

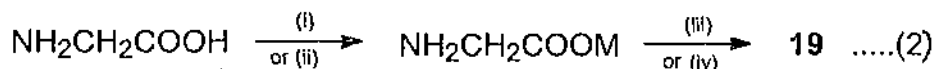
Chapter 2

Chapter 2

2. Results and Discussion

2.1 Syntheses of Potassium and/or Sodium 2-[[*(E)*-1-(2-hydroxyaryl)alkylidene]amino]acetate

The development of organotin(IV) carboxylate chemistry is highly dependent on a facile synthetic access to the ligands. The ligands used here are Schiff bases derived either from salicylaldehyde or *o*-hydroxyacetophenone with glycine. Among all reported methods, the route via alkali metal salt intermediate is found to be the most straightforward and is used for the preparation of organotin(IV) complexes. The key step in the whole preparation is the formation of alkali metal glycinate and subsequent condensation with either salicylaldehyde or *o*-hydroxyacetophenone as shown in reaction (2).



i: MOH; ii: MHCO₃; iii: Salicylaldehyde; iv: *o*-hydroxyacetophenone,
M = K or Na

19 was first obtained as a yellow liquid after condensation; upon concentration and cooling it slowly solidified to give the crystalline form of **19**, which largely simplified the purification of the product. Generally, the yields were > 60%. However, other synthetic methods were also tried to obtain free acid which either failed to give desired product in analytically pure form or could not be isolated from the reaction mixture. The various potassium or sodium salts, used for synthesizing the organotin(IV) complexes, are compiled in Table 1 along with their systematic name and abbreviation. **19** usually crystallizes as fine needles which are bright yellow in colour. They are soluble in water, MeOH, EtOH but insoluble in Et₂O, C₆H₆, CHCl₃, CH₂Cl₂ and CCl₄. In the melting point bath they decompose without melting sharply. No attempt was made to establish the constancy of their decomposition points through several recrystallizations. The crystalline product **19** was found to decompose after three days and hence freshly prepared products were used for synthesizing the organotin complexes.

Table 1: Potassium and Sodium Salts of 2-(((E)-1-(2-hydroxyaryl)alkylidene)amino)acetic acid and their Abbreviation

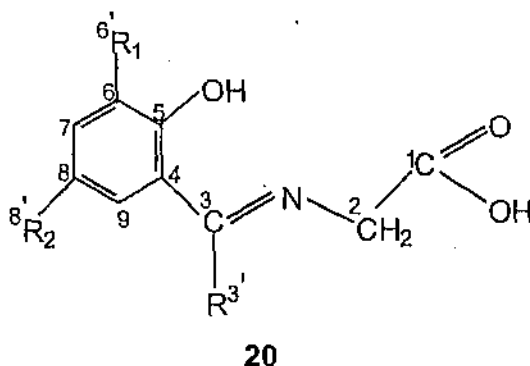
Ligand	Name	Abbreviation ^a
	Potassium 2-(((E)-1-(2-hydroxyphenyl)methylidene]amino)acetate	L ¹ HK
	Potassium 2-(((E)-1-(2-hydroxy-5-chlorophenyl)methylidene]amino)acetate	L ² HK
	Potassium 2-(((E)-1-(2-hydroxy-5-nitrophenyl)methylidene]amino)acetate	L ³ HK
	Potassium 2-(((E)-1-(2-hydroxyphenyl)ethylidene]amino)acetate	L ⁴ HK
	Sodium 2-(((E)-1-(2-hydroxyphenyl)ethylidene]amino)acetate	L ⁴ HNa
	Potassium 2-(((E)-1-(2-hydroxy-3-methylphenyl)ethylidene]amino)acetate	L ⁵ HK
	Potassium 2-(((E)-1-(2-hydroxy-5-methylphenyl)ethylidene]amino)acetate	L ⁶ HK
	Sodium 2-(((E)-1-(2-hydroxy-5-methylphenyl)ethylidene]amino)acetate	L ⁶ HNa

^a H refers to hydroxyl proton.

The synthetic details and characterization data for L^1HK-L^0HK , L^4HNa and L^0HNa are described in Chapter 4.

2.2 Triorganotin(IV) Complexes of 2-[[*E*]-1-(2-hydroxyaryl)alkylidene]amino}acetic Acid

It was discussed in Chapter 1 that the 2-[[*E*]-1-(2-hydroxyaryl)alkylidene]amino}acetic acid **20** (LHH', where H and H' denote the phenolic (-OH) and carboxyl (-COOH) protons,



respectively) are extremely efficient ligands. This class of Schiff bases form complexes with a wide variety of metals but the structural studies on organotin(IV) have only been sporadic [25-31].

In the present investigation, the bifunctional tridentate ligand forms three classes of organotin(IV) complexes, viz., (i) the triorganotin(IV) derivatives of the type R_3SnLH (ii) the diorganotin(IV) derivatives of the type $R_2SnL.nH_2O$ and (iii) the dinuclear organotin(IV) derivatives of the type $R_2SnL.R'_nSnCl_{4-n}$ ($R'=Ph$ or tBu and $n=2$ or 3). They are discussed separately in sequel.

2.2.1 Syntheses of Triorganotin(IV) Complexes, R_3SnLH ($R = Me, tBu$ or Ph)

Triorganotin(IV) complexes of 2-[[*E*]-1-(2-hydroxyaryl)alkylidene]amino}acetic acid **20** framework can be prepared in moderate yield by allowing stoichiometric amounts of R_3SnCl and potassium salts (LHM; Table 1) to react either in chloroform, benzene, methanol or a combination of these solvents. A typical reaction is shown below:



- 21: R = ⁿBu, L = L¹, 22: R = Ph, L = L¹
 23: R = Ph, L = L², 24: R = Me, L = L⁴
 25: R = ⁿBu, L = L⁴, 26: R = Ph, L = L⁴
 27: R = Me, L = L⁵, 28: R = Ph, L = L⁵
 29: R = ⁿBu, L = L⁶, 30: R = Ph, L = L⁶

The reaction can also be carried out in benzene at reflux temperature. Since LHM is insoluble, the reaction mixture turns out to be a heterogeneous system and hence prolonged reaction time is usually required for completion of the reaction and the yields were poor. A deposit of MCl was removed by filtration when CHCl₃ or benzene were used as solvents. In all other cases, the reaction mixture was evaporated to dryness and then extracted in CHCl₃ to remove MCl. The chloroform extract was concentrated to yield crude product which was washed thoroughly with petroleum ether and recrystallized using suitable solvents. In general, the solubility for the triphenyltin compounds was found to be 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. The exact synthetic methodology and reaction conditions for each of the complexes 21 - 30 are listed in Table 2 along with their characterization data.

Table 2: Characterization and Analytical Data for the Triorganotin(IV) Complexes

Complex ^a	Reaction time (h)	Crystallization solvent	Colour	Yield (%)	M.p. (°C)	Elemental analysis Found (calc.) (%)		
						C	H	N
Bu ₃ SnL ¹ H (21)	1 ^b	Chloroform	Yellow	70	Viscous liquid	54.15 (53.9)	7.26 (7.33)	3.09 (2.99)
Ph ₃ SnL ¹ H (22)	3 ^c	Chloroform	Yellow	71	156-157	61.20 (61.40)	4.35 (4.28)	2.68 (2.65)
Ph ₃ SnL ² H (23)	2 ^d	Chloroform	Yellow	42	146-148	57.50 (57.64)	3.83 (3.94)	2.60 (2.48)
Me ₃ SnL ⁴ H (24)	3 ^d	Methanol	Yellow	70	188-190	43.90 (43.86)	5.38 (5.38)	4.15 (3.93)
Bu ₃ SnL ⁴ H (25)	7 ^f	Chloroform+ petroleum ether	Yellow	50	110-112	54.39 (54.79)	7.80 (7.73)	2.84 (2.90)
Ph ₃ SnL ⁴ H (26)	3 ^e	Chloroform+ petroleum ether	Pale yellow	65	190-192	61.85 (62.03)	4.35 (4.64)	2.61 (2.58)
Me ₃ SnL ⁵ H (27)	3 ^d	Chloroform	Yellow	17	150-152	45.50 (45.44)	5.70 (5.72)	3.80 (3.78)
Ph ₃ SnL ⁵ H (28)	2 ^d	Chloroform	Yellow	40	127-128	62.68 (62.60)	4.93 (4.89)	2.48 (2.51)
Bu ₃ SnL ⁶ H (29)	3 ^d	Chloroform	Yellow	74	122-124	55.85 (55.67)	7.90 (7.92)	2.98 (2.82)
Ph ₃ SnL ⁶ H (30)	2 ^d	Chloroform	Yellow	60	182-184	62.48 (62.62)	4.87 (4.89)	2.37 (2.51)

^aComplex numbers in parentheses. In all the cases LHK was used except for 29 where LHN_a was used.

^bMethod: stirring in chloroform. ^cMethod: reflux in methanol-benzene mixture(1:1). ^dMethod: stirring in methanol. ^eMethod: reflux in methanol. ^fMethod: reflux in benzene.

Attempts to prepare the triorganotin complexes by the reaction of $(R_3Sn)_2O$, glycine and the appropriate salicylaldehyde or o-hydroxyacetophenone invariably resulted a complex mixture which could not be separated.

2.2.2 Spectroscopic Characterization of Triorganotin(IV) Complexes

Compounds 21-30 have been characterized by IR, multinuclear NMR, ^{119}Sn Mössbauer and X-ray diffraction techniques.

The 1H , ^{13}C and ^{119}Sn NMR data of the triorganotin(IV) complexes are listed in Table 3 and 4, respectively.

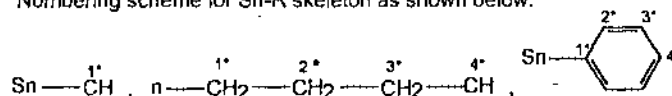
Table 3: 1H Chemical Shifts(δ , ppm)^a for the Triorganotin(IV) Complexes

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'	H-1*	H-2*	H-3*	H-4*
21	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
22	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
23	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
24	4.19, s	nd	6.89, d	7.44, t	6.87, t	7.75, d	2.63, s	-	-	0.42, s (63)	-	-	-
25	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
26	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
27	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)	-	-	-
28	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
29	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
30	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

^aSolvents: Saturated DMSO- d_6 solutions were used for complexes 24 & 26 while others were in $CDCl_3$.

^bRefer to structure 20 for numbering scheme.

^cNumbering scheme for Sn-R skeleton as shown below:



nd not detected.

Table 4: $^{13}\text{C}^{\text{a}}$ and $^{119}\text{Sn}^{\text{b}}$ Chemical Shifts (δ , ppm) for the Triorganotin(IV) Complexes

Complex	Ligand skeleton												Sn-R skeleton			
	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-3'	C-6'	C-8'	C-1*	C-2*	C-3*	C-4*
21	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
22	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
23	174.6	59.7	166.7	119.4	159.8	118.7	132.4	-	130.6	-	-	-	137.3	136.8	129.0	130.4
24	170.6	49.9	170.0	116.8	163.3	116.9	130.6	114.1	126.6	12.8	-	-	-1.71	-	-	-
25	173.8	51.6	172.7	119.4	163.7	118.7	132.4	116.9	128.0	14.8	-	-	16.6	27.7	26.9	13.6
26	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
27	173.9	51.5	172.8	118.4	162.4	127.6	133.3	116.2	125.7	16.1	15.1	-	-1.95	-	-	-
28	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
29	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
30	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

^a For numbering scheme of the ligand and Sn-R skeletons refer to structure 20 and Table 3, respectively. Coupling constants, $^nJ(^{13}\text{C}-^{119}\text{Sn})$ (Hz); For trimethyltin complexes 24 & 27: $^1J = 258$ and 200; for tributyltin complexes: $^2J = 21$, $^3J = 65$ whereas 1J and 4J could not be detected; for triphenyltin complexes: $^2J = 50$, $^3J = 64$ whereas 1J and 4J could not be detected.

^b δ (^{119}Sn) in CDCl_3 : (i) trimethyltin complexes: 24 and 27 are 134.5 and 134.7 ppm, respectively, (ii) tributyltin complexes: 21, 25 and 29 are 126.8, 121.9 and 123.9 ppm, respectively (iii) triphenyltin complexes: 26 and 28 is - 95.8 ppm.

The ^1H and ^{13}C chemical shift assignments of the triorganotin moiety are straightforward from the multiplicity patterns and/or resonance intensities [32] whereas the ligand skeletons were assigned by the multiplicity pattern and/or resonance intensities of the signals and also by the standard distortionless enhancement by polarization transfer (DEPT) experiments [33]. 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 comparison 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 $^1J(^{13}\text{C}-^{119/117}\text{Sn})$ coupling satellites in solutions owing to the solubility problem. The ^{13}C chemical shift of the *ipso*-carbon of the Sn-Ph₃ moiety is around 138 ppm in CDCl₃ solution which is typical for a tetrahedral tin atom [34]. Five-coordinated triphenyltin carboxylates have a value approximately 4 ppm higher in frequency such as is found for complex **26** 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 CDCl₃ solution. These are listed in Table 4. The triorganotin complexes exhibit a single sharp resonance at around 134 ppm for R = Me; **24** & **27**; between 121.9 and 126.8 for R = Bu; **21**, **25** & **29**, and at around -95.8 ppm for R = Ph; **26** & **28**. These are consistent with the range expected for tetrahedral triorganotin compounds [32, 35]. 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.

The solid-state IR spectra of the complexes are listed in Table 5. The complexes all display a band near 1650 cm⁻¹ which is assigned to the $\nu(\text{OCO})_{\text{asym}}$ vibration. In LHNa or LHK, this vibration appears at 1618 cm⁻¹ and 1628 cm⁻¹, respectively. The shift of this $\nu(\text{OCO})_{\text{asym}}$ band to higher wavenumber in the complexes is reported to be diagnostic of bonding between the carbonyl oxygen atom of the ligand and the triorganotin group [33]. Absorption bands believed due to the $\nu(\text{OCO})_{\text{sym}}$ stretch have been assigned since the magnitude of the $\nu(\text{OCO})_{\text{asym}} - \nu(\text{OCO})_{\text{sym}}$ (i.e. $\Delta\nu$) separation is of interest. The observed values of $\Delta\nu$, which are in the range 281 - 327 cm⁻¹,

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Table 5: Characteristic IR Bands (cm^{-1}) for the Triorganotin(IV) Complexes

Complex	$\nu(\text{OCO})_{\text{asym}}$	$\nu(\text{OCO})_{\text{sym}}$	$\Delta\nu$	$\nu(\text{Ph}(\text{C}-\text{O}))$	$\nu(\text{C}=\text{N})$
21	1648	1373	275	1259	1599
22	1644	1335	309	1257	1604
23	1643	1347	296	1265	1611
24	1649	1357	292	1261	1606
25	1650	1327	323	1260	1604
26	1651	1320	325	1259	1603
27	1649	1357	292	1261	1606
28	1630	1326	304	1260	1600
29	1650	1330	320	1269	1615
30	1630	1330	300	1258	1607

indicate a unidentate bonding mode for the carboxylate moiety [26]. For a bridging or chelating carboxylate group, $\Delta\nu$ would be expected to be $<150 \text{ cm}^{-1}$ [36], as widely observed in the infrared spectra of triorganotin carboxylates [37]. This suggests that the phenolic group occupies the fifth coordination site at the tin atom [38]. This is further substantiated by the broad IR absorptions in the region $3600\text{-}3400 \text{ cm}^{-1}$ which are reported to be due to intramolecular hydrogen bonding between the phenolic proton and the azomethine nitrogen [39]. Such intramolecular hydrogen bonding would increase the likelihood of coordination by the phenolic oxygen to the tin atom which is also reflected in the $\nu(\text{Ph}(\text{C}-\text{O}))$ vibration (see Table 5). Bands due to $\nu(\text{C}=\text{N})$ 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 **22** and **24**.

In order to obtain further structural evidence, the Mössbauer spectra of the representative complexes were recorded in the solid state (Table 6).

Table 6: ^{119}Sn Mössbauer (mm s^{-1}) Data for the Representative Triorganotin(IV) Complexes

Complex	Mössbauer data ^a			
	δ	Δ	Γ_1	Γ_2
22	1.23	2.98	0.90	0.91
23	1.18	3.03	0.92	0.97
24	1.23	3.35	0.92	0.91
26	1.23	3.02	0.91	0.91
27	1.12	3.08	0.92	0.96

^aParameters: Δ : Quadrupole splitting; δ : Isomer shifts and Γ_1 & Γ_2 : Line widths.

The isomer shift δ values which lie in the range $1.12\text{-}1.23 \text{ mm s}^{-1}$, are typical of quadrivalent organotin derivatives [40]. 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 all display a characteristic doublet absorption, indicating a single tin site. The quadrupole splitting Δ values of complexes are in the range $2.98 - 3.35 \text{ mm s}^{-1}$. Values of Δ in the range $3.0\text{-}4.1 \text{ mm s}^{-1}$ are typical for structures with a planar SnR_3 unit and two apical oxygens [40]. A similar range of values were also found in the triorganotin derivatives of amino acids with a *trans*- trigonal bipyramidal geometry [41]. The full width of half maximum (Γ_{\pm}) of these resonance absorptions are approximately 0.94 mm s^{-1} , further suggesting the presence of a single tin atom site in the structure.

2.2.3 X-ray Structures for $\text{Ph}_3\text{SnL}^1\text{H}$ (22) and $\text{Me}_3\text{SnL}^4\text{H}$ (24)

The atomic numbering scheme and the coordination around the tin atom for the complexes **22** and **24** are illustrated in Figs.1 and 3 while the packing in the unit cells are shown in Figs. 2 and 4, respectively. Selected bond lengths and bond angles are listed in Tables 7 and 8.

The triphenyltin compound **22** crystallizes in the space group $P2_1/n$ whereas the trimethyltin compound **24** adopts the $P2_1/c$ one. Both compounds exhibit the same polymeric structural motif, namely one in which the tin is five-coordinate with the three R-

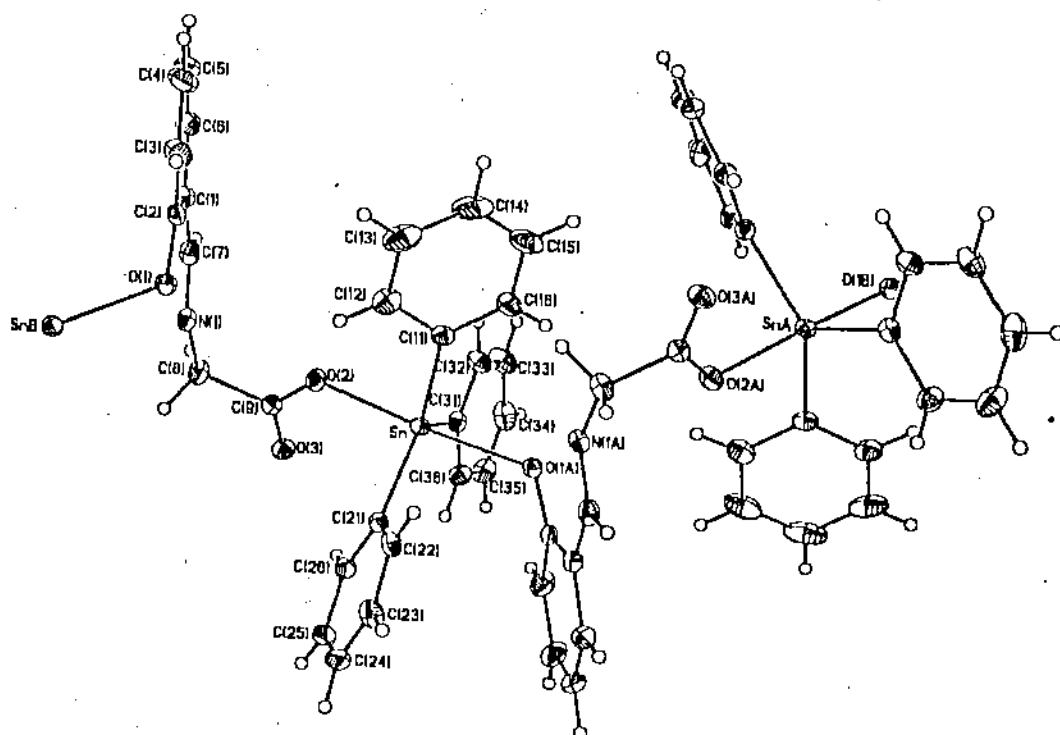


Fig. 1. Molecular structure for Ph_3SnL^1 (22)

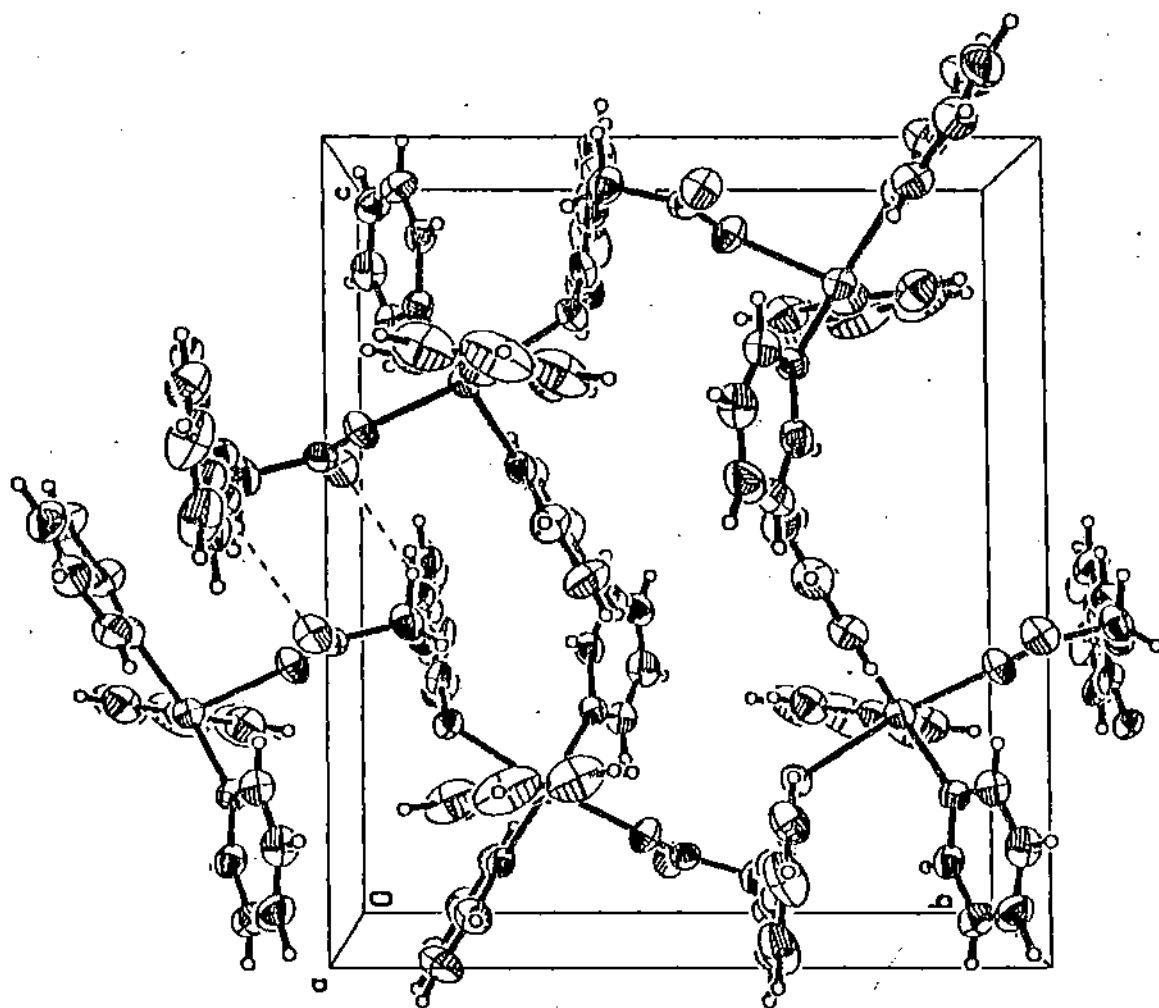


Fig. 2. The Unit cell contents for Ph_3SnL^1 (22)

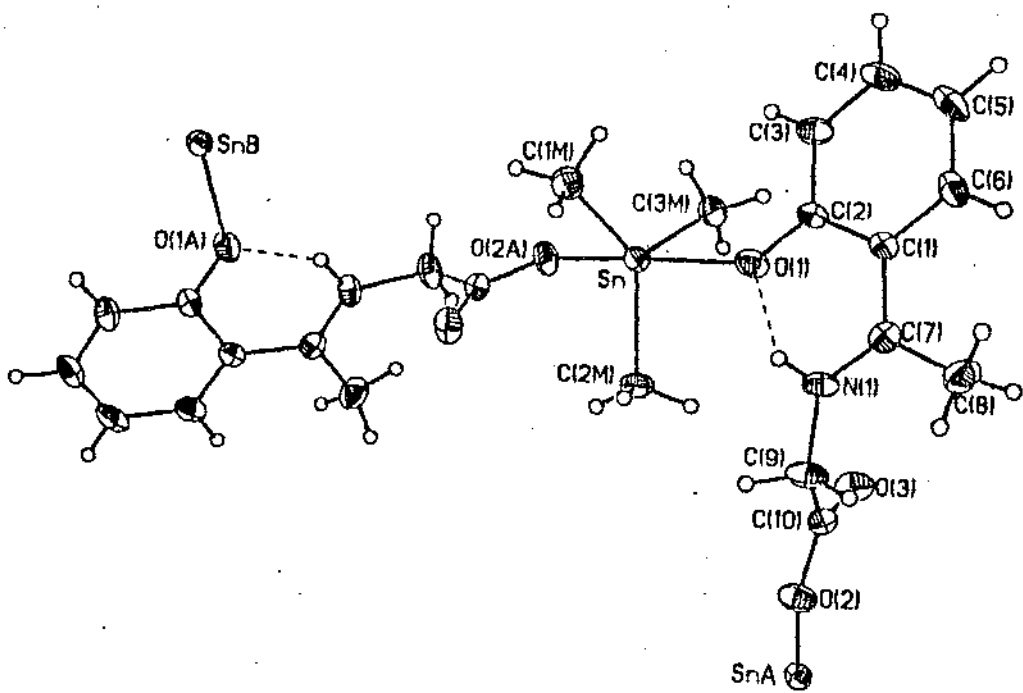


Fig. 3. Molecular structure for Me_3SnL^4 (24)

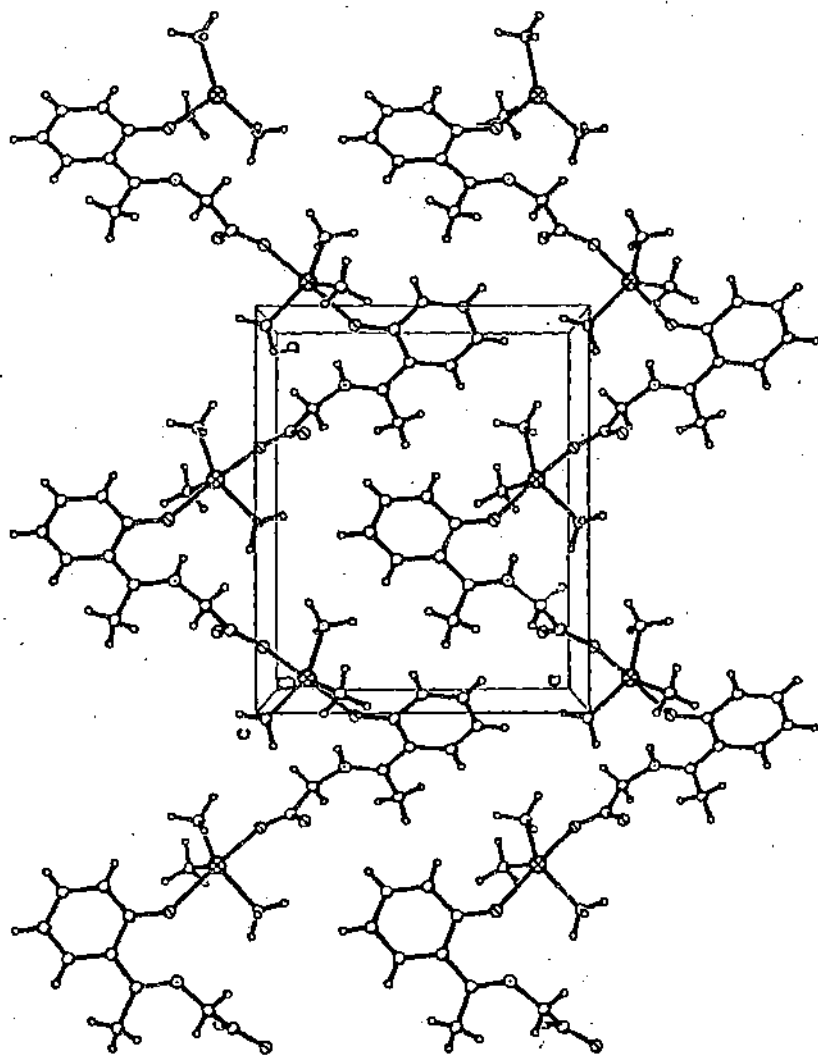


Fig. 4. The Unit cell contents for Me_3SnL^4 (24)

Table 7: Selected Bond Lengths (Å) and Bond Angles (°) for Ph₃SnL¹H (22)

Atoms	Distance	Atoms	Distance
Sn-C(31)	2.124(4)	Sn-C(21)	2.129(4)
Sn-C(11)	2.132(4)	Sn-O(2)	2.165(2)
Sn-O(1)#1	2.357(2)	O(1)-C(2)	1.312(4)
O(1)-Sn#2	2.357(2)	O(2)-C(9)	1.281(4)
O(3)-C(9)	1.226(4)	N(1)-C(7)	1.297(5)
N(1)-C(8)	1.456(5)	C(1)-C(6)	1.404(6)
C(1)-C(7)	1.432(6)	C(1)-C(2)	1.433(5)
C(2)-C(3)	1.400(5)	C(3)-C(4)	1.374(6)
C(4)-C(5)	1.393(8)	C(5)-C(6)	1.352(7)
C(8)-C(9)	1.516(5)	C(11)-C(16)	1.384(6)
C(11)-C(12)	1.402(6)	C(12)-C(13)	1.383(6)
C(13)-C(14)	1.380(9)	C(14)-C(15)	1.370(9)
C(15)-C(16)	1.385(7)	C(21)-C(26)	1.395(5)
C(21)-C(22)	1.399(5)	C(22)-C(23)	1.381(6)
C(23)-C(24)	1.392(6)	C(24)-C(25)	1.372(6)
C(25)-C(26)	1.386(5)	C(31)-C(36)	1.386(5)
C(31)-C(32)	1.400(6)	C(32)-C(33)	1.391(6)
C(33)-C(34)	1.371(7)	C(34)-C(35)	1.363(7)
C(35)-C(36)	1.380(6)		
Atoms	Angle	Atoms	Angle
C(31)-Sn-C(21)	119.69(14)	C(31)-Sn-C(11)	115.37(15)
C(21)-Sn-C(11)	124.05(14)	C(31)-Sn-O(2)	99.36(12)
C(21)-Sn-O(2)	93.63(12)	C(11)-Sn-O(2)	86.62(12)
C(31)-Sn-O(1)#1	91.66(11)	C(21)-Sn-O(1)#1	85.84(12)
C(11)-Sn-O(1)#1	83.41(12)	O(2)-Sn-O(1)#1	167.55(9)
C(2)-O(1)-Sn#2	123.9(2)	C(9)-O(2)-Sn	124.0(2)
C(7)-N(1)-C(8)	123.4(3)	C(6)-C(1)-C(7)	119.2(4)
C(6)-C(1)-C(2)	120.0(4)	C(7)-C(1)-C(2)	120.8(3)
O(1)-C(2)-C(3)	122.9(4)	O(1)-C(2)-C(1)	120.9(3)
C(3)-C(2)-C(1)	118.2(4)	C(4)-C(3)-C(2)	122.0(5)
C(3)-C(4)-C(5)	120.9(5)	C(6)-C(5)-C(4)	191.1(5)
C(5)-C(6)-C(1)	121.7(5)	N(1)-C(7)-C(1)	123.8(4)
N(1)-C(8)-C(9)	113.3(3)	O(3)-C(9)-O(2)	126.4(4)
O(3)-C(9)-C(8)	118.2(3)	O(2)-C(9)-C(8)	115.4(3)
C(16)-C(11)-C(12)	117.8(4)	C(16)-C(11)-Sn	121.4(3)
C(12)-C(11)-Sn	120.8(3)	C(13)-C(12)-C(11)	120.4(5)
C(14)-C(13)-C(12)	120.1(6)	C(15)-C(14)-C(13)	120.6(5)
C(14)-C(15)-C(16)	119.2(6)	C(11)-C(16)-C(15)	121.9(5)
C(26)-C(21)-C(22)	117.8(3)	C(26)-C(21)-Sn	123.2(3)
C(22)-C(21)-Sn	118.8(3)	C(23)-C(22)-C(21)	121.2(4)
C(22)-C(23)-C(24)	120.0(4)	C(25)-C(24)-C(23)	119.5(4)
C(24)-C(25)-C(26)	120.8(4)	C(25)-C(26)-C(21)	120.7(4)
C(36)-C(31)-C(32)	117.8(4)	C(36)-C(31)-Sn	121.9(3)
C(32)-C(31)-Sn	120.3(3)	C(33)-C(32)-C(31)	120.2(4)
C(34)-C(33)-C(32)	120.1(5)	C(35)-C(34)-C(33)	120.5(5)
C(34)-C(35)-C(36)	119.8(4)	C(35)-C(36)-C(31)	121.6(4)

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.

Table 8: Selected Bond Lengths (Å) and Bond Angles (°) for Me₃SnL¹H (24)

Atoms	Distance	Atoms	Distance
Sn-C(2M)	2.117(4)	Sn-C(3M)	2.120(3)
Sn-C(1M)	2.127(4)	Sn-O(2)#1	2.185(2)
Sn-O(1)	2.353(2)	O(1)-C(2)	1.304(4)
O(2)-C(10)	1.275(4)	O(2)-Sn#2	2.185(2)
O(3)-C(10)	1.213(3)	N(1)-C(7)	1.292(4)
N(1)-C(9)	1.447(4)	C(1)-C(6)	1.413(4)
C(1)-C(2)	1.434(4)	C(1)-C(7)	1.450(4)
C(2)-C(3)	1.408	C(3)-C(4)	1.376(5)
C(4)-C(5)	1.369(6)	C(5)-C(6)	1.377(6)
C(7)-C(8)	1.508(5)	C(9)-C(10)	1.525(4)
Atoms	Angles	Atoms	Angles
C(2M)-Sn-C(3M)	120.9(2)	C(2M)-Sn-C(1M)	118.6(2)
C(3M)-Sn-C(1M)	119.9(2)	C(2M)-Sn-O(2)#1	96.16(13)
C(3M)-Sn-O(2)#1	86.22(12)	C(1M)-Sn-O(2)#1	95.27(13)
C(2M)-Sn-O(1)	83.05(12)	C(3M)-Sn-O(1)	89.74(12)
C(1M)-Sn-O(1)	89.63(14)	O(2)#1-Sn-O(1)	174.76(9)
C(2)-O(1)-Sn	139.8(2)	C(10)-O(2)-Sn#2	123.9(2)
C(7)-N(1)-C(9)	129.4(3)	C(6)-C(1)-C(2)	118.4(3)
C(8)-C(1)-C(7)	120.3(3)	C(2)-C(1)-C(7)	121.3(3)
O(1)-C(2)-C(3)	121.8(3)	O(1)-C(2)-C(1)	120.6(3)
C(3)-C(2)-C(1)	117.5(3)	C(4)-C(3)-C(2)	121.9(4)
C(5)-C(4)-C(3)	120.7(3)	C(4)-C(5)-C(6)	119.8(3)
C(5)-C(6)-C(1)	121.7(4)	N(1)-C(7)-C(1)	118.1(3)
N(1)-C(7)-C(8)	119.6(3)	C(1)-C(7)-C(8)	122.2(3)
N(1)-C(9)-C(10)	111.9(2)	O(3)-C(10)-O(2)	127.(3)
O(3)-C(10)-C(9)	120.0(3)	O(2)-C(10)-C(9)	112.3(2)

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.

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(1A) of an 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 **22** is 359.11(14)°: [124.05(14)° + 115.37(15)° + 119.69(14)°] while the corresponding angles for **24** are 359.4(2)°: [120.9° + 119.9° + 118.6°]. These carbon-tin-carbon angles are comparable to those observed in triphenyltin *N*-salicylidene-6-aminohexanoate [42] and some other similar complexes [43]. The apical angle subtended at tin in **22** and **24** are 167.55(9)° and 174.76(9)°, respectively. The short tin-oxygen distances are Sn-O(2) = 2.165(2) Å [for **22**] and 2.185(2) Å [for **24**] and Sn-O(1A) = 2.357(2) Å [for **22**] and 2.353(2) Å [for **24**]. These values are well within the range of Sn-O bond distances usually observed for triorganotin carboxylates [44]. It is interesting to compare the phenolic oxygen-tin distances of 2.357(2) Å [for **22**] and 2.35(2) Å [for **24**], observed here, with that of 3.04 Å for triphenyltin salicylate [45], which

corresponds to a much weaker interaction, and the very similar value of 2.35 Å reported for triphenyltin *N*-salicylidene-6-aminohexanoate [42]. The short C=O distances of 1.226 (4) [for **22**] and 1.213(3) Å [for **24**] 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 $\text{Ph}_3\text{SnOCOCH}_2\text{CH}_2\text{NHCONH}_2$ (1.224(4) Å [46] and $\text{Ph}_3\text{SnOCOCMe=CHCON}(\text{CH}_2)_4$ (1.222(5) Å [47]. 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 [38, 48, 49]. 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 **22** and **24** shown in Figures 1 and 3.

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

2.3 Diorganotin(IV) Complexes of 2-(((*E*)-1-(2-hydroxyaryl)alkylidene)amino)acetic Acid

In Section 2.2 it is shown that the ligand **20** can bond to triorganotin in a fashion as shown in Figures 1 and 3. The triorganotin(IV) complexes adopt a polymeric $\text{trans-O}_2\text{SnR}_3$ 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 ligand coordinate in the zwitterionic form with the phenolic proton moved to the nearby nitrogen atom. The carboxylate group is unidentate.

In this Section, we describe herein the complexation behaviour of **20** towards diorganotin(IV) dihalides.

2.3.1 Syntheses of Diorganotin(IV) Complexes, $\text{R}_2\text{SnL}\cdot n\text{H}_2\text{O}$ (R = Me, Vin, ^tBu, Ph)

The diorganotin(IV) complexes can be prepared by reacting LHM with R_2SnCl_2 in equimolar ratio either in methanol or methanol-benzene mixture as shown below:



- | | |
|---|---|
| 31: R = Me, L = L ¹ | 32: R = ⁿ Bu, L = L ¹ |
| 33: R = Ph, L = L ¹ | 34: R = Me, L = L ² |
| 35: R = ⁿ Bu, L = L ² | 36: R = Ph, L = L ² |
| 37: R = Me, L = L ³ | 38: R = Ph, L = L ³ |
| 39: R = Me, L = L ⁴ | 40: R = ⁿ Bu, L = L ⁴ |
| 41: R = Ph, L = L ⁴ | 42: R = Vin, L = L ⁴ |
| 43: R = Ph, L = L ⁵ | 44: R = Me, L = L ⁶ |
| 45: R = Ph, L = L ⁶ | |

The completion of the reaction was monitored by ¹¹⁹Sn NMR spectroscopy. After the solvent was pumped off, the residue was extracted with chloroform and a precipitate of MCl was removed by filtration. The filtrate was concentrated to a suitable volume to yield crystals of R₂SnL.nH₂O. The complexes were characterized by elemental analyses which indicated to have compositions R₂SnL or R₂SnL.OH₂ [50]. The synthetic details and analytical results are compiled in Table 9.

Table 9: Characterization and Analytical Data for the Diorganotin(IV) Complexes

Complex ^a	Reaction Time (h)	Crystallization solvent	Colour	Yield (%)	M.p. (°C)	Elemental analysis Found (calc.) (%)		
						C	H	N
Me ₂ SnL ¹ .OH ₂ (31)	2 ^b	Chloroform + petroleum ether	Yellow	59	133-135	38.30 (38.41)	4.18 (4.40)	3.96 (4.07)
Bu ₂ SnL ¹ .OH ₂ (32)	3 ^c	Chloroform	Pale yellow	72	124-125	47.72 (47.70)	6.25 (6.36)	3.29 (3.23)
Ph ₂ SnL ¹ (33)	3 ^b	Chloroform	Yellow	70	190-191	56.00 (56.04)	3.78 (3.81)	3.29 (3.11)
Me ₂ SnL ² .OH ₂ (34)	2 ^b	Benzene + chloroform	Yellow	30	139-140	34.90 (34.92)	3.70 (3.73)	3.70 (3.70)
Bu ₂ SnL ² .OH ₂ (35)	3 ^b	Chloroform	Yellow	40	120-122	44.20 (44.14)	5.52 (5.67)	3.20 (3.30)
Ph ₂ SnL ² (36)	3 ^b	Chloroform	Yellow	45	130-132	52.15 (52.06)	3.42 (3.33)	2.95 (2.89)
Me ₂ SnL ³ .OH ₂ (37)	2 ^b	Chloroform (large volume)	Yellow	47	>250	33.90 (34.15)	3.20 (3.13)	7.30 (7.24)
Ph ₂ SnL ³ .OH ₂ (38)	3 ^b	Chloroform (large volume)	Yellow	26	226-228	49.22 (49.16)	3.44 (3.54)	5.50 (5.46)
Me ₂ SnL ⁴ .OH ₂ (39)	2 ^b	Chloroform	Yellow	53	210-211	40.30 (40.26)	4.80 (4.79)	3.90 (3.91)
Bu ₂ SnL ⁴ .OH ₂ (40)	3 ^c	Chloroform	Yellow	70	77-78	49.02 (48.90)	6.53 (6.61)	3.33 (3.17)
Ph ₂ SnL ⁴ (41)	3 ^b	Chloroform + methanol	Yellow	82	221-222	56.7 (56.9)	4.0 (4.1)	3.0 (3.0)
Vin ₂ SnL ⁴ .OH ₂ (42)	3 ^b	Benzene	Pale yellow	58	163-164	43.9 (44.0)	4.2 (4.5)	3.6 (3.7)
Ph ₂ SnL ⁵ (43)	3 ^b	Chloroform	Yellow	79	170-172	57.65 (57.78)	4.45 (4.43)	3.00 (2.83)
Me ₂ SnL ⁶ .OH ₂ (44)	2 ^b	Benzene	Pale yellow	54	138-140	42.05 (41.98)	5.15 (5.15)	3.80 (3.77)
Ph ₂ SnL ⁶ (45)	3 ^b	Chloroform	Yellow	79	236-237	57.70 (57.78)	4.40 (4.43)	2.90 (2.93)

^aComplex numbers in parentheses. ^bMethod: stirring in methanol. ^cMethod: reflux in Methanol-benzene mixture(1:1).

The compounds are yellow crystalline solids and have well defined melting points. In most cases, the crystals slowly lose the solvent of crystallization and become opaque. They are soluble in chloroform, dichloromethane, benzene, methanol, ethanol and insoluble in petroleum ether.

Attempts to synthesize $R_2SnL.nH_2O$ by reacting equimolar amounts of R_2SnO with either salicylaldehyde or *o*-hydroxyacetophenone and glycine in refluxing ethanol-benzene mixture were unsuccessful. After the reaction mixture was refluxed for 3 days, the system consisted of a pale yellow solution and red-brown powder. The liquid phase had a very little solid while the solid phase was hardly soluble, which prevented it from further characterization.

2.3.2 Spectroscopic Characterization of Diorganotin(IV) Complexes

A systematic investigation was undertaken to ascertain the structures of diorganotin(IV) complexes in the solid state by IR and ^{119}Sn Mössbauer spectroscopy. Attempts were also made to obtain single crystals for a range of samples but in most of the instances, the crystals turned opaque. However, a few complexes provided stable x-ray quality crystals to visualize the suspected molecular structures.

Diagnostically important IR bands and their assignments are presented in Table 10. The potassium salts of the ligands display two bands at around 1630 cm^{-1} and 1605 cm^{-1} that are assigned due to the $\nu(OCO)_{asym}$ and $\nu(C=N)$ stretching vibrations, respectively, in accord with earlier reports [33, 51, 52]. In diorganotin(IV) complexes, these vibrations are shifted considerably owing to coordination through the carboxyl oxygen and the imino nitrogen atoms [33]. The $\nu(OCO)_{sym}$ stretches have been detected and the magnitude of $\Delta\nu(OCO)$ is in the range $220\text{-}251\text{ cm}^{-1}$, indicate unidentate bonding through carboxylate moiety [26,51]. Coordination through the phenolic oxygen atom is reflected in the lower wavelength shifts of the $\nu(Ph-(CO))$ vibration when compared with the sodium or potassium salts [33]. A medium intensity band due to Sn-O has been detected at around 540 cm^{-1} in the complexes [53]. Thus, IR data provide reasonable evidence for complexation of the potentially multidentate ligand. However, this spectroscopy could not be utilized to detect the coordinated water molecule.

Table 10: Characteristic IR Bands (cm^{-1}) for the Diorganotin(IV) Complexes

Complex	$\nu(\text{OCO})_{\text{asym}}$	$\nu(\text{OCO})_{\text{sym}}$	$\Delta\nu$	$\nu(\text{Ph}(\text{C-O}))$	$\nu(\text{C=N})$
31	1617 ^a	1389	228	1266	1617 ^a
32	1622	1394	228	1249	1585
33	1684	1433	251	1214	1615
34	1604 ^a	1382	222	1241	1604 ^a
35	1612 ^a	1372	240	1239	1612 ^a
36	1682	1441	241	1238	1602
37	1627	1398	229	1245	1587
38	1679	1431	248	1226	1616
39	1595 ^a	1375	220	1235	1595 ^a
40	1612 ^a	1372	240	1239	1612 ^a
41	1682	1432	250	1238	1602
42	1658	1376	282	1240	1605
43	1686	1451	235	1233	1600
44	1593 ^a	1369	224	1226	1593 ^a
45	1679	1450	229	1226	1616

^avibrations due to both $\nu(\text{OCO})_{\text{asym}}$ and $\nu(\text{C=N})$ appeared as an unresolved broad peak.

Further evidence in support of structure is obtained from the ^{119}Sn Mössbauer spectra. The Mössbauer parameters are recorded in Table 11. The spectra of the complexes all display a characteristic doublet absorption, indicating a single tin site. The complexes show isomer shift δ values typical of quadrivalent organotin derivatives, similar in alkyl_2Sn (**32**, **37**, **39** and **40**) moieties and higher with respect to aryl_2Sn (**38** and **41**). The quadrupole splitting Δ values of complexes **32**, **37**, **38**, **39** and **40** are in the range $3.74 - 3.99 \text{ mm s}^{-1}$ in alkyl_2Sn and 3.61 mm s^{-1} in aryl_2Sn derivatives, suggesting a distorted *trans*- R_2Sn octahedral structures [40]. The C-Sn-C angles, calculated by Parish relation [54], vary from 141° to 170° . This further suggests that the water molecule occupy one of the equatorial plane. In contrast, complex **41** shows a lower Δ value, which agrees with a trigonal bipyramidal structure with a calculated C-Sn-C angle of 128° . Thus, Mössbauer results provide quite strong evidence in support of

structure. Further structural information on the complexes in the solid state have been obtained from the X-ray crystallography and are discussed in the Section 2.2.3.

Table 11: ^{119}Sn Mössbauer (mm s^{-1}) Data for the Representative Diorganotin(IV) Complexes

Complex	Mössbauer data ^a				C-Sn-C (°)
	δ	Δ	Γ_1	Γ_2	
32	1.33	3.79	0.92	0.92	141
37	1.29	3.99	0.95	0.92	170
38	1.16	3.61	1.0	1.0	159
39	1.21	3.74	0.90	0.92	154
40	1.40	3.87	0.95	0.98	143
41	1.15	2.88	0.89	0.98	128

^aParameters: Δ : Quadrupole splitting; δ : Isomer shifts and, Γ_1 & Γ_2 : Line widths.

The ^1H and ^{13}C NMR data of the diorganotin(IV) complexes are shown in Tables 12 and 13, respectively. The signals were assigned as described previously (See Section 2.2.2).

The ^1H and ^{13}C NMR spectra of the complexes show the expected resonances and integration.

The coordination behaviour of the complexes in solution was explored through their ^{119}Sn NMR spectra which are shown in Table 14. As discussed in Section 2.2.2 that in recording ^{119}Sn NMR in solution, non coordination solvents are preferable to coordinating ones to preclude possible changes in the coordination number of the tin atom. In present investigation, most of the complexes were found to be soluble in CDCl_3 except for complexes **34**, **37** and **38**, and hence they are excluded. The complexes all exhibit a sharp signal reflecting a single tin species in solution. The ^{119}Sn chemical shifts of dialkyltin(IV) complexes occur between -170 and -211 ppm, which fall well within the range proposed for penta-coordinate tin centers [55]. Thus, ^{119}Sn NMR results indicate that the hexa-coordinated structure of complexes in solid state (as revealed by Mössbauer spectroscopy, *vide supra*) is lost upon dissolution, indicating that a water molecule is not coordinated in solution. Diphenyltin complexes (**33**, **36**, **41**, **43** and **45**) show a sharp resonance between -335 and -352 ppm indicating a penta-coordinated tin structure in solution, which is consistent with our earlier report [33]. In conclusion, it is

suggested that in all the complexes, the tin atom is five coordinated in solution, irrespective of their different coordinations geometries in the solid state.

Table 12: ¹H Chemical Shifts (δ, ppm)^a for the Diorganotin(IV) Complexes

Complex	Ligand skeleton ^b						Sn-R skeleton ^b			
	H-2	H-6/6'	H-7	H-8/8'	H-9	H-3'	H-1*	H-2*	H-3*	H-4*
31	4.39, s	6.85, d	7.17, t	6.74, t	7.41, d	8.33, s	0.83, s (89) ^c	-	-	-
32	4.34, s	6.79, d	7.17, t	6.74, t	7.43, d	8.40, s	1.64, m	1.58, m	1.38, m	0.87, t
33	4.35, s	7.15, d	7.15, t	6.77, t	7.53, d	8.34, s	-	7.89, m	7.45, m	7.45, m
34	4.36, s	6.67, d	7.65, d	-	7.25, s	8.38, s	0.70, s (93) ^c	-	-	-
35	4.38, s	6.65, d	7.30, d	-	7.14, s	8.32, s	1.64, m	1.52, m	1.29, m	0.84, t
36	4.37, s	7.07, d	7.47, d	-	7.16, s	8.34, s	-	7.85, m	7.47, m	7.47, m
37	4.00, s	6.32, d	7.75, d	-	8.32, s	8.40, s	0.40, s (93) ^c	-	-	-
38	4.36, s	6.96, d	8.23, d	-	8.43, s	8.76, s	-	7.62, m	7.34, m	7.34, m
39	4.29, s	6.84, d	7.36, t	6.79, t	7.51, d	2.67, s	0.73, s (78) ^c	-	-	-
40	4.26, s	6.85, d	7.35, t	6.76, t	7.47, d	2.67, s	1.60, m	1.43, m	1.31, m	0.86, m
41	4.25, s	7.15, d	7.17, t	6.75, t	7.35, d	2.57, s	-	7.85, m	7.35, m	7.35, m
42	4.27, s	7.38, d	7.50, t	6.95, t	6.78, d	2.66, s	6.28, m	6.28, m	-	-
43	4.25, s	2.44, s	7.27, d	6.69, t	7.38, d	2.57, s	-	7.82, m	7.38, m	7.38, m
44	4.27, s	7.75, d	7.18, d	2.27, s	7.25, s	2.65, s	0.71, s (75) ^c	-	-	-
45	4.28, s	7.08, d	7.25, d	2.25, s	7.27, s	2.61, s	-	7.87, m	7.39, m	7.39, m

^a In CDCl₃ except for complexes 34, 37 and 38, which are in DMSO-*d*₆. ^b Refer to Table 3 numbering scheme. ^c ^J(¹H-¹¹⁹Sn) (Hz).

Table13: ^{13}C Chemical Shifts (δ , ppm)^a for the Diorganotin(IV) Complexes

Complex	Ligand skeleton ^b										Sn-R skeleton ^b			
	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-3'/6'/8'	C-1*	C-2*	C-3*	C-4*
31	172.5	57.9	172.3	117.7	168.1	122.9	137.2	117.5	135.3	-	0.09 (c)	-	-	-
32	172.9	57.7	171.4	117.3	169.5	122.7	138.0	117.2	135.6	-	26.7 (c)	26.8 (c)	22.6 (c)	13.7 (c)
33	173.0	57.0	170.4	117.1	169.4	122.8	138.3	117.8	135.6	-	137.6 (c)	136.4 (57)	128.9 (91)	130.8 (23)
34	171.7	56.6	170.1	119.3	165.1	122.9	135.0	119.2	132.4	-	0.70 (804)	-	-	-
35	171.2	58.1	171.2	117.6	167.7	124.5	137.2	121.0	133.4	-	26.1 (c)	27.0 (33)	21.1 (85)	13.5 (c)
36	172.1	57.3	170.2	117.6	167.9	124.6	138.2	122.1	133.7	-	137.3 (c)	136.4 (57)	129.7 (91)	131.0 (19)
37	171.5	56.5	170.4	135.5	170.0	121.6	131.6	115.3	129.1	-	0.20 (800)	-	-	-
38	173.0	56.8	170.4	146.0	170.0	124.8	132.8	117.5	130.4	-	137.3 (c)	134.9 (c)	129.3 (c)	130.4 (c)
39	181.7	53.3	170.4	121.1	165.7	123.5	135.9	117.9	130.5	22.9	0.08 (670)	-	-	-
40	181.4	53.5	170.7	121.1	166.1	123.5	135.8	117.6	130.3	22.9	26.7 (c)	26.9 (35)	21.0 (85)	13.5 (c)
41	182.1	53.5	170.2	120.3	166.4	123.7	136.3	117.8	130.7	22.7	137.6 (c)	136.6 (56.0)	128.8 (86)	130.5 (20.6)
42	182.7	53.3	170.3	120.6	166.2	123.5	136.0	117.9	130.5	22.8	135.0	139.5	-	-
43	182.5	53.6	170.7	128.7	164.8	119.5	136.7	117.5	131.6	23.1/ 16.9	137.9 (c)	136.5 (54)	128.9 (90)	130.7 (20)
44	181.5	53.2	170.3	126.9	163.5	123.2	137.2	120.6	129.8	22.8/ 20.5	0.30 (677)	-	-	-
45	181.9	53.5	170.3	128.2	164.4	123.6	136.7	119.9	130.2	22.7/ 20.5	137.7 (c)	136.7 (56)	128.8 (93)	130.6 (20)

^aRefer to Table 12 for solvent. ^bRefer to Table 3 for numbering scheme. ^cCould not be detected.

Table 14: ^{119}Sn NMR Data (δ , ppm) for the Diorganotin(IV) Complexes in CDCl_3

Complex	^{119}Sn
31	- 203.1
32	- 208.0
33	- 335.4
35	- 200.0
36	- 335.8
39	- 172.6
40	- 210.8
41	- 351.7
42	- 344.6
43	- 349.4
44	- 170.1
45	- 349.6

2.2.3 X-ray Structures for Ph_2SnL^4 (41), Ph_2SnL^6 (45) and $\text{Vin}_2\text{SnL}^4\cdot\text{OH}_2$ (42)

A full characterization of the complexes of the type R_2SnL were ascertained by the structural analysis in Ph_2SnL^4 (41) [33] and Ph_2SnL^6 (45) [56] while the complexes of the type $\text{R}_2\text{SnL}\cdot\text{OH}_2$ were confirmed by structural analysis in $\text{Vin}_2\text{SnL}^4\cdot\text{OH}_2$ (42) [33].

The compounds 41 and 45 crystallizes in the monoclinic space group $P2_1/c$ with $Z = 8$ and $P12_1/c1$ (No.14) with $Z = 4$, respectively. The molecular structures of 41 and 45 are shown in Figures 5 and 6 and selected interatomic parameters are collected in Tables 15 and 16, respectively. The compound 41 crystallizes with two independent molecules in the crystallographic asymmetric unit, labelled a and b, that do not differ from each other significantly. The structure is molecular with the closest intermolecular contact involving the non-hydrogen atoms of 3.382(8) Å occurring between O(2)b and C(2)b¹ (symmetry operation i: x, 0.5 - y, 0.5 + z). The coordination geometry about the tin atom is defined by two phenyl groups, an oxygen (O(1), derived from a unidentate

carboxylate group), a phenoxide O(3) atom, and the imino N(1) atom. Similar coordination, geometry has been found in related system [27]. The arrangement of the donor set is distorted trigonal bipyramidal with the two oxygen atoms defining the axial positions: O-Sn-O = 160.3(2)° for molecule a and 158.6(2)° for molecule b. Distortions from the ideal geometry may be traced to the restricted bite angles of the tridentate ligand. Neither of the five- or six- membered rings formed upon chelation are planar, as seen in the following torsion angles (value for molecule b follows in parentheses): Sn/O(1)/C(1)/C(2) = -0.2(8)° (10.5(8)°), Sn/N(1)/C(2)/C(1) = -19.7(7)° (-18.9(6)°, Sn/O(3)/C(5)/C(4) = 37.7 (8)° (42.1(7)°, and Sn/N(1)/C(3)/C(4) = 10.9(9)° (-1.6(8)°). The tin atom lies 0.0267(4) Å (0.0457 (5) Å) out of the NC₂ trigonal plane in the direction of the more tightly held O(3) atom. In addition to the differences between molecule a and b reflected in the above torsion angles, there are several minor differences in their derived interatomic parameters with the most significant of these being the Sn-O(3)-C(5) angle (Table 15). The geometry found about the tin atom in **41** is almost identical to that found about the Sn atom in **45**.

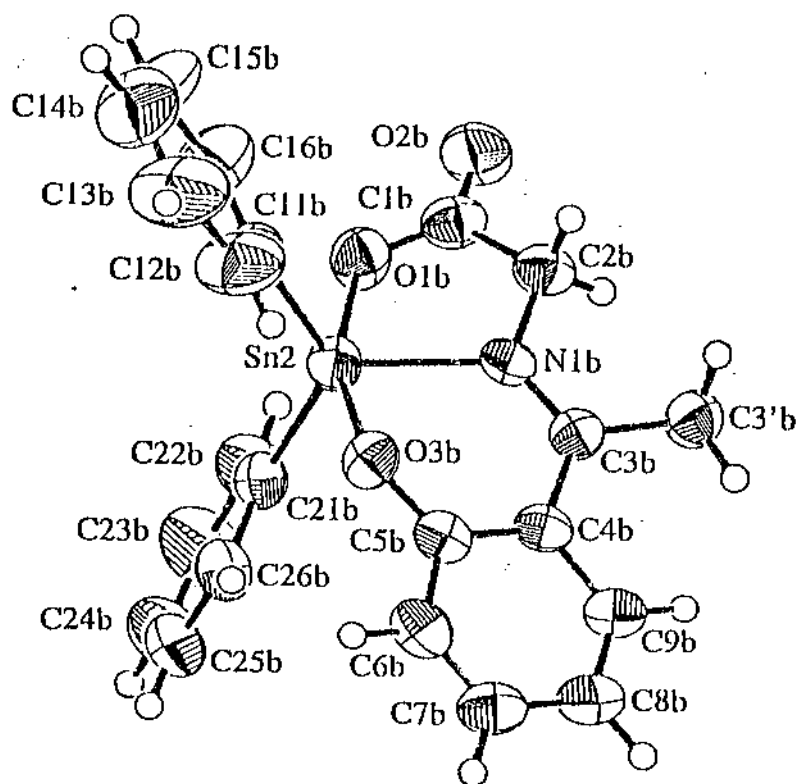
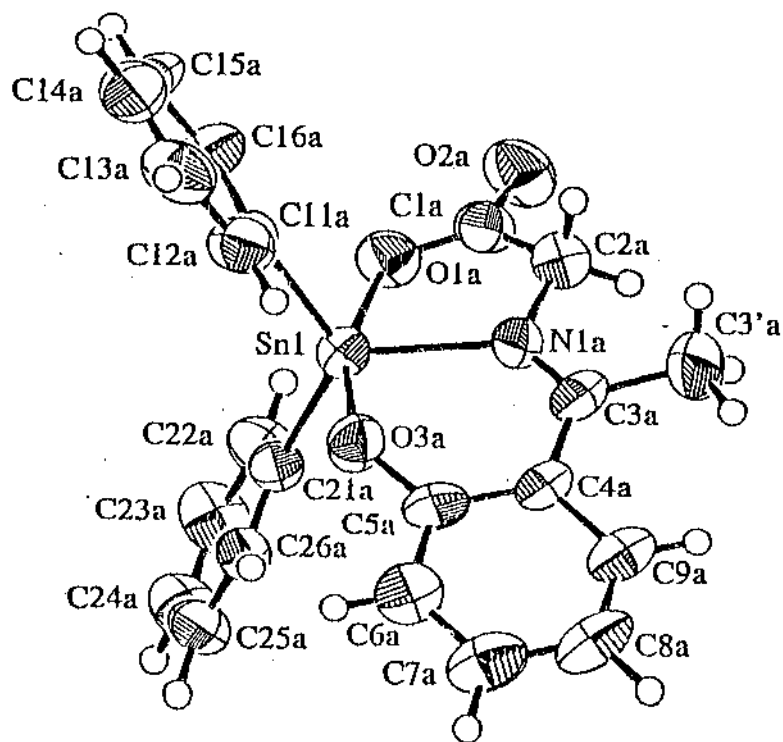


Fig. 5. Molecular structure for Ph_2SnL^4 (41)

**Table 15: Selected Bond Lengths (Å) and Bond Angles (°)
for Ph₂SnL⁴ (41)**

Atoms	Distance	Atoms	Distance
Sn(1) - O(1a)	2.127(4)	O(1a) - C(1a)	1.280(7)
Sn(1) - O(3a)	2.064(4)	O(1b) - C(1b)	1.276(8)
Sn(1) - N(1a)	2.190(5)	O(2a) - C(1a)	1.213(7)
Sn(1) - C(11a)	2.120(6)	O(2b) - C(1b)	1.217(7)
Sn(1) - C(21a)	2.138(6)	O(3a) - C(5a)	1.330(7)
Sn(2) - O(1b)	2.131(4)	O(3b) - C(5b)	1.322(7)
Sn(2) - O(3b)	2.059(4)	N(1a) - C(2a)	1.459(8)
Sn(2) - N(1b)	2.178(5)	N(1a) - C(3a)	1.285(7)
Sn(2) - C(11b)	2.102(7)	N(1b) - C(2b)	1.470(7)
Sn(2) - C(21b)	2.111(6)	N(1b) - C(3b)	1.299(7)
Atoms	Angle	Atoms	Angle
O(1a) - Sn(1) - O(3a)	160.3(2)	O(3b) - Sn(2) - C(21b)	96.5(2)
O(1a) - Sn(1) - N(1a)	77.2(2)	N(1b) - Sn(2) - C(11b)	120.2(2)
O(1a) - Sn(1) - C(11a)	96.0(2)	N(1b) - Sn(2) - C(21b)	113.4(2)
O(1a) - Sn(1) - C(21a)	93.6(2)	C(11b) - Sn(2) - C(21b)	126.2(2)
O(3a) - Sn(1) - N(1a)	83.1(2)	Sn(1) - O(1a) - C(1a)	118.8(4)
O(1a) - Sn(1) - C(11a)	92.3(2)	Sn(2) - O(1b) - C(1b)	118.6(4)
O(3a) - Sn(1) - O(21a)	95.8(2)	Sn(1) - O(3a) - C(5a)	126.7(4)
N(1a) - Sn(1) - C(11a)	113.5(2)	Sn(2) - O(3b) - C(5b)	123.1(4)
N(1a) - Sn(1) - C(21a)	120.5(2)	Sn(1) - N(1a) - N(1a)	111.5(4)
C(11a) - Sn(1) - C(21a)	126.0(2)	Sn(1) - N(1a) - C(3a)	128.2(5)
O(1b) - Sn(2) - O(3b)	158.6(2)	C(2a) - N(1a) - C(3a)	120.2(5)
O(1b) - Sn(2) - N(1b)	76.2(2)	Sn(2) - N(1b) - C(2b)	111.8(4)
O(1b) - Sn(2) - C(11b)	93.9(2)	Sn(2) - N(1b) - C(3b)	127.2(4)
O(1b) - Sn(2) - C(21b)	94.9(2)	C(2b) - N(1b) - C(3b)	120.9(5)
O(3b) - Sn(2) - N(1b)	82.6(2)	O(1a) - C(1a) - O(2a)	124.6(7)
O(3b) - Sn(2) - C(11a)	93.8(2)	O(1b) - C(1b) - O(2b)	125.4(6)

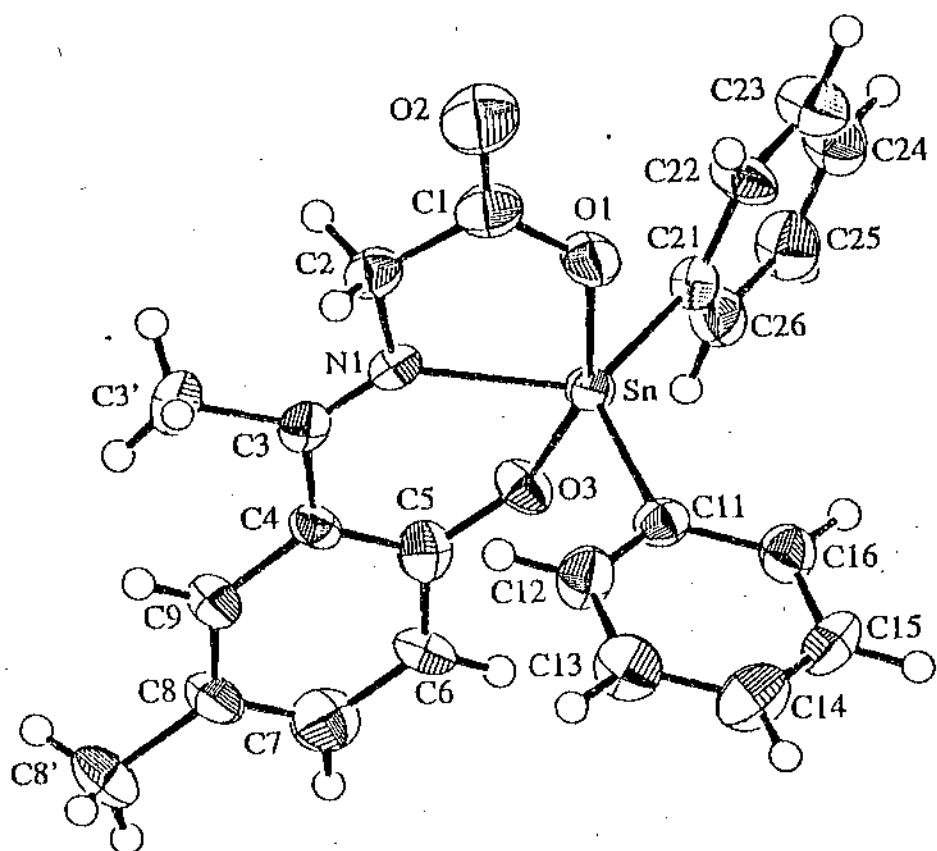


Fig. 6. Molecular structure for Ph_2SnL^6 (45)

Table 16: Selected Bond Lengths (Å) and Bond Angles (°) for Ph_2SnL^6 (45)

Atoms	Distance	Atoms	Distance
Sn-O(1)	2.122(3)	O(1)-C(1)	1.282(5)
Sn-O(3)	2.055(4)	O(2)-C(1)	1.195(7)
Sn-N(1)	2.195(3)	O(3)-C(5)	1.309(9)
Sn-C(11)	2.115(6)	N(1)-C(2)	1.473(6)
Sn-C(21)	2.115(7)	N(1)-C(3)	1.281(8)
Atoms	Angle	Atoms	Angle
O(1)-Sn-O(3)	157.7(1)	N(1)-Sn-C(21)	126.7(2)
O(1)-Sn-N(1)	77.0(1)	C(11)-Sn-C(21)	125.7(2)
O(1)-Sn-C(11)	94.1(2)	Sn-O(1)-C(1)	119.9(4)
O(1)-Sn-C(21)	90.9(2)	Sn-O(3)-C(5)	129.3(3)
O(3)-Sn-N(1)	83.2(1)	Sn-N(1)-C(2)	112.0(3)
O(3)-Sn-C(11)	101.5(2)	Sn-N(1)-C(3)	128.3(3)
O(3)-Sn-C(21)	92.8(2)	C(2)-N(1)-C(3)	119.6(4)
N(1)-Sn-C(11)	107.1(2)	O(1)-C(1)-O(2)	125.2(7)

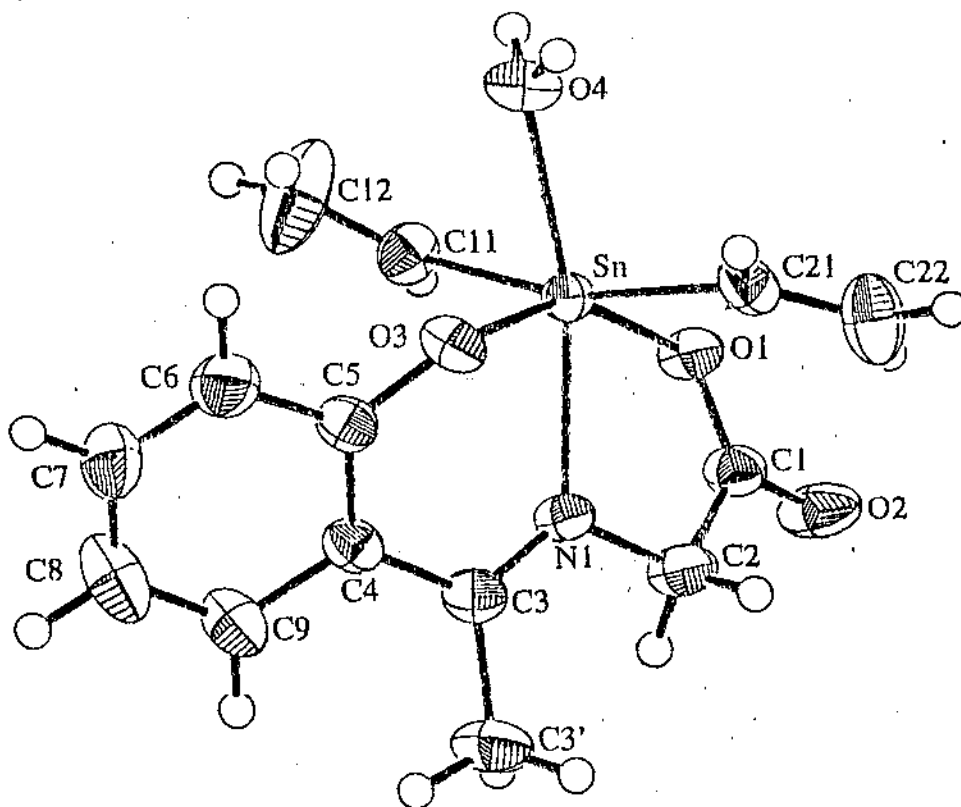


Fig. 7. Molecular structure for Vin_2SnL^4 (42)

Table 17: Selected Bond Lengths (Å) and Bond Angles (°) for Vin_2SnL^4 (42)

Atoms	Distance	Atoms	Distance
Sn-O(1)	2.249(4)	O(1)-C(1)	1.263(6)
Sn-O(3)	2.105(4)	O(2)-C(1)	1.234(6)
Sn-O(4)	2.358(4)	O(3)-C(5)	1.334(6)
Sn-N(1)	2.254(4)	N(1)-C(2)	1.468(7)
Sn-C(11)	2.101(5)	N(1)-C(3)	1.299(6)
Sn-(21)	2.100(5)		
Atoms	Angle	Atoms	Angle
O(1)-Sn-O(3)	152.4(1)	O(4)-Sn-C(21)	84.1(2)
O(1)-Sn-N(1)	72.8(1)	N(1)-Sn-C(21)	97.7(2)
O(1)-Sn-C(11)	86.3(2)	N(1)-Sn-C(11)	97.2(2)
O(3)-Sn-C(21)	90.0(2)	C(11)-Sn-C(21)	162.8(2)
O(3)-Sn-O(4)	79.9(0)	Sn-O(1)-C(21)	117.9(3)
O(3)-Sn-N(1)	79.6(1)	Sn-O(3)-C(1)	121.6(3)
O(3)-Sn-C(11)	99.2(2)	Sn-N(1)-C(5)	112.6(3)
O(4)-Sn-C(21)	91.8(2)	Sn-N(1)-C(2)	127.9(4)
O(4)-Sn-N(1)	158.7(1)	C(2)-N(1)-C(3)	119.5(4)
O(4)-Sn-C(11)	85.1(2)	O(1)-C(1)-O(2)	125.1(5)

The final structure is that of **42** ($R_2SnL.OH_2$ type), which was shown to be five-coordinate in solution (Section 2.3.2, see NMR discussion) but six-coordinate in the solid-state owing to the coordination of a water molecule. The molecular structure of the complex **42** (crystallizes with space group $P1$ and $Z = 2$) is shown in Figure 7 and selected interatomic parameters are listed in Table 17. The geometry is distorted octahedral with the two vinyl groups occupying *trans* positions ($C-Sn-C = 162.8(2)^\circ$) above and below a NO_3 equatorial plane. Similar coordination geometries to those seen in **42** have been found in some related 2,6-pyridinedicarboxylate [57,58] and *N*-methyliminodiacetate [58] structures, however, in these structures, association (2.5 - 2.8 Å) via one of the carboxylate oxygen atoms leads to the formation of centrosymmetric dimers featuring central Sn_2O_2 cores. In **42**, the closest $Sn-O(1)'$ intermolecular contact is 3.319(4) Å (symmetry operation $i: 1-x, 1-y, 1-z$).

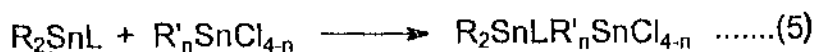
Thus, X-ray results confirm the formulation of both types of complexes (R_2SnL and $R_2SnL.OH_2$) in the solid state. This has also been reflected in ^{119}Sn Mössbauer results. ^{119}Sn NMR results indicated that $R_2SnL.OH_2$ type complexes dissociate in non-coordinating solvent giving rise to a five-coordinate tin similar to that observed for R_2SnL type complexes.

2.4 Dinuclear Organotin(IV) Complexes of 2-(((*E*)-1-(2-hydroxyaryl)alkylidene)amino)acetic acid

In earlier Sections 2.2 and 2.3, we have shown the coordination behaviour of 2-(((*E*)-1-(2-hydroxyaryl)alkylidene)amino)acetic acid **20** towards triorganotin(IV) and diorganotin(IV). Their structures have been investigated in solid state and in solution, we describe herein the formation of dinuclear organotin(IV) complexes derived from **20**.

2.4.1 Syntheses of Dinuclear Organotin(IV) Complexes, $R_2SnL.R'_nSnCl_{4-n}$ ($R=Ph$ or tBu and $n=2$ or 3)

Reaction of the diorganotin(IV) complexes (R_2SnL , refer to Chapter 2.3) with R'_nSnCl_{4-n} in benzene at reflux temperature result in the smooth formation of dinuclear molecular adduct of composition $R_2SnL.R'_nSnCl_{4-n}$ which can be isolated as yellow crystalline solid in good yield.



46:R = Ph, n = 3

47:R = ^tBu, n = 2

The synthetic and analytical data are listed in Table 18.

Table 18: Characterization and Analytical Data for the Dinuclear Organotin(IV) Complexes

Complex ^a	Reaction time (h)	Crystallization solvent	Colour	Yield (%)	M.p. (°C)	Elemental analysis Found (calc.) (%)		
						C	H	N
Ph ₂ SnL ^a .SnPh ₃ Cl (46)	2 ^b	Chloroform	Yellow	65	199-200	56.5 (56.6)	4.0 (4.0)	1.5 (1.7)
^t Bu ₂ SnL ^a . ^t Bu ₂ SnCl ₂ (47)	2 ^c	Chloroform	Yellow	55	132-133	42.8 (42.9)	6.2 (6.2)	1.9 (1.9)

^aComplex numbers in parentheses. ^bMethod: reflux in benzene. ^cMethod: stirring in methanol.

Diorganotin(IV) complex of composition R₂SnL can readily be reacted with R₂SnCl₂ to obtain dinuclear complex containing R₂Sn/R₂Sn species. There is no report in the extant literature of any metal complex having been isolated and characterized apart from a very recent examples [31]. Similarly, diorganotin(IV) compound **41** undergoes an unprecedented adduct formation with Ph₃SnCl to produce **46** which possesses a diorganotin(IV) and a triorganotin(IV) moiety connected via a carbonyl oxygen. The examples of such donor-acceptor complexes are rare. The complexes are stable in air and highly soluble in most common organic solvents.

2.4.2 Spectroscopic Characterization of Dinuclear Organotin(IV) Complexes

In the solid-state IR spectrum of **41**, the ν(OCO)_{asym} band at 1682 cm⁻¹ has found to be shifted in **46** and appears at 1627 cm⁻¹. The shift of the ν(OCO)_{asym} band at ca. 55 cm⁻¹ to a lower wavenumbers in **46** confirms the interaction of Ph₃SnCl with the carbonyl

Table 19: Characteristic IR Bands (cm⁻¹) for the Dinuclear Organotin(IV) Complexes

Complex	ν(OCO) _{asym}	ν(OCO) _{sym}	ν(Ph(C-O))	ν(C=N)
46	1627	1432	1236	1603
47	1681	1436	1237	1603

oxygen atom of complex **41** (Table 19). In contrast to this, in compound **47** exhibits no shift of $\nu(\text{OCO})_{\text{asym}}$ band although such carbonyl oxygen \rightarrow Sn coordination is indicated in X-ray structure (see Section 2.4.3) [33]. The extent of shifts could be attributed to the donor-acceptor properties.

The ^{119}Sn Mössbauer spectrum of **46** (Fig.8) shows asymmetric absorption with large values of full-width at half height, and was fitted as two doublets with different

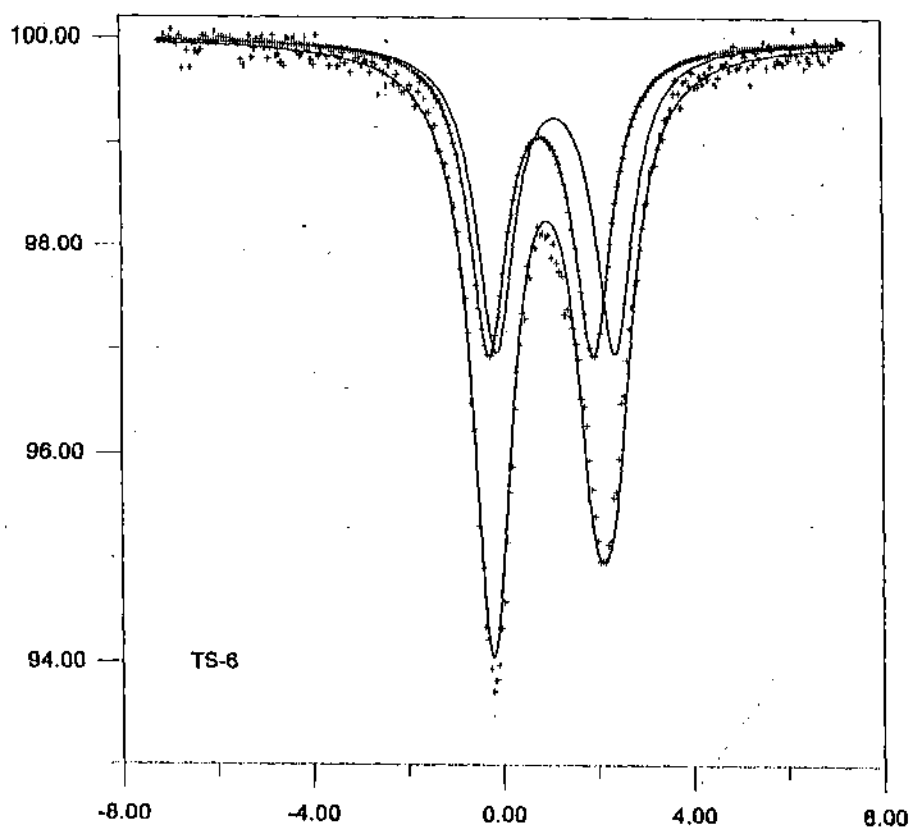


Fig. 8. ^{119}Sn Mössbauer spectrum for $\text{Ph}_2\text{SnL}^4 \cdot \text{Ph}_3\text{SnCl}$ (**46**)

parameter values; hence the occurrence of two different tin sites can be inferred [50]. The Mössbauer parameters are listed in Table 20.

Table 20: ^{119}Sn Mössbauer (mm s^{-1}) Data for $\text{Ph}_2\text{SnL}^4\cdot\text{Ph}_3\text{SnCl}$ (**46**)

Complex	δ		Δ		Mössbauer data ^a		C-Sn-C (°)
	δ_1	δ_2	Δ_1	Δ_2	Γ_1	Γ_2	
46	0.75		2.20		1.00	1.00	107
	1.14		2.50		0.86	0.86	

^aParameters: Δ : Quadrupole splitting; δ : isomer shifts and Γ_1 & Γ_2 : Line widths.

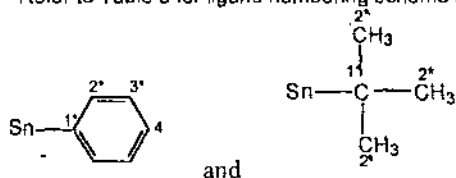
A doublet shows a Δ value (2.20 mm s^{-1}) that can be set as the lowest in *cis*- R_2Sn trigonal bipyramidal derivatives [40]. This $\text{Ph}_2\text{Sn-O}_2\text{N}$ trigonal bipyramidal geometry matches with the X-ray structure (*vide infra*) except for the C-Sn-C calculated angle; the corresponding δ value is also low, and this can arise from the electron withdrawal of the ligands to the tin. The second doublet can be attributed to a Ph_3Sn moiety in a trigonal bipyramidal geometry, with the oxygen and chlorine atoms as axial ligands. The percentage areas of the two doublets are similar, indicating equal amounts of di- and tri-organotin moieties.

Compounds **46** and **47** were characterized by ^1H and ^{13}C NMR (Table 21). The ^1H and ^{13}C NMR spectra of the complexes show the expected resonances and integration. ^{119}Sn NMR spectroscopy has been utilized to probe the solution-state structures in order to ascertain whether the observed association in the solid-state persisted in solution (Table 22). Compound **46** gives two ^{119}Sn resonances of almost equal intensity (-49.9 ppm and -351.4 ppm) in CH_2Cl_2 solution. The signal at -351.4 ppm is assigned to the five-coordinate tin center in the Ph_2SnL^4 core (refer to Section 2.3.2) and the resonance at -49.9 ppm is assigned to the Ph_3SnCl moiety (*cf* -47.0 ppm for Ph_3SnCl in CH_2Cl_2 solution). A similar spectrum was obtained when equimolar amounts of Ph_2SnL^4 (**41**) and Ph_3SnCl were mixed in the same solvent, which indicates that compound **46** completely dissociates into **41** and Ph_3SnCl under these conditions.

Table 21: ^1H and ^{13}C NMR Data (δ , ppm) for the Dinuclear Organotin(IV) Complexes

Proton/ Carbon No. ^a	46		47	
	^1H	^{13}C	^1H	^{13}C
1	-	182.0	-	181.2
2	4.24, s	53.6	4.25, s	53.9
3	-	170.2	-	170.9
4	-	120.4	-	120.8
5	-	166.6	-	167.2
6	7.15, d	123.9	6.87, d	123.7
7	7.17, t	136.4	7.45, d	135.6
8	6.75, t	117.9	6.72, t	117.0
9	7.35, d	130.8	7.34, t	130.2
3'	2.59, s	22.8	2.67, s	22.8
1*	-	137.6 ^b 137.5 ^c	-	29.8
2*	7.85, m	136.1 ^b 136.7 ^c	1.26, s	40.7
3*	7.35, m	128.9 ^b 129.1 ^c	-	-
4*	7.35, m	130.7 ^b 130.5 ^c	-	-

^aRefer to Table 3 for ligand numbering scheme and, for Sn-R skeleton see below:



^b and ^c represent signals due to Sn-Ph₂ and Sn-Ph₃, respectively. Coupling constants for 46: $^nJ(^{13}\text{C}-^{119}\text{Sn})^b$ are $^2J = 55.7$, $^3J = 90.5$, $^4J = 21.1$ and $^nJ(^{13}\text{C}-^{119}\text{Sn})^c$ are $^2J = 54.4$, $^3J = 65.5$, $^4J = 13.2$ Hz.

Table 22: ^{119}Sn NMR Data (δ , ppm) for the Dinuclear Organotin(IV) Complexes

Complex	^{119}Sn
46	- 48.2, - 350.3
47	57.2, - 302.4

Cooling the solution of 46 to $-10\text{ }^\circ\text{C}$ causes only a minor shift of the low-frequency ^{119}Sn resonance (-350.9) but a more substantive shift of the higher frequency resonance (-83.5 ppm) (Fig. 9).

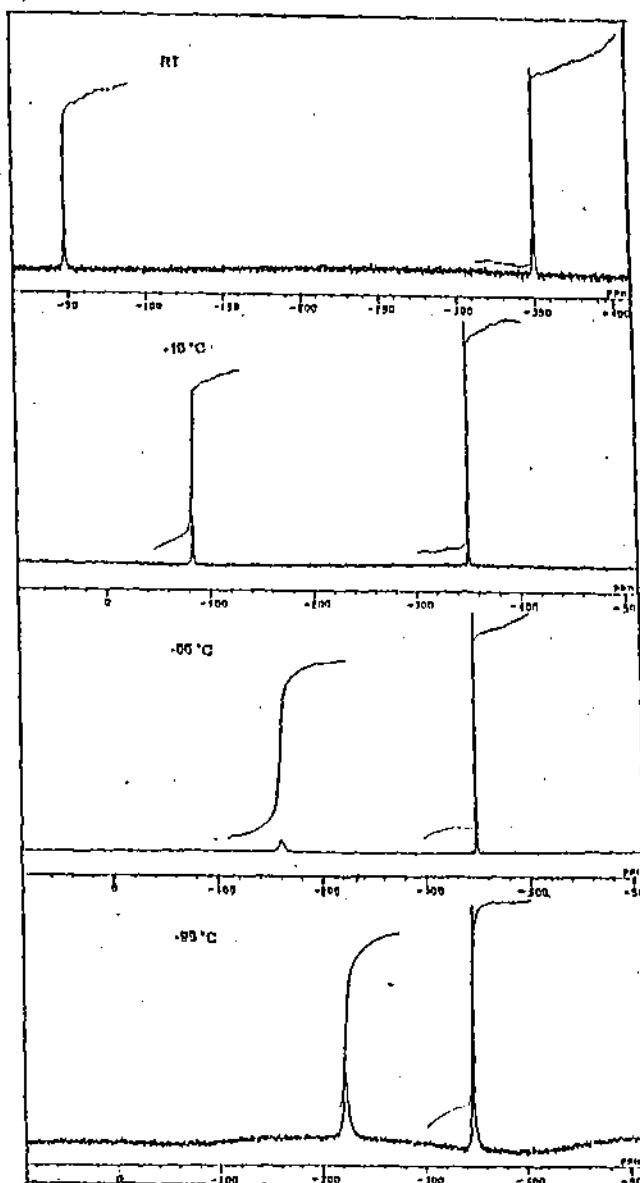


Fig. 9. Temperature dependence ^{119}Sn NMR spectrum for $\text{Ph}_2\text{SnL}^4 \cdot \text{Ph}_3\text{SnCl}$ (46)

At $-95\text{ }^{\circ}\text{C}$, the two ^{119}Sn resonances occur at -223.0 and -347.4 ppm, which indicates that the equilibrium between Ph_3SnCl and **41** has moved substantively toward formation of **46**. The ^{119}Sn shift of the adducted Ph_3SnCl is comparable to that found for other similar five-coordinate species [59]: ($\text{Ph}_3\text{SnClO}_2^-$: -251 at $-95\text{ }^{\circ}\text{C}$ in CH_2Cl_2 ; $\text{Ph}_3\text{SnCl}\cdot\text{pyridine}$: -219 in pyridine at room temperature). Such molecular adduct formation was also confirmed by ^{119}Sn NMR spectra at room temperature of a CH_2Cl_2 solution of **41** to which an equimolar amount of Ph_2SnCl_2 was added shows resonances at -114.0 (cf -33 ppm for Ph_2SnCl_2 at room temperature [59]) and -348.0 ppm, indicating substantial adduct formation. On cooling, the resonances at -114.0 moves progressively to lower frequency, and at $-95\text{ }^{\circ}\text{C}$, the ^{119}Sn NMR spectrum contains two resonances at -236.8 and -342.7 ppm. Clearly, the magnitude of the interaction between **41** and an additional tin moiety is dependent on the Lewis acidity of the latter.

The ^{119}Sn NMR spectrum at room temperature of a CH_2Cl_2 solution of **47** shows resonances at 57.2 (cf 56.0 for $^t\text{Bu}_2\text{SnCl}_2$ in CH_2Cl_2) and -302.4 ppm, indicating negligible interaction between these two species in solution. The magnitude of the interaction is not changed much on cooling the solution to $-95\text{ }^{\circ}\text{C}$ (47.8 and -297.8 ppm). Thus, ^{119}Sn NMR shows extensive adduct formation at low temperature but extensive dissociation at room temperature.

2.4.3 X-ray Structures for $\text{Ph}_2\text{SnL}^4\cdot\text{Ph}_3\text{SnCl}$ (**46**) and $^t\text{Bu}_2\text{SnL}^4\cdot^t\text{Bu}_2\text{SnCl}_2$ (**47**)

A full characterization of dinuclear organotin(IV) complexes of composition $\text{R}_2\text{SnL}\cdot\text{R}'_n\text{SnCl}_{4-n}$ was achieved by the structural analyses in $\text{Ph}_2\text{SnL}^4\cdot\text{Ph}_3\text{SnCl}$ (**46**) and $^t\text{Bu}_2\text{SnL}\cdot^t\text{Bu}_2\text{SnCl}_2$ (**47**). The crystal structures reveal a monomeric 1:1 donor-acceptor dinuclear tin complexes.

The bright yellow complexes (**46** and **47**) crystallize both in the triclinic space groups $P1$ with $Z = 2$. The molecular structures of **46** and **47** are illustrated in Figures 10 and 11 and selected interatomic parameters are listed in Tables 23 and 24, respectively. In **46**, the closest non-hydrogen intermolecular contact in the lattice of $3.455(9)$ Å occurs between C(11) and C(16)^l (symmetry operation $l: -x, 1-y, 1-z$). The compound is dinuclear and may be considered as an adduct formed between Ph_2SnL^4 (**41**) and Ph_3SnCl . A comparison of chemically equivalent geometric parameters for **41** (refer to Section 2.3.3) with those about the Sn(1) atom in **46** shows a remarkable consistency;

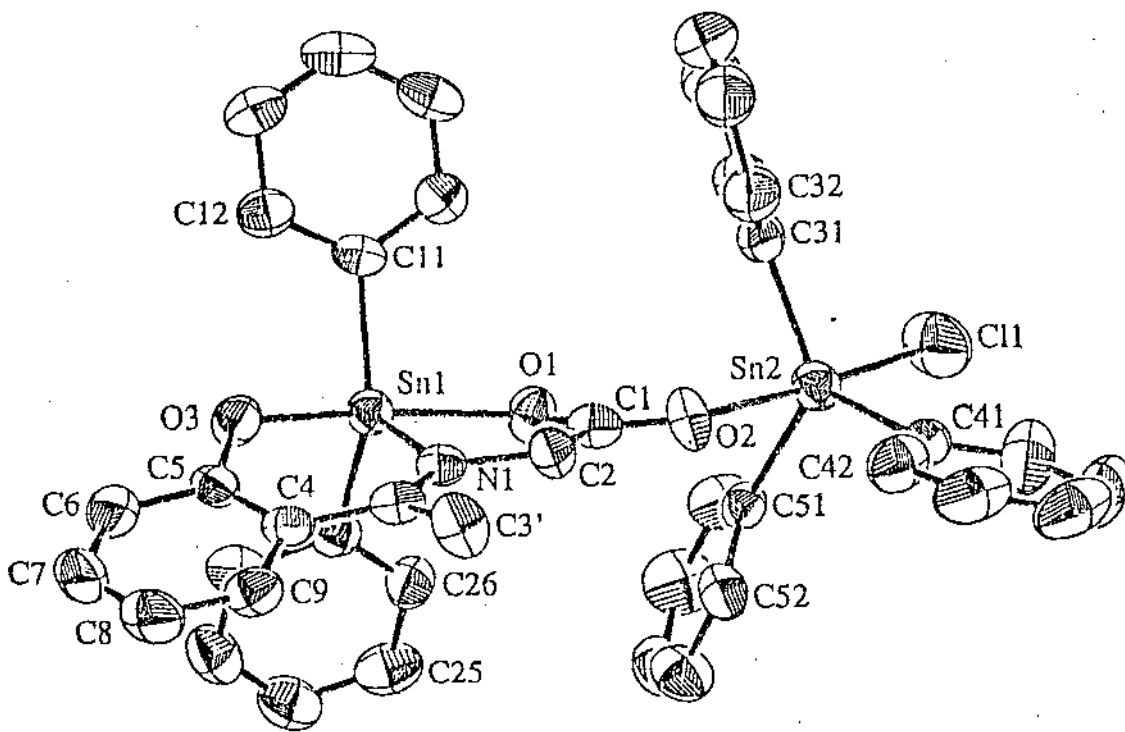


Fig. 10. Molecular structure for $\text{Ph}_2\text{SnL}^4 \cdot \text{Ph}_3\text{SnCl}$ (46)

**Table 23: Selected Bond Lengths (Å) and Bond Angles (°)
for Ph₂SnL⁴.Ph₃SnCl (46)**

Atoms	Distance	Atoms	Distance
Sn(1) - O(1)	2.167(5)	O(2) - C(1)	1.236(1)
Sn(1) - O(3)	2.055(5)	O(3) - C(5)	1.312(7)
Sn(1) - N(1)	2.174(6)	N(1) - C(2)	1.461(1)
Sn(1) - C(11)	2.127(7)	N(1) - C(3)	1.293(9)
Sn(1) - C(21)	2.122(8)	Sn(2) - Cl(1)	2.446(3)
O(1) - C(1)	1.272(1)	Sn(2) - O(2)	2.453(5)
Atoms	Angle	Atoms	Angle
O(1) - Sn(1) - O(3)	160.1(2)	C(11) - Sn(1) - C(21)	137.4(3)
O(1) - Sn(1) - N(1)	76.3(2)	Sn(1) - O(1) - C(1)	117.9(5)
O(1) - Sn(1) - C(11)	93.2(2)	Sn(1) - O(3) - C(5)	127.4(5)
O(1) - Sn(1) - C(21)	94.0(3)	Sn(1) - N(1) - C(2)	112.7(4)
O(3) - Sn(1) - N(1)	84.0(3)	Sn(1) - N(1a) - C(3)	127.8(5)
O(3) - Sn(1) - C(11)	92.0(3)	C(2) - N(1) - C(3)	119.5(6)
O(3) - Sn(1) - O(21)	95.2(3)	O(1) - C(1) - O(2)	125.5(5)
N(1) - Sn(1) - C(11)	111.8(3)	Cl(1) - Sn(2) - O(2)	176.5(2)
N(1) - Sn(1) - C(21)	110.8(2)		

the Sn(1) atom lies 0.0376(5) Å out of the trigonal plane in the direction of the O(3) atom. The only significant difference in the coordination geometries is found in the C-Sn-C angle, which has expanded to 137.4(3)° in **46** compared with 126.0(2)° and 126.2(2)° for molecules a and b, respectively, in **41**. The other major difference between the geometries may be related to the formation of the O(2)-Sn(2) interaction. Thus, the Sn(1)-O(1) bond is longer in **46** owing to the withdrawal of electron density from O(2) and donation to the Sn(2) atom via the carboxylate group. This is also manifested in the apparent lengthening of the C(1)-O(2) bond in **46** compared with the comparable distances in **41**, i.e. consistent with the IR results. The geometry about the Sn(2) atom is also distorted trigonal bipyramidal with the Cl and O(2) atoms defining the axial positions. The Sn(2) atom lies 0.2057(5) Å above the C₃ trigonal plane.

The presence of bidentate bridging carboxylate residue in organotin carboxylate structures is well established [44,60], however, this is the first example of an isolated ditin structure with different R groups held together in this fashion, i.e., in which the two tin atoms are not connected via an organo link. Further, crystal structures of mixed diorgano/triorgano tin are rare, with one example containing a Sn-Sn bond [61] and the other having the tin centers linked via a central platinum atom [62].

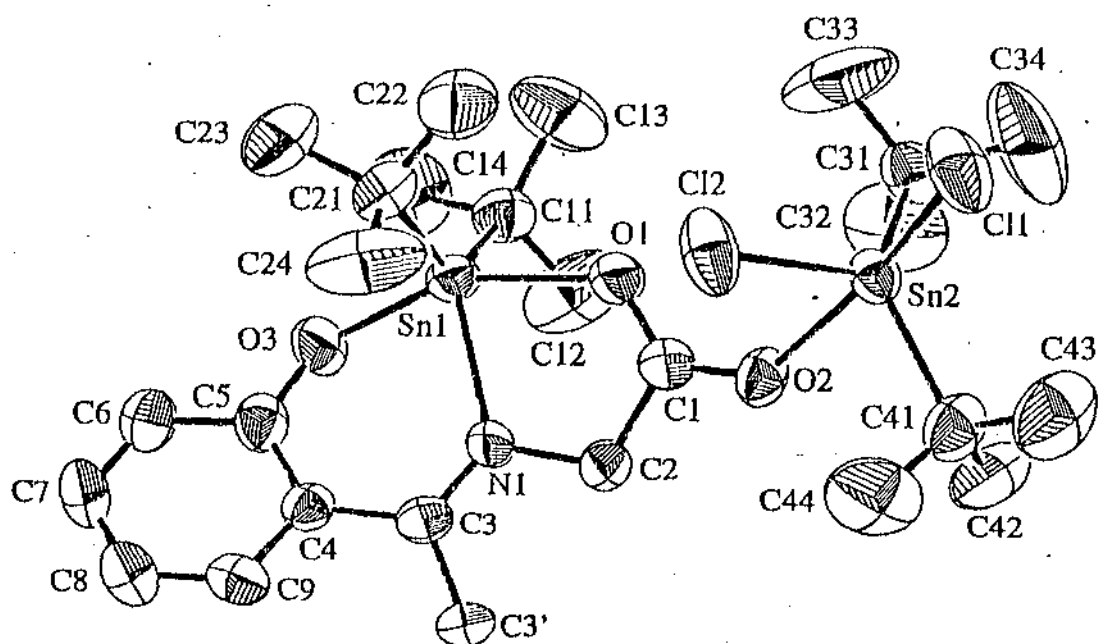


Fig. 11. Molecular structure for ${}^1\text{Bu}_2\text{SnL}^4 \cdot {}^1\text{Bu}_2\text{SnCl}_2$ (47)

Table 24: Selected Bond Lengths (Å) and Bond Angles (°) for ${}^t\text{Bu}_2\text{SnCl}_2 \cdot \text{Bu}_2\text{SnCl}_2$ (**47**)

Atoms	Distance	Atoms	Distance
Sn(1) - O(1)	1.184(4)	N(1) - C(2)	1.474(8)
Sn(1) - O(3)	2.057(4)	N(1) - C(3)	1.307(8)
Sn(1) - N(1)	2.190(5)	Sn(2) - Cl(1)	2.480(2)
Sn(1) - C(11)	2.148(8)	Sn(2) - Cl(2)	2.370(2)
Sn(1) - C(21)	2.152(8)	Sn(2) - O(2)	2.335(2)
O(1) - C(1)	1.254(8)	Sn(2) - C(31)	2.156(8)
O(2) - C(1)	1.256(7)	Sn(2) - C(41)	2.160(8)
O(3) - C(5)	1.335(8)		
Atoms	Angle	Atoms	Angle
O(1) - Sn(1) - O(3)	155.0(2)	Sn(1) - O(1) - C(1)	120.5(4)
O(1) - Sn(1) - N(1)	74.6(2)	Sn(1) - O(3) - C(5)	125.9(4)
O(1) - Sn(1) - C(11)	91.6(2)	Sn(1) - N(1) - C(2)	113.7(4)
O(1) - Sn(1) - C(21)	95.2(2)	Sn(1) - N(1) - C(3)	128.4(4)
O(3) - Sn(1) - N(1)	81.7(2)	C(2) - N(1) - C(3)	117.9(6)
O(3) - Sn(1) - C(11)	93.4(2)	O(1) - C(1) - O(2)	127.6(6)
O(3) - Sn(1) - O(21)	101.4(3)	Cl(2) - Sn(2) - O(2)	66.89(7)
N(1) - Sn(1) - C(11)	120.2(3)	Cl(1) - Sn(2) - O(2)	166.5(1)
N(1) - Sn(1) - C(21)	112.8(3)	Cl(2) - Sn(2) - O(2)	79.9(1)
C(11) - Sn(1) - C(21)	126.4(3)	C(31) - Sn(2) - C(41)	125.3(3)

A similar structure to **46** is found for **47** (Fig.11). In this case, the adduct involves two diorganotin centers similar to that reported in ref. 31. A distorted trigonal-bipyramidal geometry is found about the Sn(1) atom in which the Sn atom lies 0.0930(5) Å out of the NC_2 plane in the direction of the O(3) atom. With the exception of the elongation of the Sn(1)-C bonds in **47**, the geometry is essentially as found in **46**; however, it is noted that the disparity in the C-O(1), O(2) distances is not as pronounced in **47** owing to the shorter Sn(2)-O(2) interaction of 2.335(2) Å, a result that may be correlated with the enhanced Lewis acidity of ${}^t\text{Bu}_2\text{SnCl}_2$ compared with Ph_3SnCl . The strength of the Sn(2)-O(2) contact is responsible for the elongation of the Sn(2)-Cl(2) bond; O(2)-Sn(2)-Cl(2) is 166.5(1)°.

2.5 Biological Properties of Organotin(IV) Complexes

The chemistry of the metal complexes of 2-[[*E*]-1-(2-hydroxyaryl)alkylidene]amino acetic acid framework **20** has developed not only from an inorganic point of view, but also because of possible biological interest due to their possible use as potential pyridoxylidene amino acid systems [63]. In addition, organotin compounds of related system shown to possess a wide range of biological properties [53, 63, 64]. Recently, diorgano- and triorganotin complexes of **20** were tested *in vitro* against several bacteria (*Streptococcus faecalis*, *Klebsiella pneumoniae*, *Escherichia coli*, *Pseudomonas aeruginosa*, *Staphylococcus aureus*) and fungi (*Candida albicans*, *Cryptococcus neoformans*, *Sporotrichum schenckii*, *Trichophyton mentagrophytes*, *Aspergillus fumigatus*) [63] and found to be active. The inhibitory effects of all the organotin complexes were found to be fairly greater than those of the parent organotin compounds. Furthermore, this class of organotin compounds were tested for antitumour activities *in vitro* against human tumour cell lines, viz., MCF-7, EVSA-T, WiDr, IGROV, M19 MEL, A498 and H226 [53]. These compounds were found to be more active against all the cell lines than carboplatin and cisplatin. However, they all are less active than methotrexate and doxorubicin. Recently, antitumour screenings of related organotin complexes were carried out on a panel of 60 human tumour cell lines derived from seven cancer types (leukemia, lung, colon, central nervous system, melanoma, ovarian and renal cancers) and the results are reported in ref. 64. In view of these, we have also investigated the antitumour properties of some selected organotin(IV) complexes.

2.5.1 Evaluation of Antitumour Properties of Organotin(IV) Complexes

Three different types of complexes, Ph_2SnL^4 (**41**), $\text{Ph}_2\text{SnL}^4 \cdot \text{Ph}_3\text{SnCl}$ (**46**) and $^t\text{Bu}_2\text{SnL}^4 \cdot ^t\text{Bu}_2\text{SnCl}_2$ (**47**) were selected for evaluation of antitumour properties. The effect of the organotin(IV) complexes **42**, **46**, **47** and L^4HNa on the survivability of mice are shown in Table 25. The sodium salt L^4HNa is found to be non-toxic to mice at 30 mg kg^{-1} . It has been observed that L^4HNa is highly soluble in water, and a very high dosage (50 mg kg^{-1} in aqueous solution) does not cause the death of any mice. All the organotin complexes studied in the experiment are highly toxic to mice. The complex **41**

Table 25: Effect of Organotin Compounds 41, 46, 47 and L⁴HNa on the Survivability of the Mouse *in vivo*

Parameters	Control	Sodium salt		Organotin complexes					
		L ⁴ Na		41		46		47	
Dose(mg kg ⁻¹)	No drug	6	30	6	30	6	30	6	30
Cells(X10 ⁶)per ml ascites fluid	168 ± 10.20	180 ± 16.32	178.3 ± 16.5	76 ± 20.5	-	-	-	-	-
Total volume (ml) tumour cells + ascites fluid	7.3 ± 1.45	5 ± 0.6	6 ± 0.6	4 ± 0.77	-	-	-	-	-
Total packed cell volume (ml)	5.2 ± 0.40	3.1 ± 0.3	3.5 ± 0.8	3.1 ± 0.6	-	-	-	-	-
Mean survival time (MST) (days)	32.5 ± 2.69	30.2 ± 3.16	29 ± 3.5	19.1 ± 4.6	02	10	02	11.2	04
T/C ^a (%)	100	93	90	59	6.15	30.76	6.15	35	11.3

^aT/C is the ratio of the MST of treated mice to MST of control mice.

is less toxic than 46 and 47. Although the exact cause of toxicity was not studied, it could be due to free radical generation from the organotins to the living system [53]. T/C values (using the NCI protocol for screening new anticancer drugs) [65] showed that neither L⁴HNa nor the organotin complexes possess any antitumour properties. Further studies with the organotin complexes were not undertaken owing to their toxicity.