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THE CRYSTAL STRUCTURES OF TRIBUTYLTIN AND TRIPHENYLTIN ESTERS OF 2-BENZOYLBENZOIC ACID

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Abstract—Tin-199m Mössbauer parameters and IR spectra for triorganotin 2-benzoylbenzoates indicate a *trans*-C_3SnO_2 trigonal bipyramidal geometry in the solid state. This configuration was confirmed by X-ray diffraction. Molecules of tributyltin 2-benzoylbenzoate and triphenyltin 2-benzoylbenzoate are ketonic oxygen-bridged into a polymeric chain; the carboxylate carbonyl oxygen is not involved in coordination.

Triorganotin(IV) carboxylates are generally five-coordinate carboxylate-bridged polymers whose repeat units are propagated in a zigzag or helical manner in the crystal lattice.[1] A substituent in the carboxylate group carrying a donor atom makes possible an alternative bonding to carboxyl bridging. This option is adopted in triorganotin esters of 3-ureidopropionic acid,[2] citraconic acid monopyrrolidide,[3] and 1-uracilacetic acid,[4] whose Sn—O bridges occur through the amido carbonyl oxygen. But with triphenyltin 3-benzoylpropionate[5] the polymeric chain is carboxylate-bridged and the ketonic oxygen is not involved in coordination. Thus, based on Mössbauer studies for triorganotin derivatives of 2-benzoylbenzoic acid a five-coordinate configuration with carboxyl bridging was proposed for the tin atom.[6] As the ultimate demonstration of whether or not a ketonic oxygen in the triorganotin esters of keto carboxylic acid is involved in coordination must come from diffraction studies, we undertook the X-ray structure determination of tributyltin 2-benzoylbenzoate (**1**) and triphenyltin 2-benzoylbenzoate (**2**).

EXPERIMENTAL

Preparation

The triorganotin 2-benzoylbenzoates, **1** and **2**, were prepared by a published method.[6] Recrystallization of the product from the reaction mixture

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Table 1. Physical properties of triorganotin 2-benzoylbenzoates

	$2\text{-}C_6H_5COC_6H_4COOSnBu^n_3$ **1**	$2\text{-}C_6H_5COC_6H_4COOSnPh_3$ **2**
M.p. (°C)	61–62 [60–61]	107–108 [106–107]
IR absorptions (cm^{-1})		
ν_{asym}(OCO)	1662 vs; 1596 s; 1579 s [1664 vs; 1597 s; 1578 s]	1650 vs; 1595 s; 1576 s [1648 vs; 1594 s; 1576 s]
ν_{sym}(OCO)	1338 vs [1336 vs]	1334 s; 1314 vs [1334s; 1314 vs]
$\Delta\nu$ range	324–241 [328–243]	336–242 [334–242]
Mössbauer data (mm s^{-1})		
Isomer shift	1.44 ± 0.01 [1.46 ± 0.03]	1.32 ± 0.01 [1.31 ± 0.03]
Quadrupole splitting	3.46 ± 0.03 [3.50 ± 0.06]	3.07 ± 0.03 [3.16 ± 0.06]

Published values[6] in square parentheses.

Table 2. Crystal data and refinement details for $2\text{-}C_6H_5COC_6H_4COOSnBu^n_3$ (**1**) and $2\text{-}C_6H_5COC_6H_4COOSnPh_3$ (**2**)

	1	**2**
Formula	$C_{26}H_{36}O_3Sn$	$C_{32}H_{24}O_3Sn$
Formula weight	514.2	575.2
Cell dimensions (mm)	$0.30 \times 0.30 \times 0.45$	$0.10 \times 0.20 \times 0.40$
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$P2_12_12$
a (Å)	10.380(4)	13.073(3)
b (Å)	13.028(5)	20.462(4)
c (Å)	20.230(8)	9.752(2)
β (°)	101.11(1)	
Volume (Å^3)	2684(2)	2608.6(13)
Z (molecules/cell)	4	4
D_{calc} (Mg m^{-3})	1.272	1.465
μ (mm^{-1})	0.973	1.011
$F(000)$	1064	1160
2Θ range (°)	3.0 to 50.0	3.5 to 48.0
Index ranges h	$0 \rightarrow 12$	$0 \rightarrow 14$
k	$0 \rightarrow 15$	$0 \rightarrow 22$
l	$-24 \rightarrow 23$	$0 \rightarrow 11$
Reflections collected	5003	2347
Independent reflections	4735 ($R_{int} = 5.61\%$)	2347
Observed reflections	2195 ($F > 6.0\sigma(F)$)	2159 ($F > 4.0\sigma(F)$)
R_f (unique reflections)	0.061	0.022
R_w (unique reflections)	0.076	0.028
R_f (all reflections)	0.112	0.025
R_w (all reflections)	0.086	0.028
Goodness-of-fit	1.87	0.88
Largest and mean Δ/σ	0.232, 0.026	0.010, 0.002
Last D-map		
Deepest hole (e Å^{-3})	−0.73	−0.45
Highest peak (e Å^{-3})	0.79	0.32

in 60–80°C petroleum ether : benzene solvent (1 : 3) yielded crystals suitable for X-ray analysis. The melting points, IR stretching absorptions and Mössbauer data for **1** and **2** are recorded in Table 1.

X-ray crystallography of **1** *and* **2**

Single crystals were mounted on a thin glass fibre on a Siemens R3m/V automatic diffractometer fitted with a graphite monochromatized Mo-K_α radiation, $\lambda = 0.71073$ Å. The ω-scan method was employed to measure the reflections. The intensity data were reduced and corrected for Lorentz and polarization factors. The absorption corrections were made using a semi-empirical method by psi-scan. The crystal structures were solved by direct methods using the Siemens SHELXTL PLUS[7] and refined by a full-matrix least-squares procedure. The crystal data and refinement parameters are given in Table 2 and selected inter-atomic distances and bond angles in Table 3.

Supplementary materials including non-hydrogen and hydrogen atomic coordinates and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre, and observed and calculated structure factors are available upon request from the corresponding author.

Table 3. Selected bond lengths (Å) and bond angles (°) for 2-$C_6H_5COC_6H_4COOSnBu^n_3$ (**1**) and 2-$C_6H_5COC_6H_4COOSnPh_3$ (**2**)

	1	2
Sn(1)—O(1)	2.109(7)	2.107(3)
Sn(1)—O(2)	3.077(8)	2.888(3)
Sn(1)—O(3′)	2.675(10)	2.880(4)
Sn(1)—C(15)	2.095(12)	2.133(4)
Sn(1)—C(19)	2.127(10)	2.126(4)
Sn(1)—C(23)	2.115(8)	2.119(5)
C(7)—O(1)	1.296(13)	1.302(6)
C(7)—O(2)	1.229(12)	1.217(6)
C(8)—O(3)	1.192(12)	1.230(6)
O(1)—Sn(1)—O(3′)	178.1(6)	173.7(3)
O(1)—Sn(1)—C(15)	98.3(4)	101.1(1)
O(1)—Sn(1)—C(19)	92.8(3)	94.3(1)
O(1)—Sn(1)—C(23)	100.9(3)	98.1(1)
C(15)—Sn(1)—C(19)	114.4(4)	113.7(2)
C(15)—Sn(1)—C(23)	123.5(4)	126.7(2)
C(19)—Sn(1)—C(23)	117.0(4)	113.8(2)
Sn(1)—O(1)—C(7)	117.9(6)	111.6(3)
O(1)—C(7)—O(2)	123.0(9)	122.2(4)

RESULTS AND DISCUSSION

The Mössbauer data and the observed IR absorption frequencies for carboxylic antisymmetric, ν_{asym}(OCO), and symmetric, ν_{sym}(OCO), stretching vibrations for the triorganotin carboxylates, **1** and **2**, recorded in Table 1 are in agreement with published values.[6] The assignment of the ν_{asym}(OCO) band is complicated by the presence of the ν(C=O) stretching vibration, which is observed in the region 1662–1650 cm^{-1}. Nevertheless, the magnitude of the $\nu_{\text{asym}}(\text{OCO}) - \nu_{\text{sym}}(\text{OCO})$ [i.e. $\Delta\nu$] separation is of interest. For a bridging or chelating carboxylate group[8] $\Delta\nu$ would be expected to be $\leqslant 150$ cm^{-1}, as widely observed in the IR spectra of triorganotin carboxylates.[9] The observed values of $\Delta\nu$ for **1** and **2**, which are in the range of 241–336 cm^{-1}, indicate a unidentate bonding mode for the carboxylate moiety.[10,11] However, the quadrupole splitting values of 3.46 and 3.07 mm s^{-1} for **1** and **2**, respectively, are in the range commonly encountered and predicted for *trans*-trigonal bipyramidal triorganotin compounds.[12] Thus, a *trans*-R_3SnO_2 structural motif for **1** and **2** would infer participation of the ketonic oxygen of 2-benzoylbenzoic acid. This conclusion was confirmed by the results of the X-ray structural analysis for **1** and **2**.

The X-ray crystal structures of **1** and **2** with atom labelling are shown in Figs 1 and 2, respectively. The carbon locations for one of the butyl groups [C(24)—C(26)] in **1** are poor owing to dynamic or static disorder. As expected for a R_3SnO_2 structural motif, the tin(IV) atom in **1** and **2** is found to be five coordinate (Figs 1 and 2) with the three organo substituents occupying the equatorial positions of a trigonal bipyramid and the apical sites taken by a carboxyl oxygen, O(1), and the ketonic oxygen, O(3′), of a neighbouring molecule. The Sn atom is 0.103 Å for **1** and 0.111 Å for **2** away from the trigonal plane in the direction of O(1) while the Σ(C—Sn—C) angles are 354.9(4)° for **1** and 354.2(2)° for **2**. The axial angle formed by the two oxygens, [O(1)—Sn(1)—O(3′)], is 178.1(6)° and 173.7(3)° for **1** and **2**, respectively, and the tin ketonic oxygen intermolecular contact, [Sn(1)—O(3′)], of 2.675(10) Å for **1** and 2.880(4) Å for **2** is within the sum of the respective Van der Waals' radii (3.70 Å).[13] Nevertheless, this newly observed tin—ketonic oxygen distance is comparable with the tin—aldehydic oxygen distance of 2.680 Å reported for the 1,1-dichlorodimethyltin–salicylaldehyde adduct.[14] The weak tin—ketonic oxygen bridging is due to the close proximity of the carboxylate carbonyl oxygen, O(2), which is located at 3.077(8) Å for **1** and 2.888(3) Å for **2** from its tin atom.

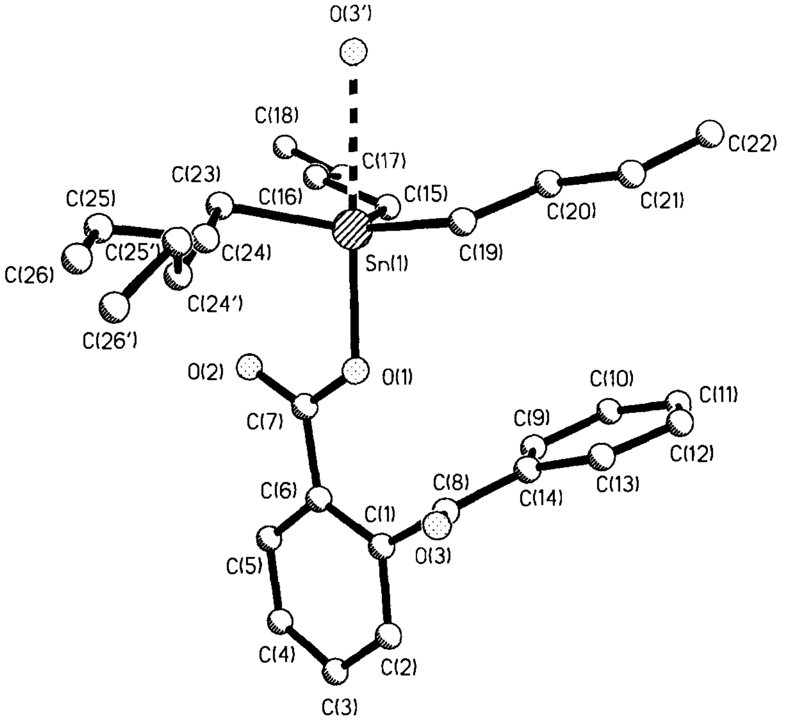

Fig. 1. Molecular structure and crystallographic numbering scheme employed for 2-$C_6H_5COC_6H_4COOSnBu^n_3$.

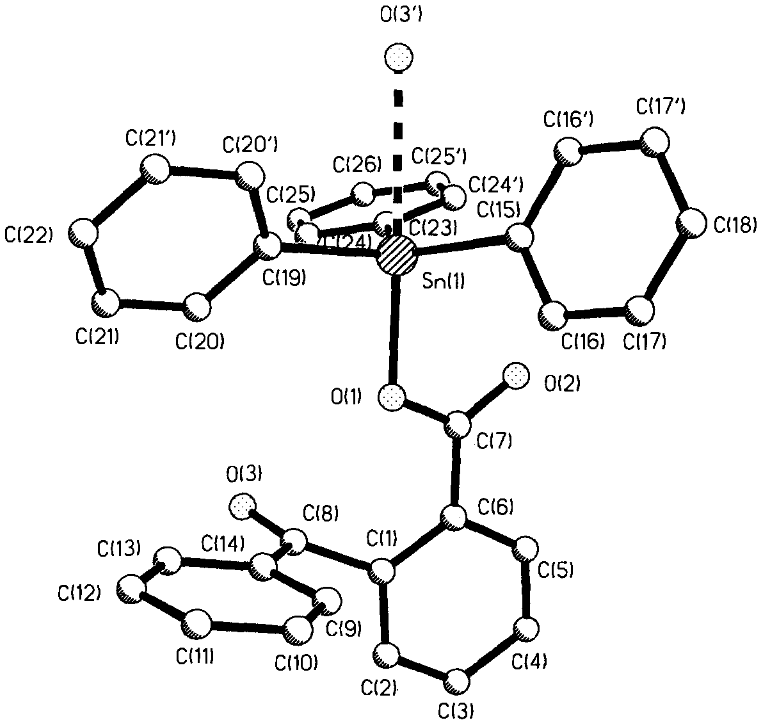

Fig. 2. Molecular structure and crystallographic numbering scheme employed for 2-$C_6H_5COC_6H_4COOSnPh_3$.

The atoms of the ketonic system, C(1), C(8), C(14), and O(3), for **1** and **2** are coplanar to within ±0.022 Å, while the atoms, Sn(1), O(1), C(1), C(2), C(3), C(4), C(5), C(6), C(7), and O(2) for **1** and **2** are coplanar to within ±0.046 Å. The dihedral angle between these planes is in the range 105.2–89.6° and corresponds primarily to a rotation about the C(1)—C(8) bond (Figs 1 and 2). In the absence of such a rotation, ketonic oxygen bridging as observed for the title compounds will result in severe crowding between the ketonic and the carboxylic oxygens.

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