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^{1}H, ^{13}C, AND ^{119}Sn NMR, IR, MASS, THERMAL, AND BIOLOGICAL STUDIES OF ORGANOTIN(IV) DERIVATIVES OF 4-*p*-(CHLOROPHENYL)-2-PHENYL-5-THIAZOLEACETIC ACID

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ABSTRACT

A series of di- and triorganotin(IV) carboxylates of 4-*p*-(chlorophenyl)-2-phenyl-5-thiazoleacetic acid has been synthesized and characterized by various instrumental techniques such as infrared, ^{1}H, ^{13}C, ^{119}Sn NMR, mass spectrometry and thermal analysis. These compounds were also tested for their

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antibacterial and antifungal activities to study their biological significance.

INTRODUCTION

Organotin compounds of oxygen and nitrogen donor ligands are well known for their biological activity.[1–4] Recently, organotin(IV) complexes of sulfur-containing ligands have received considerable attention.[5,6] In view of the diverse fields of applications of organotin complexes, we have synthesized and characterized a number of organotin complexes with various donor ligands.[7–14] Some of these were subjected to X-ray crystal analysis[15–18] and have found biological[19,20] and industrial applications.[21] In continuation of our previous work we have synthesized some complexes of the general formulae R_2SnL_2 and R_3SnL, L = 4-*p*-(chlorophenyl)-2-phenyl-5-thiazole acetic acid anion (Fig. 1). These complexes have been characterized by elemental analyses, infrared, multinuclear (^1H, ^{13}C, ^{119}Sn) NMR and mass spectrometry. Thermal analysis was performed for the complexes to study their energy of activation and order of decomposition reactions. The compounds showed high activity against various bacteria and fungi. The crystal analysis for Me_3SnL shows the coordination of one H_2O molecule with the Sn atom.[22]

RESULTS AND DISCUSSION

The reported compounds of type (a) and (b) were prepared by the reaction of the ligand salt (method I) with the respective organotin chlorides [Eqs. (1) and (2)] or by the reaction of ligand acid (method II) and organotinoxide or hydroxide [Eqs. (3) and (4)].

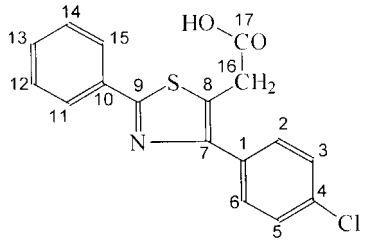


Figure 1. Structure of the ligand (HL).

$$R_2SnCl_2 + 2NaL \longrightarrow R_2SnL_2 + 2NaCl \quad (1)$$

$$R_3SnCl + NaL \longrightarrow R_3SnL + NaCl \quad (2)$$

$$R_2SnO + 2HL \longrightarrow R_2SnL_2 + H_2O \quad (3)$$

$$R_3SnOH + HL \longrightarrow R_3SnL + H_2O \quad (4)$$

Type (a) R_2SnL_2

Compound No.	**(1)**	**(2)**	**(3)**	**(4)**	**(5)**
R	Me	Et	*n*-Bu	Ph	Bz

Type (b) R_3SnL

Compound No.	**(6)**	**(7)**	**(8)**	**(9)**
R	Me	*n*-Bu	Ph	Bz

All the compounds are colourless crystalline solids. Their physical data, *i.e.*, melting points, % yield and CHN analysis are reported in Table I.

Infrared Spectroscopy

The infrared spectra have been recorded in the range of 4000-250 cm^{-1} as KBr/CsBr discs and important bands for structural assignments are given in Table II. The broad band at 2930–2590 cm^{-1} due to ν(OH) present in the spectrum of the ligand is absent in the spectra of the corresponding organotin derivatives, thus showing deprotonation of the carboxylic acid group. The Δν values [$\Delta\nu = \nu_{asym}(COO) - \nu_{sym}(COO)$] has been used to predict the mode of tin carboxylate interaction.[23] There is donation of charge density from C=O:→ to the electropositive tin metal, which slightly increase the C=O bond length, hence, the absorption frequency decreases and carboxylate acts as bidentate ligand in the solid state. The complexation of tin(IV) with the ligand is further confirmed by the absence of Sn–Cl vibrations at *ca.* 333 cm^{-1}, and the presence of Sn–O bands in the range 450–500 cm^{-1}.

Table I. Physical Data for Organotin(IV) Carboxylates[a]

Compound No.	Molecular Formula (Formula Weight)	M.p. (°C)	Yield (%)	%C Cald./Exp.	%H Cald./Exp.
(1)	$C_{36}H_{28}Cl_2N_2O_4S_2Sn$ (806)	82–83	70	53.60/53.77	3.47/3.60
(2)	$C_{38}H_{32}Cl_2N_2O_4S_2Sn$ (834)	95–97	79	54.68/54.95	3.84/3.92
(3)	$C_{42}H_{40}Cl_2N_2O_4S_2Sn$ (890)	123–24	83	56.62/55.96	4.44/4.22
(4)	$C_{46}H_{32}Cl_2N_2O_4S_2Sn$ (930)	96–97	84	59.35/58.88	3.44/3.85
(5)	$C_{48}H_{36}Cl_2N_2O_4S_2Sn$ (958)	108–110	78	60.12/60.05	3.76/4.09
(6)	$C_{20}H_{22}ClNO_3SSn$ (510.5)	71–72	73	47.01/46.70	4.31/3.95
(7)	$C_{29}H_{38}ClNO_2SSn$ (618.5)	141–42	70	56.26/55.90	6.14/6.38
(8)	$C_{35}H_{26}ClNO_2SSn$ (678.5)	84–85	78	61.90/62.00	3.83/4.12
(9)	$C_{38}H_{32}ClNO_2SSn$ (720.5)	91–92	80	63.29/63.42	4.44/4.72

[a]Compound **(6)** contains an H_2O molecule.

Table II. Infrared Data for the Investigated Compounds[a]

Compounds	$\nu(COO)_{asym}$	$\nu(COO)_{sym}$	$\Delta\nu$	ν(Sn–C)	ν(Sn–O)
(1)	1632 s	1442 s	190	555 s, 522 w	468 w
(2)	1625 s	1437 s	188	580 s, 535 m	472 w
(3)	1616 s	1440 s	176	556 w, 528 m	465 m
(4)	1614 s	1456 s	158	556 s	482 s
(5)	1631 s	1440 s	191	570 w, 530 m	479 m
(6)	1619 s	1430 s	184	554 w, 520 w	460 m
(7)	1610 s	1430 s	180	582 m, 528 m	462 w
(8)	1616 s	1460 s	156	548 w, 504 w	460 m
(9)	1614 s	1452 s	162	558 s, 508 w	470 w

[a]s, strong; m, medium; w, weak.

NMR

^{1}H NMR spectra of the investigated compounds show the absence of OH signals at 11.0 ppm for COO<u>H</u> of the ligand which indicate the bonding of tin with the ligand moiety through the deprotonated carboxylic oxygen. The ligand shows a complex pattern for aromatic protons which remains almost the same in the tin compounds (Table III). However, additional signals due to the organic groups attached to tin appear in the region 0.5–1.7 ppm (R = Me, Et, Bu) and 7.5–7.8 ppm (R = Ph, Bz). The ^{13}C and ^{119}Sn NMR data, along with the coupling constants $^{n}J(^{119}Sn, ^{13}C)$ are listed in Table III. Deshielding of the protons H(11) and (15) and H(12) and (14) is observed in all complexes which should be due to the electropositive nature of the tin. A σ-charge donation from the COO^{-} donor to the tin atom decreases the electron density of the ligand and produces deshielding. All the shifts are downfield except for H(2) and (6), H(3) and (5) and H(13) which are shifted upfield, probably due to the ring current effect.

The involvment of the carboxylic group in bonding to tin is confirmed by the resonances ascribed C(16) and C(8) which exhibit the greatest shifts upon coordination (Table IV). The remaining resonances due to the aromatic carbon atoms do not shift significantly on bonding to tin. The greatest downfield shift is observed for the carboxylic carbon, C(17), while all the remaining carbon atoms shift downfield by ~0.8–6.0 ppm.

Using the ^{1}J values in Lockhart's equation,[24] in compounds **(1)**, **(3)**, **(6)** and **(7)** the predicted C–Sn–C angles are 131.5, 131.5, 110 and 110.9°, respectively, which confirms the characteristic tetrahedral environment of tin in non-coordinating solvents.

The values of δ ^{119}Sn define the region of various coordination numbers of the central tin atom.[5] According to data in Table IV, all compounds show a tetrahedral environment around tin in solution (Fig. 2).

Thermal Studies

The degradation of organotin complexes gave identical patterns of decomposition. Horowitz[25] and Coats and Redfern[26] formulae were used for TG curves to determine the energy of activation (E_a) and order of reaction (n).

The ligand decomposes in two steps. In the first step CH_3COOH, C_6H_5Cl and C_6H_5CN evolve over the temperature range of 230–400 °C. The order of the reaction is "0" and the energy of activation is

Table III. ^{1}H NMR Data of the Investigated Compounds[a–d]

^{1}H	HL	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
(2), (6)	7.27 d	7.08 d	7.05 d	7.10 d	7.04 d	7.12 d	7.06 d	7.10 d	7.08 d	7.15 d
	(8.11)	(7.89)	(7.86)	(7.92)	(7.79)	(7.88)	(7.83)	(7.85)	(7.90)	(7.81)
(3), (5)	7.31 d	7.27 d	7.25 d	7.25 d	7.25 d	7.27 d	7.23 d	7.25 d	7.24 d	7.25 d
	(8.30)	(7.92)	(7.90)	(7.91)	(7.82)	(7.91)	(7.90)	(7.88)	(7.93)	(7.86)
(11), (15)	7.64 d	8.13 d	8.16 d	8.16 d	8.15 d	8.15 d	8.07 d	8.12 d	8.18 d	8.20 d
	(8.44)	(8.21)	(8.35)	(8.31)	(8.38)	(8.30)	(8.29)	(8.28)	(8.29)	(8.30)
(12), (14)	7.47 m	7.79 m	7.80 m	7.79 m	7.81 m	7.79 m	7.76 m	7.77 m	7.76 m	7.75 m
(13)	7.37 m	7.32 m	7.34 m	7.34 m	7.33 m	7.32 m	7.34 m	7.34 m	7.33 m	7.34 m
(16)	1.9 s	2.39 s	2.38 s	2.39 s	2.40 s	2.39 s	2.39 s	2.38 s	2.40 s	2.38 s
*CH_2	–	–	–	–	–	2.90 s	–	–	–	2.95 s
α	–	1.2 s	1.38 m	1.87–1.75 m	–	–	0.69 s	1.87–1.70 m	–	–
		[80.0]	[111.2]				[55.8, 58.2]			
β	–	–	1.80 t	1.45–1.39 m	7.98 d	7.62 d	–	1.45–1.40 m	7.94 d	7.69 d
					(7.52)	(7.33)			(7.61)	(7.44)
γ	–	–	–	1.45–1.39 m	7.70 d	7.45 d	–	1.45–1.40 m	7.66 d	7.49 d
					(7.49)	(7.41)			(7.55)	(7.40)
δ	–	–	–	0.91 t	7.50 m	7.50 m	–	0.81 t	7.46 m	7.56 m
				(7.32)				(7.29)		

[a]Chemical shift in ppm, multiplicity is given as s, singlet; d, doublet; t, triplet; m, multiplet.
[b]Coupling constants in H_z are in parentheses $^{n}J(^{1}H, ^{1}H)$ and $^{2}J[^{119}Sn, ^{1}H]$ in Hz.
[c]HL = Ligand (Fig. 1); numbering scheme is according to Fig. 1.
[d]*CH_2 from benzyl group.

Table IV. ^{13}C NMR Data of the Investigated Compounds[a–d]

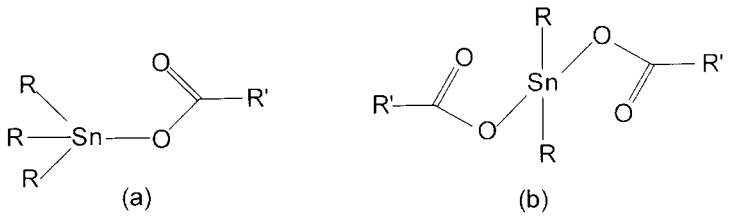
^{13}C	HL	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
(1)	137.6	136.8	136.8	136.8	136.9	136.7	136.7	136.8	136.5	136.3
(2), (6)	113.0	112.2	112.2	112.2	110.6	112.2	113.9	112.0	112.5	112.3
(3), (5)	129.2	135.8	135.9	135.9	136.0	135.9	136.2	136.0	136.1	136.5
(4)	125.3	131.6	131.7	131.7	131.5	131.5	131.5	130.9	131.7	131.2
(7)	124.9	128.8	128.8	128.8	128.8	128.8	128.5	129.0	128.7	128.6
(8)	126.4	133.5	133.5	133.5	132.9	133.9	133.0	133.5	133.7	133.5
(9)	152.7	148.0	148.0	148.0	148.2	148.0	147.5	148.0	147.9	147.6
(10)	138.4	137.9	137.8	137.8	137.4	137.8	137.6	137.4	137.6	137.0
(11), (15)	126.5	134.9	134.8	135.8	134.9	135.2	134.5	134.8	134.8	134.3
(12), (14)	128.6	134.6	134.7	134.7	134.5	134.7	134.6	135.0	134.7	134.4
(13)	124.8	128.1	128.1	128.1	128.2	128.0	128.0	128.1	128.0	128.0
(16)	14.6	21.1	21.0	21.0	20.6	20.9	21.0	21.0	21.0	21.2
(17)	180.4	170.0	172.7	170.6	170.0	172.0	171.7	172.0	172.0	172.0
$*CH_2$	–	–	–	–	–	24.0	–	–	–	23.7
α	–	5.6 [630]	18.4	18.2 [568.5]	136.9	137.0	−1.67 [378, 399]	18.4 [362.5]	139.0	136.5
β	–	–	9.4	27.1	135.5	129.0	–	26.9	136.5	129.2
γ	–	–	–	26.8	129.0	130.5	–	26.7	129.2	130.5
δ	–	–	–	14.0	130.7	126.0	–	14.0	130.5	126.5
^{119}Sn	–	−115.6	−149.3	−144.2	−290.0	−238.6	137.5	124.0	−113.4	−18.9

[a]Chemical shift in ppm.

[b]Coupling constants $^1J[^{119}Sn, ^{13}C]$ in Hz are in brackets.

[c]HL = Ligand (Fig. 1); numbering scheme is according to Fig. 1.

[d]$*CH_2$ from benzyl group.



R = Me **(1)**, Et **(2)**, *n*-Bu **(3)**, Ph **(4)**, Bz **(5)** R = Me **(6)**, *n*-Bu **(7)**, Ph **(8)**, Bz **(9)**

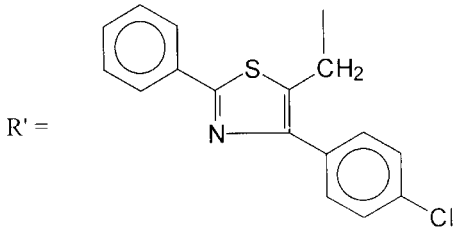


Figure 2. Proposed structures (a) for triorganotin(IV) carboxylates and (b) for diorganotin(IV) dicarboxylates in non-coordinating solvents.

18.42 kcal/mol. In the second step only sulfur evolves in the temperature range of 470–595 °C. The order of this step is also "0" and the energy of activation is 6.84 kcal/mol. The residue contains only carbon in this case. The thermal degradation of compounds **(6)** and **(4)** takes place in three steps, whereas the remaining compounds decompose in two steps. The various fragments evolved, their activation energy and order of reactions are reported in Tables V and VI.

Mass Spectrometry

The monoisotopic mass fragmentation of the individual compounds are reported in the experimental section. The molecular ion peak of these complexes has not been observed like in previous reports.[27,28] Two representative compounds and the ligand are discussed here for their mass fragmentation while the remaining compounds follow an analogous patterns. The primary fragmentation of the ligand takes place due to the loss of the carboxylate group followed by two routes of fragmentation: (i) loss of chlorine forming $[C_{16}H_{11}NS]^+$ and subsequent loss of C_9H_6S and

Table V. Proposed Degradation Pattern for Organotin(IV) Carboxylates

Compound	Temp. Range (°C)	Evolved Compd.	Remaining Compd.	Weight Loss % Calcd.	Weight Loss % Obs.
HL	230–400	CH_3COOH, C_6H_5Cl, C_6H_5CN	C_2S	83.6	84.0
	470–595	S	2C	09.70	08.60
(3)	270–456	$C_{16}H_{11}ClNS$	$SnC_{26}H_{29}ClNO_4S$	32.00	32.26
	498–718	$C_{17}H_{11}ClNO_2S$		40.10	40.33
		CO	Bu_2SnO		
(4)	55–360	L	Ph_2SnL	35.30	37.96
	360–480	PhC_9H_4ClNS	$PhSnCOOCH_2$	29.11	30.26
	520–735	Ph	SnCOOC	08.29	07.96
(6)	196–500	3Me, H_2O	$SnC_{17}H_{11}ClNO_2S$	12.33	12.20
	560–690	$C_{17}H_{11}ClNS$	SnO_2	66.07	65.72
(7)	287–480	3Bu	$SnC_{17}H_{11}ClNO_2S$	27.67	29.33
	530–625	$C_{17}H_{11}ClNS$	SnO_2	47.98	46.09
(8)	200–545	$C_{16}H_{12}ClNS$	Ph_3SnO_2C	41.11	42.45
	545–665	2Ph, CO_2	PhSn	29.20	29.39
(9)	217–510	$C_{15}H_{11}ClNS$	Bz_3SnOOC	39.51	39.25
	524–728	2Bz, C_6H_5	$SnC_2H_2O_2$	35.97	36.11

CN forming $[C_6H_5CN]^+$ and $[C_6H_5]^+$ ions, respectively and (ii) loss of C_6H_5CN forming $[C_9H_6SCl]^+$ and subsequent loss of CS and C_2HCl forming $[C_8H_6Cl]^+$ and $[C_6H_5]^+$ ions, respectively. A third route was observed by the loss of chlorine from $[C_9H_6SCl]^+$ and C_6H_5CN from $[C_{16}H_{11}NS]^+$ with the formation of $[C_9H_6S]^+$ at m/z 146 which on further loss of C_2H_2 results in $[C_7H_4S]^+$ ion at m/z 120. The fragmentation pattern of the ligand is given in Fig. 3.

The compound **(6)** follows two routes of fragmentation. In the first route it gives a peak at m/z 478 after the loss of one methyl radical, which further gives a peak of the ligand ion at m/z 328 after losing the $Sn(CH_3)_2$ radical. The ligand ion adopts almost the same pattern of fragmentation as given in Fig. 3. In the second route, the compound shows a peak of $[Sn(CH_3)_3]^+$ at 165 which gives a peak of $[Sn]^+$ at 120 after loosing 3 CH_3 radicals (Fig. 4).

Table VI. Energy of Activation and Order of Reaction for Organotin(IV) Carboxylates[a,b]

Compound	Temp. Range (°C)	T_s (°C)	Horowitz (E_a)	Redfern's Method	
				E_a	n
L	316–400	361.92	27.92	28.90	1.25
	511–576	556.8	18.25	14.18	1.00
(3)	276–457	312.65	22.98	18.81	0.75
	490–710	633.75	42.05	39.24	1.00
(4)	56–360	288.30	17.86	18.23	1.00
	360–480	362.70	14.27	16.96	1.25
	521–720	585.20	22.12	25.23	0.80
(6)	194–500	287.64	17.45	16.84	1.00
	567–686	583.74	25.96	24.77	1.00
(7)	296–466	329.94	21.60	22.04	0.66
	496–593	558.36	40.87	36.97	1.00
(8)	194–342	258.26	33.44	34.83	1.00
	518–560	583.30	22.31	25.94	1.25
(9)	216–482	274.85	26.53	27.74	1.25
	500–728	595.35	26.60	22.77	1.25

[a]E_a = Energy of activation Kcal/mol.
[b]n = Order of the reaction.

Compound **(3)**, after giving rise to the fragments $[C_{17}H_{11}ClNO_2SSnBu_2]^+$ at m/z 562 and $[C_{17}H_{11}ClNO_2SSn]^+$ at m/z 448 fragments by two routes. In the first route, the ligand ion is formed after losing an Sn radical, which undergoes fragmentation almost in the same way as in Fig. 3. Whereas the second route ends with $[Sn]^+$ at m/z 120, after giving rise to different fragments at their respective m/z values.

Biological Activity

Biological activity tests of the compounds were carried out against various bacteria and fungi by the "agar diffusion technique".[29] All the compounds were screened for antibacterial and antifungal activity. The results are given in Tables VII and VIII.

The screening test shows that the butyl and phenyltin carboxylates are the most potent candidates against the tested bacteria. The activity of the

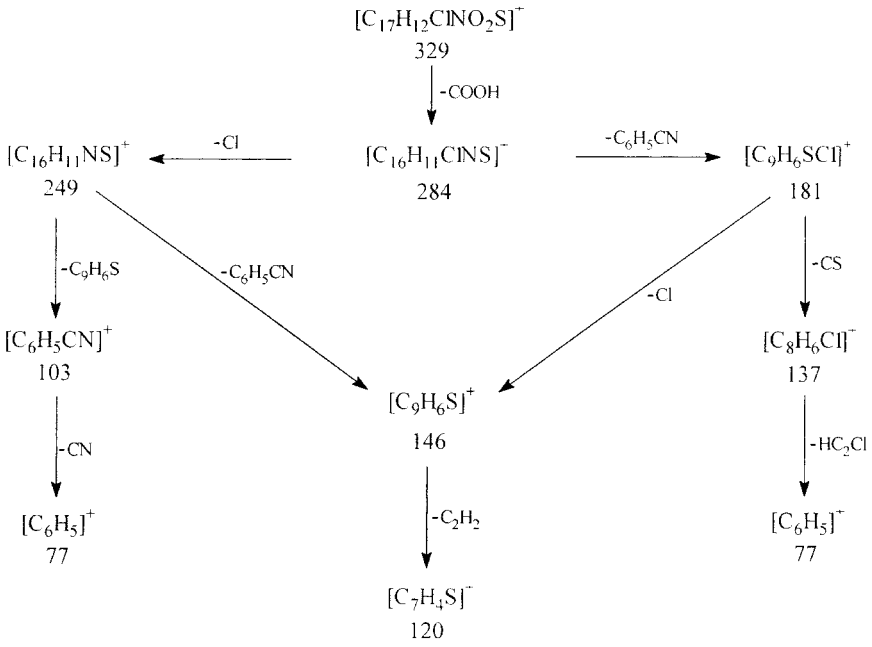


Figure 3. Proposed mass fragmentation pattern of the ligand.

other derivatives varies according to their R groups. However, all of these compounds are active against *E. coli* (Table VII).

Earlier reports show that higher antifungal activity is associated with tributyltin and triphenyltin compounds.[30] In the present case most of the compounds show high antifungal activity against the tested fungi. Fentiazac is also active against some species of the tested fungi while in some cases like *Aspergillus niger*, it is inactive, but trimethyl- and tributyltin derivatives are highly active against this fungus. In the present series diphenyltin, tribenzyltin and dibenzyltin carboxylates, comparatively, are more active (Table VIII).

Brine Shrimps (*Artemia salina*), a tiny crustacean, have been used for the determination of toxicity of the organotin carboxylates. The results are given in Table IX. Previous reports[30,31] show that the toxicity of organotin compounds depends upon the nature of the organic group. The highest toxicity being shown by compounds having three tin carbon (Sn–C) bonds.

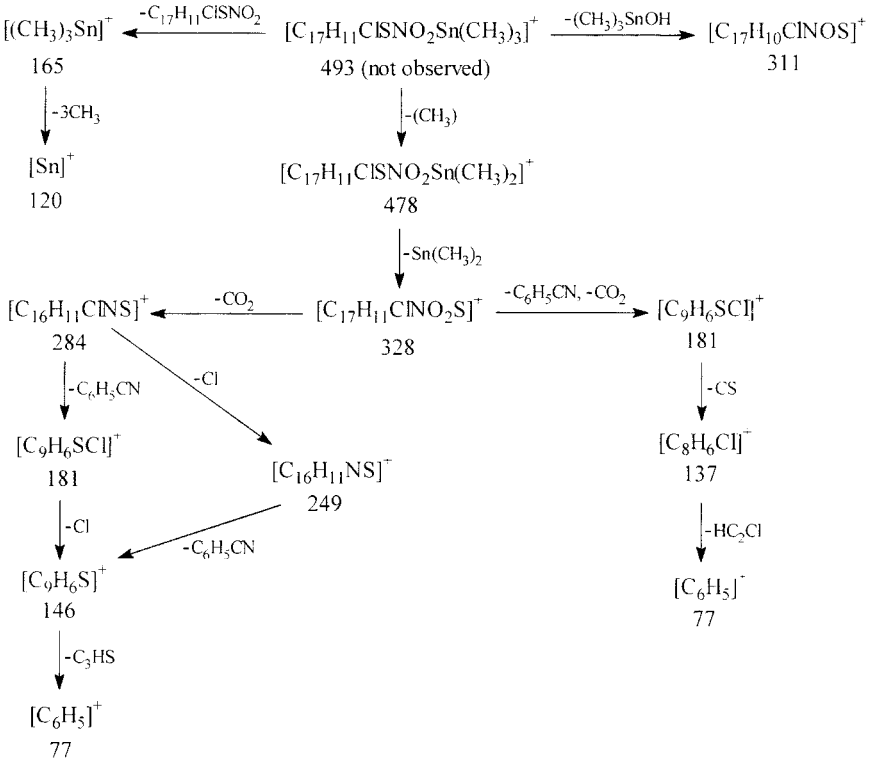


Figure 4. Proposed mass fragmentation pattern for compound **(6).**

EXPERIMENTAL

Chemicals

All solvents used were purchased from Merck, Germany and were dried before use according to the standard methods.[32] Di- and triorganotin chlorides were purchased from Aldrich, USA, whereas organotin oxides and hydroxides were obtained from Strem, USA. All of these chemicals were of analytical reagent grade and were used without further purification. 4-(*p*-Chlorophenyl)-2-phenyl-5-thiazoleacetic acid (Fentiazac/Donoerest) was kindly provided by Wyeth Pharmaceutical Co. Ltd., Pakistan, and was recrystallized from benzene and dried over P_2O_5 under vacuum (m.p. 161–62 °C).

Table VII. Antibacterial Activity of Organotin(IV) Carboxylates[a–c]

Bacterium	(3)	(4)	(5)	(6)	(7)	(8)	(9)	HL	S_1	S_2
Corynebacterium diptheriae	16	13	9	n.a.	11	14	6	6	13	12
Streptococcus ryogenes	7	13	8	n.a.	7	14	7	6	17	18
Streptococcus aureus	12	15	10	n.a.	16	15	7	6	18	19
Proteus mirabillis	12	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	6	18	17
Escherichia coli	12	12	8	7	14	8	8	7	18	19
Shigella boydii	7	n.a.	6	n.a.	7	6	6	6	16	17
Pseudomonas aeroginosa	n.a.	n.a.	7	n.a.	8	n.a.	8	n.a.	19	18

[a]Inhibition zone in mm, 100 μg/100 μL.
[b]S_1 and S_2, Standards ampicilline and tobramycine, 10 μg/100 μL.
[c]n.a., No activity.

Table VIII. Antifungal Activity for Organotin(IV) Carboxylates[a–c]

	Organotin Carboxylates							
Fungus	HL	(3)	(4)	(5)	(6)	(7)	(8)	(9)
Allescheria boydii	+++	−	+++	+++	−	−	−	+++
Aspergillus niger	−	−	++	−	+++	+++	−	−
Candida albicans	+	−	−	+	−	−	−	++
Curvularia lunata	+++	−	++	++	+++	+++	+++	−
Drechslera restrata	+++	+	+++	+++	+++	+++	−	+++
Nigrospora oryzae	−	−	+++	+++	−	+++	−	++
Microsporum canis	+++	+++	+++	−	+++	+++	−	+++
Pleurotus ostreatus	+++	+++	+++	+++	+++	−	+++	+++
Stachybotrys atra	++	−	++	+++	+++	+++	−	+++
Trichophyton mentagophyte	+++	+	+++	+++	−	+++	−	+++

[a]Strong inhibition (+++) (60–80%); medium inhibition, (++) (50–60%); weak inhibition, (+) (30–50%); no inhibition (−).
[b]Incubation period, 7–10 days; incubation temp., 27–29 °C.
[c]Medium used: Sabouraud Dextrose Agar; Conc. used for sample, 200 μg/mL of medium.

Instrumentation

Melting points were determined in capillary tubes using an electrothermal melting point apparatus model MP-D Mitamura Riken Kogyo (Japan) and are uncorrected. Infrared spectra were recorded within the

Table IX. Toxicity Data for Organotin(IV) Carboxylates[a]

Compound	Toxicity		
	Upper Value	Lower Value	LD_{50}
HL	–	–	>100
(3)	2.3652	0.8677	1.5089
(4)	2.3474	0.4724	0.2126
(5)	–	–	>100
(6)	3.0608	1.2884	1.9266
(7)	1.4535	0.2400	0.8197
(8)	1.6801	0.5953	0.3404
(9)	–	–	>100

[a]Upper value = dose in μg/mL at which maximum organisms die; Lower value = dose in μg/mL at which death of organism starts; LD_{50} = Lethal dose at which 50% organisms die.

range 4000–600 cm^{-1} in KBr and 600–200 cm^{-1} in CsBr pellets on a Perkin Elmer 3300 spectrometer (USA). The ^{1}H, ^{13}C and ^{119}Sn NMR spectra were recorded on a Bruker ARX 250 spectrometer (Germany), using $CDCl_3$ as an internal reference for ^{1}H and ^{13}C [δ ^{1}H ($CDCl_3$) = 7.24: δ ^{13}C ($CDCl_3$) = 77.0] and Me_4Sn as external reference for ^{119}Sn [Ξ (Sn) = 37.290665]. Thermal analysis were carried out in nitrogen (N_2) by a Netzsch simultaneous thermal analyzer STA-429 while mass data were recorded on a 70 eV mass spectrometer model MAT 8500 Finnigan (Germany).

Synthesis

Since organotin halides and their derivatives are air- and moisture-sensitive; all glassware was completely dried at 140 °C and reactions were carried out under argon. Two synthetic routes were used for the preparation of complexes.

Method (a) Sodium ethoxide was prepared by reacting 100 mL of ethanol with 0.1 mole (2.3 g) of sodium metal in a two-neck 250 mL round bottom flask equipped with a condenser, ice bath and magnetic stirrer. After completion of the reaction 0.1 mole (32.98 g) of the ligand acid was added to it. The mixture was refluxed for 3–4 h and after cooling the appropriate organotin chloride (0.1 mole in the case of triorganotin compounds and

0.05 mole in the case of diorganotin compounds) was added with constant stirring. The mixture was refluxed for 5–6 h and was allowed to stand overnight at room temperature. The sodium chloride formed was filtered and ethanol was removed under reduced pressure and the solid formed was recrystallized from an appropriate solvent.

Method (b) Stoichiometric amounts of the ligand acid (0.01 mole, 3.298 g) and organotin oxide (0.005 mole) or hydroxide (0.01 mole) were refluxed in 100 mL dry toluene for 3–4 h. Water formed was continuously removed using a Dean and Stark apparatus. Toluene was then removed completely under reduced pressure in a high vacuum. The residue was treated with activated charcoal in chloroform and filtered. The filtrate was concentrated and kept at low temperature (−5 °C). The formed solid mass was recrystallized from an appropriate solvent.

Compound (1)

Recrystallized from dichloromethane. MS, m/z (%) [fragment]: 806 (not observed) $[Me_2Sn(C_{17}H_{11}ClNO_2S)_2]^+$, 791 (78) $[MeSn(C_{17}H_{11}ClNO_2S)_2]^+$, 776 (62) $[Sn(C_{17}H_{11}ClNO_2S)_2]^+$, 476 (100) $[Me_2\ Sn(C_{17}H_{11}ClNO_2S)]^+$, 463 (55) $[Me\ Sn(C_{17}H_{11}ClNO_2S)]^+$, 448 (40) $[Sn(C_{17}H_{11}ClNO_2S)]^+$, 404 (32) $[Sn(C_{16}H_{11}ClNS)]^+$, 328 (45) $[C_{17}H_{11}ClNO_2S]^+$, 284 (36) $[C_{16}H_{11}ClNS]^+$, 276 (21) $[C_{17}H_{10}NOS]^+$, 249 (15) $[C_{16}H_9OS]^+$, 181 (37) $[C_9H_6ClS]^+$, 150 (52) $[Me_2Sn]^+$, 146 (18) $[C_9H_6S]^+$, 120 (28) $[Sn]^+$.

Compound (2)

Recrystallized from dichloromethane. MS, m/z (%) [fragment]: 834 (not observed) $[Et_2Sn(C_{17}H_{11}ClNO_2S)_2]^+$, 805 (20) $[EtSn(C_{17}H_{11}ClNO_2S)_2]^+$, 776 (35) $[Sn(C_{17}H_{11}ClNO_2S)_2]^+$, 477 (25) $[EtSn(C_{17}H_{11}\ ClNO_2S)]^+$, 448 (55) $[Sn(C_{17}H_{11}ClNO_2S)]^+$, 404 (100) $[Sn(C_{16}H_{11}ClNS)]^+$, 328 (60) $[C_{17}H_{11}ClNO_2S]^+$, 311 (32) $[C_{17}H_{10}ClNOS]^+$, 276 (27) $[C_{17}H_{10}\ NOS]^+$, 249 (22) $[C_{16}H_9OS]^+$, 181 (37) $[C_9H_6ClS]^+$, 149 (38) $[C_6H_6Cl]^+$, 120 (28) $[Sn]^+$.

Compound (3)

Recrystallized from dichloromethane and *n*-hexane (1:1). MS, m/z (%) [fragment]: 890 (not observed) $[(C_{17}H_{11}ClNO_2S)_2SnBu_2]^+$, 562 (90) $[(C_{17}H_{11}ClNO_2SSnBu_2]^+$, 448 (20) $[(C_{17}H_{11}ClNO_2SSn]^+$, 328 (30) $[(C_{17}H_{11}NO_2ClS)]^+$, 312 (72) $[SnC_{10}H_8SO_2]^+$, 284 (85) $[C_{16}H_{11}ClNS]^+$, 236 (42)

$[SnC_4H_4O_2S]^+$, 181 (63) $[C_9H_6SCl]^+$, 149 (100) $[C_9H_6Cl]^+$, 120 (38) $[Sn]^+$, 69 (87) $[HC_3S]^+$, 32 (64) $[S]^+$.

Compound (4)

Recrystallized from dichloromethane and *n*-hexane (1:1). MS, m/z (%) [fragment]: 930 (not observed) $[(Ph)_2\ Sn(C_{17}H_{11}ClNSO_2)_2]^+$, 602 (5) $[(Ph)_2SnC_{17}H_{11}ClNO_2S]^+$, 567 (20) $[(Ph)_2SnC_{17}H_{11}NO_2S]^+$, 328 (5) $[C_{17}H_{11}ClNO_2S]^+$, 312 (65) $[PhSnC_5H_7OS]^+$, 284 (27) $[C_{16}H_{11}ClNS]^+$, 249 (12) $[C_6H_5SnSOH_4]^+$, 181 (15) $[C_9H_6SCl]^+$, 120 (10) $[Sn]^+$, 77 (100) $[C_6H_5]^+$.

Compound (5)

Dibenzyltin dichloride was prepared by the reported method.[33] The Compound **(5)** was recrystallized from dichloromethane. MS, m/z (%) [fragment]. 958 (5) $[(Bz)_2Sn(C_{17}H_{11}NO_2ClS)_2]^+$, 867 (35) $[(Bz)Sn(C_{17}H_{11}NO_2ClS)_2]^+$, 776 (58) $[Sn(C_{17}H_{11}NO_2ClS)_2]^+$, 539 (100) $[(Bz)Sn(C_{17}H_{11}NO_2ClS)]^+$, 448 (25) $[Sn(C_{17}H_{11}NO_2ClS)]^+$, 404 (42) $[SnC_{16}H_{11}\ ClNS]^+$, 328 (32) $[C_{17}H_{11}ClNO_2S]^+$, 311 (100) $[C_{17}H_{10}ClNOS]^+$, 276 (13) $[C_{17}H_{10}NOS]^+$, 249 (18) $[C_{16}H_9OS]^+$, 181 (39) $[C_9H_6SCl]^+$, 149 (22) $[C_9H_6Cl]^+$, 120 (41) $[Sn]^+$.

Compound (6)

Recrystallized from dichloromethane. MS, m/z (%) [fragment]: 511 (not observed) $[C_{17}H_{11}ClSNO_2Sn(CH_3)_3H_2O]^+$, 478 (12) $[C_{17}H_{11}ClSNO_2Sn(CH_3)_2]^+$, 311 (25) $[C_{17}H_{11}NSO_2H_2O]^+$, 328 (10) $[C_{17}H_{11}ClNO_2S]^+$, 284 (40) $[C_{16}H_{11}ClNS]^+$, 249 (18) $[C_{16}H_{11}NS]^+$, 181 (30) $[C_9H_6SCl]^+$, 165 (100) $[(CH_3)_3Sn]^+$, 146 (35) $[C_9H_6S]^+$, 137 (20) $[C_8H_6Cl]^+$, 120 (10) $[Sn]^+$, 103 (12) $[C_6H_5CN]^+$, 77 (8) $[C_6H_5]^+$.

Compound (7)

Recrystallized from dichloromethane. MS, m/z (%) [fragment]: 619 (not observed) $[C_{17}H_{11}ClNO_2SSn(Bu)_3]^+$, 489 (3) $[C_{20}H_{16}SNClO_2Sn]^+$, 402 (40) $[(Bu)C_{10}H_6O_2SClSn]^+$, 375 (14) $[C_{12}H_{12}SClO_2Sn]^+$, 328 (28) $[C_{17}H_{11}ClNO_2S]^+$, 312 (85) $[C_{10}H_5ClO_2Sn]^+$, 284 (40) $[C_{16}H_{11}ClNS]^+$, 249 (17)

$C_{16}H_{11}NS]^+$, 181 (30) $[C_9H_6SCl]^+$, 120 (27) $[Sn]^+$, 90 (47) $[C_7H_6]^+$, 69 (100) $[C_3HS]^+$, 32 (24) $[S]^+$.

Compound (8)

Recrystallized from chloroform and dichloromethane (1:1). MS, m/z (%) [fragment]: 679 (not observed) $[(Ph)_3Sn(C_{17}H_{11}NO_2ClS)]^+$, 602 (75) $[(Ph)_2SnC_{17}H_{11}NO_2ClS]^+$, 567 (24) $[(Ph)_2SnC_{17}H_{11}NO_2S]^+$, 533 (10) $[(Ph)_2SnC_{17}H_9NO_2]^+$, 328 (7) $[C_{17}H_{11}ClNO_2S]^+$, 312 (28) $[PhSnC_5H_7OS]^+$, 284 (20) $[C_{16}H_{11}ClNS]^+$, 274 (75) $[(Ph)_2Sn]^+$, 181 (19) $[C_9H_6SCl]^+$, 197 (7) $[(Ph)Sn]^+$, 168 (64) $[C_8H_5SCl]^+$, 134 (30) $[C_8H_3Cl]^+$, 120 (12) $[Sn]^+$, 103 (43) $[C_6H_5CN]^+$, 89 (33) $[C_7H_5]^+$, 77 (24) $[C_6H_5]^+$.

Compound (9)

Tribenzyltin chloride was prepared by the reported method.[33] The compound **(9)** was recrystallized from dichloromethane. MS, m/z (%) [fragment]: 721 (not observed) $[(Bz)_3SnC_{17}H_{11}NO_2ClS]^+$, 563 (50) $[(Bz)_3SnC_7H_5ClNO_2]^+$, 539 (8) $[(Bz)SnC_{17}H_{11}NO_2ClS]^+$, 448 (11) $[SnC_{17}H_{11}ClNO_2S]^+$, 404 (4) $[SnC_{16}H_{11}ClNS]^+$, 328 (18) $[C_{17}H_{11}ClNO_2S]^+$, 311 (100) $[C_{17}H_{10}ClNOS]^+$, 276 (33) $[C_{17}H_{10}NOS]^+$, 249 (21) $[C_{16}H_9OS]^+$, 181 (33) $[C_9H_6SCl]^+$, 149 (50) $[C_9H_6Cl]^+$, 120 (15) $[Sn]^+$.

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