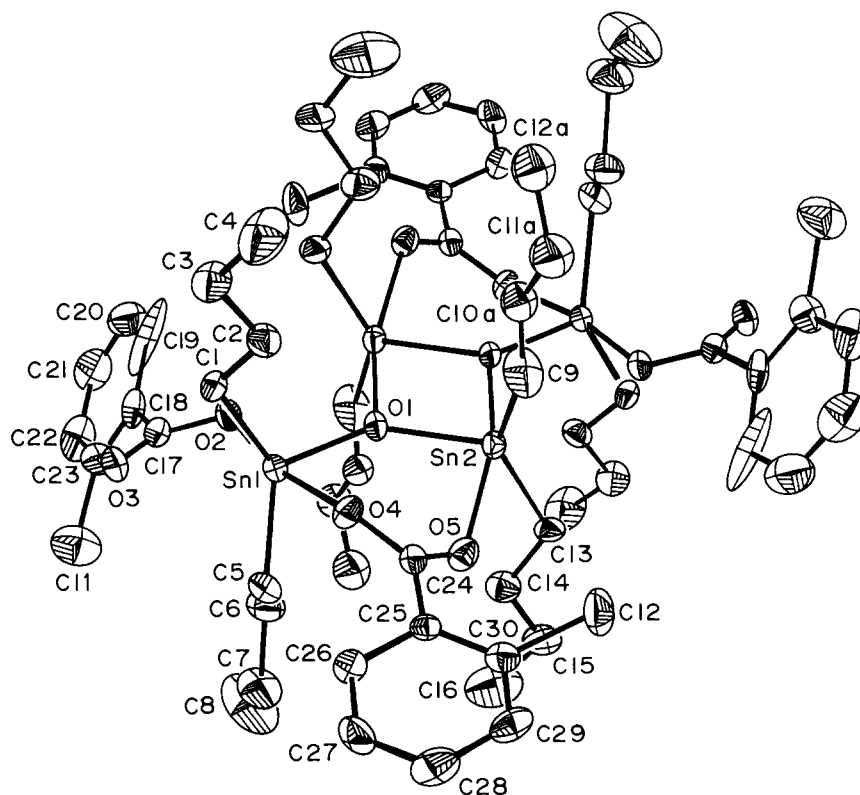

Fig. 2. ORTEP plot of $[(n\text{-}Bu_2SnO_2CC_6H_4\text{-}o\text{-}Cl)_2]_2$ (**2**) (thermal ellipsoids at 30% probability level) showing the atomic numbering scheme. Hydrogen atoms are omitted for clarity.

Table 3
Selected bond lengths (Å) and angles (°) for **1**

Bond lengths

Sn(1)–O(1)	2.034(6)	Sn(1)–O(2)	2.178(5)
Sn(1)–O(4)	2.288(6)	Sn(1)–C(1)	2.135(9)
Sn(1)–C(5)	2.120(7)	Sn(2)–O(1)	2.050(6)
Sn(2)–O(5)	2.261(6)	Sn(2)–C(9)	2.116(12)
Sn(2)–C(13)	2.145(9)	Sn(2)–O(1A)	2.177(4)
O(1)–Sn(2A)	2.177(4)	O(2)–C(17)	1.299(12)
O(3)–C(17)	1.208(11)	O(4)–C(25)	1.269(12)
O(5)–C(25)	1.277(13)	C(1)–C(2)	1.513(12)
C(2)–C(3)	1.506(16)	C(3)–C(4)	1.489(18)
C(5)–C(6)	1.444(14)	C(6)–C(7)	1.530(14)
C(7)–C(8)	1.297(26)	C(9)–C(10A)	1.149(23)
C(9)–C(10B)	1.117(31)	C(10A)–C(11A)	1.710(35)
C(10B)–C(11B)	1.671(35)	C(11A)–C(12)	1.060(35)
C(11B)–C(12)	1.682(42)	C(13)–C(14)	1.471(11)
C(14)–C(15)	1.492(14)	C(15)–C(16)	1.501(17)
C(17)–C(18)	1.523(10)	C(18)–C(19)	1.376(11)
C(18)–C(23)	1.414(11)	C(19)–C(20)	1.366(15)
C(20)–C(21)	1.371(14)	C(21)–C(22)	1.397(14)
C(22)–C(23)	1.345(11)	C(23)–C(24)	1.518(11)
C(25)–C(26)	1.489(10)	C(26)–C(27)	1.390(14)
C(26)–C(31)	1.389(14)	C(27)–C(28)	1.358(12)
C(28)–C(29)	1.383(17)	C(29)–C(30)	1.354(18)
C(30)–C(31)	1.372(12)	C(31)–C(32)	1.538(18)
Sn(1) ⋯ O(3)	2.992(6)		
Sn(2) ⋯ O(2A)	2.929(6)		

Bond angles

O(1)–Sn(1)–O(2)	80.1(2)	O(1)–Sn(1)–O(4)	89.4(2)
O(2)–Sn(1)–O(4)	168.9(2)	O(1)–Sn(1)–C(1)	115.4(3)
O(2)–Sn(1)–C(1)	95.6(3)	O(4)–Sn(1)–C(1)	85.6(3)
O(1)–Sn(1)–C(5)	108.9(3)	O(2)–Sn(1)–C(5)	100.9(3)
O(4)–Sn(1)–C(5)	85.8(3)	C(1)–Sn(1)–C(5)	134.8(4)
O(1)–Sn(2)–O(5)	89.4(2)	O(1)–Sn(2)–C(9)	105.7(5)
O(5)–Sn(2)–C(9)	91.1(4)	O(1)–Sn(2)–C(13)	116.0(3)
O(5)–Sn(2)–C(13)	82.7(3)	C(9)–Sn(2)–C(13)	137.7(5)
O(1)–Sn(2)–O(1A)	76.4(2)	O(5)–Sn(2)–O(1A)	163.8(2)
C(9)–Sn(2)–O(1A)	100.1(4)	C(13)–Sn(2)–O(1A)	96.4(3)
Sn(1)–O(1)–Sn(2)	132.8(2)	Sn(1)–O(1)–Sn(2A)	123.0(3)
Sn(2)–O(1)–Sn(2A)	103.6(2)	Sn(1)–O(2)–C(17)	111.9(4)
Sn(1)–O(4)–C(25)	127.6(5)	Sn(2)–O(5)–C(25)	130.6(5)
Sn(1)–C(1)–C(2)	117.1(7)	C(1)–C(2)–C(3)	113.3(10)
C(2)–C(3)–C(4)	113.8(13)	Sn(1)–C(5)–C(6)	118.3(6)
C(5)–C(6)–C(7)	113.3(9)	C(6)–C(7)–C(8)	116.7(13)
Sn(2)–C(9)–C(10A)	141.3(15)	Sn(2)–C(9)–C(10B)	136.3(16)
C(9)–C(10A)–C(11A)	124.5(19)	C(9)–C(10B)–C(11B)	123.2(22)
C(10A)–C(11A)–C(12)	109.0(25)	C(11B)–C(11A)–C(12)	116.7(41)
C(10B)–C(11B)–C(12)	127.1(23)	Sn(2)–C(13)–C(14)	117.4(8)
C(13)–C(14)–C(15)	115.3(10)	C(14)–C(15)–C(16)	115.6(12)
O(2)–C(17)–O(3)	125.0(7)	O(2)–C(17)–C(18)	113.6(8)
O(3)–C(17)–C(18)	121.4(9)	C(17)–C(18)–C(19)	118.6(7)
C(17)–C(18)–C(23)	123.3(6)	C(19)–C(18)–C(23)	118.1(8)
C(18)–C(19)–C(20)	121.9(9)	C(19)–C(20)–C(21)	119.7(9)
C(20)–C(21)–C(22)	119.3(9)	C(21)–C(22)–C(23)	121.2(8)
C(18)–C(23)–C(22)	119.8(7)	C(18)–C(23)–C(24)	120.3(7)
C(22)–C(23)–C(24)	119.9(7)	O(4)–C(25)–O(5)	121.2(7)
O(4)–C(25)–C(26)	118.4(9)	O(5)–C(25)–C(26)	120.3(9)
C(25)–C(26)–C(27)	116.1(8)	C(25)–C(26)–C(31)	122.8(9)
C(27)–C(26)–C(31)	121.0(7)	C(26)–C(27)–C(28)	121.0(10)
C(27)–C(28)–C(29)	118.6(10)	C(28)–C(29)–C(30)	119.5(9)
C(29)–C(30)–C(31)	124.1(11)	C(26)–C(31)–C(30)	115.7(10)
C(26)–C(31)–C(32)	121.8(8)	C(30)–C(31)–C(32)	122.6(11)

Symmetry equivalent positions: A, $-x$, $-y$, $-z$.

For 1, the observed axial O(2)–Sn(1)–O(4) and O(5)–Sn(2)–O(1A) angles are 168.9(2)° and 163.8(2)°, respectively and the C(1)–Sn(1)–C(5) and C(9)–Sn(2)–C(13) angles are 134.8(4)° and 137.7(5)° respectively. Similarly for 2, the axial O(2)–Sn(1)–O(4) and O(5)–Sn(2)–O(1') angles are 169.7(3)° and 163.1(3)° respectively, and the C(1)–Sn(1)–C(5) and C(9)–Sn(2)–C(13) angles are 135.4(5)° and 136.3(7)° respectively. The Sn–O coordinate bonds in 1 (Sn(1)–O(3), 2.992(6) Å; Sn(2)–O(2A), 2.929(6) Å) and also those in 2 (Sn(1)–O(3), 3.012(8) Å; Sn(2)–O(2'), 2.975(8) Å) are the longest intramolecular and intermolecular Sn–O dis-

tances so far reported. The intermolecular distances are less than 0.8 Å shorter than the sum (3.67 Å) of the van der Waal's radii.

The intramolecular and intermolecular Sn–O coordinate bond distances and the C–Sn–C bond angles for some tetra-n-butyl-distannoxane derivatives are summarized in Table 7. It will be seen that the C–Sn–C bond angle in general decreases with increasing Sn ← O coordinate bond distance. It is also evident that, if these coordinate bond distances in a compound are less than 2.9 Å, then the C–Sn–C bond angles are greater than 140°, presumably indicating stronger Sn–O interactions.

Table 4
Summary of crystal data, data collection and structural refinement for 2

Crystal data	
Unit-cell parameters	
a (Å)	11.764(3)
b (Å)	12.206(3)
c (Å)	13.336(2)
α (°)	84.51(2)
β (°)	81.68(2)
γ (°)	64.23(2)
Volume (Å³)	1705.5(2)
Crystal system	Triclinic
Space group	$P\bar{1}$ (No. 2)
Empirical formula	$C_{30}H_{44}Cl_2O_5Sn_2$
Formula weight	792.9
Z; $F(000)$	2; 796
Density (calculated) (Mg m⁻³)	1.544 Mg/m³
Absorption coefficient (μ) (mm⁻¹)	1.661
Absorption correction	Transmission factors, 0.88–1.07
Data collection	
Radiation	Mo Kα (λ = 0.71073 Å)
Monochromator	Highly oriented graphite crystal
Temperature (K)	296
2θ range (°)	4.0–50.0
Scan type	2θ–θ
Scan speed (° min⁻¹)	Constant 8.00 in ω (for details see text)
Scan width	1.732 + 0.350 tan θ
Scan time : background time	2 : 1
Index ranges	$0 \leqslant h \leqslant 13, - 13 \leqslant k \leqslant 14, - 15 \leqslant l \leqslant 15$
Total number of reflections collected	6487
Number of independent reflections	6030 (R_{int} = 1.33%)
Number m of unique data used	3753 ($F > 4.0\sigma(F)$)
Solution and refinement	
Number n parameters refined	337
Data-to-parameter ratio m/n	11.1 : 1
Final R indices (observed data)	
R (%)	5.01
wR (%)	7.33
Goodness of fit S	2.04
Largest shift/error Δ/σ	0.014
Largest Difference Peak $\Delta \rho_{max}$	2.26 (electrons Å⁻³)
Largest Difference Hole	−0.80 (electrons Å⁻³)

$R = (\Sigma \| \| F_o \| - \| F_c \| \| / \Sigma \| F_o \|)$; $wR = [\Sigma w(\| F_o \| - \| F_c \|)^2 / \Sigma w \| F_o \|^2]^{1/2}$; $S = [\Sigma w(\| F_o \| - \| F_c \|)^2 / (m - n)]^{1/2}$.

Similarly an increase in the Sn–O distances from 2.9 to 3.11 Å results in an increase in the observed C–Sn–C bond angle from 133 to 138°, indicating relatively weak Sn–O interactions.

Owing to the extremely low solubility of **3** in common organic solvents, no X-ray quality crystals could be obtained. However, the IR spectra (KBr) show broad absorptions at 3450 and 3190 cm^{-1} assignable to the OH stretching mode and indicate hydrogen bonding. When the compound is warmed at 60°C for 10–15 min with chloroform, a spectral shift to 3240–3120 cm^{-1}

occurs, which may indicate breakdown of the solid state structure. This is supported by the presence of five ^{119}Sn NMR signals between -158 and -205 ppm [21].

The ^{119m}Sn Mössbauer spectra show the isomer shift δ and quadrupole splitting ΔE_Q at 1.37 and 3.42 mm s^{-1} respectively for **1**, 1.36 and 3.40 mm s^{-1} respectively for **2** and 1.35 and 3.50 mm s^{-1} respectively for **3**. The values of the ratio ($\rho = E_Q/\delta$) of 2.5–2.6 suggest that the coordination number of the tin atoms in the compounds is greater than 4. With the availability of C–Sn–C bond angle data from X-ray studies, ΔE_Q

Table 5

Atomic coordinates and equivalent isotropic displacement coefficients for **2**

	x $(\times 10^{-4})$	y $(\times 10^{-4})$	z $(\times 10^{-4})$	U_{eq} [a] (10^{-3}Å^{-2})
Sn(1)	5004(1)	2259(1)	5307(1)	50(1)
Sn(2)	5840(1)	4697(1)	5985(1)	49(1)
Cl(1)	6057(5)	29(5)	1777(3)	148(3)
Cl(2)	7739(5)	2940(3)	8733(3)	125(3)
O(1)	5115(6)	3886(5)	5125(5)	54(3)
O(2)	4411(7)	2807(6)	3774(5)	59(3)
O(3)	4418(8)	998(7)	3755(6)	72(4)
O(4)	5515(7)	2056(6)	6924(5)	65(3)
O(5)	6919(7)	2841(7)	6777(6)	69(4)
C(1)	3227(9)	2320(10)	5993(7)	59(5)
C(2)	2645(11)	3041(11)	6893(9)	74(6)
C(3)	1433(12)	2977(14)	7361(10)	97(8)
C(4)	885(17)	3606(19)	8325(13)	163(15)
C(5)	6833(10)	874(9)	4935(8)	70(5)
C(6)	7482(12)	919(12)	3963(12)	101(7)
C(7)	8829(14)	−110(16)	3776(15)	143(11)
C(8)	9434(19)	−197(20)	2798(18)	253(21)
C(9)	4529(16)	5329(17)	7267(12)	122(10)
C(10A)	3454(28)	5978(26)	7442(22)	92(8)
C(10B)	4516(31)	5191(30)	8168(27)	110(10)
C(11A)	2706(38)	6301(36)	8522(28)	113(11)
C(11B)	3416(36)	5852(33)	8913(27)	117(11)
C(12A)	1417(37)	6983(36)	8608(28)	129(12)
C(12B)	2282(41)	5929(38)	8669(30)	126(13)
C(13)	7701(9)	4529(10)	5484(9)	67(5)
C(14)	8522(11)	3528(12)	4827(10)	88(7)
C(15)	9808(11)	3462(13)	4478(11)	94(7)
C(16)	10540(16)	2520(20)	3768(14)	179(14)
C(17)	4343(9)	1937(10)	3340(7)	54(5)
C(18)	4139(8)	2253(8)	2230(4)	67(6)
C(19)	3207	3374	1936	229(21)
C(20)	3047	3655	912	140(11)
C(21)	3820	2815	183	127(12)
C(22)	4751	1694	478	116(11)
C(23)	4911	1413	1502	81(6)
C(24)	6495(10)	2121(9)	7196(8)	56(5)
C(25)	7153(9)	1262(8)	8023(7)	48(4)
C(26)	7194(11)	104(10)	8048(8)	68(6)
C(27)	7841(13)	−743(10)	8765(11)	87(7)
C(28)	8399(12)	−498(14)	9462(10)	90(7)
C(29)	8345(11)	667(13)	9439(9)	85(7)
C(30)	7753(10)	1508(10)	8708(9)	68(5)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor, i.e. $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i a_j$. Both A and B have a structure occupancy factor of 0.5.

values for **1** and **2** can be calculated by use of the Sham–Bancroft equation [22]. The average calculated values for the tin atoms in a compound (3.33 mm s^{-1} for **1** and 3.36 mm s^{-1} for **2**) are in good agreement with experimental values, namely 3.41 mm s^{-1} for **1** and 3.40 mm s^{-1} for **2**.

Table 6
Selected bond lengths (Å) and angles (°) for **2**

Bond lengths			
Sn(1)–O(1)	2.035(7)	Sn(1)–O(2)	2.203(7)
Sn(1)–O(4)	2.284(7)	Sn(1)–C(1)	2.130(11)
Sn(1)–C(5)	2.102(9)	Sn(2)–O(1)	2.064(8)
Sn(2)–O(5)	2.299(7)	Sn(2)–C(9)	2.086(15)
Sn(2)–C(13)	2.119(11)	Sn(2)–O(1')	2.179(6)
Cl(1)–C(23)	1.689(8)	Cl(2)–C(30)	1.745(14)
O(1)–Sn(2')	2.179(6)	O(2)–C(17)	1.294(15)
O(3)–C(17)	1.197(14)	O(4)–C(24)	1.295(16)
O(5)–C(24)	1.240(15)	C(1)–C(2)	1.457(15)
C(2)–C(3)	1.503(20)	C(3)–C(4)	1.476(23)
C(5)–C(6)	1.416(18)	C(6)–C(7)	1.538(17)
C(7)–C(8)	1.382(29)	C(9)–C(10A)	1.166(31)
C(9)–C(10B)	1.196(39)	C(10A)–C(11A)	1.563(45)
C(10B)–C(11B)	1.479(45)	C(11A)–C(12A)	1.369(53)
C(11B)–C(12B)	1.379(69)	C(13)–C(14)	1.459(16)
C(14)–C(15)	1.486(19)	C(15)–C(16)	1.440(23)
C(17)–C(18)	1.519(11)	C(24)–C(25)	1.495(13)
C(25)–C(26)	1.391(17)	C(25)–C(30)	1.358(18)
C(26)–C(27)	1.378(16)	C(27)–C(28)	1.337(24)
C(28)–C(29)	1.393(24)	C(29)–C(30)	1.368(16)
Sn(1) · · · O(3)	3.012(8)		
Sn(2) · · · O(2')	2.975(8)		

Bond angles			
O(1)–Sn(1)–O(2)	80.4(3)	O(1)–Sn(1)–O(4)	89.9(3)
O(2)–Sn(1)–O(4)	169.7(3)	O(1)–Sn(1)–C(1)	115.7(3)
O(2)–Sn(1)–C(1)	95.2(3)	O(4)–Sn(1)–C(1)	85.7(3)
O(1)–Sn(1)–C(5)	108.2(4)	O(2)–Sn(1)–C(5)	99.6(3)
O(4)–Sn(1)–C(5)	86.9(4)	C(1)–Sn(1)–C(5)	135.4(5)
O(1)–Sn(2)–O(5)	89.4(3)	O(1)–Sn(2)–C(9)	106.6(7)
O(5)–Sn(2)–C(9)	92.0(5)	O(1)–Sn(2)–C(13)	116.6(4)
O(5)–Sn(2)–C(13)	82.9(4)	C(9)–Sn(2)–C(13)	136.3(7)
O(1)–Sn(2)–O(1')	75.8(3)	O(5)–Sn(2)–O(1')	163.1(3)
C(9)–Sn(2)–O(1')	99.8(4)	C(13)–Sn(2)–O(1')	96.5(3)
Sn(1)–O(1)–Sn(2)	131.5(3)	Sn(1)–O(1)–Sn(2')	123.8(4)
Sn(2)–O(1)–Sn(2')	104.2(3)	Sn(1)–O(2)–C(17)	112.3(6)
Sn(1)–O(4)–C(24)	126.3(6)	Sn(2)–O(5)–C(24)	128.4(7)
Sn(1)–C(1)–C(2)	116.9(10)	C(1)–C(2)–C(3)	113.3(13)
C(2)–C(3)–C(4)	114.5(16)	Sn(1)–C(5)–C(6)	118.7(7)
C(5)–C(6)–C(7)	114.8(12)	C(6)–C(7)–C(8)	116.8(15)
Sn(2)–C(9)–C(10A)	137.3(18)	Sn(2)–C(9)–C(10B)	137.7(18)
C(9)–C(10A)–C(11A)	125.8(28)	C(9)–C(10B)–C(11B)	125.1(28)
C(10A)–C(11A)–C(12A)	119.0(33)	C(10B)–C(11B)–C(12B)	113.5(36)
Sn(2)–C(13)–C(14)	117.5(10)	C(13)–C(14)–C(15)	115.5(14)
C(14)–C(15)–C(16)	113.2(16)	O(2)–C(17)–O(3)	124.7(9)
O(2)–C(17)–C(18)	111.8(9)	O(3)–C(17)–C(18)	123.4(11)
C(17)–C(18)–C(19)	120.8(4)	C(17)–C(18)–C(23)	119.2(4)
Cl(1)–C(23)–C(18)	123.8(3)	Cl(1)–C(23)–C(22)	116.2(3)
O(4)–C(24)–O(5)	122.4(9)	O(4)–C(24)–C(25)	117.9(10)
O(5)–C(24)–C(25)	119.7(11)	C(24)–C(25)–C(26)	116.2(10)
C(24)–C(25)–C(30)	125.3(10)	C(26)–C(25)–C(30)	118.4(9)
C(25)–C(26)–C(27)	118.6(13)	C(26)–C(27)–C(28)	113.3(13)
C(27)–C(28)–C(29)	117.7(12)	C(28)–C(29)–C(30)	119.9(14)
Cl(2)–C(30)–C(25)	121.4(8)	Cl(2)–C(30)–C(29)	16.7(11)
C(25)–C(30)–C(29)	121.8(13)		

Symmetry equivalent positions: $1 - x$, $1 - y$, $1 - z$.

Table 7
Comparison of X-ray structural parameters for $[Bu_2SnO_2CX)_2O]_2$

X	Sn(2)–O(2) (Å)	C–Sn–C (°)	Sn(1)–O(3) (Å)	C–Sn–C (°)	Reference
2-methylthio-3-pyridine	2.793(6)	140.7(4)	2.984(7)	135.3(5)	[7]
C_4H_3S	2.830(8)	143.6(5)	2.867(8)	139.6(4)	[17]
C_6H_4–o-NH_2	2.79(2)	149.0(4)	2.84(1)	136.0(3)	[18]
	2.72(1)	140.0(3)	3.11(2)	137.0(4)	
CCl_3	2.68(2)	143.0(2)	3.06(2)	137.0(2)	[19]
C_6H_4–o-NO_2	2.798(6)	137.9(3)	3.054(6)	133.2(2)	[8]
C_6H_4–o-OMe	2.781(7)	144.4(5)	2.861(7)	139.0(3)	[20]
	2.787(7)	145.6(3)	2.736(7)	138.8(3)	
C_6H_4–o-Me	2.929(5)	137.7(5)	2.992(6)	134.8(4)	Present work
C_6H_4–o-Cl	2.975(8)	136.3(7)	3.012(8)	135.4(5)	Present work

If there is no effect of hydrogen bonding on the C–Sn–C bond angle in the solid state, the quadrupole splitting value for 3 can be used to compute a value for the average C–Sn–C angle of 138.2°. This, however, would have to be confirmed by an X-ray study.

Acknowledgments

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