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Journal of Organometallic Chemistry 654 (2002) 100–108

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

The synthesis and structural characterization of some triorganotin(IV) complexes of 2-{[(*E*)-1-(2-hydroxyaryl)alkylidene]amino}acetic acid. Crystal and molecular structures of $Ph_3Sn(2\text{-}OHC_6H_4C(H)=NCH_2COO)$ and $Me_3Sn(2\text{-}OHC_6H_4C(CH_3)=NCH_2COO)$

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Abstract

Triorganotin(IV) derivatives of 2-{[(*E*)-1-(2-hydroxyaryl)alkylidene]amino}acetic acid have been synthesized and characterized by ^1H, ^{13}C, ^{119}Sn-NMR, ^{119}Sn Mössbauer and IR spectroscopic techniques in combination with elemental analyses. The crystal structures of triphenyltin 2-{[(*E*)-1-(2-hydroxyphenyl)methylidene]amino}acetate and trimethyltin 2-{[(*E*)-1-(2-hydroxyphenyl)ethylidene]amino}acetate are reported. The X-ray structures reveal that the complexes adopt a polymeric *trans*-O_2SnC_3 trigonal bipyramidal configuration with the R groups in the equatorial positions and the axial locations occupied by a carboxylate oxygen from the ligand and the phenolic oxygen of the ligand on an adjacent complex. The ligands coordinate in the zwitterionic form with the phenolic proton moved to the nearby nitrogen atom. There is hydrogen bonding between this proton and the phenolic oxygen. The carboxylate group is unidentate. The spectroscopic evidence in combination with ^{119}Sn Mössbauer data suggest that the other complexes adopt similar polymeric structures in the solid state. © 2002 Published by Elsevier Science B.V.

Keywords: Organotin; Carboxylates; 2-{[(*E*)-1-(2-hydroxyaryl)alkylidene]amino}acetic acid; NMR; Mössbauer; X-ray

1. Introduction

Organotin carboxylates have a variety of biocidal activities [1–3] along with an interesting range of structural variations [4] which have led to the proposal of some structure–activity relationships [5]. The structure–activity relationship studies suggest that triorganotin carboxylates with either an isolated tetrahedral tin center or a *trans*-R_3SnO_2 geometry around the tin atom show significantly greater biocidal activity than compounds with the monomeric *cis*-R_3SnO_2 structural type [3,5]. However, two types of bridging are known for the *trans*-R_3SnO_2 configuration of organotin carboxylates. The most commonly encountered structure is polymeric in which the carboxylate groups behave as bridging bidentate ligands and the pentacoordinated tin atoms have distorted trigonal bipyramidal geometries. Alternatives to carboxylate bridging for the *trans*-R_3SnO_2 structural moiety have been reported for triorganotin carboxylates containing either donor substituent groups [6,7] or a labile phenolic group in the ester function [8]. Consequently, in recent years there has been an upsurge in the synthesis of organotin carboxylates of substituted benzoic acids. These studies have revealed new structural possibilities [9] and, more recently, certain derivatives have been demonstrated to

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0022-328X/02/$ - see front matter © 2002 Published by Elsevier Science B.V.
PII: S0022-328X(02)01387-6

possess exciting cytotoxic activity [10]. We have recently reported the coordination behavior of 2-{[(*E*)-1-(2-hydroxyaryl)alkylidene]amino}acetic acid towards the $R_2Sn(IV)$ moiety [11,12]. Moreover, these diorganotin complexes were used as coordinating ligands to form uncommon mixed dinuclear organotin species in which the two tin atoms are connected via the carbonyl atom of the ligand [11].

As a continuation of our studies on such interesting systems, we now report the synthesis and characterization of a series of new triorganotin(IV) complexes derived from sodium or potassium 2-{[(*E*)-1-(2-hydroxyaryl)alkylidene]amino}acetate (LHM, Fig. 1).

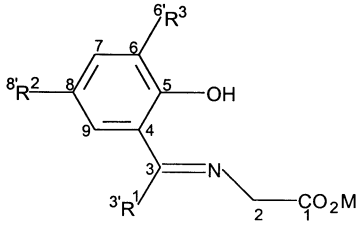
2. Experimental

2.1. Materials

Me_3SnCl (Merck), Bu_3SnCl (Merck) and Ph_3SnCl (Fluka AG) were used without further purification. Glycine (Aldrich), 2-hydroxyacetophenone (Aldrich), 2-hydroxybenzaldehyde (Fluka), 2-hydroxy-5-chlorobenzaldehyde (Kodak) were of reagent grade whereas 2-hydroxy-5-methylacetophenone and 2-hydroxy-3-methylacetophenone were gift samples. All the solvents used in the reactions were of AR grade and dried using standard literature procedures.

2.2. Physical measurements

Carbon, hydrogen and nitrogen analyses were performed with a Perkin–Elmer 2400 series II instrument. IR spectra in the range 4000–400 cm^{-1} were obtained on a Perkin–Elmer 983 spectrophotometer with samples investigated as KBr discs. The ^1H, ^{13}C and ^{119}Sn-NMR spectra were acquired on a Bruker ACF 300 spectrometer and measured at 300.13, 75.47 and 111.92 MHz, respectively. The ^1H, ^{13}C spectra were referenced to Me_4Si while ^{119}Sn chemical shifts were referenced to Me_4Sn, all set at 0.00 ppm. ^{119}Sn Mössbauer spectra of the complexes in the solid state were obtained at liquid-nitrogen temperature on a conventional constant acceleration spectrometer equipped with a CRYO cryostat and a ^{119}Sn Mössbauer source. The velocity calibration was made using a ^{57}Co Mössbauer source, and an iron foil enriched to 95% in ^{57}Fe (DuPont Pharma Italia, Firenze, Italy) was used as the absorber. The $Ca^{119m}SnO_3$ and ^{57}Co sources, 10 mCi, were procured from Ritverc, St. Petersburg, Russia.



(LHM)

Abbreviation[a]	R^1	R^2	R^3
L^1HM	H	H	H
L^2HM	H	Cl	H
L^3HM	CH_3	H	H
L^4HM	CH_3	H	CH_3
L^5HM	CH_3	CH_3	H

[a] H and M represent the hydroxyl proton and Na or K, respectively.

Fig. 1. Ligands used in the present work.

2.3. X-ray crystallography

The intensity data for yellow blocked shaped crystals of complexes **2** and **4** were measured at 293 K on a Rigaku AFC6S diffractometer fitted with graphite monochromatized Mo–K_α radiation ($\lambda = 0.71073$ Å) using the omega scan technique. Empirical corrections were made from psi-scan curves [13]. The structures were solved by direct methods. All hydrogen atoms were given calculated positions. Neutral atom scattering factors were taken from the literature [14]. All computations were performed using the TEXSAN system of crystal structure solving programmes [15]. All refinements were performed by full-matrix least-squares on F^2. The data were corrected for Lorentz and polarization effects.

2.4. Preparation of sodium and potassium salts of 2-{[(*E*)-1-(2-hydroxyaryl)alkylidene]amino}acetate

The sodium (L^3HNa and L^5HNa) or potassium (L^2HK, L^3HK and L^5HK) salts of 2-{[(*E*)-1-(2-hydroxyaryl)alkylidene]amino}acetic acid were prepared by reacting equimolar amounts of sodium or potassium glycinate with either 2-hydroxyacetophenone or 2-hydroxybenzaldehyde [11], as appropriate, while L^1HK and L^4HK were prepared under cold conditions (−10 °C) according to the reported procedure [16]. The salts of the ligands were recrystallized from methanol and obtained in >60% yield as yellow crystalline solids. The characterization data for L^1HK, L^2HK, L^4HK, L^5HK and L^5HNa are recorded in Tables 1 and 4 while for L^3HK and L^3HNa are reported in [11].

2.5. Synthesis of the triorganotin complexes

Three typical methods are described below.

Table 1
Synthetic and analytical data for the triorganotin(IV) complexes

Complex	Reaction time (h)	Crystallization solvent	Color	Yield (%)	M.p. (°C) [f]	Elemental analysis Found (Calc.) (%)		
						C	H	N
Bu_3SnL^1 H (**1**)	1 [a]	Chloroform	Yellow	70	Viscous liquid	54.15 (53.99)	7.26 (7.33)	3.09 (2.99)
Ph_3SnL^1 H (**2**)	3 [b]	Chloroform	Yellow	71	156–57	61.20 (61.40)	4.35 (4.39)	2.68 (2.65)
Ph_3SnL^2 H (**3**)	2 [c]	Chloroform	Yellow	42	146–48	57.50 (57.64)	3.83 (3.94)	2.60 (2.48)
Me_3SnL^3 H (**4**)	3 [d]	Methanol	Yellow	70	188–90	43.90 (43.86)	5.38 (5.38)	4.15 (3.93)
Bu_3SnL^3 H (**5**)	7 [e]	Chloroform + petroleum ether	Yellow	50	110–12	54.39 (54.79)	7.80 (7.73)	2.84 (2.90)
Ph_3SnL^3 H (**6**)	3 [d]	Chloroform + petroleum ether	Pale yellow	65	190–92	61.85 (62.03)	4.35 (4.64)	2.61 (2.58)
Me_3SnL^4 H (**7**)	5 [c]	Chloroform	Yellow	17	150–52	45.40 (45.44)	5.70 (5.72)	3.80 (3.78)
Ph_3SnL^4 H (**8**)	2 [c]	Chloroform	Yellow	40	127–28	62.68 (62.60)	4.93 (4.89)	2.48 (2.51)
Bu_3SnL^5 H (**9**)	3 [a]	Chloroform	Yellow	74	122–24	55.85 (55.67)	7.90 (7.92)	2.98 (2.82)
Ph_3SnL^5 H (**10**)	2 [c]	Chloroform	Yellow	60	182–84	62.48 (62.62)	4.87 (4.89)	2.37 (2.51)

[a] Method: stirring in chloroform.
[b] Method: reflux in methanol–benzene mixture (1:1).
[c] Method: stirring in methanol.
[d] Method: reflux in methanol.
[e] Method: reflux in benzene.
[f] The decomposition points of the K–Na-salts of the corresponding ligands are 216–218 °C (L^1HK), > 250 °C (L^2HK), 205 °C (L^4HK), 259 °C (L^5HK) and 214 °C (L^5HNa).

2.5.1. Ph_3SnL^1H (**2**)

Ph_3SnCl (1.77 g, 4.60 mmol) in benzene (25 ml) was added dropwise with continuous stirring to L^1HK (1.0 g, 4.60 mmol) in 50 ml methanol. The reaction was then refluxed for 3 h and the solvent was distilled off to dryness using a rotary evaporator. The residue was washed with petroleum ether, extracted into hot chloroform and filtered. The yellow-colored extract was distilled off (up to 50% of the initial solvent volume) and kept at room temperature (r.t.) for crystallization. On the following day, the solid was isolated by filtration and recrystallized from methanol and chloroform mixture. Slow evaporation of methanol and chloroform solutions (1:1 v/v) of the product deposited shining block-like crystals suitable for structural studies.

2.5.2. Me_3SnL^3H (**4**)

Me_3SnCl (0.80 g, 4.01 mmol) in methanol (30 ml) was added dropwise with continuous stirring to a hot methanol solution (50 ml) containing either L^3HNa (0.863 g, 4.01 mmol) or L^3HK (0.927 g, 4.01 mmol). The reaction mixture was heated at reflux temperature for 3 h and then the solvent was removed using a rotary evaporator. The yellow mass was washed thoroughly with hot petroleum ether, extracted into chloroform and filtered. The yellow product obtained upon concentration of the chloroform extract was recrystallized from methanol which upon slow evaporation yielded yellow block crystals suitable for structural studies.

2.5.3. Bu_3SnL^3H (**5**)

The compound was prepared by reacting Bu_3SnCl (0.64 g, 1.96 mmol) and L^3HK (0.454 g, 1.96 mmol) in anhydrous benzene (50 ml) under reflux conditions for 7 h. The reaction mixture was filtered while hot and the filtrate was evaporated to dryness. The yellow jelly-like residue was cooled in a freezing mixture and then petroleum ether was added drop wise to yield a crude product. This was washed thoroughly with petroleum ether and finally recrystallized from chloroform and petroleum ether (1:1 v/v).

3. Results and discussion

3.1. Syntheses

Triorganotin(IV) complexes of 2-{[(*E*)-1-(2-hydroxyaryl)alkylidene]amino}acetic acid can be prepared in moderate yield by allowing stoichiometric amounts of R_3SnCl and sodium or potassium 2-{[(*E*)-1-(2-hydroxyaryl)alkylidene]amino}acetate to react in chloroform, benzene, methanol or a combination of these solvents as shown in equation (1):

$$LHM + R_3SnCl \rightarrow R_3SnLH + MCl \quad (1)$$

(LHM as described in Fig. 1 and R = Me, Bu or Ph).

The exact synthetic methodology and reaction conditions for each of the complexes are reported in Table 1 along with their characterization data. In general, the solubility for the triphenyltin compounds was found to be very poor, even in hot chloroform. A large amount of chloroform was needed to extract the pure triphenyltin compounds, however, the other triorganotin compounds were readily extracted. Attempts to prepare the triorganotin complexes by the reaction of $(R_3Sn)_2O$ with glycine and the appropriate salicylaldehyde or

Table 2
^{1}H chemical shifts (δ, ppm) [a] for the triorganotin(IV) complexes

Complex	Ligand skeleton[b]									Sn–R skeleton[c]			
	H-2	H-5	H-6	H-7	H-8	H-9	H-3′	H-6′	H-8′	1*	2*	3*	4*
1	4.35, s	16.2, brs	6.85, d	7.29, t	6.77, t	6.94, d	8.34, s	–	–	1.26, m	1.26, m	1.59, m	0.90, t
2	4.32, s	13.2, brs	6.87, d	7.26, t	6.81, t	7.18, d	8.22, s	–	–	–	7.72, m	7.42, m	7.42, m
3	4.47, s	13.2, brs	6.91, d	7.20, d	–	7.23, s	8.26, s	–	–	–	7.72, m	7.46, m	7.46, m
4	4.19, s	Nd	6.89, d	7.44, t	6.87, t	7.75, d	2.63, s	–	–	0.42, s (63)	–	–	–
5	4.35, s	16.1, brs	6.92, d	7.26, t	6.75, t	7.50, d	2.30, s	–	–	1.32, m	1.32, m	1.62, m	0.95, t
6	3.21, s	15.6, brs	5.76, d	6.29, t	5.71, t	6.56, d	1.19, s	–	–	–	6.85, m	6.41, m	6.41, m
7	4.32, s	16.5, brs	–	7.17, d	6.66, t	7.37, d	2.31, s	2.26, s	–	0.58, s(59)	–	–	–
8	4.44, s	16.2, brs	–	7.18, d	6.68, t	7.40, d	2.29, s	2.24, s	–	–	7.77, m	7.45, m	7.45, m
9	4.34, s	16.2, brs	6.84, d	7.08, d	–	7.29, s	2.28, s	–	2.27, s	1.32, m	1.32, m	1.62, m	0.91, t
10	4.12, s	16.1, brs	6.62, d	7.02, d	–	7.28, s	2.20, s	–	2.10, s	–	7.78, m	7.36, m	7.36, m

n.d., Not detected.

[a] Solvents: Saturated DMSO-d_6 solutions were used for complexes **4** and **6** while others were in $CDCl_3$.

[b] Refer to Fig. 1 for numbering scheme.

[c] Numbering scheme for Sn–R skeleton as shown below:

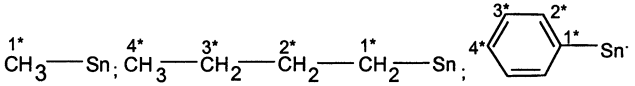


Table 3
^{13}C [a] and ^{119}Sn [b] chemical shifts (δ, ppm) for the triorganotin(IV) complexes

Complex	Ligand skeleton												Sn–R skeleton				^{119}Sn-NMR
	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-3′	C-6′	C-8′	1*	2*	3*	4*	
1	173.9	60.5	167.5	118.7	161.3	117.1	132.4	118.4	131.6	–	–	–	16.6	27.8	27.1	13.7	126.8
2	174.9	59.8	167.7	119.8	161.3	118.5	133.7	117.1	131.6	–	–	–	136.9	136.6	128.8	132.6	[b]
3	174.6	59.7	166.7	119.4	159.8	118.7	132.4	–	130.6	-	–	–	137.3	136.8	129.0	130.4	[b]
4	170.6	49.9	170.0	116.8	163.3	116.9	130.6	114.1	126.6	12.8	–	–	−1.71	–	–	–	134.5
5	173.8	51.6	172.7	119.4	163.7	118.7	136.4	116.9	128.0	14.8	–	–	16.6	27.7	26.9	13.6	121.9
6	171.4	49.9	169.5	116.6	163.5	117.0	130.8	114.1	126.7	12.7	–	–	141.2	134.4	126.3	126.9	−95.8
7	173.9	51.5	172.8	118.4	162.4	127.6	133.3	116.2	125.7	16.1	15.1	–	−1.95	–	–	–	134.7
8	175.1	51.4	165.1	118.6	161.7	117.4	133.3	116.4	125.7	16.0	15.1	–	137.6	136.9	128.9	130.3	−95.8
9	174.1	51.8	172.6	125.9	161.2	119.2	133.4	118.4	128.1	14.9	–	20.7	16.7	27.8	27.1	13.7	123.9
10	173.0	52.2	171.8	124.7	162.3	118.5	133.7	117.6	130.9	14.7	–	20.4	137.3	136.4	127.9	128.3	[b]

[a] Refer to Fig. 1 and Table 2 for numbering scheme of the ligand and Sn–R skeletons, respectively; coupling constants, $^{n}J(^{13}C-^{117/119}Sn)$ (Hz): for trimethyltin complexes **4** and **7** $^{1}J = 258$ and 200; for tributyltin complexes: $^{2}J = 21$, $^{3}J = 65$ whereas ^{1}J and ^{4}J could not be detected; for triphenyltin complexes: $^{2}J = 50$, $^{3}J = 64$ whereas ^{1}J and ^{4}J could not be detected.
[b] Not recorded due to solubility problem.

hydroxyacetophenone invariably resulted a complex mixture which could not be separated.

3.2. NMR data

The ^{1}H and ^{13}C-NMR data of the triorganotin complexes are shown in Tables 2 and 3, respectively. The ^{1}H and ^{13}C chemical shift assignments of the triorganotin moiety is straightforward from the multiplicity patterns and/or resonance intensities [17] whereas the ligand skeletons were assigned by the multiplicity patterns and/or resonance intensities of the signals and also by the standard distortionless enhancement by polarization transfer (DEPT) experiments [11], wherever required. The efforts to use the NMR data in the elucidation of the coordination mode of the ligand and the geometries of the complexes were not successful since (i) it was not possible to isolate the free acid, making comparisons with it difficult, and (ii) the solvents used for the spectra (DMSO-d_6 in some cases) were not all the same and this could influence the nature of the coordination sphere.

None of the triorganotin complexes exhibit $^{1}J(^{13}C-^{119/117}Sn)$ coupling satellites in solution owing to the solubility problem. The ^{13}C chemical shift of the *ipso*-carbon of the $SnPh_3$ moiety is around 138 ppm in $CDCl_3$ solution which is typical for a tetrahedral tin atom [18]. Five-coordinated triphenyltin carboxylates have a value ca. 4 ppm higher in frequency such as is found for complex **6** in DMSO-d_6 solution.

In recording ^{119}Sn-NMR spectra of organotin(IV) complexes in solution, non-coordinating solvents are preferable to coordinating ones to preclude possible changes in the coordination number of the tin atom. In the present investigation, a few complexes were found to be suitable for recording ^{119}Sn-NMR spectra in $CDCl_3$ solution. These are listed in Table 3. The organotin complexes exhibit a single sharp resonance at around 134 ppm for R = Me; **4** and **7**; between 121.9 and 126.8 for R = Bu; **1**, **5** and **9**, and at around −95.8 ppm for R = Ph; **6** and **8**. These are consistent with the range expected for tetrahedral triorganotin compounds [17,19]. Thus, ^{119}Sn-NMR results indicate that the five-coordinated polymeric structure of solids (as revealed by X-ray and Mössbauer, vide infra) is lost upon dissolution giving rise to four-coordinate monomeric structures in solution.

3.3. IR data

The solid-state IR spectra of the complexes (Table 4) all display a band near 1650 cm^{-1} which is assigned to the $\nu(OCO)_{asym}$ vibration. In the sodium and potassium 2-{[(*E*)-1-(2-hydroxyaryl)alkylidene]amino}acetate, this vibration appears at 1618 and 1628 cm^{-1}, respectively. The shift of this $\nu(OCO)_{asym}$ band to higher wave number in the complexes is reported to be diagnostic of bonding between the carbonyl oxygen atom of the ligand and the triorganotin group [11]. Absorption bands believed due to the $\nu(OCO)_{sym}$ stretch have been assigned since the magnitude of the $\nu(OCO)_{asym}-\nu(OCO)_{sym}$ (i.e. $\Delta\nu$) separation is of interest. The observed values of $\Delta\nu$, which are in the range 281–327 cm^{-1}, indicate a unidentate bonding mode for the carboxylate moiety [8]. For a bridging or chelating carboxylate group, $\Delta\nu$ would be expected to be <150 cm^{-1} [20], as widely observed in the infrared spectra of triorganotin carboxylates [21]. This suggests that the phenolic group occupies the fifth coordination site at the tin atom [22]. This is further substantiated by the broad IR absorptions in the region 3600–3400 cm^{-1} which are reported to be due to intramolecular hydrogen bonding between the phenolic proton and the azomethine nitrogen [23]. Such intramolecular hydrogen bonding would

Table 4
IR data (cm^{-1}) for the ligands and triorganotin(IV) complexes

Complex	$\nu(OCO)_{asym}$	$\nu(OCO)_{sym}$	$\Delta\nu$	ν(Ph–(CO))	ν(CN)
L^1HK	1640	–	–	1281	1607
1	1648	1373	275	1259	1599
2	1644	1335	309	1257	1604
L^2HK	1633	–	–	1260	1604
3	1643	1347	296	1265	1611
4	1649	1357	292	1261	1606
5	1650	1327	323	1260	1604
6	1651	1326	325	1259	1603
L^4HK	1629	–	–	1250	1603
7	1649	1357	292	1261	1606
8	1630	1326	304	1260	1600
L^5HK	1645	–	–	1266	1615
L^5HNa	1640	–	–	1270	1603
9	1650	1330	320	1269	1615
10	1630	1330	300	1258	1607

Table 5
^{119}Sn Mössbauer (mm s^{-1}) data for the representative triorganotin(IV) complexes

Complex	Mössbauer data [a]			
	δ	Δ	Γ_1	Γ_2
2	1.23	2.98	0.90	0.91
3	1.18	3.03	0.92	0.97
4	1.23	3.35	0.92	0.91
6	1.23	3.02	0.91	0.91
10	1.12	3.08	0.92	0.96

[a] Parameters: δ: isomer shifts; Δ: quadrupole splitting and Γ_1 and Γ_2: line widths.

increase the likelihood of coordination by the phenolic oxygen to the tin atom which is also reflected in the ν(Ph–(CO)) vibration (see Table 4). Bands due to ν(C=N) have been detected in the complexes at around 1605 cm^{-1} and showed no change when compared with the ligand values, indicating non-participation of the azomethine nitrogen in bonding to tin. Thus, the spectroscopic data suggest that the structures of these triorganotin carboxylates may well involve bridging by phenolic oxygen atoms. This conclusion was confirmed by the results of X-ray structural analysis for complexes **2** and **4**.

Table 6
Crystallographic data for **2** and **4**

Parameters	**2**	**4**
Empirical formula	$C_{27}H_{23}NO_3Sn$	$C_{13}H_{19}NO_3Sn$
Formula weight	528.15	355.98
Crystal size (mm)	0.42 × 0.54 × 0.48	0.06 × 0.66 × 0.33
Colour and morphology	Yellow, block	Yellow, block
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a (Å)	10.7790(12)	10.7327(14)
b (Å)	13.3111(13)	13.010(2)
c (Å)	16.1450(19)	10.5513(14)
β (^{0})	91.132(9)	90.458(9)
V (Å^3)	2316.0(4)	1473.3(4)
Z	4	4
D_{calc} (g cm^{-3})	1.515	1.605
Temperature (K)	293(2)	293(2)
Absorption coefficient (mm^{-1}), F(000)	1.132, 1064	1.734, 712
θ Range for data collection (°)	2.2–27.5	2.5–30.0
Reflections collected	5591	3876
Independent reflections	5316 (R_{int} = 0.0257)	3744 (R_{int} = 0.0254)
Absorption correction	Empirical	Semi- empirical from psi-scans
Max/min transmission	0.273 and 0.222	1.000 and 0.449
Refinement method	Full-matrix least-square on F^2	Full-matrix least-square on F^2
Data/restraints/parameters	5316/0/315	3744/0/190
Goodness-of-fit on F^2	1.01	1.05
Final R indices ($I > 2\sigma(I)$)	R_1 = 0.039, wR_2 = 0.081	R_1 = 0.031, wR_2 = 0.077
R indices (all data)	R_1 = 0.062, wR_2 = 0.089	R_1 = 0.041, wR_2 = 0.083
Extinction coefficient	Not applied	0.0013(3)
Largest difference peak and hole (e Å^{-3})	0.49 and −0.35	0.50 and −0.45

3.4. Mössbauer data

In order to obtain further structural evidence, the Mössbauer spectra of the representative complexes have been recorded in the solid state (Table 5). The isomer shift (δ) values, which lie in the range 1.12–1.23 mm s^{-1}, are typical of quadrivalent organotin derivatives [24]. This means that the total s-electron density at the tin nucleus is essentially the same for all the complexes. This consistency of s-electron density about the tin atom suggests that there is no significant difference in the coordination around the tin atom with changes in the ligand substituents. The spectra of the complexes show a characteristic doublet absorption indicating a single tin site and the quadrupole splitting (Δ) values lie in the range 2.98–3.35 mm s^{-1}. Values of Δ in the range 3.0–4.1 mm s^{-1} are typical for structures with a planar SnR_3 unit and two apical oxygens [24]. A similar range of values were also found in the triorganotin derivatives of amino acids with a *trans*-trigonal bipyramidal geometry [25]. The full width of half maximum ($\Gamma\pm$) of these resonance absorptions are ca. 0.94 mm s^{-1}, further suggesting the presence of a single tin atom site in the structure.

3.5. X-ray diffraction analysis for Ph_3SnL^1H (**2**) and Me_3SnL^4H (**4**)

Pertinent crystallographic parameters are summarized in Table 6. The atomic numbering scheme and the

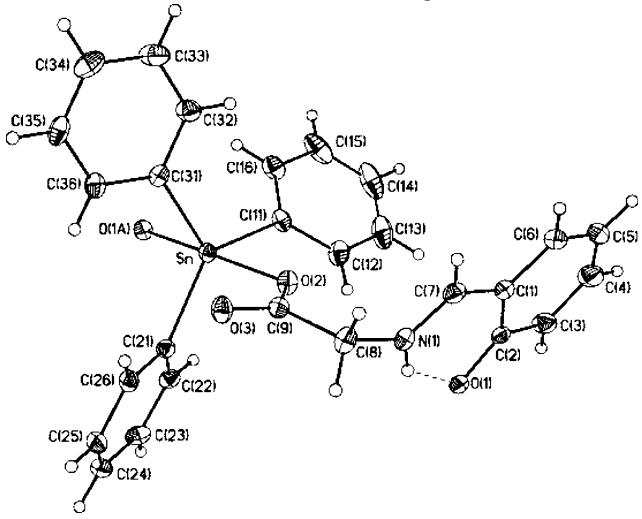


Fig. 2. Molecular structure and crystallographic numbering scheme for **2**.

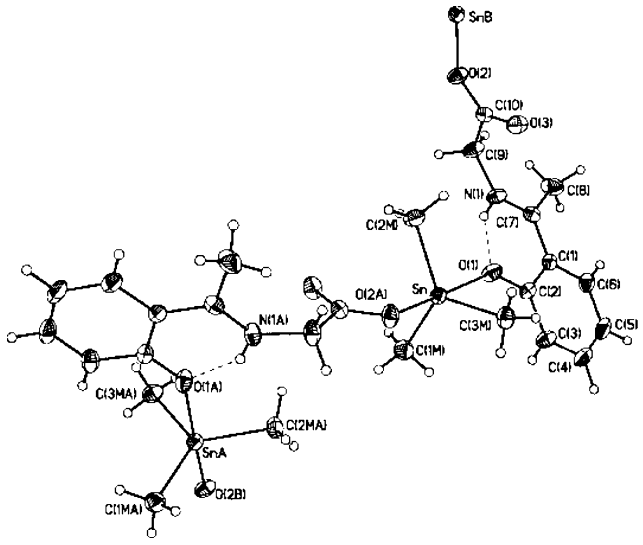


Fig. 3. Molecular structure and crystallographic numbering scheme

Table 7
Selected bond lengths (Å) and angles (°) for the organotin complex **2**

Bond lengths			
Sn–C(31)	2.125(4)	C(11)–Sn–O(1A)	83.41(12)
Sn–C(21)	2.128(4)	O(2)–Sn–O(1A)	167.59(9)
Sn–C(11)	2.133(4)	C(2)–O(1)–Sn(2)	124.0(2)
Sn–O(2)	2.164(2)	C(9)–O(2)–Sn	124.0(2)
Sn–O(1A)	2.357(2)	C(7)–N(1)–C(8)	124.1(4)
O(1)–C(2)	1.311(4)	C(6)–C(1)–C(7)	119.0(4)
O(1)–Sn(2)	2.357(2)	C(2)–C(1)–C(7)	120.9(3)
O(2)–C(9)	1.282(4)	O(1)–C(2)–C(3)	122.8(4)
O(3)–C(9)	1.225(4)	O(1)–C(2)–C(1)	121.0(3)
N(1)–C(7)	1.295(5)	N(1)–C(7)–C(1)	124.0(4)
N(1)–C(8)	1.453(5)	N(1)–C(8)–C(9)	113.3(3)
C(1)–C(7)	1.431(6)	O(3)–C(9)–O(2)	126.4(4)
C(8)–C(9)	1.51(6)	O(3)–C(9)–C(8)	118.1(3)
Bond angles			
C(31)–Sn–C(21)	119.71(14)	O(2)–C(9)–C(8)	115.4(3)
C(31)–Sn–C(11)	115.45(15)	C(16)–C(11)–Sn	121.3(3)
C(21)–Sn–C(11)	123.96(14)	C(12)–C(11)–Sn	120.9(3)
C(31)–Sn–O(2)	99.32(12)	C(26)–C(21)–Sn	123.2(3)
C(21)–Sn–O(2)	93.64(12)	C(22)–C(21)–Sn	118.8(3)
C(11)–Sn–O(2)	86.64(12)	C(36)–C(31)–Sn	121.9(3)
C(31)–Sn–O(1A)	91.66(11)	C(32)–C(31)–Sn	120.3(3)
C(21)–Sn–O(1A)	85.83(11)		

Symmetry transformations used to generate equivalent atoms: #1 $-x+3/2$, $y-1/2$, $-z+1/2$; #2 $-x+3/2$, $y+1/2$, $-z+1/2$.

coordination around the tin atom for the complexes **2** and **4** are illustrated in Figs. 2 and 3, respectively. Selected bond lengths and bond angles are listed in Table 7 (for **2**) and Table 8 (for **4**).

Both compounds exhibit the same polymeric structural motif, namely one in which the tin is five-coordinate with the three R groups occupying the equatorial positions and the axial positions of the trigonal bipyramid being occupied by a carboxylate oxygen, O(2), and the phenolic oxygen, O(1), of an

Table 8
Selected bond lengths (Å) and angles (°) for the organotin complex **4**

Bond lengths			
Sn–C(2M)	2.117(4)	C(2M)–Sn–O(1)	83.05(12)
Sn–C(3M)	2.120(3)	C(3M)–Sn–O(1)	89.74(12)
Sn–C(1M)	2.127(4)	C(1M)–Sn–O(1)	89.63(14)
Sn–O(2)#1	2.185(2)	O(2)#1–Sn–O(1)	174.76(9)
Sn–O(1)	2.353(2)	C(2)–O(1)–Sn	139.83(19)
O(1)–C(2)	1.304(4)	C(10)–O(2)–Sn#2	123.92(18)
O(2)–C(10)	1.275(4)	C(7)–N(1)–C(9)	129.4(3)
O(2)–Sn#2	2.185(2)	C(6)–C(1)–C(2)	118.4(3)
O(3)–C(10)	1.213(3)	C(6)–C(1)–C(7)	120.3(3)
N(1)–C(7)	1.292(4)	C(2)–C(1)–C(7)	121.3(3)
N(1)–C(9)	1.447(4)	O(1)–C(2)–C(3)	121.8(3)
C(1)–C(7)	1.450(4)	O(1)–C(2)–C(1)	120.6(3)
C(7)–C(8)	1.508(5)	N(1)–C(7)–C(1)	118.1(3)
C(9)–C(10)	1.525(4)	N(1)–C(7)–C(8)	119.6(3)
Bond angles			
C(2M)–Sn–C(3M)	120.91(17)	C(1)–C(7)–C(8)	122.2(3)
C(2M)–Sn–C(1M)	118.65(17)	N(1)–C(9)–C(10)	111.9(2)
C(3M)–Sn–C(1M)	119.85(16)	O(3)–C(10)–O(2)	127.7(3)
C(2M)–Sn–O(2)#1	96.16(13)	O(3)–C(10)–C(9)	120.0(3)
C(3M)–Sn–O(2)#1	86.22(12)	O(2)–C(10)–C(9)	112.3(2)
C(1M)–Sn–O(2)#1	95.28(13)		

Symmetry transformations used to generate equivalent atoms: #1 $-x+2$, $y-1/2$, $-z+1/2$; #2 $-x+2$, $y+1/2$, $-z+1/2$.

adjacent molecule. The ligand is coordinating in the form of a zwitterion and the carboxylate group is monodentate. The sum of the carbon–tin–carbon angles in the trigonal plane of complex **2** is 359.21(14)° while the sum of the corresponding angles for **4** is 359.41(17)°. These carbon–tin–carbon angles are comparable to those observed in triphenyltin *N*-salicylidene-6-aminohexanoate [26] and some other similar complexes [27]. The apical angle subtended at tin in **2** and **4** are 167.59(9) and 174.76(9)°, respectively. The short tin–oxygen distances are Sn–O(carboxylate) = 2.164(2) Å [for **2**] and 2.185(2) Å [for **4**] and Sn–O(phenolic) = 2.357(2) [for **2**] and 2.353(2) Å [for **4**]. The former values are well within the range of Sn–O bond distances usually observed for triorganotin carboxylates [4]. It is interesting to compare the phenolic oxygen–tin distances of 2.357(2) Å [for **2**] and 2.353(2) Å [for **4**], observed here, with that of 3.04 Å for triphenyltin salicylate [28], which corresponds to a much weaker interaction, and the very similar value of 2.35 Å reported for triphenyltin *N*-salicylidene-6-aminohexanoate [26]. The short C=O distances of 1.225(4) [for **2**] and 1.213(3) Å [for **4**] indicate that the free carbonyl group on the ligand is not involved in coordination with another tin atom. Similar C=O bond lengths have also been reported for corresponding non-bridging carbonyl groups in the compounds $Ph_3SnOCOCH_2CH_2NHCONH_2$ (1.224(4) Å [29], and $Ph_3SnOCOCMe{=}CHCON(CH_2)_4$ (1.222(5) Å) [30]. Proton transfer from oxygen to nitrogen atoms via hydrogen bonding, and the formation of zwitterion intermediates in similar

molecules to those discussed here, is quite commonly encountered [22,31,32]. Thus, the labile phenolic oxygen is rendered susceptible to coordination with the tin atom. This makes possible the formation of a series of Sn–O(phenolic) bridges leading to the zigzag polymeric structure of complexes **2** and **4** shown in Figs. 2 and 3.

Similarities in the spectroscopic data suggest that the other triorganotin(IV) complexes reported here adopt similar structures in the solid state.

4. Conclusion

Triorganotin carboxylates assume one of several structural motifs [9], ranging from monomeric four- or five-coordinate species to five-coordinate polymers which usually involve bidentate carboxylate groups. The compounds which form the subject of this study, however, have ligands with phenolic groups in close proximity to nitrogen atoms. The resultant zwitterionic forms of the ligands coordinate through monodentate carboxylate groups and the phenolic oxygen. This series of compounds all exhibit the same polymeric *trans*-O_2SnC_3 trigonal bipyramidal structural motif, namely one with the three R groups occupying the equatorial positions and the axial positions being occupied by a carboxylate oxygen and the phenolic oxygen of an adjacent molecule.

The biological activity of these compounds is currently being investigated.

5. Supplementary data

Full tables of bond lengths and angles, tables of non-hydrogen and hydrogen atomic coordinates, anisotropic thermal parameters for non-hydrogen atoms are available upon quoting the CCDC deposition numbers 161785 and 161784 for **2** and **4**, respectively. Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

The financial support of the Department of Science and Technology, New Delhi, India (Grant No. SP/S1/F26/98, TSBB) and the support of the MURST, Italy (60%, ER) are gratefully acknowledged

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