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Syntheses and Solid-State Structures of Some Dialkyltin Derivatives of α-Methoxy- and α-Acetoxy-phenylacetic Acids

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Several di-n-butyltin and diethyltin biscarboxylates and distannoxanes of α-methoxy- and α-acetoxy-phenylacetic acids were synthesized and (two of) their structures were studied by means of X-ray diffraction analysis as well as by means of IR and Mössbauer spectroscopies. It was shown for $\{[(n\text{-Bu})_2SnOC(O)CH(OMe)Ph]_2O\}_2$ that there is an interaction between the OMe group and one of the endocyclic tin atoms, resulting in a distorted pentagonal-bipyramidal geometry with the pentagonal plane defined by five O atoms and an uncommon seven coordination number for this tin atom. Spectral data indicate that biscarboxylates have *trans*-octahedral structures.

Keywords: organotin biscarboxylates; distannoxanes; coordination bonds

INTRODUCTION

Diorganotin carboxylates often show promising antitumour activity, as has been found, for example, for a number of substituted benzoates.[1-8] We have synthesized some di-n-butyltin and diethyltin derivatives of α-methoxy- and α-acetoxy-phenylacetic acids: $\{[Et_2SnOC(O)CH(OAc)Ph]_2O\}_2$ (**1**); $\{[(n\text{-Bu})_2SnOC(O)CH(OMe)Ph]_2O\}_2$ (**2**); $(n\text{-Bu})_2Sn[OC(O)CH(OMe)Ph]_2$ (**3**); $R_2Sn[OC(O)CH(OAc)Ph]_2$ where R=Et (**4**) or n-Bu (**5**), in order to study their structures by means of X-ray diffraction analysis as well as by IR and Mössbauer spectroscopies and to test their biological activities; the dialkyltin biscarboxylates described here are being screened for antitumour activities at the National Cancer Institute, Bethesda, MD, USA.

EXPERIMENTAL

The compounds **1–5** were obtained by the interaction of R_2SnO, R=Et, n-Bu, and the appropriate acid in $CHCl_3$ in the molar ratio 1:1 for **1** and **2**, and in C_6H_6 in the molar ratio 1:2 for **3–5**. The reactions were carried out in the presence of excess 2,2-dimethoxypropane to absorb water. The yields were about 85–90%. Results of the elemental analyses are reported in Table 1 together with melting points.

Intensity data for colourless crystals of **1** and **2** were measured at room temperature on a CAD-4 Enraf Nonius diffractometer (Mo-K_α radiation, graphite monochromator, ω-scanning). Crystal data for **1** and **2** and the conditions of X-ray experiments are given in Table 2. No absorption or extinction corrections were applied. The positions of the tin atoms were determined by the Patterson method, and the other atoms were found from Fourier and difference Fourier syntheses. In structure 1 the hydrogen atoms were placed in calculated positions and included in the structure factor calculations but not refined. All non-hydrogen atoms were refined anisotropically. Structure determinations were carried out with the SDP package.[9] Final fractional atomic coordinates for **1** and **2** are given in Tables 3 and 4 respectively, bond distances and angles in Tables 5 and 6.

IR spectra were recorded as Nujol and hexachlorobutadiene mulls on a Perkin–Elmer grating spectrometer, model 983G, with CsI windows.

^{119}Sn Mössbauer spectra were measured with constant acceleration and a triangular waveform, using a Laben 8001 multichannel analyser, and a

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Table 1 Physical and analytical data for diorganotin carboxylates

No.	Compound	M.p. (°C)	Analysis: found (Calcd) (%) C	H
1	$\{[Et_2SnOC(O)CH(OAc)Ph]_2O\}_2$	179–180	44.2 (44.4)	5.0 (5.0)
2	$\{[(n\text{-}Bu)_2SnOC(O)CH(OMe)Ph]_2O\}_2$	94–95	49.1 (49.2)	6.7 (6.8)
3	$(n\text{-}Bu)_2Sn[OC(O)CH(OMe)Ph]_2$	78–79	55.5 (55.4)	6.6 (6.4)
4	$Et_2Sn[OC(O)CH(OAc)Ph]_2$	114–115	51.6 (51.2)	5.3 (5.0)
5	$(n\text{-}Bu)_2Sn[OC(O)CH(OAc)Ph]_2$	102–104	54.3 (54.3)	5.9 (5.8)

Mössbauer closed-refrigerator system [model 21 sc Cryodyne Cryocooler (CTI-Cryogenics, USA)].

RESULTS AND DISCUSSION

The structures and atomic numbering schemes for **1** and **2** are depicted in Figs 1 and 2 respectively. The dicarboxylatotetraorganodistannoxanes **1** and **2** are centrosymmetric dimers. Their structures are built up around a planar four-membered Sn_2O_2 unit. The two exocyclic Sn(2) atoms are connected to the bridging O atoms of the Sn_2O_2 ring.

There are two distinct carboxylate moieties in the structures. The first type of carboxylate group O(2)–C(9)–O(3) (Figs 1, 2) is bidentate and bridges both the endocyclic and exocyclic Sn atoms, the Sn–O bonds being asymmetric [Δ(Sn–O) 0.064 Å for **1** and 0.153 Å for **2**]. Noteworthy is the absence of any contacts between the tin atoms and the O atoms of OAc (for **1**) or OMe (for **2**) groups of this 'bridging' type of carboxylate ligand.

The second type of COO group (O(5)–C(20)–O(6), Figs 1, 2) coordinates the Sn(2) atom in the monodentate mode and at the same time forms weaker interactions to exocyclic and endocyclic tin atoms: Sn(2)–O(5) and Sn(1)–O(6). A distinctive feature of structure **2** consists in the

Table 2 Crystal data for $\{[Et_2SnOC(O)CH(OAc)Ph]_2O\}_2$ (**1**) and $\{[(n\text{-}Bu)_2SnOC(O)CH(OMe)Ph]_2O\}_2$ (**2**)

	1	**2**
Formula	$C_{28}H_{38}O_9Sn_2$	$C_{34}H_{54}O_7Sn_2$
Molecular weight	755.99	812.19
Cell dimensions:		
a (Å)	8.876 (2)	13.248 (3)
b (Å)	12.765 (4)	14.123 (4)
c (Å)	15.346 (4)	13.202 (4)
α (°)	103.95 (3)	114.76 (2)
β (°)	109.12 (2)	92.80 (3)
γ (°)	90.50 (2)	116.20 (3)
Cell volume (Å^3)	1587	1928
Space group: Symbol	$P\bar{1}$	$P\bar{1}$
No.	2	2
Z	2	2
Calculated density (g/cm^3)	1.582	1.399
μ(Mo$K\alpha$) (mm^{-1})	1.62	1.34
Crystal dimensions (mm)	0.4 × 0.35 × 0.25	0.35 × 0.30 × 0.3
2θ range (°)	0–50	0–50
No. of reflections measured	6368	6673
No. of reflections observed ($I > 3\sigma(I)$)	4638	3910
R	0.045	0.046
R_w	0.048	0.047

Table 3 Fractional atomic coordinates for $\{[Et_2SnOC(O)CH(OAc)Ph]_2O\}_2$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Sn(1)	0.10175(6)	0.04179(4)	0.11618(3)	C(9)	0.2181(9)	0.2996(6)	0.2018(5)
Sn(2)	−0.03557(6)	−0.24684(4)	0.02871(3)	C(10)	0.308(1)	0.3964(6)	0.2848(5)
O(1)	−0.0313(6)	−0.0986(3)	0.0029(3)	C(11)	0.455(1)	0.4378(6)	0.2686(5)
O(2)	0.2348(7)	0.2066(4)	0.2118(4)	C(12)	0.592(1)	0.3879(8)	0.2866(7)
O(3)	0.1334(9)	0.3254(5)	0.1284(4)	C(13)	0.724(1)	0.431(1)	0.2726(8)
O(4)	0.3627(7)	0.3675(5)	0.3746(4)	C(14)	0.713(1)	0.520(1)	0.2374(8)
O(6)	0.0722(7)	−0.1482(4)	0.1762(3)	C(15)	0.577(1)	0.5683(9)	0.2187(8)
O(7)	0.2188(7)	−0.2297(5)	0.3951(4)	C(16)	0.446(1)	0.5298(8)	0.2342(7)
O(8)	0.1131(9)	0.3632(7)	0.3746(5)	C(17)	0.250(1)	0.3540(8)	0.4137(6)
O(5)	0.0801(9)	−0.3105(5)	0.2063(4)	C(18)	0.323(1)	0.327(1)	0.5087(6)
O(9)	−0.0307(9)	−0.2221(7)	0.3946(7)	C(20)	0.109(1)	−0.2118(6)	0.2331(5)
C(1)	0.329(1)	−0.0143(6)	0.1294(6)	C(21)	0.193(1)	−0.1524(7)	0.3379(5)
C(2)	0.448(1)	0.061(1)	0.1186(9)	C(22)	0.353(1)	−0.0970(7)	0.3533(5)
C(3)	−0.077(1)	0.0791(9)	0.1787(7)	C(23)	0.476(1)	−0.1546(8)	0.3401(6)
C(4a)*	−0.146(3)	0.162(2)	0.187(2)	C(24)	0.625(1)	−0.104(1)	0.3549(8)
C(4)*	−0.066(2)	0.098(2)	0.270(1)	C(25)	0.645(1)	0.007(1)	0.3816(7)
C(5)	0.179(1)	−0.3188(8)	0.0250(8)	C(26)	0.526(1)	0.0658(9)	0.3940(7)
C(6)	0.179(2)	−0.424(2)	−0.015(1)	C(27)	0.378(1)	0.0165(8)	0.3807(6)
C(7)	−0.266(1)	−0.2838(9)	0. 0381(8)	C(28)	0.094(1)	−0.2614(9)	0.4175(7)
C(8)	−0.311(2)	−0.213(1)	0.106(1)	C(29)	0.135(2)	−0.3487(8)	0.4703(7)

Occupation factors for starred atoms are equal to 0.5.

coordination of the OMe group of this second type of carboxylate ligand to the endocyclic tin atom: O(7)–Sn(1). The disposition of the structural units in **1** makes impossible such kind of interaction for the OAc group, because the last one is directed away from the rest of the

Table 4 Fractional atomic coordinates for $\{[(n\text{-}Bu)_2SnOC(O)CH(OMe)Ph]_2O\}_2$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Sn(1)	0.56556(5)	0.59445(4)	0.44814(5)	C(13)	0.335(1)	−0.218(1)	0.116(1)
Sn(2)	0.42348(5)	0.28078(5)	0.23312(5)	C(14)	0.439(1)	−0.181(1)	0.187(1)
O(1)	0.4698(4)	0.4052(4)	0.4006(4)	C(15)	0.481(1)	−0.090(1)	0.306(1)
O(2)	0.3449(5)	0.1944(4)	0.4530(5)	C(16)	0.410(1)	−0.0369(9)	0.349(1)
O(3)	0.6898(6)	0.8661(5)	0.7350(5)	C(17)	0.097(1)	−0.035(1)	0.426(1)
O(4)	0.1985(7)	−0.0348(6)	−0.4093(6)	C(20)	0.5532(7)	0.4544(7)	0.1409(6)
O(5)	0.5064(5)	0.3638(5)	0.0456(5)	C(21)	0.6289(7)	0.5759(7)	0.1485(7)
O(6)	0.5405(4)	0.4509(4)	0.2362(4)	C(22)	0.7383(7)	0.5826(7)	0.1136(7)
O(7)	0.6588(5)	0.6690(5)	0.2663(5)	C(23)	0.7342(9)	0.549(1)	−0.0012(9)
C(1)	0.7380(7)	0.6189(8)	0.4649(8)	C(24)	0.838(1)	0.557(1)	−0.034(1)
C(2)	0.810(1)	0.673(1)	0.572(2)	C(25)	0.9362(9)	0.598(1)	0.045(1)
C(3)	0.934(1)	0.678(2)	0.592(2)	C(26)	0.939(1)	0.630(1)	0.159(1)
C(4)*	0.981(2)	0.735(3)	0.547(3)	C(27)	0.8370(8)	0.624(1)	0.1943(9)
C(4A)*	0.935(3)	0.583(4)	0.506(5)	C(28)	0.704(1)	0.7878(7)	0.2773(9)
C(5)	0.4257(7)	0.5986(7)	0.3643(7)	C(31)	0.5257(9)	0.190(1)	0.187(1)
C(6)	0.3769(7)	0.6688(8)	0.4518(9)	C(32)	0.640(1)	0.273(1)	0.206(1)
C(7)	0.2677(8)	0.6531(9)	0.377(1)	C(33)	0.681(1)	0.151(2)	0.160(2)
C(8)	0.228(1)	0.730(1)	0.468(2)	C(34)	0.819(2)	0.277(2)	0.180(2)
C(9)	0.2997(8)	0.1133(7)	0.3487(8)	C(35)	0.2678(9)	0.2434(8)	0.1272(8)
C(10)	0.2270(9)	−0.0218(7)	0.3126(8)	C(36)	0.220(1)	0.127(1)	0.013(1)
C(11)	0.3052(9)	−0.0758(7)	0.2739(8)	C(37)	0.113(2)	0.113(1)	−0.057(1)
C(12)	0.267(1)	−0.1643(9)	0.158(1)	C(38)	0.931(2)	0.003(2)	0.173(2)

Occupation factors for starred atoms are equal to 0.5.

Table 5 Selected interatomic distances (Å) and angles (°) in $\{[\mathrm{Et_2SnOC(O)CH(OAc)Ph}]_2\mathrm{O}\}_2$ (**1**)

Sn(1)–Sn(1)′	3.321(1)	Sn(1)–C(3)	2.109(11)	Sn(2)–C(7)	2.153(13)
Sn(1)–O(1)	2.179(4)	Sn(2)–O(1)	2.027(5)	O(2)–C(9)	1.236(10)
Sn(1)–O(1)′	2.038(5)	Sn(2)–O(3)′	2.240(5)	O(3)–C(9)	1.254(9)
Sn(1)–O(2)	2.304(4)	Sn(2)–O(6)	2.193(4)	O(6)–C(20)	1.299(10)
Sn(1)–O(6)	2.832(6)	Sn(2)–O(5)	2.896(7)	O(5)–C(20)	1.224(10)
Sn(1)–C(1)	2.107(8)	Sn(2)–C(5)	2.134(11)		
O(1)–Sn(1)–O(1)′	76.1(2)	C(1)–Sn(1)–C(3)	147.4(4)	O(5)–Sn(2)–C(7)	82.8(4)
O(1)–Sn(1)–O(2)	168.7(2)	O(1)–Sn(2)–O(3)′	90.5(2)	C(5)–Sn(2)–C(7)	141.2(4)
O(1)–Sn(1)–O(6)	64.9(2)	O(1)–Sn(2)–O(6)	81.1(2)	Sn(1)–O(1)–Sn(1)′	103.9(2)
O(1)–Sn(1)–C(1)	95.2(2)	O(1)–Sn(2)–O(5)	130.6(2)	Sn(1)–O(1)–Sn(2)	120.4(2)
O(1)–Sn(1)–C(3)	97.4(3)	O(1)–Sn(2)–C(5)	110.2(4)	Sn–(1)′–O(1)–Sn(2)	135.1(2)
O(1)′–Sn(1)–O(2)	92.6(2)	O(1)–Sn(2)–C(7)	108.3(4)	Sn(1)–O(2)–C(9)	131.2(4)
O(1)′–Sn(1)–O(6)	141.0(1)	O(3)′–Sn(2)–O(6)	171.1(2)	Sn(2)′–O(3)–C(9)	136.6(5)
O(1)′–Sn(1)–C(1)	107.2(3)	O(3)′–Sn(2)–O(5)	138.6(2)	Sn(1)–O(6)–Sn(2)	92.3(2)
O(1)′–Sn(1)–C(3)	105.0(3)	O(3)′–Sn(2)–C(5)	85.7(3)	Sn(1)–O(6)–C(20)	155.9(4)
O(2)–Sn(1)–O(6)	126.4(2)	O(3)′–Sn(2)–C(7)	89.2(4)	Sn(2)–O(6)–C(20)	109.1(4)
O(2)–Sn(1)–C(1)	87.1(2)	O(6)–Sn(2)–O(5)	49.5(2)	Sn(2)–O(5)–C(20)	77.6(5)
O(2)–Sn(1)–C(3)	86.5(3)	O(6)–Sn(2)–C(5)	94.3(3)	O(2)–C(9)–O(3)	126.7(6)
O(6)–Sn(1)–C(1)	79.2(3)	O(6)–Sn(2)–C(7)	96.2(3)	O(6)–C(20)–O(5)	123.7(7)
O(6)–Sn(1)–C(3)	79.1(3)	O(5)–Sn(2)–C(5)	76.1(4)		

Coordinates of atoms labelled with a prime (′) are produced by symmetry operation $\bar{x}$, $\bar{y}$, $\bar{z}$.

molecule. The oxygen atom O(7) of the OMe group in **2** forms a relatively close contact with Sn(1) at 3.107 Å, which is significantly less than the sum of the van der Waals radii for Sn and O of 3.7 Å,[10] and should be considered as a bonding interaction. The geometry of the fragment under consideration is indicative of this coordination, the angles at the O(7) oxygen atom (Fig. 2, Table 6) having almost ideal values characteristic for compounds with an 'ether' oxygen–tin coordina-

Table 6 Selected interatomic distances (Å) and angles (°) in $\{[\mathrm{(n\text{–}Bu)_2SnOC(O)CH(OMe)Ph}]_2\mathrm{O}\}_2$ (**2**)

Sn(1)–Sn(1)′	3.348(1)	Sn(1)–C(1)	2.140(10)	Sn(2)–C(31)	2.19(2)
Sn(1)–O(1)	2.162(5)	Sn(1)–C(5)	2.147(11)	Sn(2)–C(35)	2.151(12)
Sn(1)–O(1)′	2.071(6)	Sn(2)–O(1)	2.004(4)	O(2)–C(9)	1.249(9)
Sn(1)–O(2)′	2.338(5)	Sn(2)–O(3)′	2.185(7)	O(3)–C(9)	1.254(14)
Sn(1)–O(6)	2.572(5)	Sn(2)–O(5)	3.204(7)	O(5)–C(20)	1.216(7)
Sn(1)–O(7)	3.107(7)	Sn(2)–O(6)	2.190(5)	O(6)–C(20)	1.296(11)
O(1)–Sn(1)–O(1)′	75.5(2)	O(6)–Sn(1)–C(1)	80.3(3)	O(5)–Sn(2)–C(35)	74.3(3)
O(1)–Sn(1)–O(2)′	164.2(2)	O(6)–Sn(1)–C(5)	81.7(3)	O(6)–Sn(2)–C(31)	100.5(4)
O(1)–Sn(1)–O(6)	66.4(2)	O(7)–Sn(1)–C(1)	73.3(4)	O(6)–Sn(2)–C(35)	95.5(3)
O(1)–Sn(1)–O(7)	119.9(2)	O(7)–Sn(1)–C(5)	75.6(3)	C(31)–Sn(2)–C(35)	129.1(4)
O(1)–Sn(1)–C(1)	98.0(3)	C(1)–Sn(1)–C(5)	148.9(4)	Sn(1)–O(1)–Sn(1)′	104.5(2)
O(1)–Sn(1)–C(5)	97.6(3)	O(1)–Sn(2)–O(3)′	91.9(2)	Sn(1)–O(1)–Sn(2)	118.4(3)
O(1)′–Sn(1)–O(2)′	88.8(2)	O(1)–Sn(2)–O(5)	120.1(2)	Sn(1)′–O(1)–Sn(2)	136.6(3)
O(1)′–Sn(1)–O(6)	141.9(2)	O(1)–Sn(2)–O(6)	77.0(2)	Sn(1)′–O(2)–C(9)	135.2(7)
O(1)′–Sn(1)–O(7)	164.5(1)	O(1)–Sn(2)–C(31)	116.5(4)	Sn(2)′–O(3)–C(9)	138.4(4)
O(1)′–Sn(1)–C(1)	104.0(3)	O(1)–Sn(2)–C(35)	114.1(3)	Sn(2)–O(5)–C(20)	72.7(5)
O(1)′–Sn(1)–C(5)	105.9(3)	O(3)′–Sn(2)–O(5)	147.4(2)	Sn(1)–O(6)–Sn(2)	97.1(2)
O(2)′–Sn(1)–O(6)	129.3(2)	O(3)′–Sn(2)–O(6)	168.9(2)	Sn(1)–O(6)–C(20)	138.9(5)
O(2)′–Sn(1)–O(7)	75.8(2)	O(3)′–Sn(2)–C(31)	85.5(5)	Sn(2)–O(6)–C(20)	121.3(4)
O(2)′–Sn(1)–C(1)	87.5(3)	O(3)′–Sn(2)–C(35)	87.8(4)	O(2)–C(9)–O(3)	123.7(8)
O(2)′–Sn(1)–C(5)	84.6(3)	O(5)–Sn(2)–O(6)	43.3(1)	O(5)–C(20)–O(6)	122.6(8)
O(6)–Sn(1)–O(7)	53.5(2)	O(5)–Sn(2)–C(31)	85.2(5)		

Coordinates of atoms labelled with a prime (′) are produced by symmetry operation $1-x$, $1-y$, $1-z$.

tion bond.[11] On the other hand, due to the steric hindrance of MeO→Sn interaction, the Sn(1)–O(6) bond distance becomes shorter, and Sn(2)–O(5) becomes longer. In the case of **2** they have minimal (2.572 Å) and maximal (3.205 Å) values respectively in comparison with other dicarboxylatotetraorganodistannoxanes of this structural type.[2–4, 12] Analogous bond distances in **1** are 2.832 Å and 2.896 Å, respectively.

Thus, if both strong and weak interactions in the structures under consideration are taken into account, then the geometry about the Sn(1) atom can be described as being based on a distorted octahedron with a basal plane defined by four O atoms in the case of **1**, the tin atom displacement from this plane being 0.006 Å. The inclusion of the O(7) atom in the coordination polyhedron in the case of **2** results in a distorted pentagonal-bipyramidal geometry with the pentagonal plane defined by five O atoms as shown in Fig. 2, the displacement from this plane being 0.05 Å for plane-forming oxygen atoms and 0.006 Å for Sn(1). Only one other example where the coordination number of the tin atoms (the exocyclic ones) was found to be more than six in the distannoxane derivative $\{[R_2SnOC(O)R']_2O\}_2$ is available in the literature.[13] As in the case of **2**, this phenomenon arises as a result of the interaction with the Sn atom of an additional donor atom (a pyridine N atom) in R′.

Nevertheless, it has to be mentioned that the endocyclic tin atom, Sn(1), forms five 'significant' bonds in **1** and **2** if the weak interactions are not taken into account. Then the Sn(1) coordination polyhedron would be best described as distorted trigonal-bipyramidal in both structures. Similarly, coordination numbers six or five can be ascribed to the exocyclic tin atom Sn(2), depending on inclusion or non-inclusion of the O(5) oxygen atom in its coordination polyhedron.

As usual,[3–8, 14] Mössbauer spectroscopy does not reveal two different types of tin atoms in

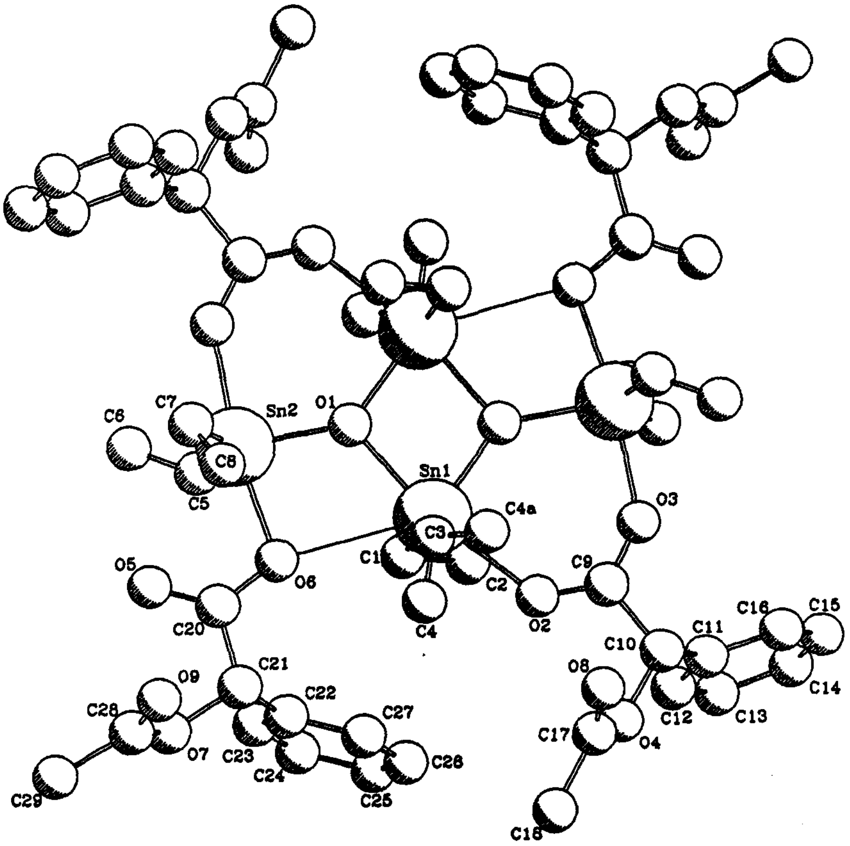

Figure 1 The structure and atomic numbering scheme for $\{[Et_2SnOC(O)CH(OAc)Ph]_2O\}_2$ (**1**).

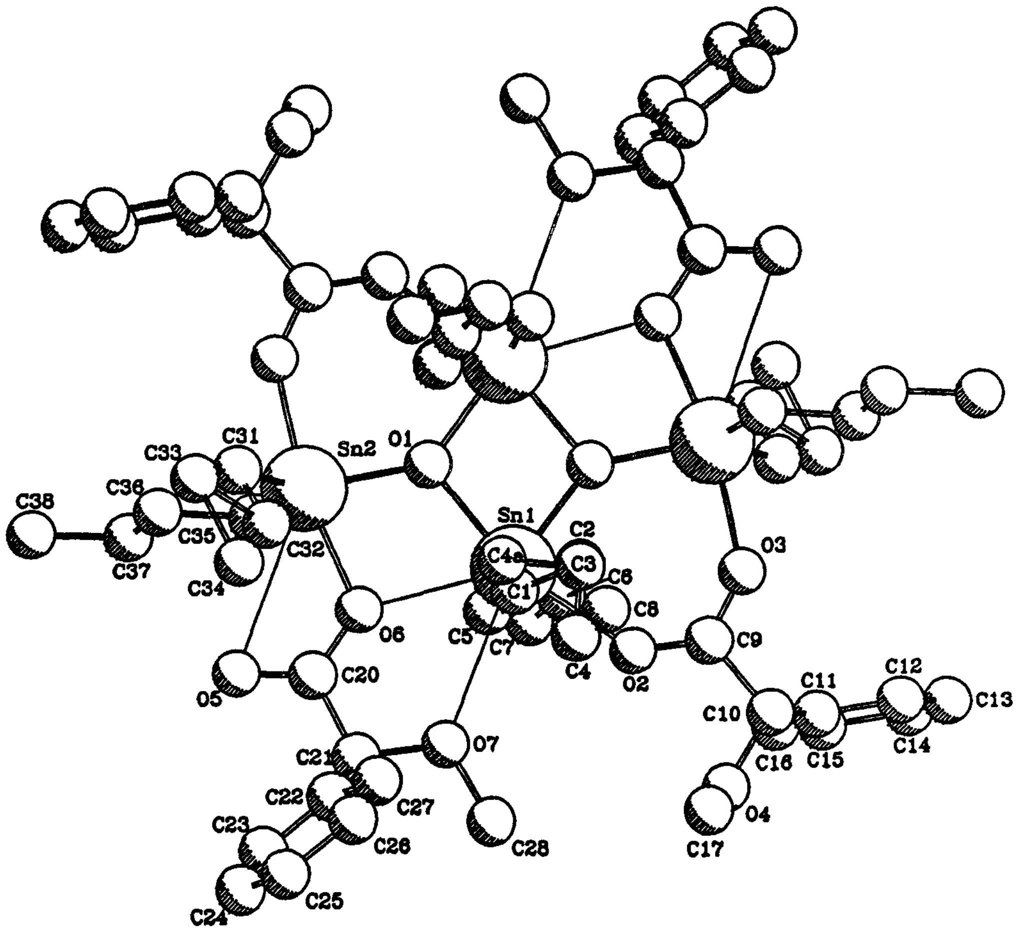

Figure 2 The structure and atomic numbering scheme for $\{[(n\text{-}Bu)_2SnOC(O)CH(OMe)Ph]_2O\}_2$ (**2**).

compounds **1** and **2**. The Mössbauer spectrum for each compound consists of a symmetric unbroadened doublet. Isomer shifts (IS) and quadrupole splittings (QS) of the resonant peaks are given in Table 7. Using the crystallographically determined bond angles C–Sn–C, the

Table 7 Mössbauer and IR spectroscopic data for diorganotin carboxylates

Compound no.	IS[a] (mm s^{-1})	QS[b] (mm s^{-1})	ν_{as}(COO) (cm^{-1})	ν_s(COO) (cm^{-1})	$\Delta\nu$(COO) (cm^{-1})
1	1.35	3.49	1602 s	1412 s	190
			1651 vs	1372 vs	279
2	1.31	3.35	1598 s	1402 s	196
			1654 vs	1330 vs	324
3	1.44	3.59	1611 vs	1402 vs	209
4	1.58	4.02	1600 vs	1400 vs	200
5	1.52	3.87	1615 vs	1402 vs	213

[a] Isomer shift, IS, ∓ 0.03 mm s^{-1} with respect to $BaSnO_3$.
[b] Nuclear quadrupole splitting, QS, ∓ 0.02 mm s^{-1}.
Abbreviations: s, strong; vs, very strong.

Table 8 QS values calculated[14, 15] for tin atoms in compounds **1** and **2**

Compound no.	Atom	C–Sn–C (deg)	QS_{calc} (mm s^{-1})	QS_{av} (mm s^{-1})
1	Sn(1)	147.4	3.64	3.55
	Sn(2)	141.2	3.46	
2	Sn(1)	148.9	3.68	3.37
	Sn(2)	129.1	3.05	

QS values can be calculated for each tin atom by means of the Sham–Bancroft equation[15] (Table 8).

The average values obtained are in good agreement with the experimental QS values (Table 7) which are commonly found for this class of distannoxane derivatives and indicate an average coordination number for tin atoms of greater than four.[3–8, 14]

In the IR spectra of **1** and **2** in the COO stretching vibration region, two pairs of ν(COO) bands are present (Table 7). One of them ($\Delta\nu$(COO)$<200\ \mathrm{cm}^{-1}$) can be attributed to a bridging carboxylate group, the other to a non-bridging, essentially monodentate, COO group, being in accordance with the structures established by means of X-ray diffraction analysis.

The solid-state structures of diorganotin biscarboxylates **3**, **4** and **5** have been determined by spectral methods only. Mössbauer and IR spectroscopy data for them are given in Table 7. The QS values obtained are in good agreement with those calculated in terms of the point-charge model formalism assuming idealized *trans*-R_2SnO_4 octahedral environments around the tin atom[16, 17] and characteristic for this class of compounds.[4, 7, 8, 18] By use of the Sham–Bancroft equation,[15] the C–Sn–C angles for biscarboxylates **3**, **4** and **5** are estimated to be 146°, 174° and 156°. respectively. Thus Mössbauer evidence suggests that the $R_2Sn(OC(O)R')_2$ reported here adopt either monomeric chelate structure **A** or polymeric structure **B** (Fig. 3) arising from bridging carboxylate groups.

The same conclusion could be deduced from the infrared spectra of **3**–**5**. The positions of $\nu_{s,\,as}$(COO) bands and $\Delta\nu$(COO) values (Table 7), which are close to those of COO vibrational bands of $R_3SnOC(O)CH(OX)Ph$ (R=Me, n-Bu; X=Me, Ac),[19] where carboxylate groups were found to form the bridging polymeric structures, are indicative of the bidentate (chelating or bridging) carboxylate group function.

The OAc groups of biscarboxylates **4** and **5** as well as of $R_3SnOC(O)CH(OAc)Ph$[19] do not participate in a coordination to tin, $COO_{acet.}$ bands in their IR spectra being centred near 1740 cm^{-1} and 1230 cm^{-1}. These positions are almost the same as those of appropriate bands of a 'free' α-acetoxyphenylacetic acid and distannoxane derivative **1** where the absence of any contact between OAc group and tin atoms is established by X-ray diffraction analysis.

All of the available spectral data for compounds **3**–**5** point to six-coordinated structures with *trans*-R_2SnO_4 octahedral geometries around the tin atoms, but do not allow one to distinguish the two types of structures **A** and **B**. Though the definitive choice between **A** and **B** seems to be impossible without X-ray diffraction evidence, analysis of the literature data clearly favours the monomeric structure **A**, where the tin atom is octahedrally surrounded by two asymmetrically chelating carboxylate groups. This type of structure has been established crystallographically for a number of the diorganotin biscarboxy-

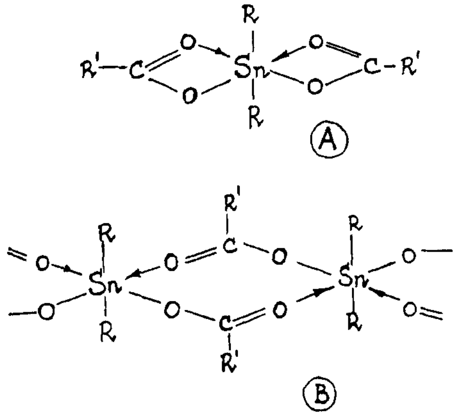

Figure 3 The solid-state structures of diorganotin biscarboxylates **3**, **4** and **5**.

lates,[2, 12, 18, 20, 21] whereas the polymeric one has never been confirmed for this class of compounds.

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