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Structural chemistry of organotin carboxylates

IV *. Synthesis and spectroscopic properties of diorganotin(IV) complexes with *o*-anisic acid. The crystal and molecular structure of $\{[{}^n\text{Bu}_2\text{Sn}(2\text{-MeOC}_6\text{H}_4\text{COO})]_2\text{O}\}_2$

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Abstract

Reactions of diorganotin(IV) oxides with *o*-anisic acid in 1/1 and 1/2 stoichiometry afford complexes of the type $\{[\text{R}_2\text{Sn}(2\text{-MeOC}_6\text{H}_4\text{COO})]_2\text{O}\}_2$ (I) and $[\text{R}_2\text{Sn}(2\text{-MeOC}_6\text{H}_4\text{COO})_2]$ (II) (R = Me, Et, ⁿPr, ⁿBu), respectively. These complexes have been characterized by elemental analyses, IR and NMR (¹H, ¹³C and ¹¹⁹Sn) spectroscopy, and I shown to adopt a dimeric ladder structure whereas II has the usual monomeric diorganotin dicarboxylate structure. The oxygen atom of the methoxy group of the ligand does not participate in bonding to the tin atom. This conclusion is supported by an X-ray diffraction study. The compound $\{[{}^n\text{Bu}_2\text{Sn}(2\text{-MeOC}_6\text{H}_4\text{COO})]_2\text{O}\}_2$, (Id), showed that in solid Id there are two unique, centrosymmetric dimers in the asymmetric unit. The individual molecules conform to the tetraorganostannoxane structure, with six-coordination being assigned to both the endocyclic and exocyclic tin atoms after consideration of close intermolecular tin to oxygen contacts. Crystals are triclinic with space group $P\bar{1}$ and unit cell dimensions a 13.503(3), b 24.226(4), c 11.917(1) Å, α 102.21(1), β 108.54(2), and γ 89.92(1)°. The structure was refined by a blocked-matrix least-squares procedure to final $R = 0.052$ for 5505 reflections with $I \geq 2.5\sigma(I)$.

For Part III, see ref. 7.

Introduction

The study of organotin compounds are of current interest owing to their wide range of applications such as biocides [1-4] and as homogeneous catalysts in industry [5,6]. In general the biocidal activity of organotin compounds is influenced greatly by the structure of the molecule and the coordination number of the tin atom(s) [3-5]. Recently we have investigated organotin compounds containing carboxylate ligands which have an additional hetero-donor atom (e.g. N, O or S) residing on the R' group, that is, potentially tridentate ligands, in order to examine what effect the presence of the heteroatom has on the structure adopted by these compounds [6,7]. As a part of our continuing programme in this area we have synthesized and structurally characterized diorganotin(IV) compounds of the potentially tridentate ligand *o*-anisic acid, and the results of this study are reported herein.

Results

Treatment of R₂SnO with *o*-anisic acid in 1/1 and 1/2 stoichiometry yields {[R₂Sn(2-MeOC₆H₄COO)]₂O}₂ (Ia, R = Me; Ib, R = Et; Ic, R = ⁿPr; Id, R = ⁿBu) and [R₂Sn(2-MeOC₆H₄COO)₂] (IIa, R = Me; IIb, R = Et; IIc, R = ⁿPr; IIId, R = ⁿBu), respectively; Table 1. The asymmetric ν(COO) band appears in the region 1590-1615 cm⁻¹, and represents a shift to lower wavenumber from that found for the free acid. A strong, broad band in the region 630-645 cm⁻¹ for I can be assigned to the ν(Sn-O-Sn) mode [5].

The ¹H NMR spectra showed the expected integration and peak multiplicities. The methyl groups attached to tin in the compound IIa showed a singlet (δ 1.10 ppm; ²J(Sn-H) 82 Hz) and the magnitude of ²J is comparable to that for

Table 1

Physical and analytical data for diorganotin (IV) complexes of *o*-anisic acid.

Compound	M.p. (°C)	Recrystallization solvent	Yield (%)	Analysis (Found (Calcd.) (%))		
				C	H	Sn
{[Me ₂ Sn(2-MeOC ₆ H ₄ COO)] ₂ O} ₂ (Ia)	203	CH ₂ Cl ₂ /hexane	72	38.60 (39.01)	4.09 (4.25)	37.66 (38.55)
{[Et ₂ Sn(2-MeOC ₆ H ₄ COO)] ₂ O} ₂ (Ib)	170	CH ₂ Cl ₂ /hexane	69	42.56 (42.90)	5.05 (5.10)	35.02 (35.33)
{[ⁿ Pr ₂ Sn(2-MeOC ₆ H ₄ COO)] ₂ O} ₂ (Ic)	120	C ₆ H ₆ /hexane	51	46.37 (46.19)	6.01 (5.81)	32.13 (32.61)
{[ⁿ Bu ₂ Sn(2-MeOC ₆ H ₄ COO)] ₂ O} ₂ (Id)	90-95	hexane	83	48.63 (49.02)	6.44 (6.43)	29.70 (30.27)
[Me ₂ Sn(2-MeOC ₆ H ₄ COO) ₂] (IIa)	85	CH ₂ Cl ₂ /hexane	62	47.46 (47.93)	4.26 (4.47)	27.23 (26.31)
[Et ₂ Sn(2-MeOC ₆ H ₄ COO) ₂] (IIb)	80-83	CH ₂ Cl ₂ /hexane	46	49.38 (50.14)	4.98 (5.05)	24.80 (24.77)
[ⁿ Pr ₂ Sn(2-MeOC ₆ H ₄ COO) ₂] (IIc)	60-63	CH ₂ Cl ₂ /hexane	60	51.70 (52.10)	5.34 (5.56)	23.43 (23.40)
[ⁿ Bu ₂ Sn(2-MeOC ₆ H ₄ COO) ₂] (IIId)	60-63	hexane	76	53.70 (53.86)	5.98 (6.03)	22.24 (22.18)

Table 2
 ^{119}Sn (^1H) and ^{13}C (^1H) NMR data of organotin(IV) complexes with *o*-anisic acid.

Compound	$\delta(^{119}\text{Sn})$ (^1H) (ppm)	$\delta(\text{Sn}-\text{C})$ (ppm)	^{13}C (^1H) NMR data ^a (δ , ppm)							
			OMe	COO	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)
2-MeOC ₆ H ₄ COOH	-	-	56.4	166.3	121.5	158.2	111.8	134.9	117.4	133.0
{[Me ₂ Sn(2-MeOC ₆ H ₄ COO)] ₂ O} ₂ (Ia)	-176, -183	8.9, 7.3	55.6	173.0	123.5	158.3	111.7	132.3	120.1	131.3
{[Et ₂ Sn(2-MeOC ₆ H ₄ COO)] ₂ O} ₂ (Ib)	-203, -210	21.3 (728 Hz) ^b 20.2 (722 Hz) ^b 9.6, 9.4	55.4	173.0	124.1	158.1	111.5	131.8	119.6	130.8
{[ⁿ Pr ₂ Sn(2-MeOC ₆ H ₄ COO)] ₂ O} ₂ (Ic)	-206, -210	30.9, 30.2, 18.6 18.5, 18.3	55.4	174.4	124.1	158.0	111.5	131.6	119.8	130.5
{[ⁿ Bu ₂ Sn(2-MeOC ₆ H ₄ COO)] ₂ O} ₂ (Id)	-199, -203	28.2, 26.7, 27.2 26.7, 13.3	55.3	173.1	124.1	157.8	111.4	131.4	119.8	130.3
[Me ₂ Sn(2-MeOC ₆ H ₄ COO)] ₂ ^c (IIa)	-125	4.6 ¹ J(¹¹⁹ Sn- ¹³ C) 666 Hz; ¹ J(¹¹⁷ Sn- ¹³ C) 639 Hz	55.6	172.6	120.1	159.0	111.6	133.8	119.7	132.7
[Et ₂ Sn(2-MeOC ₆ H ₄ COO)] ₂ (IIb)	-155	17.7, 9.6	56.1	174.6	120.1	159.7	112.0	134.1	120.1	133.2
[ⁿ Pr ₂ Sn(2-MeOC ₆ H ₄ COO)] ₂ (IIc)	-150	27.8, 18.3, 17.7	56.0	174.0	120.1	159.0	112.0	134.0	120.1	133.0
[ⁿ Bu ₂ Sn(2-MeOC ₆ H ₄ COO)] ₂ (IIId)	-149	25.0 (599 Hz) ^b 26.1 (102 Hz) ^b 26.5, 13.4	55.9	174.0	120.0	159.5	111.8	133.7	120.0	132.8

^a Interpretation is based on the reported ^{13}C NMR data for similar compounds. ^b $^1J(^{119}/^{117}\text{Sn}-^{13}\text{C})$ values. ^c Contains small impurity of {[R₂Sn(2-MeOC₆H₄COO)]₂O}₂.

[Me₂Sn(OAc)₂] [8] (82.5 Hz), indicating approximate octahedral geometry in solution. Ia displayed two resonances (δ 0.92 ppm, $^2J(\text{Sn-H})$ 89 Hz exocyclic, and δ 0.98 ppm, 2J 91 Hz, endocyclic) as expected for tetraorganodistannoxanes. The OMe proton resonance of the *o*-anisic acid moiety in the free acid and in the complexes appeared at ca. δ 3.8 ppm, while signals from the aromatic protons (H(3), H(4), H(5) and H(6)) appeared as complex multiplets in the region δ 6.78–8.03 ppm. The singlet at δ 9.95 due to the hydroxyl proton in *o*-anisic acid was absent from the spectra of the complexes.

The ¹³C NMR spectra (Table 2) of II and I displayed one and two sets of Sn–R resonances, respectively. Owing to the low intensities of the Sn–R resonances, identification of $^1J(\text{Sn-C})$ from spectral noise was not possible in all cases. Ligand carbons in all cases appeared as singlets. As for the ¹H resonances (see above) the ¹³C resonances of the OMe group showed little change from their positions for the free ligand, suggesting that the OMe part of the carboxylic acid is not involved in bonding to the tin atom. The ¹¹⁹Sn NMR spectra of II displayed a single resonance in the region –125 to –150 ppm; in contrast the ¹¹⁹Sn NMR spectra of I exhibited two signals in the region –176 to –210 ppm.

The NMR data for II can be best interpreted in terms of the common diorganotin dicarboxylate structure; i.e. the tin atom is octahedrally surrounded by two asymmetrically chelating carboxylate groups [8]. The value of $^1J(\text{Sn-C})$ is as expected, and by use of Lockhart's equation [9] the C–Sn–C angle for IIa is calculated to be 135°, close to the angle observed for [Me₂Sn(OAc)₂] [8].

The ¹³C and ¹¹⁹Sn NMR data for the complexes I are consistent with a dimeric tetraorganostannoxane structure [9,10]. Although at least two different types of carboxylate groups are present (as revealed by the X-ray analysis; see below), only single resonances are observed for the COO group in the ¹³C spectra of I. This may be due to either accidental magnetic equivalence of the carbonyl carbon atoms or a dynamic equilibrium between possible isomeric structures. Recently, asymmetric distannoxane dimers have been studied by ¹¹⁹Sn NMR spectroscopy [11] and the existence of a dynamic equilibrium between various possible tetraorganodistannoxanes has been suggested.

The crystal structure analysis of {[ⁿBu₂Sn(2-MeOC₆H₄COO)]₂O}₂ (Id) reveals that there are two unique tetraorganostannoxane moieties in the triclinic unit cell each of which is disposed about a crystallographic centre of inversion such that two half formula units comprise the asymmetric unit. Selected interatomic bond distances and angles are given in Table 3, and the numbering scheme employed is shown in Fig. 1. To a first approximation the two molecules (designated a and b, respectively) comprising the asymmetric unit are equivalent. Each features the now familiar planar Sn₂O₂ four-membered ring, with two ⁿBu₂Sn(2-MeOC₆H₄COO) units being attached at each bridging oxygen atom.

In both molecules there are two distinct carboxylate groups. One, defined by O(2) and O(3), bridges both tin atoms and the other, defined by O(4) and O(5), functions essentially in the monodentate mode. In addition, each tin atom forms two σ bonds to two *n*-butyl groups. As a consequence the corresponding tin atoms in both molecules exist in similar coordination environments.

The endocyclic tin atom, Sn(1), forms five short bonds: two to the O(1) atoms, one to the O(2) atom, and two to the *n*-butyl groups. In addition the Sn(1) atom makes a close contact of 2.781(7) Å (2.787(7) Å for molecule b) with the O(4) atom.

Table 3

Selected bond distances (Å) and angles (°) for $\{[{}^n\text{Bu}_2\text{Sn}(2\text{-MeOC}_6\text{H}_4\text{COO})]_2\text{O}\}_2$

	Molecule a	Molecule b
Sn(1)–O(1)	2.161(6)	2.034(7)
Sn(1)–O(1')	2.041(6)	2.163(7)
Sn(1)–O(2)	2.286(6)	2.297(6)
Sn(1)–O(4)	2.781(7)	2.787(7)
Sn(1)–C(17)	2.13(1)	2.13(2)
Sn(1)–C(21)	2.10(1)	2.15(2)
Sn(2)–O(1)	2.036(6)	2.036(6)
Sn(2)–O(3)	2.275(8)	2.281(6)
Sn(2)–O(4)	2.160(7)	2.182(6)
Sn(2)–O(5)	2.861(7)	2.736(7)
Sn(2)–C(25)	2.13(1)	2.13(1)
Sn(2)–C(29)	2.15(1)	2.11(2)
C(1)–O(2)	1.26(1)	1.25(1)
C(1)–O(3)	1.26(2)	1.24(2)
C(9)–O(4)	1.27(2)	1.28(2)
C(9)–O(5)	1.25(1)	1.21(1)
O(1)–Sn(1)–O(1')	75.3(2)	75.0(2)
O(1)–Sn(1)–O(2)	165.0(3)	89.3(3)
O(1)–Sn(1)–O(4)	64.8(3)	139.5(3)
O(1)–Sn(1)–C(17)	95.9(3)	111.6(3)
O(1)–Sn(1)–C(21)	97.8(4)	102.5(3)
O(1')–Sn(1)–O(2)	90.2(3)	162.2(3)
O(1')–Sn(1)–O(4)	140.0(3)	64.9(3)
O(1')–Sn(1)–C(17)	107.5(3)	95.0(3)
O(1')–Sn(1)–C(21)	107.7(3)	98.1(3)
O(2)–Sn(1)–O(4)	129.8(3)	131.2(3)
O(2)–Sn(1)–C(17)	84.6(3)	88.1(3)
O(2)–Sn(1)–C(21)	89.6(3)	98.2(3)
O(4)–Sn(1)–C(17)	80.5(3)	78.2(3)
O(4)–Sn(1)–C(21)	76.5(3)	78.9(3)
C(17)–Sn(1)–C(21)	144.4(5)	145.6(3)
O(1)–Sn(2)–O(3)	91.3(3)	89.3(3)
O(1)–Sn(2)–O(4)	80.1(3)	79.7(3)
O(1)–Sn(2)–O(5)	130.1(3)	130.2(3)
O(1)–Sn(2)–C(25)	110.8(3)	116.1(3)
O(1)–Sn(2)–C(29)	109.1(3)	104.6(3)
O(3)–Sn(2)–O(4)	171.3(3)	168.5(3)
O(3)–Sn(2)–O(5)	138.6(3)	140.5(3)
O(3)–Sn(2)–C(25)	83.5(3)	86.6(3)
O(3)–Sn(2)–C(29)	86.5(3)	88.5(3)
O(4)–Sn(2)–O(5)	50.1(3)	50.7(3)
O(4)–Sn(2)–C(25)	99.5(3)	95.9(3)
O(4)–Sn(2)–C(29)	96.3(3)	97.7(3)
O(5)–Sn(2)–C(25)	83.0(3)	78.5(3)
O(5)–Sn(2)–C(29)	78.7(3)	80.6(3)
C(25)–Sn(2)–C(29)	139.0(3)	138.8(3)
Sn(1)–O(1)–Sn(1')	104.7(2)	105.0(2)
Sn(1)–O(1)–Sn(2)	119.5(2)	134.6(2)
Sn(1)–O(1)–Sn(2')	135.0(2)	120.9(2)
Sn(1)–O(2)–C(1)	137.0(3)	126.8(3)
Sn(2)–O(3)–C(1)	134.4(3)	128.7(3)
Sn(2)–O(5)–C(9)	76.4(3)	82.1(3)
O(2)–C(1)–O(3)	122.4(8)	127.7(8)
O(4)–C(9)–O(5)	128.5(8)	120.4(8)

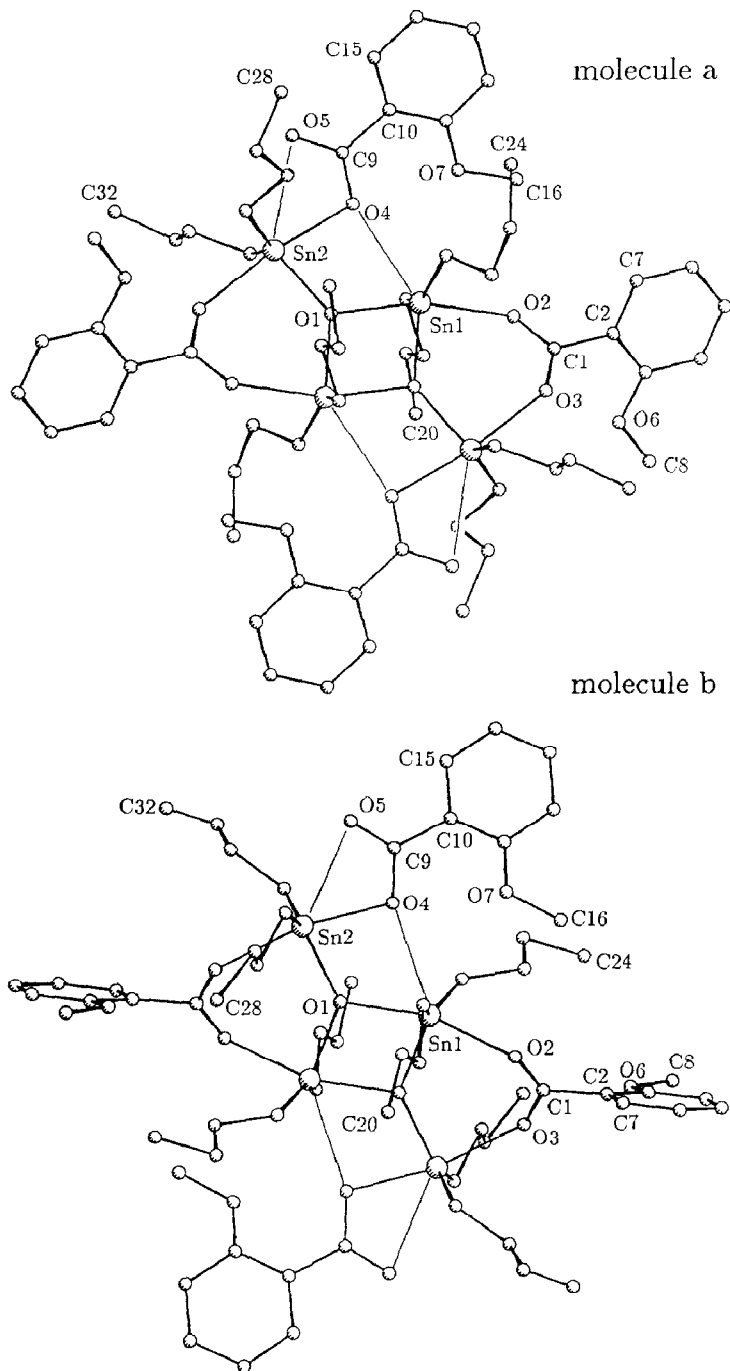


Fig. 1. Molecular structure and crystallographic numbering scheme for $\{[{}^n\text{Bu}_2\text{Sn}(2\text{-MeOC}_6\text{H}_4\text{-COO})_2\text{O}]\}_2$.

These contacts are significantly less than 3.7 \AA , the sum of the Van der Waals radii for these atoms [12]. The Sn(1) atom is therefore best described as six-coordinate. A distinct coordination geometry is found for the exocyclic Sn(2) atom, for which an

Sn–O bond is formed with both the bridging and monodentate carboxylate groups as well as with the bridging O(1) atom of the Sn₂O₂ moiety; there are also two additional bonds to n-butyl groups. The Sn(2) atom also forms a weak interaction with O(5), derived from the monodentate carboxylate group, of 2.861(7) Å (2.736(7) Å for molecule b), and thus this atom may also be considered as six coordinate.

Noteworthy in the structure is the absence of a significant contact between the tin atoms and the O atom of the OMe group of *o*-anisic acid. The structure found here for {[ⁿBu₂Sn(2-MeOC₆H₄COO)]₂O}₂ contrasts with that found for {[ⁿBu₂Sn(2-pic)]₂O}₂ (where 2-pic is 2-pyridinecarboxylate) in which the hetero N atoms of the 2-pic ligands do form significant contacts with the Sn atoms [6]. The structure of {[ⁿBu₂Sn(2-MeOC₆H₄COO)]₂O}₂ does, however, have several precedents [13–17] showing closely similar gross geometric features, i.e. a Sn₂O₂ unit with two bridging and two essentially monodentate carboxylate ligands.

As can be seen from Table 3 and the foregoing discussion, the intermolecular parameters for the two unique molecules in the asymmetric unit are quite similar. The most obvious difference however, can be seen from Fig. 1, viz. that there is a twist about the C(1)–C(2) bond of the *o*-anisic acid function (exaggerated in the diagram) that distinguishes molecules a and b such that the torsion angles O(2)C(1)C(2)C(3) is –120.7° for molecule a and –133.3° for molecule b.

Experimental

o-Anisic acid and Bu₂SnO were obtained from Koch Light Laboratories Ltd. and Fluka Chemicals A.G., respectively. Dried analytical grade solvents were used in all

Table 4

Crystal data and refinement details for {[ⁿBu₂Sn(2-MeOC₆H₄COO)]₂O}₂

Formula	C ₆₄ H ₁₀₀ O ₁₄ Sn ₄
Mol.wt.	1568.2
Crystal system	triclinic
Space group	$P\bar{1}$
<i>a</i> , Å	13.503(3)
<i>b</i> , Å	24.226(4)
<i>c</i> , Å	11.917(1)
α , deg.	102.21(1)
β , deg.	108.54(2)
γ , deg.	89.92(1)
<i>V</i> , Å ³	3603.3
<i>Z</i>	2 (tetramers)
<i>D_c</i> (g cm ⁻³)	1.445
<i>F</i> (000)	1592
μ , cm ⁻¹	13.05
Transmission factors (max./min.)	0.823; 0.489
θ limits (°)	1.0–25.0
No. of data collected	10388
No. of unique data	9416
No. of unique reflections used with $I \geq 2.5\sigma(I)$	5505
<i>R</i>	0.052
<i>g</i>	0.0027
<i>R_w</i>	0.063
Residual ρ_{\max} (e Å ⁻³)	0.78

Table 5

Fractional atomic coordinates ($\times 10^5$ for Sn; $\times 10^4$ for remaining atoms) for $\{[{}^n\text{Bu}_2\text{Sn}(2\text{-MeOC}_6\text{H}_4\text{COO})]_2\text{O}\}_2$

Atom	x	y	z
Sn(1A)	3967(5)	138(3)	38192(6)
Sn(2A)	8874(6)	13414(3)	60582(6)
Sn(1B)	45491(5)	50751(3)	35717(6)
Sn(2B)	46423(6)	36081(3)	41479(6)
O(1A)	384(5)	506(3)	5552(5)
O(2A)	82(6)	-651(3)	2047(6)
O(3A)	-179(6)	-1482(3)	2418(6)
O(4A)	1470(5)	1076(3)	4552(5)
O(5A)	1982(7)	1989(3)	5017(7)
O(6A)	-1698(8)	-1845(4)	-34(8)
O(7A)	1545(7)	671(3)	2209(7)
O(1B)	4886(5)	4467(3)	4553(5)
O(2B)	4282(6)	4388(3)	1830(6)
O(3B)	3610(5)	3642(3)	2235(5)
O(4B)	5576(6)	3756(3)	6066(6)
O(5B)	5420(8)	2841(4)	5536(10)
O(6B)	1731(6)	3481(5)	245(8)
O(7B)	6274(8)	4078(5)	8578(7)
C(1A)	-34(9)	-1182(5)	1736(9)
C(2A)	15(6)	-1454(3)	522(6)
C(3A)	-837(6)	-1789(3)	-346(6)
C(4A)	-771(6)	-2049(3)	-1480(6)
C(5A)	147(6)	-1972(3)	-1746(6)
C(6A)	999(6)	-1637(3)	-877(6)
C(7A)	933(6)	-1377(3)	257(6)
C(8A)	-2636(14)	-2163(7)	-939(15)
C(9A)	1985(9)	1491(5)	4457(10)
C(10A)	2720(6)	1382(4)	3696(7)
C(11A)	2501(6)	958(4)	2638(7)
C(12A)	3247(6)	848(4)	2050(7)
C(13A)	4212(6)	1161(4)	2520(7)
C(14A)	4431(6)	1584(4)	3577(7)
C(15A)	3685(6)	1695(4)	4166(7)
C(16A)	1270(15)	278(6)	1048(12)
C(17A)	-745(8)	465(5)	2740(10)
C(18A)	-1819(9)	126(5)	2160(11)
C(19A)	-2627(11)	511(6)	1510(14)
C(20A)	-3730(16)	214(10)	1126(22)
C(21A)	1982(10)	-155(6)	4344(12)
C(22A)	2332(24)	-737(10)	4130(31)
C(23A)	3555(21)	-784(12)	4511(24)
C(24A)	4204(41)	-325(19)	4323(49)
C(25A)	2331(10)	1481(6)	7519(12)
C(26A)	3280(13)	1260(8)	7217(17)
C(27A)	4233(20)	1450(11)	8408(20)
C(28A)	5360(32)	1511(26)	8389(59)
C(29A)	-332(9)	1826(5)	5167(11)
C(30A)	-320(11)	2436(6)	5875(13)
C(31A)	-1301(12)	2716(7)	5183(15)
C(32A)	-1089(19)	3326(9)	5953(22)

Table 5 (continued)

Atom	x	y	z
C(1B)	3766(8)	3923(5)	1547(8)
C(2B)	3421(6)	3657(3)	181(6)
C(3B)	2388(6)	3439(3)	-424(6)
C(4B)	2078(6)	3173(3)	-1652(6)
C(5B)	2802(6)	3125(3)	-2276(6)
C(6B)	3835(6)	3343(3)	-1672(6)
C(7B)	4145(6)	3609(3)	-443(6)
C(8B)	661(12)	3269(11)	-346(18)
C(9B)	5782(10)	3268(5)	6305(11)
C(10B)	6546(8)	3209(5)	7484(9)
C(11B)	6814(8)	3619(5)	8568(9)
C(12B)	7589(8)	3526(5)	9596(9)
C(13B)	8095(8)	3023(5)	9540(9)
C(14B)	7826(8)	2613(5)	8457(9)
C(15B)	7052(8)	2706(5)	7429(9)
C(16B)	6437(16)	4554(8)	9649(15)
C(17B)	5862(10)	5343(5)	3143(12)
C(18B)	6680(11)	4902(6)	3194(15)
C(19B)	7704(14)	5156(8)	3115(18)
C(20B)	8481(21)	4708(12)	3445(27)
C(21B)	2906(11)	5153(6)	3284(13)
C(22B)	2030(17)	4946(12)	2068(20)
C(23B)	968(19)	5118(10)	2283(23)
C(24B)	172(41)	4729(21)	1155(37)
C(25B)	3260(8)	3288(5)	4355(11)
C(26B)	2230(9)	3569(5)	3788(11)
C(27B)	1347(10)	3349(6)	4194(12)
C(28B)	323(15)	3568(10)	3401(20)
C(29B)	5833(12)	3318(7)	3422(14)
C(30B)	5618(15)	2767(8)	2389(17)
C(31B)	6570(16)	2678(10)	1860(20)
C(32B)	6297(36)	2054(13)	1316(43)

experiments. The IR spectra were recorded as Nujol/Fluorolube mulls on a Perkin Elmer 577 spectrophotometer. The ^1H , ^{13}C and ^{119}Sn NMR spectra were recorded with CDCl_3 solutions on a Varian FT-80 A NMR spectrometer, operating at 79.54, 20.00 and 29.63 MHz, respectively. Chemical shifts are reported in ppm from internal chloroform (7.26 ppm for ^1H and 77.6 ppm for ^{13}C) and from external 33% Me_4Sn in C_6D_6 for ^{119}Sn . Tin was estimated as SnO_2 . Microanalyses were performed by Analytical Chemistry Division of the Badha Atomic Research Centre.

Synthesis

Preparation of $[\{\text{Bu}_2\text{Sn}(2\text{-MeOC}_6\text{H}_4\text{COO})\}_2\text{O}]_2$. To a benzene suspension of Bu_2SnO (1.18 g, 4.74 mmol) was added a benzene solution (ca. 60 ml) of *o*-anisic acid (0.72 g, 4.76 mmol). The mixture was heated under reflux with stirring for 2 h. Water formed during the reaction was removed azeotropically with a Dean and Stark trap. The clear solution thus obtained was evaporated under vacuum to leave a white crystalline solid, which was recrystallized from hexane in 82% yield. The oxides Ia, Ib and Ic were prepared similarly, but with benzene/methanol as a

solvent in the case of Ia and Ib. Similar reactions in 1/2 stoichiometry afforded $[\text{R}_2\text{Sn}(2\text{-MeOC}_6\text{H}_4\text{COO})_2]$ (II). Pertinent data for these complexes are given in Table 1.

Crystallography

Intensity data for 10388 reflections were measured on an Enraf-Nonius CAD4F diffractometer by use of graphite monochromatized Mo- K_α radiation and the $\omega/2\theta$ scan technique. The net intensity values of three reference reflections decreased to ca. 91% of their original values during the course of the data collection and the data were scaled to allow for this. The data were also corrected for Lorentz and polarization effects and for absorption [17]. Of the reflections measured ($\theta_{\text{max}} 25^\circ$) 9416 were unique ($R_{\text{amalg}} 0.016$), and of these 5505 satisfied the $I \geq 2.5\sigma(I)$ criterion of observability. Relevant crystal data and refinement details are given in Table 4.

The structure was solved by direct-methods and refined by a blocked-matrix least-squares procedure based on F [18]. The crystallographic asymmetric unit is comprised of two half tetraorganostannoxane molecules, each situated about a centre of inversion. Owing to high thermal motion in the structure, the eight unique n-butyl groups were refined with constrained C-C bond distances of 1.55(2) Å. The Sn, O and non-phenyl C atoms were refined with anisotropic thermal parameters and the phenyl rings were refined as hexagonal rigid groups with individual isotropic thermal parameters; hydrogen atoms were not included in the model. An empirical extinction correction, 0.00030(5), was applied to the data. Refinement with a weighting scheme of the form $w = [\sigma^2(F) + g(F)^2]^{-1}$ converged to final values of $R = 0.052$, $R_w = 0.063$, and $g = 0.0027$.

Fractional atomic coordinates are listed in Table 5 and the numbering scheme used is shown in Fig. 1 (diagram drawn with the PLUTO program [19]). Scattering factors for all atoms were those incorporated in the SHELX76 program system [18]. Other crystallographic data are available from the authors (E.R.T.T.).

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