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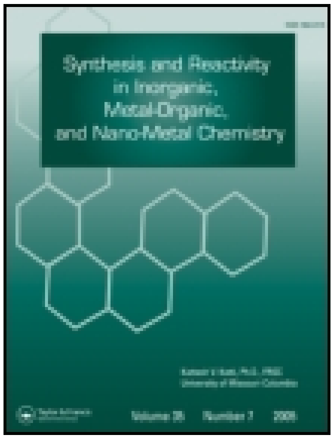

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SYNTHESIS AND SPECTRAL STUDIES OF TRI- AND DIORGANOTIN(IV) COMPLEXES WITH 5-BENZOYL-α-METHYL-2-THIOPHENEACETIC ACID: CRYSTAL STRUCTURE OF [$(CH_3)_3Sn(C_{14}H_{11}O_3S)$]

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SYNTHESIS AND SPECTRAL STUDIES OF TRI- AND DIORGANOTIN(IV) COMPLEXES WITH 5-BENZOYL-α-METHYL-2-THIOPHENEACETIC ACID: CRYSTAL STRUCTURE OF $[(CH_3)_3Sn(C_{14}H_{11}O_3S)]$

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ABSTRACT

A series of tri- and diorganotin(IV) complexes of the general formula $R_{4-n}SnL_n$ (where $R = CH_3$, C_4H_9, C_6H_6, C_7H_7, $n = 1, 2$ and HL = 5-benzoyl-α-methyl-2-thiopheneacetic acid) have been sythesized by the reaction of tri- and diorganotin-

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(IV) chloride(s) with the silver salt of the ligand in $CHCl_3$ solution. All of the compounds have been characterized by IR, conductance measurement, multinuclear (^1H, ^{13}C, ^{119}Sn) NMR, UV-Vis and mass spectrometery. An X-ray crystal structure of the representative compound $(CH_3)_3SnL$ confirms a trigonal bipyramid around the tin atom, having the space group $P2_{1/a}$ with a monoclinic crystal system.

INTRODUCTION

Organotin(IV) compounds are well-known by their applications in the chemical industry, agriculture and other fields of human activities.[1–3] Recent studies have shown that organotin(IV) derivatives may exhibit antitumour activities.[4,5] The biocidal activity of organotin compounds is believed to be greatly dependent on the structure of the molecule and the coordination number of the tin atom.[6–8] Organotin(IV) derivatives with monodentate organic ligands show different behaviour in the solutions of different solvents and in the solid state. It has been observed that triorganotin(IV) carboxylates and diorganotin(IV) dicarboxylates form monomeric chelate complexes with an intermediate state between monodentate and bidentate, called anisobidentate, carboxylic groups in noncoordinating solvents. Most of the triorganotin(IV) carboxylates are of polymeric nature in the solid state. Previously, we have synthesized and characterized various organotin(IV) derivatives of donor ligands. We have also reported their structural chemistry as well as some of their biological applications. In this paper we report the synthesis, spectroscopic characterization and crystal structure of the triorganotin(IV) derivative of 5-benzoyl-α-methyl-2-thiopheneacetic acid commonly known as surgam (Fig. 1), one of the most frequently used analgesic, antipyretic and anti-inflammatory drugs.

RESULTS AND DISCUSSION

A series of tri- and diorganotin(IV) carboxylates have been prepared as shown by the following Eqs. (1) and (2)

$$R_3SnCl + AgL \longrightarrow R_3SnL + AgCl \tag{1}$$

$$R_2SnCl_2 + 2AgL \longrightarrow R_2SnL_2 + 2AgCl \tag{2}$$

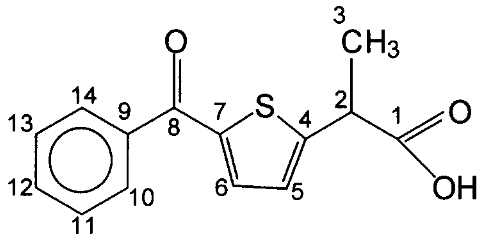


Figure 1. Numbering scheme and structure of 5-Benzoyl-α-methyl-2-thiophene-acetic acid (surgam).

The complexes are quite stable in air, and are white, crystalline solids which are mostly soluble in common organic solvents. The complexes are sufficiently soluble in absolute ethanol to enable their molar conductance to be measured. The molar conductances of 10^{-3} M solutions of the complexes (Table I) in absolute ethanol lie in the range of 4–15 $\mu S/cm^2$ indicating their non-electrolytic nature.[9]

Electronic Spectra

The spectra of the ligand and its complexes were recorded in absolute ethanol. The various bands observed were assigned to interligand and charge transfer or $n \rightarrow \pi^*$ transitions according to their energies and intensities.

The spectra of the complexes exhibit bands in the range of 198–250 nm, which may be due to the $\pi \rightarrow \pi^*$ inter-ligand transitions of the aromatic moiety of the ligand.[10] Furthermore, there is a sharp band observed in the 253–270 nm region in the spectra of the complexes, which could be assigned as a charge-transfer band. It is known[11] that metal/metalloids are capable of forming dπ-pπ bonds with ligands containing nitrogen or oxygen as donor atoms. The tin atom has vacant 5d orbitals and hence L → M bonding can take place by acceptance of a pair of electrons from an oxygen donor atom of the ligand.

Infrared Spectroscopy

Infrared spectra were recorded in the range of 4000–250 cm^{-1} as KBr/CsBr pellets and the important bands for structural assignments are summarized in Table II.

Table I. Conductance Measurement[a] and Physical Data of Organotin(IV)-Surgam Complexes

Comp. No.	Compounds	Empirical Formula (Formula wt.)	Yield (%)	M. p. (°C)	%C Calc. (Found)	%H Calc. (Found)	Conductance μS/cm^2
(1)	Bu_2SnL_2	$C_{36}H_{40}O_6S_2Sn$ (752)	82.8	65–67	57.45 (57.41)	5.32 (5.32)	23.25
(2)	Bu_3SnL	$C_{26}H_{38}O_3SSn$ (550)	77.75	53–55	56.73 (56.67)	6.91 (6.85)	9.75
(3)	Me_2SnL_2	$C_{30}H_{28}O_6S_2Sn$ (668)	68.0	b	53.89 (53.70)	4.19 (4.25)	8.25
(4)	Me_3SnL	$C_{17}H_{20}O_3SSn$ (424)	79.0	115–17	48.11 (47.95)	4.72 (4.65)	14.75
(5)	Ph_2SnL_2	$C_{40}H_{32}O_6S_2Sn$ (792)	45.3	65–70	60.60 (60.35)	4.04 (3.95)	13.25
(6)	Ph_3SnL	$C_{32}H_{25}O_3SSn$ (610)	72.9	70–80	62.95 (63.10)	4.26 (4.35)	12.25
(7)	Bz_2SnL_2	$C_{42}H_{36}O_6S_2Sn$ (820)	56.8	112–14	61.46 (61.70)	4.39 (4.14)	4.25
(8)	Bz_3SnL	$C_{35}H_{32}O_3SSn$ (652)	50.3	b	64.42 (64.30)	4.91 (4.77)	3.95
HL	Ligand	$C_{14}H_{13}O_3$ (260)	–	96–7	–	–	–

[a] In absolute ethanol at 27 °C.
[b] Semi solid.

Table II. Infrared Data (cm^{-1}) of Organotin(IV) Derivatives of 5-Benzoyl-α-methyl-2-thiopheneacetic Acid

		ν(COO)				
S. No.	Compounds	asym	sym	Δν	ν(Sn-C)	ν(Sn-O)
(1)	Bu_2SnL_2	1628 vs	1378 s	250	533 ms	452 m
(2)	Bu_3SnL	1635 vs	1361 s	274	518 s	466 w
(3)	Me_2SnL_2	1630 s	1381 m	249	516 vs	450 w
(4)	Me_3SnL	1630 m	1358 s	272	555 vs	477 s
(5)	Ph_2SnL_2	1633 w	1350 w	283	540 m	450 s
(6)	Ph_3SnL	1632 s	1361 s	271	533 w	454 vs
(7)	Bz_2SnL_2	1627 s	1394 s	233	544 m	456 m
(8)	Bz_3SnL	1633 w	1350 m	283	550 w	453 s
(9)	Ligand	1731 vs	1392 s	339	–	–
(10)	Ligand-Ag	1627 s	1362 s	265	–	–

Characteristic vibrational frequencies have been identified by comparing the spectra of the organotin derivatives with their precursors and with various reported analogous compounds.[12,13] The absorptions of interest in the spectra of the complexes are ν(COO), ν(Sn-C), ν(Sn-O) and ν(Sn-Cl). The absence of a broad band with several maxima in the range of 2900–2500 cm^{-1} and the presence of ν(Sn-O) in the 500–400 cm^{-1} range indicates the deprotonation of -COOH and formation of a new Sn-O bond.

The infrared studies indicated that the ν(CO) absorption of benzoyl in all the complexes either remains at the same position or shifts slightly to higher frequency compared to the free acid. The carboxylates generally have two strongly coupled C=O bonds with bond strengths intermediate between C=O and C-O. These give a strong asymmetric stretching band near 1650–1550 cm^{-1} and a weaker symmetrical stretching band near 1400 cm^{-1}. If the magnitude of the separation Δν, $[\Delta\nu = \nu(COO)_{asym} - \nu(COO)_{sym}]$ is comparable to that of the silver salt of the acid, the bidentate nature of the carboxylate group is confirmed. In most of the complexes the Δν values are higher than that of the silver salt, the presence of bidentate carboxylates is not supported. However, a weak intermolecular interaction of the -COO group in the solid state in some cases may be present. In all of the complexes bands in the region 445–400 cm^{-1} are assigned to Sn-O.[14–18] Complexation of tin(IV) with the ligand is further confirmed by the absence of a Sn-Cl vibration at 333 cm^{-1}.

^{1}H NMR Spectroscopy

The ^{1}H NMR spectral data (Tables III and IV) further support the composition of the new complexes suggested by IR, UV-Vis and conductance measurements. ^{1}H NMR spectra were recorded for the free ligand and the complexes in $CDCl_3$ and in all the cases the signals of all the protons have been identified.

The ^{1}H NMR spectrum of the ligand exhibits a quartet at 4.12 ppm for the CH proton and a doublet at 1.64 ppm for the $-CH_3$ protons attached to the -CH carbon of the acetate moiety. Similarly, all the other signals in the pure ligand were observed in the organotin complexes with slight shifts. Signals for the aromatic protons of the ligand and the phenyltin moiety appear as multiplets in the range of 7.29–7.73 ppm.

In the tri- and dibenzyltin derivatives methylene protons are observed as singlets with tin satellites [3.02 ppm, $^2J(^{119}\text{Sn-}^1\text{H}) = 82.94$ Hz, 2.91 ppm, $^2J(^{119}\text{Sn-}^1\text{H}) = 70.80$ Hz, respectively]. These values are comparable with the values of tri- and dimethyltin chlorides confirming the tetrahedral environment around tin.[19] The C-Sn-C angle (Table V), calculated by Lockhart's equation,[20] also supports the assignment of tetrahedral geometery.

The butyl groups are observed as poorly resolved multiplets. No evidence was found for the coordination of the sulfur atom present in the ligand with the tin.

^{13}C NMR Spectroscopy

^{13}C NMR data of the investigated compounds are given in Tables VI and VII. Resonances in the butyl, methyl and benzyltin derivatives are well resolved due to the presence of all unique carbon atoms. ^{13}C spectra of the phenyl derivatives were much more complicated. However, in all of these cases, some signals are of sufficient intensity to suggest overlap.

The coupling constant values $^1J(^{119}\text{Sn-}^{13}\text{C})$ in the range of 353.0–395.0 Hz correspond to the magnitude of the bond angles C-Sn-C of about 108–111° (Table V).[21] These data suggest that in these compounds the carboxylic groups are bound to the tin atom either monodentately or anisobidentately (intermediate between mono- and bidentate) with a slight participation of bonding interaction between the tin atoms and carbonyl group oxygen atoms or as bridging. Hence, when dissolved in non-coordinating solvents, compounds **(2)**, **(4)** and **(6)** are present either as monomeric pseudo-tetrahedral molecules (Fig. 2a) or as strongly deformed *cis*-trigonal-bipyramidal molecular complexes with an anisobidentate chelate carboxylic group (Fig. 2b) or as *trans* polymeric form (Fig. 2c).

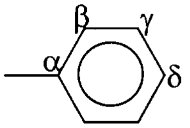
Table III. ^{1}H NMR Data[a,b,c,d] (δ, ppm) of Triorganotin(IV) 5-Benzoyl-α-methyl-2-thiophene Acetates

Compound H-No.	**(2)** Bu_3SnL	**(4)** Me_3SnL	**(6)** Ph_3SnL	**(8)** Bz_3SnL
2	4.01 [1H, q ($^{3}J = 7.22$)]	4.03 [1H, q ($^{3}J = 7.14$)]	3.81 [1H, q ($^{3}J = 7.13$)]	3.68 [1H, q ($^{3}J = 9.13$)]
3	1.59 [3H, d ($^{3}J = 7.22$)]	1.57 [3H, d ($^{3}J = 7.13$)]	1.41 [3H, d ($^{3}J = 7.11$)]	1.38 [3H, d ($^{3}J = 9.19$)]
5	6.98 [1H, d ($^{3}J = 3.86$)]	6.97 [1H, d ($^{3}J = 3.87$)]	6.88 [1H, d ($^{3}J = 3.75$)]	6.98 [1H, d ($^{3}J = 3.03$)]
6	7.46 [1H, d ($^{3}J = 3.9$)]	7.45 [1H, d ($^{3}J = 3.78$)]	7.45 [1H, d ($^{3}J = 3.35$)]	7.44 [1H, d ($^{3}J = 2.72$)]
10,14	7.80 [2H, dd ($^{3}J = 8.25$, $^{3}J = 1.68$)]	7.82 [2H, dd ($^{3}J = 8.27$, $^{3}J = 1.30$)]	7.79 [2H, dd ($^{3}J = 7.11$, $^{3}J = 1.42$)]	7.78 [2H, dd ($^{3}J = 6.59$, $^{3}J = 1.5$)]
11,12, 13	7.42–7.52 [3H, m]	7.44–7.54 [3H, m]	7.43–7.54 [3H, m]	7.38–7.51 [3H, m]
α	0.91 [6H, m]	0.55 [9H, s] $^{2}J[(^{117}Sn\text{-}^{1}H) = 56.02]$ $^{2}J[(^{119}Sn\text{-}^{1}H) = 58.39]$	7.32–7.52 [15H, m]	2.91 [6H, s]
β	1.21–1.34 [6H, m]			7.29–7.48 [15H, m]
γ	1.50–1.56 [6H, m]			
δ	0.85 [9H, t J = 7.2]			

[a]Chemical shift (δ) in ppm, $^{3}J(^{1}H\text{-}^{1}H)$ in Hz, $^{2}J[^{119/117}Sn\text{-}^{1}H]$ in Hz in parenthesis, Multiplicity is given by: s, singlet; d, doublet; t, triplet; q, quartet and m, multiplet.

[b]Numbering is according to Fig. 1.

[c]



$\overset{\alpha}{C}H_2\overset{\beta}{C}H_2\overset{\gamma}{C}H_2\overset{\delta}{C}H_3$

$\overset{\alpha}{C}H_2\overset{\beta}{C}H_3$

$\overset{\alpha}{C}H_3$

[d]In case of benzyl (Bz) CH_2 is α.

Table IV. ^{1}H NMR Data[a,b,c,d] (δ, ppm) of Diorganotin(IV) 5-Benzoyl-α-methyl-2-thiophene Acetate

Compound H-No.	**(HL)** Surgam	**(1)** Bu_2SnL_2	**(3)** Me_2SnL_2	**(5)** Ph_2SnL_2	**(7)** Bz_2SnL_2
2	4.05 [2H, q (^{3}J = 7.14)]	4.12 [2H, q (^{3}J = 7.1)]	3.90 [2H, q (^{3}J = 6.98)]	4.40 [2H, q (^{3}J = 6.91)]	3.81 [2H, q (^{3}J = 6.9)]
3	1.64 [6H, d (^{3}J = 7.14)]	1.64 [6H, d (^{3}J = 7.17)]	1.48 [6H, d (^{3}J = 6.91)]	1.61 [6H, d (^{3}J = 7.08)]	1.40 [6H, d (^{3}J = 7.1)]
5	7.05 [2H, d (^{3}J = 3.84)]	7.20 [2H, d (^{3}J = 3.88)]	6.86 [2H, d (^{3}J = 3.73)]	7.02 [2H, d (^{3}J = 3.87)]	6.88 [2H, d (^{3}J = 3.75)]
6	7.46 [2H, d (^{3}J = 3.10)]	7.47 [2H, d (^{3}J = 3.45)]	7.32 [2H, d (^{3}J = 3.96)]	7.47 [2H, d (^{3}J = 3.62)]	7.46 [2H, d (^{3}J = 3.40)]
10,14	7.81 [2H, d (^{3}J = 7.84)]	7.79 [4H, d (^{3}J = 7.84)]	7.67 [4H, d (^{3}J = 6.9)]	7.79 [4H, d (^{3}J = 7.75)]	7.78 [4H, d (^{3}J = 7.1)]
11,13	7.48 [4H, m]	7.43 [4H, m]	7.39 [4H, m]	7.42 [4H, m]	7.43 [4H, m]
12	7.54 [2H, m]	7.54 [2H, m]	7.64 [2H, m]	7.55 [2H, m]	7.54 [2H,m]
α	–	0.86–0.92 [4H, m]	0.83 6H, s ^{2}J[(^{117}Sn-^{1}H) = 78.67] ^{2}J[(^{119}Sn-^{1}H) = 81.35]	7.68–7.73 [10H, m]	3.02 4H, s ^{2}J[(^{117}Sn-^{1}H) = 70.80] ^{2}J[(^{119}Sn-^{1}H) = 82.94]
β	–	1.25–1.45 [4H, m]	–	–	7.35–7.51 [10H, m]
γ	–	1.72 [4H, m]	–	–	–
δ	–	0.86–0.92 [4H, m]	–	–	–

[a] Chemical shift (δ) in ppm, ^{3}J(^{1}H-^{1}H) in Hz, ^{2}J[$^{119/117}$Sn-^{1}H] in Hz in parenthesis, Multiplicity is given by: s, singlet; d, doublet; t, triplet; and m, multiplet.

[b] Numbering is according to Fig. 1.

[c] See footnotes of Table III for α, β, γ, δ.

[d] In case of benzyl (Bz) CH_2 is α.

Table V. (C-Sn-C) Angles (°) Based on NMR Parameters

Compound No.	Compounds	[$^1J(^{119}Sn-^{13}C)$] (Hz)	[$^2J(^{119}Sn-^1H)$] (Hz)	Angles (°)	
				^1J	^2J
(2)	Bu_3SnL	353.04	25.67	107.72	108.82
(3)	Me_2SnL_2	544.53	78.67	124.50	124.52
(4)	Me_3SnL	395.00	58.39	111.40	111.54
(7)	Bz_2SnL_2	565.16	70.82	126.30	126.33

The $\delta(^{13}C)$ chemical shift values of carboxylic groups in these compounds (Table VI) are practically identical with or even higher than the same shift values for the carboxylate anion. These shifts suggest a coordination number of six. This geometry is further supported by the magnitudes of

Table VI. ^{13}C NMR Data[a,b] (δ, ppm) of Diorganotin(IV) Derivatives of 5-Benzoyl-α-methyl-2-thiopheneacetic Acid

Compound ^{13}C No.	**HL** Surgam	**(1)** Bu_2SnL_2	**(3)** Me_2SnL_2	**(5)** Ph_2SnL_2	**(7)** Bz_2SnL_2
1	178.528	–	181.75	177.811	181.73
2	41.392	41.578	41.61	41.645	41.52
3	18.972	19.867	19.658	19.0746	19.4028
4	137.87	142.630	152.75	151.852	152.66
5	126.42	126.406	132.171	132.259	132.135
6	134.925	135.017	134.917	134.964	134.769
7	151.58	138.262	142.290	142.404	142.199
8	188.129	188.157	188.033	188.069	187.933
9	124.44	138.262	137.950	137.988	137.990
10	129.123	129.298	129.072	129.106	129.026
11	128.423	128.633	128.372	128.428	128.520
12	132.27	132.406	126.050	126.392	125.762
13	128.423	128.633	128.372	128.428	128.374
14	129.123	129.298	129.072	129.106	128.967
CH_2[a]	–	–	–	–	32.16
α	–	26.476	4.63	137.897	128.594
β	–	29.914	–	134.259	128.520
γ	–	26.805	–	133.007	128.374
δ	–	13.715	–	131.747	126.224

[a] CH_2 of benzyl group, chemical shifts (δ) in ppm.

[b] See footnotes of Table III for α, β, γ, δ.

Table VII. ^{13}C NMR Data[a,b] (δ, ppm) of Triorganotin(IV) Complexes with 5-Benzoyl-α-methyl-2-thiopheneacetic Acid

Compound ^{13}C No.	**(2)** Bu_3SnL	**(4)** Me_3SnL	**(6)** Ph_3SnL	**(8)** Bz_3SnL
1	177.365	177.546	178.335	180.087
2	42.650	42.460	42.602	43.633
3	19.929	20.028	19.955	19.544
4	155.087	154.835	154.023	153.484
5	131.960	132.016	132.046	132.951
6	134.830	134.944	134.754	134.748
7	141.650	141.793	141.846	142.006
8	188.074	188.153	188.019	188.125
9	138.650	138.190	137.711	137.958
10	129.036	129.077	129.161	129.726
11	128.305	128.321	128.428	128.929
12	125.536	125.564	126.392	126.950
13	128.305	128.321	128.428	128.501
14	129.036	129.077	129.106	129.296
CH_2[a]	–	–	–	34.538
α	26.513	−2.335	137.897	129.014
β	29.667	–	134.259	129.395
γ	27.811	–	133.007	127.598
δ	13.621	–	131.747	124.850

[a] CH_2 of benzyl group, chemical shifts (δ) in ppm.

[b] See footnotes of Table III for α, β, γ, δ.

bond angles of about 124–127° as calculated[21] from the coupling constants $^1J(^{119}Sn\text{-}^{13}C)$ (545–565 Hz) (Table V). Accordingly the compounds **(2)**, **(4)**, **(6)** and **(8)** are present in non-coordinating solvents as monomeric species.

^{119}Sn NMR Spectroscopy

The ^{119}Sn chemical shifts increase as the coordination number of the tin atom increases from four to five to six and seven and usually produces a large upfield shift of $\delta(^{119}Sn)$. The chemical shift values $\delta(^{119}Sn)$ of compounds **(2)**, **(4)** and **(6)** in $CDCl_3$ are 123.7, −177.34 and −99.29 ppm (Table VIII) and are typical of tris(1-butyl), methyl and phenyltin(IV) compounds with a coordination number of four of the central tin atom.[22]

In $CDCl_3$, compounds **(1)**, **(3)**, **(5)** and **(7)** (Table VIII) exhibit chemical shifts $\delta(^{119}Sn)$ at −136.35, 180.26, 225.26 and −238.32 ppm, respectively.

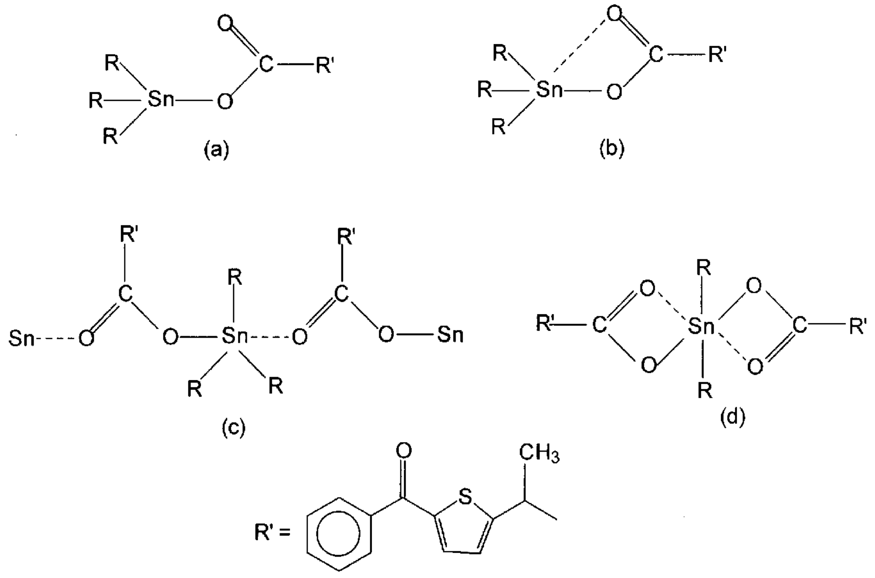


Figure 2. Proposed geometries of the organotin(IV) carboxylates.

This region is characteristic of diorganotin(IV) compounds with the coordination number around the tin atom equal to five (trigonal-bipyramidal) or four plus two (deformed octahedron, or a trapezoidal bipyramid with four strong and two somewhat weaker bonds)[23] around the tin atom (Fig. 2d). Multinuclear NMR spectroscopy of the diorganotin dicarbox-

Table VIII. ^{119}Sn NMR Data (δ, ppm) of Organotin(IV) Derivatives of 5-Benzoyl-α-methyl-2-thiopheneacetic Acid

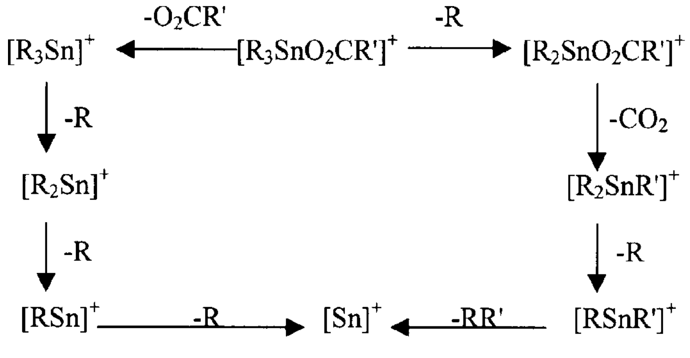
Compound No.	Compound	^{119}Sn NMR
(1)	Bu_2SnL_2	−136.35
(2)	Bu_3SnL	123.723
(3)	Me_2SnL_2	180.265
(4)	Me_3SnL	−177.337
(5)	Ph_2SnL_2	−225.263
(6)	Ph_3SnL	−99.292
(7)	Bz_2SnL_2	−238.32
(8)	Bz_3SnL	38.65
(HL)	Ligand	–

ylates suggests a coordination number of tin greater than five due to the increased polarizability of the phenyl groups. The increased shielding of the tin atom and shifting of δ(^{119}Sn) values to higher field support this suggestion.[24]

Mass Spectrometry

The fragmentation patterns of tri- and diorganotin(IV) carboxylates of 5-benzoyl-α-methyl-2-thiopheneacetic acid are described in Figs. 3 and 4. The resulting fragmentation data are recorded in Tables IX and X. The molecular ion peak in almost all of the derivatives is not observed. In the triorganotin(IV) derivatives the major fragmentation observed is due to the loss of the ligand moiety from the tin derivatives. Successive fragmentation is observed by the loss of R groups (Me, Bu, Ph, Bz) until the Sn^+ ion is obtained. In an alternative route, R groups are eliminated first and in the next step one molecule of CO_2 is evolved from the ligand moiety attached to the tin atom. In the successive steps the remaining substituents are evolved from the tin atom.

In the diorganotin derivatives fragmentation takes place according to the schemes in Figs. 3 and 4. The main fragmentation observed is due to the loss of a ligand molecule followed by the loss of CO_2 from the second ligand. The successive loss of R groups and the loss of the remaining part of the ligand proceed until Sn^+ is obtained. An alternative route suggests that a



R = *n*-Bu, Me, Ph and Bz

Figure 3. Fragmentation pattern of triorganotin(IV) carboxylate.

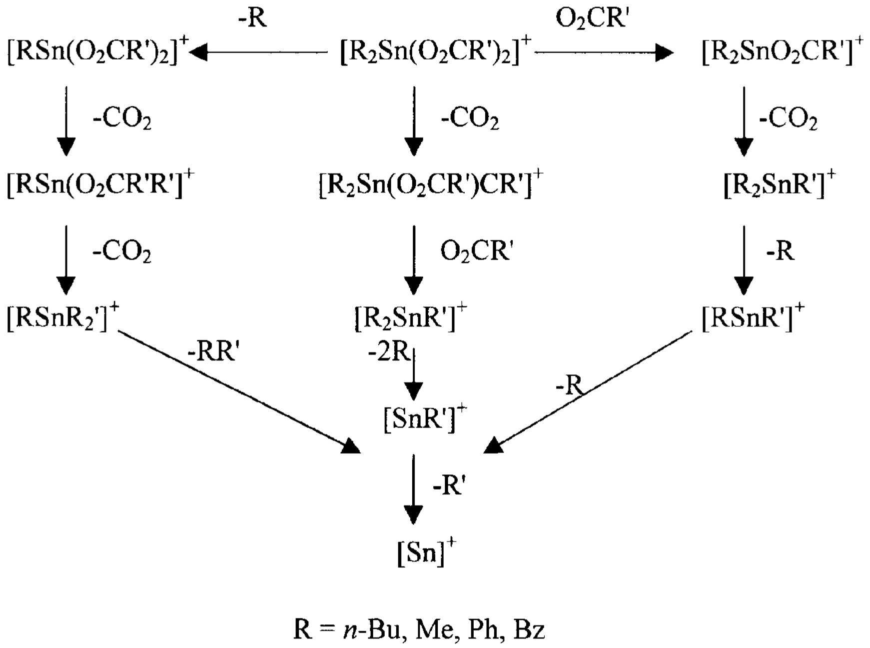


Figure 4. Fragmentation pattern of diorganotin(IV) dicarboxylates.

loss of an R group occurs first followed by the successive loss of two CO_2 molecules and then the remaining groups. The third route proposed is the loss of a CO_2 molecule followed by the elimination of one ligand and then by the loss of the R groups.

Single Crystal X-Ray Analysis

The immediate environment around the Sn atom in $(CH_3)_3SnL$ is shown in Fig. 5 and selected interatomic parameters are listed in Table XI. The coordination around the tin atom is distorted trigonal bipyramidal, with the three methyl carbon atoms forming a trigonal plane and the two carboxylate oxygen atoms are at the axial positions.

The Sn-C bond lengths [2.096(11), 2.104(11) and 2.135(10) Å] in the equatorial plane are equal within the experimental error (Table XI), but Sn-O1 [2.195(7) Å] and Sn-O2 [2.456(7) Å] bond distances in the *trans* coordination are very different. Within the carboxylate groups, somewhat unequal C-O bond lengths are also observed [C4-O1, 1.287(12) and C4-O2,

Table IX. Mass Spectral Data (m/z) of Triorganotin(IV) 5-Benzoyl-α-methyl-2-thiophene Acetates

Mass Fragment	Bu **(2)**	Inte. (%)	Me **(4)**	Inte. (%)	Ph **(6)**	Inte. (%)	Bz **(8)**	Inte. (%)
$[R_3SnC_{14}H_{11}SO_3]^+$	550	2	424	–	610	–	652	–
$[R_2SnC_{14}H_{11}SO_3]^+$	493	78	409	15	533	5	561	4
$[R_2SnC_{13}H_{11}SO]^+$	449	17	365	18	489	2	517	1
$[RSnC_{13}H_{11}SO]^+$	392	2	350	8	412	2	426	2
$[RSn]^+$	177	58	135	22	197	50	211	5
$[R]^+$	57	75	15	–	77	35	91	100
$[C_{14}H_{11}SO_3]^+$	260	8	260	5	260	1	260	1
$[R_3Sn]^+$	291	30	165	82	351	100	393	5
$[R_2Sn]^+$	234	28	150	100	274	28	302	100
$[S/SnH]^+$	120	22	120	20	120	10	120	2
$[C_{13}H_{11}SO]^+$	215	60	215	40	215	30	215	78

1.223(12) Å]. From these observations one could conclude that the shorter Sn-O distance indicates a covalent bond and the longer Sn-O distance indicates a coordinate covalent bond, as the C4-O2 bond keeps some of its double bond nature. The O1-Sn1-O2 angle is 175.5(3)°. The central

Table X. Mass Spectral Data (m/z) for Diorganotin(IV) Derivatives of 5-Benzoyl-α-methyl-2-thiophene Acetates

Mass Fragment	Bu **(1)**	Int. (%)	Me **(3)**	Int. (%)	Ph **(5)**	Int. (%)	Bz **(7)**	Int. (%)
$[R_2SnC_{28}H_{22}S_2O_6]^+$	752	n.o	668	n.o	792	n.o	820	n.o
$[R_2SnC_{14}H_{11}SO_3]^+$	493	38	409	2	533	2	561	12
$[R_2SnC_{13}H_{11}SO]^+$	449	8	365	2	489	2	517	12
$[RSnC_{13}H_{11}SO]^+$	392	5	350	5	412	1	426	8
$[SnC_{13}H_{11}SO]^+$	335	12	135	2	335	2	335	5
$[C_{13}H_{11}SO]^+$	215	100	215	100	215	100	215	100
$[RSnC_{28}H_{22}S_2O_6]^+$	695	n.o	653	–	715	–	729	–
$[RSnC_{27}H_{22}S_2O_4]^+$	651	–	609	–	671	–	685	5
$[R_2SnC_{26}H_{22}S_2O_2]^+$	607	–	565	2	627	–	641	–
$[SnC_{14}H_{11}SO_3]^+$	379	5	379	5	379	–	379	18
$[C_{14}H_{11}SO_3]^+$	260	81	260	12	260	8	260	2
$[Sn^+/SnH]^+$	120	12	120	5	120	2	120	–
$[R]^+$	57	58	15	–	77	80	91	17
$[R_2SnC_{27}HS_2O_4]^+$	708	10	624	5	748	–	776	–

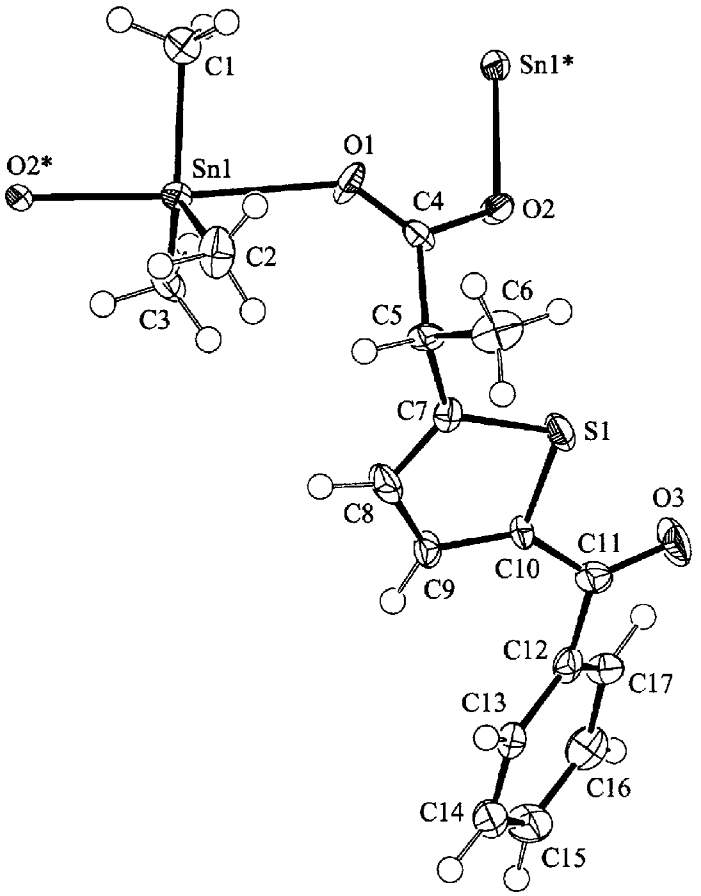


Figure 5. X-ray crystal structure of trimethyltin(IV)-5-benzoyl-α-methyl-2-thiophene acetate.

trimethyltin group bridges two neighbouring 5-benzoyl-α-methyl-2-thiopheneacetic acid ligands *via* carboxylate moieties to form one-dimensional polymeric chains running along the A axis (Fig. 5). Similar polymeric chain structures of triorganotin compounds with carboxylate bridges also have been reported in the literature.[25–29] The 5-benzoyl-α-methyl-2-thiopheneacetic acid (surgam) ligand is not planar. The two rings form an interplanar angle of 40.2(16)°. All the other bond distances and angles within the ligand have their expected values.

Table XI. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for Trimethyltin(IV) 5-Benzoyl-α-methyl-2-thiophene Acetate

Atom	X	Y	Z	B_{eq}
Sn(1)	0.22902 (5)	0.12319(8)	0.05440(5)	1.520(14)
S(1)	0.3872(2)	−0.0962(3)	−0.3243(2)	2.66(7)
O(1)	0.2313(6)	−0.0701(8)	−0.0540(5)	2.28(18)
O(2)	0.2708(6)	−0.2152(7)	−0.1607(5)	2.00(18)
O(3)	0.5507(6)	−0.1831(8)	−0.4248(6)	3.3(2)
C(1)	0.1664(9)	−0.0178(12)	0.1388(9)	2.8(3)
C(2)	0.1159(9)	0.2121(12)	−0.0543(9)	2.7(3)
C(3)	0.3941(8)	0.1343(11)	0.0551(8)	2.1(2)
C(4)	0.2548(8)	−0.0951(10)	−0.1323(8)	1.7(2)
C(5)	0.2514(8)	0.0128(11)	−0.2117(8)	1.6(2)
C(6)	0.1538(9)	−0.0090(13)	−0.2911(9)	2.8(3)
C(7)	0.3504(8)	0.0204(10)	−0.2481(7)	1.5(2)
C(8)	0.4244(9)	0.1192(12)	−0.2292(8)	2.4(3)
C(9)	0.5096(8)	0.1014(11)	−0.2757(7)	1.8(2)
C(10)	0.5022(8)	−0.0103(11)	−0.3310(7)	1.8(2)
C(11)	0.5719(9)	−0.0728(12)	−0.3880(8)	2.2(3)
C(12)	0.6735(8)	−0.0068(11)	−0.3979(7)	1.8(2)
C(13)	0.6847(8)	0.1294(12)	−0.4099(7)	1.7(2)
C(14)	0.7800(10)	0.1846(11)	−0.4191(8)	2.4(3)
C(15)	0.8664(8)	0.1002(13)	−0.4186(9)	2.7(3)
C(16)	0.8544(9)	−0.0377(13)	−0.4070(8)	2.7(3)
C(17)	0.7596(9)	−0.0904(11)	−0.3957(8)	2.2(3)
H(1)	0.1535	0.0244	0.1960	3.4010
H(2)	0.1022	−0.0523	0.1031	3.4010
H(3)	0.2150	−0.00894	0.1555	3.4010
H(4)	0.0960	0.2971	−0.0326	3.2423
H(5)	0.1447	0.2238	−0.1110	3.2423
H(6)	0.0558	0.1554	−0.0683	3.2423
H(7)	0.4266	0.0522	0.0790	2.5259
H(8)	0.4053	0.1491	−0.0088	2.5259
H(9)	0.4237	0.2064	−0.0955	2.5259
H(10)	0.2425	0.0971	−0.1825	1.9537
H(11)	0.0921	−0.0006	−0.2640	3.4100
H(12)	0.1526	0.0566	−0.3404	3.4100
H(13)	0.1563	−0.0964	−0.3179	3.4100
H(14)	0.4185	0.1932	−0.1880	2.8638
H(15)	0.5672	0.1621	−0.2691	2.0984
H(16)	0.6255	0.1866	−0.4118	2.0800
H(17)	0.7870	0.2792	−0.4258	2.9496
H(18)	0.9325	0.1363	−0.4261	3.2620
H(19)	0.9127	−0.0958	−0.4068	3.2095
H(20)	0.7529	−0.1845	−0.3864	2.6219

Table XII. Anisotropic Displacement Parameters for Trimethyltin(IV) 5-Benzoyl-α-methyl-2-thiophene Acetate

Atom	U11	U22	U33	U12	U13	U23
Sn(1)	0.0230(3)	0.0.160(3)	0.0192(4)	−0.0008(4)	0.0052(3)	0.0017(4)
S(1)	0.0422(18)	0.0224(18)	0.0422(19)	0.0145(14)	0.0223(15)	0.0163(14)
O(1)	0.046(5)	0.030(5)	0.011(4)	0.014(4)	0.007(4)	−0.001(4)
O(2)	0.044(5)	0.014(4)	0.022(4)	0.009(4)	0.016(4)	0.004(3)
O(3)	0.043(5)	0.026(5)	0.064(7)	−0.008(4)	0.026(5)	−0.025(5)
C(1)	0.044(8)	0.034(8)	0.033(7)	−0.013(6)	0.013(6)	−0.006(6)
C(2)	0.040(7)	0.028(7)	0.030(7)	0.016(6)	−0.004(6)	−0.003(6)
C(3)	0.029(6)	0.020(6)	0.028(6)	-0.009(6)	-0.001(5)	-0.001(6)
C(4)	0.027(6)	0.015(6)	0.017(6)	−0.007(5)	−0.007(5)	0.004(5)
C(5)	0.025(6)	0.016(6)	0.022(6)	0.005(5)	0.006(5)	0.009(5)
C(6)	0.025(7)	0.045(8)	0.040(8)	0.012(6)	0.010(6)	0.011(7)
C(7)	0.023(6)	0.017(6)	0.014(6)	0.006(5)	−0.001(5)	0.001(5)
C(8)	0.039(7)	0.014(6)	0.039(7)	−0.001(6)	0.009(5)	−0.006(6)
C(9)	0.022(6)	0.023(7)	0.020(6)	−0.004(5)	0.000(4)	−0.007(5)
C(10)	0.030(6)	0.019(6)	0.017(6)	−0.009(5)	0.002(5)	−0.006(5)
C(11)	0.037(7)	0.023(7)	0.021(7)	−0.004(5)	0.003(5)	0.006(5)
C(12)	0.032(6)	0.020(6)	0.013(6)	0.004(5)	−0.001(5)	0.001(5)
C(13)	0.026(6)	0.022(6)	0.018(6)	0.003(6)	0.002(4)	−0.003(6)
C(14)	0.049(8)	0.023(7)	0.018(7)	−0.003(6)	−0.004(6)	0.004(5)
C(15)	0.021(6)	0.041(9)	0.043(8)	−0.005(6)	0.012(5)	0.000(7)
C(16)	0.032(7)	0.041(8)	0.028(7)	0.006(6)	0.003(6)	0.001(6)
C(17)	0.031(6)	0.029(7)	0.024(7)	−0.006(5)	0.009(5)	0.003(5)

The anisotropic displacement factor exponent takes the form: $\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + \sim\sim\sim\sim\sim\sim\sim\sim\sim +2b^*c^*U_{23}kl))$.

EXPERIMENTAL

All of the tri- and diorganotin chlorides except the benzyl derivatives were procured from Aldrich or Fluka and the tri- and dibenzyltin chlorides were prepared by the reported method.[30] All of the solvents were dried before use by the literature methods.[31] The ligand, 5-benzoyl-α-methyl-2-thiopheneacetic acid, was extracted with chloroform from the commercially available tablets (surgam) and was purified by crystallization in dichloromethan before use.

Instrumentation

Melting points were determined in a capillary tube using an MP.D Mitamura Riken Kogyo (Japan) electrothermal melting point apparatus.

Table XIII. Bond Lengths (Å) for Trimethyltin(IV) 5-Benzoyl-α-methyl-2-thiophene Acetate

Atoms	Distances	Atoms	Distances
Sn(1)-O(1)	2.456(7)	Sn(1)-O(2)	2.195(7)
Sn(1)-C(1)	2.096(11)	Sn(1)-C(2)	2.104(11)
Sn(1)-C(3)	2.135(10)	S(1)-C(7)	1.106(10)
S(1)-C(10)	1.733(10)	O(1)-C(4)	1.223(12)
O(2)-C(4)	1.287(12)	O(3)-C(11)	1.222(13)
C(4)-C(5)	1.543(13)	C(5)-C(6)	1.537(15)
C(5)-C(7)	1.469(13)	C(7)-C(8)	1.361(14)
C(8)-C(9)	1.393(14)	C(9)-C(10)	1.349(14)
C(10)-C(11)	1.453(15)	C(11)-C(12)	1.499(15)
C(12)-C(13)	1.374(15)	C(12)-C(17)	1.385(14)
C(13)-C(14)	1.378(14)	C(14)-C(15)	1.395(15)
C(15)-C(16)	1.392(16)	C(16)-C(17)	1.370(14)

Infrared absorption spectra were recorded as KBr/CsBr pellets on a Spectrum 1000 Perkin Elmer FT-IR, spectrometer. ^{1}H, ^{13}C and ^{119}Sn NMR spectra were recorded on a Bruker AM 250 spectrometer (Germany), using $CDCl_3$ as an internal reference [δ ^{1}H ($CDCl_3$) $=$ 7.23: δ ^{13}C ($CDCl_3$) = 77.0]. ^{119}Sn NMR spectra were obtained on Brucker 250ARX spectrometer (Germany) with Me_4Sn [$\Xi = 37.296665$ MHz] as an external reference. Mass spectral data were measured on a MAT 8500 Finnigan (Germany) mass spectrometer. UV absorption spectra were recorded on a Perkin Elmer UV-Vis Lambda 2S spectrometer, while conductance measurements were made on a model DDS-11A (China) conductometer. X-ray single crystal analysis

Table XIV. Non-bonded Contacts for Trimethyltin(IV) 5-Benzoyl-α-methyl-2-thiophene Acetate

Atoms	Distances	ADC	Atoms	Distances	ADC
S(1)-C(17)	3.580(12)	44504	O(1)-C(2)	3.129(14)	54502
O(1)-C(3)	3.355(14)	54502	O(2)-C(1)	3.115(14)	54502
O(2)-C(2)	3.189(13)	54502	O(2)-C(3)	3.189(13)	54502
O(3)-C(15)	3.395(14)	64404	O(3)-C(13)	3.511(13)	65403
C(2)-C(8)	3.569(16)	45504	C(8)-C(14)	3.546(16)	45504
C(14)-C(17)	3.400(15)	65402			

ADC (Atom Designator Code).

Table XV. Bond Angles (°) for Trimethyltin(IV) 5-Benzoyl-α-methyl-2-thiophene Acetate

Atoms	Angle	Atoms	Angle
O(1)-Sn(1)-O(2)	175.5(3)	O(1)-Sn(1)-C(1)	83.1(4)
O(1)-Sn(1)-C(2)	87.9(4)	O(1)-Sn(1)-C(3)	85.2(3)
O(2)-Sn(1)-C(1)	93.1(4)	O(2)-Sn(1)-C(2)	95.8(4)
O(2)-Sn(1)-C(3)	94.9(4)	C(1)-Sn(1)-C(2)	113.7(5)
C(1)-Sn(1)-C(3)	121.6(5)	C(2)-Sn(1)-C(3)	122.7(5)
C(7)-S(1)-C(10)	92.5(5)	Sn(1)-O(1)-C(4)	138.9(7)
Sn(1)-O(2)-C(4)	16.5(6)	O(1)-C(4)-C(2)	123.3(9)
O(1)-C(4)-C(5)	122.2(10)	O(2)-C(4)-C(5)	113.9(9)
C(4)-C(5)-C(6)	109.7(9)	C(4)-C(5)-C(7)	112.3(9)
C(6)-C(5)-C(7)	113.8(9)	S(1)-C(7)-C(5)	123.3(8)
S(1)-C(7)-C(8)	110.1(8)	C(5)-C(7)-C(8)	126.6(10)
C(7)-C(8)-C(9)	114.0(10)	C(8)-C(9)-C(10)	113.5(10)
S(1)-C(10)-C(9)	110.0(8)	S(1)-C(10)-C(11)	116.5(8)
C(9)-C(10)-C(11)	135.3(10)	O(3)-C(11)-C(10)	120.3(11)
O(3)-C(11)-C(12)	118.9(11)	C(10)-C(11)-C(12)	120.6(10)
C(11)-C(12)-C(13)	113.8(10)	C(11)-C(12)-C(17)	116.8(10)
C(13)-C(12)-C(17)	119.4(10)	C(12)-C(13)-C(14)	121.3(10)
C(13)-C(14)-C(15)	119.3(11)	C(14)-C(15)-C(16)	119.0(11)
C(15)-C(16)-C(17)	120.9(11)	C(12)-C(17)-C(16)	120.0(11)

was made on a Rigaku AFC6S diffractometer with graphite monochromated Mo-Kα radiation.

Extraction of the Acid Ligand

Surgam tablets were ground to a fine powder, dissolved in dry chloroform and stirred vigorously for 5 ~ 10 min. The solution was allowed to stand for 15 min and then filtered through a sintered glass crucible. The filtrate was evaporated under reduced pressure, and the resulting solid mass obtained was recrystallized in chloroform. The purity was checked by TLC and its melting point (m. p. = 96–97 °C).

Preparation of the Silver Salt of Acid Ligand

To a 0.01 M ethanol solution of the acid ligand a 0.01 M aqueous solution of sodium bicarbonate was added dropwise with constant stirring.

When the effervescence had ceased, a 0.01 M solution of silver nitrate was added dropwise. A creamy white precipitate was formed and the mixture was stirred for 15 min and then filtered through the Büchner funnel. The resulting solid was washed twice with dry ethanol and kept in vacuum desicator in the dark over P_2O_5.

General Procedure for the Synthesis of the Organotin Acetates

Triorganotin chloride (0.01 mol) or diorganotin dichloride (0.005 mol) in dry chloroform (25 mL) was added dropwise with constant stirring to a suspension of the silver salt of 5-benzoyl-α-methyl-2-thiophene acetic acid in dry chloroform (25 mL) in a 250 mL two-necked round bottom flask equipped with a water cooled condenser and magnetic stirring bar. The reaction mixture was refluxed for 7–8 h under helium atmosphere and then was allowed to stand overnight at room temperature. The formed silver chloride was filtered and the solvent of the filtrate was removed under reduced pressure. The solid mass left was recrystallized in dichloromethan/*n*-hexane (1:1).

Crystal Structure of Trimethyltin(IV) 5-Benzoyl-α-methyl-2-thiophene Acetate (4)

A crystal of approximate dimensions 0.50×0.30×0.20 mm was grown from a chloromethane/*n*-hexane mixture (80:20) and was used for data collection.

Crystal data: $C_{17}H_{20}O_3SSn$, M = 423.09 monoclinic, a = 12.934(3), b = 9.938(4), c = 14.079(4) Å, β = 100.77° (2), V = 1777.8 (9) Å,[3] space group $P2_{1/a}$, Z = 4, Dc = 1.581 g/cm^3, $\mu(M_o\text{-}K\alpha) = 15.63\ \text{cm}^{-1}$, F(000) = 848.00.

Data were measured at room temperature on a Rigaku AFC-6S diffractometer fitted with graphite monochromatized Mo-K_α radiation, λ = 0.71069 Å. A total of 3508 reflections were measured, of which 3354 were unique with the $I>2\alpha(I)$ data corrected for the Lorentz-polarization effect[32] and for absorption employing the DIFABS programe.[33] In the final least squares cycles all atoms were allowed to vibrate anisotropically. Hydrogen atoms were included at the calculated positions. Final residuals after ten cycles of least squares were R = 0.054, $R_w = 0.063$, for a weighting scheme of $w = 1/\sigma^2(F_o) = [\sigma^2{}_c(F_o) + P^2/4F^2{}_o]^{-1}$. Maximum and minimum residual densities were 1.47 and $-1.62\text{e}\,\text{Å}^{-3}$, respectively. Final fractional atomic coordinates are given in Table XI. The asymmetric unit is shown in Fig. 5, along with the labeling scheme used.

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