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Crystal and molecular structures of tris(*p*-methoxyphenyl)- and tris(2,4,6-trimethylphenyl)tin(IV) acetates

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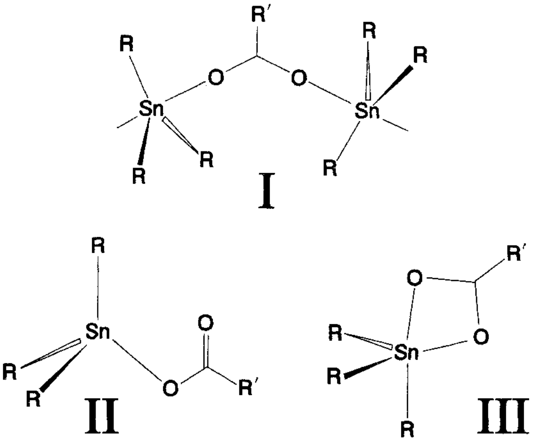
The crystal and molecular structures of tris(*p*-anisyl)tin acetate (1) (*p*-anisyl = *p*-methoxyphenyl) and trimesityltin acetate (2) (mesityl = 2,4,6-trimethylphenyl) have been determined. Both have monomeric structures with the acetate group acting as an asymmetric bidentate ligand. Bond valence analysis of (1) and (2) and other Ph_3SnO_2CR suggest however that the carboxylate ligand effectively occupies a single bonding position at tin. Thus in (1) and (2) the tin atom is in a chemical environment equivalent to that found in four-coordinate $R_3Sn–X$ systems based on tetrahedral geometry.

Keywords: Triorganotin carboxylate, triaryltin acetate, X-ray structure, bond valence analysis

1 INTRODUCTION

Triorganotins have had several important applications as commercial biocides[1,2] with triphenyltin acetate being active against potato blight (*Phytophtora infestans*) as well as other fungi. Thus, perhaps because of their biocidal importance, there have been numerous crystal structure determinations of triorganotin carboxylates reported and these have been reviewed recently in this journal.[3] All bridged R_3SnCO_2R structures examined to date have been described as bridged polymeric-*trans*-O_2SnR_3 (I), or monomeric with either tetrahedral-$OSnR_3$ (II) or trigonal bipyramidal-*cis*-O_2SnR_3 (III) geometries, the last being implicated with significantly decreased biological activity.[4] The qualitative distinction between a polymeric or a monomeric structure for each R_3SnCO_2R can also be made using IR,[5] Mössbauer[6] or more recently solid-state ^{114}Sn NMR[7] data. Thus early workers[6, 8-10] showed that most Ph_3SnO_2CR complexes, where R is an alkyl group, adopt polymeric structures, but increasing bulkiness of R may cause the compound to be monomeric. In contrast, practically all triphenyltin substituted benzoates are monomers in the solid state,[11-17] the exception being the *o*-chlorobenzoate[14] which is polymeric, a structural change ascribed to both steric and electronic factors.

The two compounds whose structures are reported here have been synthesized as part of a study of the effects of substitution at the phenyl rings on the spectroscopic and biological properties and structures of various Ar_4Sn and Ar_3SnX systems.[18] For evaluation of fungicidal activity we have chosen the series with X = OAc or OH to enable a direct comparison to be made with the triphenyl compounds now in use.[1,2] Whilst nearly all Ar_3SnOAc prepared to date have structure **I** like Ph_3SnOAc,[19] IR data show that replacement of *para*-H with CH_3O causes a change to a monomeric structure which may correlate with the lack



Structures 1 to 3

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of fungicidal activity of tris(*p*-anisyl)tin acetate.[20] More recently we have prepared several *meta*- and *ortho*-substituted Ar_3SnOAc including trimesityltin acetate. Whilst it is not surprising that IR data show this compound is monomeric like the corresponding fluoride and hydroxide,[21] X-ray diffraction studies of both monomeric acetates were undertaken for comparison with the early report of monomeric tricylcohexyltin acetate[22] which has more recently been reclassified as a borderline weakly associated polymer.[23]

EXPERIMENTAL

Tris(*p*-anisyl)tin bromide was a previous preparation[24] whilst trimesityltin bromide was prepared by the literature method.[21,25] Silver acetate was prepared fresh and benzene distilled from sodium as required for the syntheses which were carried out in the absence of light. Other experimental details were as described earlier.[18]

Preparations

Tris(*p*-anisyl)tin acetate (1)

A mixture of tris(*p*-anisyl)tin bromide (2.49 g) and silver acetate (4.19 g) was stirred in benzene (150 cm^3) for 24 h at room temperature and then filtered. The filtrate was concentrated *in vacuo* and the oil stirred with cold cyclohexane (~10 cm^3). The crude *product* was filtered and the above process repeated several times. The combined crude (1.41 g) was redissolved in boiling cyclohexane (350 cm^3) and the solution allowed to evaporate slowly at room temperature for 12 days to give white crystals. Yield 30%; m.p. 108–110 °C; IR (cm^{-1}), Nujol: 1646 [$\nu_{as}(CO_2)$], 1305 [$\nu_s(CO_2)$]; $CDCl_3$ soln: 1639 [$\nu_{as}(CO_2)$], 1317 [$\nu_s(CO_2)$]. Analysis: Calcd for $C_{23}H_{24}O_5Sn$: C, 55.35; H, 4.85. Found: C, 54.75; H, 4.86%.

Trimesityltin acetate (2)

Trimesityltin bromide (2.04 g) in benzene (50 cm^3) was stirred with silver acetate (2.17 g) for 2 days at room temperature. The filtrate was concentrated *in vacuo* to an oil which was then treated successively with ethanol (2 × 25 cm^3) and then methanol (30 cm^3), each time the mixture being evaporated at room temperature under vacuum, to give the white *product*. Slow evaporation of the filtrate gave the crystals used here. The crude product was dissolved in ethanol (20 cm^3) and acetone (10 cm^3) and the solution slowly evaporated under bench vacuum for 2 days to produce fine crystals. Yield 40%; m.p. 138 °C (dec); IR (cm^{-1}), Nujol: 1656 [$\nu_{as}(CO_2)$], 1286 [$\nu_s(CO_2)$]. Analysis: Calcd for $C_{29}H_{36}O_2Sn$: C, 65.07; H, 6.78. Found: C, 65.09; H, 6.98%.

X-ray structure analysis

Data collection for both compounds followed previous procedures;[26,27] the specific parameters are given in Table 1. For **1**, intensity was checked every hour using seven standard reflections with the largest fluctuation (±9.9%) due to slow decomposition during collection. For **2**, three standard reflections were measured every hour, the largest fluctuation (±2.0%) being random. The structures were solved by the Patterson method followed by difference Fourier calculations. Refinement based on F (full matrix least squares) with all non-hydrogen atoms having anisotropic thermal parameters, and hydrogen atoms assigned isotropic thermal parameters and initially placed in ideal positions [$d(C\text{–}H) = 1.08$ Å; $U_{iso} = 0.05$ Å^2] and then refined in the last cycles, gave the results shown in Table 1.

Scattering curves for the non-hydrogen atoms were from Cromer and Mann,[28] and those for the hydrogen atoms from Stewart *et al.*[29] The anomalous dispersion of tin was included.[30] Programs used were modified versions of NRC-2, data reduction, NRC-10, bond distances and angles, and NRC-22, mean planes;[31] SHELX-76;[32] and ORTEP.[33] Final atomic coordinates and isotropic temperature factors are listed in Table 2 whilst selected bond lengths and angles are listed in Table 3. The numbering schemes for the molecules are given in Fig. 1 and Fig. 2 shows the unit cells for the compounds. The remaining data are on deposit with the Cambridge X-ray Structure Database, anisotropic temperature factors, hydrogen atom parameters, phenyl ring data, hydrogen atom bond lengths and angles, least-squares planes, torsion angles, structure factors and the stereoview of the unit cell, being Tables S1–S7 and Fig. S1 for (**1**), and Tables S8–S14 and Fig. S2 for (**2**) respectively.

Results and Discussion

These two compounds are the first unambiguously monomeric triorganotin acetates to be characterized, the shortest intermolecular tin–oxygen

Table 1. Crystallographic parameters

Parameter	1	2
(a) Crystal data		
Formula	$C_{23}H_{24}O_5Sn$	$C_{29}H_{36}O_2Sn$
M_r	499.13	535.29
Crystal system	Triclinic	Monoclinic
Space group	$P1$	$P2_1/n$
a (Å)	9.994(2)	12.457(3)
b (Å)	10.651(6)	16.087(6)
c (Å)	11.156(4)	13.088(4)
α deg	76.12(3)	90
β (deg)	76.50(3)	91.98(2)
γ (deg)	82.58(3)	90
V (Å^3)	1117.6(8)	2625(14)
Z	2	4
D_x (Mg m^{-3})	1.483	1.354
Radiation	Cu$K\alpha$	Mo$K\alpha$
Wavelength (Å)	1.54178	0.71069
μ (mm^{-1})	9.54	1.00
$F(000)$	504	1104
T_m (K)	295	225
(b) Structure determination details[a]		
Crystal dimensions (mm)	$0.11\{011,0\bar{1}\bar{1}\} \times 0.28\{023,023\} \times 0.33\{100,\bar{1}\bar{1}\bar{1}\}$	$0.34\{100,\bar{1}00\} \times 0.34\{010,0\bar{1}0\} \times 0.46\{001,00\bar{1}\}$
Scan width (°)	$1.00 + 0.14 \tan\theta$	$1.00 + 0.35 \tan\theta$
h, k, l range	$0 \rightarrow 12, -12 \rightarrow 12, -12 \rightarrow 13$	$0 \rightarrow 14, 0 \rightarrow 19, -15 \rightarrow 15$
Number of measured reflections	8326	18029
Number of unique reflections	4229	4605
$R_{merge} = \Sigma I - \langle I \rangle) \Sigma I$	0.042	0.013
Reflections with $I \geqslant 3\sigma(I)$	3808	3984
Absorption correction		
Grid	$10 \times 10 \times 10$	—
Transmission-factor range	0.08–0.42	—
Parameters refined	360	434
$R = \Sigma \|\|F_0\| - \|F_c\|\|\Sigma\|F_0\|$	0.037	0.017
$wR = [\Sigma w(\|F_0\| - \|F_c\|)^2 / \Sigma wF_0^2]$	0.047	0.022
$S = [\Sigma w(\|F_0\| - \|F_c\|)^2/(m-n)]$	1.78	1.49
Weights, w^{-1}	$\sigma^2(F) + 0.0016 F^2$	$\sigma^2(F) + 0.0001 F^2$
Shift-to-σ ratio		
Maximum	0.22	0.46
Average	0.02	0.06
Final ΔF map, eÅ^{-3}	0.86–0.40 (10 peaks), 0.93–1.44Å from tin	No peaks, only background
Background, $\leq \pm$eÅ^{-3}	0.30	0.11

[a] Nonius CAD-4 diffractometer, scan speed 4 deg min^{-1}, scan type ω/2θ.

Table 2. Atomic coordinates and equivalent isotropic temperature factors ($\times 10^3$)

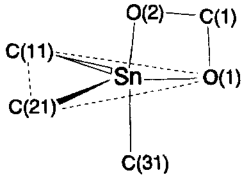
1. Tris(*p*-methoxyphenyl)tin(IV) acetate ($\times 10^4$, Sn $\times 10^5$)

Atom	x	y	z	U_{eq}
Sn	21745(2)	11210(2)	57639(2)	46
O(1)	3892(3)	1579(3)	6244(3)	59
O(2)	3280(3)	3480(3)	5161(3)	67
O(10)	3243(4)	1467(3)	−79(3)	77
O(20)	−3161(3)	4270(3)	8043(4)	74
O(30)	2676(4)	−4838(3)	8218(4)	84
C(1)	4059(5)	2804(4)	5790(4)	57
C(2)	5236(7)	3288(6)	6098(7)	95
C(11)	2517(4)	1280(4)	3794(4)	46
C(12)	2635(4)	2454(4)	2894(4)	52
C(13)	2862(5)	2483(4)	1625(4)	58
C(14)	2976(4)	1342(4)	1204(4)	55
C(15)	2859(5)	166(4)	2072(4)	58
C(16)	2616(5)	151(4)	3343(4)	55
C(17)	3250(7)	346(6)	−549(5)	85
C(21)	401(4)	2178(4)	6592(4)	51
C(22)	−275(5)	3170(4)	5840(4)	60
C(23)	−1446(5)	3860(4)	6340(5)	63
C(24)	−1963(4)	3564(4)	7632(4)	57
C(25)	−1304(5)	2604(4)	8410(4)	63
C(26)	−133(5)	1916(4)	7882(4)	59
C(27)	−3971(7)	3775(6)	9212(6)	92
C(31)	2295(4)	−869(4)	6689(4)	49
C(32)	3549(4)	−1540(4)	6863(4)	59
C(33)	3636(5)	−2857(4)	7376(5)	65
C(34)	2480(5)	−3541(4)	7722(4)	59
C(35)	1225(5)	−2900(5)	7573(5)	71
C(36)	1143(5)	−1577(4)	7059(5)	67
C(37)	1577(7)	−5630(5)	8362(7)	96

2. Tris(2,4,6-trimethylphenyl)tin(IV) acetate ($\times 10^5$)

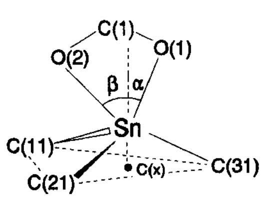
Atom	x	y	z	U_{eq}
Sn	5464(1)	32133(1)	19695(1)	24
O(1)	−2268	42230(8)	13432(10)	32
O(2)	−18321(11)	36326(10)	14667(13)	50
C(1)	−12774(15)	41990(13)	11697(15)	35
C(2)	−17002(18)	49570(17)	6326(19)	55
C(11)	−2093(14)	21661(12)	12330(14)	29
C(12)	−2220(15)	21103(13)	1649(15)	34
C(13)	−6745(16)	14171(14)	−3169(15)	39
C(14)	−11249(15)	7773(13)	2285(16)	37
C(15)	−11414(15)	8523(12)	12837(16)	35
C(16)	−7056(15)	15359(12)	17955(14)	29
C(17)	2105(20)	27894(16)	−5014(17)	51
C(18)	−16128(19)	336(16)	−3100(19)	54
C(19)	−8297(18)	15944(13)	29394(16)	40
C(21)	6094(14)	32758(11)	36187(14)	27
C(22)	14200(15)	28098(12)	41210(15)	31
C(23)	15689(16)	28708(13)	51729(16)	37
C(24)	9323(17)	33831(13)	57481(15)	38
C(25)	1311(16)	38295(12)	52491(15)	35
C(26)	−490(14)	37857(11)	41944(14)	29
C(27)	21300(17)	22175(14)	35546(17)	44
C(28)	10979(23)	34188(18)	68944(18)	60
C(29)	−9690(16)	42653(14)	37150(16)	39
C(31)	21428(14)	35659(12)	15471(14)	27
C(32)	25159(14)	43616(11)	18331(14)	28
C(33)	35775(15)	45740(12)	16667(16)	36
C(34)	42808(15)	40325(13)	12090(17)	41
C(35)	38979(16)	32611(13)	9156(18)	40
C(36)	28521(15)	30088(12)	10884(16)	33
C(37)	18066(15)	50011(12)	23099(15)	34
C(38)	54375(18)	42629(16)	10554(25)	57
C(39)	25543(17)	21353(14)	7833(20)	48

distances being between molecules related by inversion centres, i.e. for **1**, d[Sn–O(1)($1-x$, $-y$, $1-z$)] 4.980(3) Å, d[Sn–O(2)($1-x$, $-y$, $1-z$)] 6.341(3) Å, and for **2**, d[Sn–O(1)($-x$, $1-y$, $-z$)] 5.987(1) Å, d[Sn–O(2)($-x$, $1-y$, $-z$)] 7.003(2) Å, all being much greater than the Sn–O van der Waals value of 3.70 Å.[34] As with earlier reports of monomeric Ph_3SnO_2CR,[11-14,16] both **1** and **2** may be considered as distortions of ideal structure **III** as shown in model **A**. For **1**, O(1) lies within the plane given by Sn,O(2),C(31), the dihedral angle between this plane and that formed from C(11),C(21),O(1) is 88.2°, whilst O(2)–Sn–C(31) is 147.8°. Moreover O(1)–Sn–C(31) approaches the 'ideal' value of 90°. However the displacement of tin from the equatorial plane (0.596 Å) and the large $C_{(ax)}$–Sn–$C_{(eq)}$ angles both suggest the degree of distortion from the ideal trigonal bipyramid is considerable. Model **A** appears even less appropriate for **2** with O(1) being 0.547 Å out of the plane given by Sn,O(2),C(31), this plane being at 78.8° with that formed from C(11),C(21),O(1) and the angle O(2)–Sn–C(31) is 140.8°, while tin is even more displaced from the equatorial plane (0.623 Å).



A

Molloy *et al.* have questioned the above description[15,17,35] and instead suggested that R_3SnCO_2R monomers are distorted tetrahedral systems (model **B**). Thus bond angles around the central tin atom show no systematic change towards trigonal bipyramidal geometry while average C–Sn–C values, (**1**) 113° and (**2**) 114°, are comparable with those found for Ph_3SnX ($X = Cl, Br$).[36, 37] These latter are clearly monomeric with four-coordinate tin. Furthermore, in each case the tin atom lies out of the plane defined by C(11),C(21),C(31) a distance [0.573 Å (**1**), 0.531 Å (**2**)] also indicative of quasi-tetrahedral geometry about tin. Finally, as in other monomer structures, the secondary Sn–O(2) interactions are considerably less than the van der Waals value, a situation taken by several authors as indicative of weak bonding. In contrast Molloy *et al.* have maintained, with some theoretical justification,[17] that the distortions caused by the close approach of O(2) are due to steric rather than electronic factors and that the number of bonds to tin does not expand beyond four.



B

Table 3. Selected bond distances (Å) and angles (deg)

1. Tris(p-methoxyphenyl)tin(IV) acetate

Bonds			
Sn–O(1)	2.060(3)	Sn–O(2)	2.747(3)
Sn–C(11)	2.112(4)	O(1)–C(1)	1.299(5)
Sn–C(21)	2.117(4)	O(2)–C(1)	1.218(6)
Sn–C(31)	2.125(4)	C(1)–C(2)	1.482(9)
Angles			
O(1)–Sn–C(11)	110.47(14)	Sn–C(11)–C(12)	124.5(3)
O(1)–Sn–C(21)	109.55(14)	Sn–C(11)–C(16)	118.5(3)
O(1)–Sn–C(31)	96.03(14)	Sn–C(21)–C(22)	120.2(3)
O(2)–Sn–C(11)	85.61(13)	Sn–C(21)–C(26)	122.2(3)
O(2)–Sn–C(21)	82.82(13)	Sn–C(31)–C(32)	121.5(3)
O(2)–Sn–C(31)	147.80(13)	Sn–C(31)–C(36)	121.3(3)
C(11)–Sn–C(21)	116.69(15)	Sn–O(1)–C(1)	109.2(3)
C(11)–Sn–C(31)	109.48(15)	Sn–O(2)–C(1)	78.4(3)
C(21)–Sn–C(31)	112.70(16)	O(1)–C(1)–O(2)	120.7(4)
		O(1)–C(1)–C(2)	115.3(4)
		O(2)–C(1)–C(2)	124.0(5)

2. Tris(2,4,6-trimethylphenyl)tin(IV) acetate

Bonds			
Sn–O(1)	2.0460(13)	Sn–O(2)	3.0915(14)
Sn–C(11)	2.1431(19)	O(1)–C(1)	1.323(2)
Sn–C(21)	2.1596(18)	O(2)–C(1)	1.216(2)
Sn–C(31)	2.1609(17)	C(1)–C(2)	1.494(3)
Angles			
O(1)–Sn–C(11)	104.47(6)	Sn–C(11)–C(12)	119.27(13)
O(1)–Sn–C(21)	111.34(6)	Sn–C(11)–C(16)	121.67(13)
O(1)–Sn–C(31)	96.61(6)	Sn–C(21)–C(22)	116.36(13)
O(2)–Sn–C(11)	70.84(6)	Sn–C(21)–C(26)	124.31(13)
O(2)–Sn–C(21)	101.78(5)	Sn–C(31)–C(32)	118.01(13)
O(2)–Sn–C(31)	140.76(6)	Sn–C(31)–C(36)	122.70(13)
C(11)–Sn–C(21)	119.10(7)	Sn–O(1)–C(1)	119.75(11)
C(11)–Sn–C(31)	119.10(7)	Sn–O(2)–C(1)	71.27(12)
C(21)–Sn–C(31)	103.97(7)	O(1)–C(1)–O(2)	122.57(18)
		O(1)–C(1)–C(2)	112.85(17)
		O(2)–C(1)–C(2)	124.49(19)

In many solid-state structures, chemical bonds are not well defined, the difficulty being to decide which interatomic distances correspond to bonds. Quite different impressions of a structure can be created depending on how the bonds are selected, as instanced by models proposed here for the bonding in R_3SnCO_2R monomers. To shed more light on this problem we have applied the Bond Valence Method which has been extensively used by Brown[38] including an analysis of the structural chemistry of acetate ions bound to a variety of cations.[39]

The Bond Valence Model assumes that the valence, V_i, of an atom, i, is shared between the bonds it forms so that each bond can be assigned a bond strength or *bond valence* (S_{ij}) where

$$V_i = \sum S_{ij} \qquad [1]$$

Since bond strengths decrease as bond lengths increase, bond valence (S_{ij}) varies inversely with bond length (R_{ij}) (Eqn [2]):

$$S_{ij} = S_0(R_{ij}/R_0)^{-N} \qquad [2]$$

where $S_0 = 1.00$ v.u. (valence unit) and R_0 and N are empirical parameters. These are determined by ensuring the best fit to the Valence Sum Rule (Eqn [1]) where summations are over all bonds formed by the atom i using a large number of

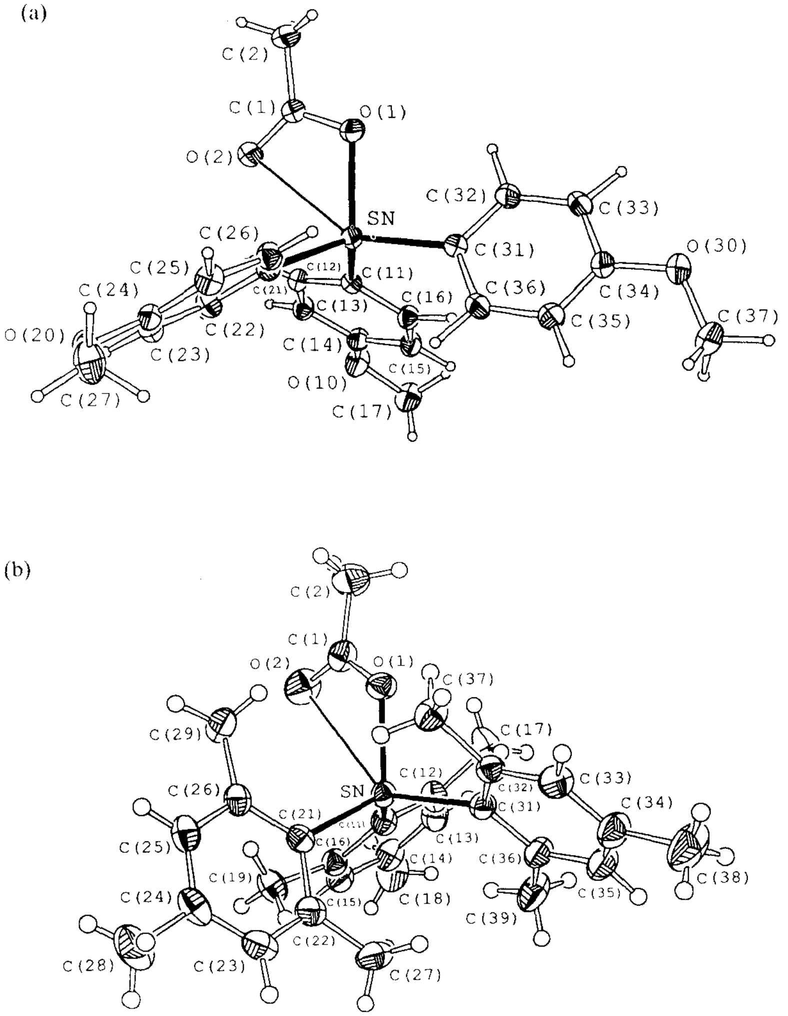


Figure 1. View of the molecule with the numbering scheme used. (a) (p-$CH_3OCF_6H_4)_3SnO_2CCH_3$. (b) $[2,4,6\text{-}(CH_3)_3C_6H_2]_3SnO_2CCH_3$.

structures. Experimental bond lengths can then be used to determine bond valences (Eqn. [2]) followed by empirical atom valences (Eqn [1]) which are usually within 0.05 v.u. of the ideal integer value. In making the summation it is usual to ignore bonds with valences less than 0.03 v.u., this amount corresponding to a van der Waals distance. When the empirical and ideal valence values do not agree, this may indicate that the bonding model assumed is incorrect or that a partial ionic charge resides on the atom in question.

We have calculated Sn–O and Sn–C bond valence values for a selection of Ph_3SnO_2CR systems as well as for the structures reported here using parameters given by Brown[39] (Sn–O, $R_0 = 1.94$ Å, $N = 5.5$; Sn–C_{sp^2}, $R_0 = 2.15$ Å, $N = 3.5$), and these are listed in Table 4. Compounds **1**, **2** and **4**–**8** typify the monomeric bonding situation with average $S_{\mathrm{SnO(1)}} = 0.71(4)$ v.u. and average $S_{\mathrm{SnO(2)}} = 0.14(4)$ v.u. Moreover, any variation in $S_{\mathrm{SnO(1)}}$, e.g. **5**, is balanced by an opposite change in $S_{\mathrm{SnO(2)}}$, keeping the total Sn–O bond valence value almost constant [0.86(2) v.u.]. Only **3** deviates from this pattern, perhaps because of packing of the very large R groups in the crystal lattice causing an overall compression of the coordination sphere around tin. Even in this case the doubling of $S_{\mathrm{SnO(2)}}$ is partially compensated by a decrease in $S_{\mathrm{SnO(1)}}$. Although the principal tin–

oxygen bond is Sn–O(1), the secondary interaction, Sn–O(2), is sufficient to indicate that the carboxylate group acts as an anisobidentate ligand in these compounds. However, in solution, ^{119}Sn NMR data for Ph_3SnO_2CR[15] and Ar_3SnOAc (Wharf, I, unpublished results) show these monomeric systems contain four-coordinate tin whilst for the two structures reported here near-coincidence of infrared values for solid and solution spectra e.g. for **1** would suggest these two compounds have the same structure in both the solid state and solution. Thus with $\Sigma S_{SnO} < 1$ and $\Sigma S_{SnC} > 3$ for **1–8**, we suggest that the RCO_2 ligand is effectively occupying *one* bonding position, leaving these R_3SnX systems with essentially four-coordinate tin. This contrasts with the values $\Sigma S_{SnO} = 1.07$ and $\Sigma S_{SnC} = 2.90$ v.u. found for Ph$_3$SnOC(Ph)CHCO(Ph) which is monomeric with five-coordinate tin in both the solid state[43] and in solution.[15] Lastly we note that in all R_3SnO_2CR monomers, the principal Sn–O bond always tilts towards one of the tin–carbon bonds, meaning both Sn–O bonds are inclined to the Sn–X bonding axis (model **B**), which for simplicity we have defined as the extension of the line between the mid-point C(x) of the C(11),C(21),C(31) plane, and tin. Thus (α, β) angles are (14.6°, 37.2°) (**1**) and (16.0°, 30.2°) (**2**), which then give resultant ΣS_{SnO} values of 0.82 v.u. and 0.79 v.u. respectively along the Sn–X bond axis. These compare well with $S_{SnX} = 0.80$ (X = Cl) and 0.85 (X = Br) for Ph_3SnX from spectroscopic data.[44]

The structures **9–14** are also consistent with each carboxylate group occupying a *single* bonding position at tin. Thus **9** with carboxylate groups

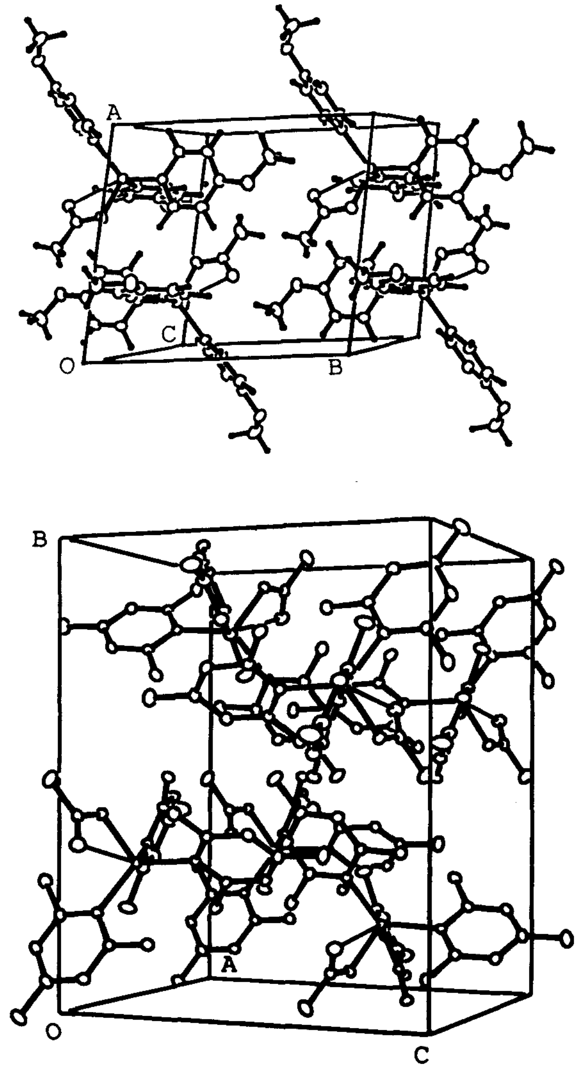


Figure 2. Packing diagram of the cell. (a) $(p\text{-}CH_3OC_6H_4)_3SnO_2CCH_3$. (b) $[2,4,6\text{-}(CH_3)_3C_6H_2]_3SnO_2CCH_3$.

Table 4. Tin coordination bond valences (*S*) in Ph_3SnO_2CR

Cpd	$S_{SnO(1)}$	$S_{SnO(2)}$	$S_{SnO(2')}$	ΣS_{SnO}	ΣS_{SnC}	V_{Sn}
1	0.72	0.15	—	0.87	3.16	4.03
2	0.75	0.08	—	0.83	2.97	3.80
3	0.70	0.27	—	0.97	3.13	4.10
4	0.74	0.12	—	0.86	3.12	3.98
5	0.62	0.22	—	0.88	3.09	3.97
6	0.73	0.14	—	0.87	3.11	3.98
7	0.72	0.14	—	0.86	3.11	3.96
8	0.69	0.14	—	0.83	3.15	3.98
9	0.43	0.05	—	0.91	3.08	3.99
	0.38	0.05	—			
10	0.53	0.06	(0.31)^a	0.91	3.13	4.04
11	0.55^b	0.03^b	(0.36)^{b,c}	0.94	3.13	4.07
	0.57^d	0.06^d	0.18^{d,e}	0.81	3.12	3.93
12	0.48^f	0.05	0.38^e	0.91	3.18	4.09
	0.48	0.04	0.38^e	0.90	3.14	4.04
13	0.52	0.06	0.35^e	0.93	3.10	4.03
14	0.50	0.03	0.32^e	0.85	3.07	3.92

Key: **1**, **2**, this work; **3**, R = $[(CH_3)(OH)C_6H_3N_2]C_6H_4$;[11] **4**, R = *p* – ClC_6H_4;[14] **5**, R = *o*-$(CH_3)_2NC_6H_4$;[12] **6**, R = *o*-$CH_3OC_6H_4$;[13] **7**, R = *p*-$CH_3SC_6H_4$;[13] **8** R = C_4H_3S;[16] **9**, R = $\frac{1}{2}(2,6\text{–}C_6H_3N)$;[40] **10**, R = CCl_3, L = CH_3OH;[41]; **11**, see text;[14] **12**, R = H;[42] **13**, R = CH_3;[19] **14**, R = *o*-ClC_6H_4.[14]

[a] Sn–O(H)CH_3. [b] Bonds to Sn(1). [c] Sn–OH_2. [d] Bonds to Sn(2). [e] Intermolecular Sn- -O(2′) bond. [f] Two molecules per asymmetric unit.

occupying the *trans*-axial positions may be compared with the structure of $Ph_3SnBr_2^-$,[45] with axial ΣS_{SnO} values of 0.48 and 0.43 being similar to $\Sigma S_{SnX} = 0.46$ (X = Cl) and 0.42 (X = Br) found for $Ph_3SnX_2^-$ from spectroscopic data.[44] In the same way, in **10**, the trichloroacetate ion occupies an axial position *trans* to a neutral ligand, in this case methanol. The slightly higher ΣS_{SnO} value of 0.59 for the tin–anion interaction is the same as that found for the axial Sn–Cl bond in $Ph_3SnCl \cdot HMPA$.[44] Compound **11** [(H_2O)-$Ph_3SnOC(R)OSnPh_3(O_2CR)$, R = *o*-$ClC_6H_4$] has RCO_2 groups occupying axial positions opposite 'neutral' ligands in the same way as in **10** with one RCO_2 bound to Sn(1) (*trans* to H_2O) but with the O(2) of this group now donating to Sn(2) forming the weaker axial Sn(2)–O bond opposite the other RCO_2 group uniquely occupying an axial position at Sn(2). This *asymmetric* bridging pattern provides the model for polymeric Ph_3SnO_2CR (**12–14**) and contradicts the symmetric ideal structure (**I**) usually assumed.

Bond valence analysis of the carboxylate group, using $R_0 = 1.37$ Å and $N = 4.4$ for the C–O bond, provides further insight to the differing modes of acetate ligand behaviour. Thus, in **1**, $S_{O(1)C(1)} = 1.26$ and $S_{O(2)C(1)} = 1.68$, giving $V_{O(1)} = 1.98$ and $V_{O(2)} = 1.83$ v.u. Since, ideally, $V_O = 2$, the difference found on O(2) clearly represents the partial negative charge of the polar tin–acetate interaction. In contrast, for Ph_3SnOAc $S_{O(1)C(1)} = 1.43$ and $S_{O(2)C(1)} = 1.49$ giving $V_{O(1)} = 1.95$ and $V_{O(2)} = 1.55$ for attachment to one tin atom. However, the unused valence at O(2) is now available for formation of a bond to the neighbouring tin atom, yielding a new $V_{O(2)} = 1.90$. This results in somewhat stronger tin–oxygen bonding overall.

This bond valence analysis suggests that a *trans*-polymeric structure will be the choice for R_3SnO_2CR' systems. However the preference is slight and is overcome if the central tin atom is prevented from becoming five-coordinate, which is the case for the two structures reported here, i.e. either by electronic interactions reducing the Lewis acidity at tin (**1**) or steric hindrance preventing increased coordination at the tin (**2**). Other factors that may tip the balance in favour of the monomeric form are the delocalization of the negative charge on the O(2) through the rest of the RCO_2 ligand or other lattice interactions including hydrogen bonding with O(2). However, regardless of the structure chosen, the carboxylate group always acts as an asymmetric bidentate ligand, but effectively occupying a single coordination site on the tin atom.

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