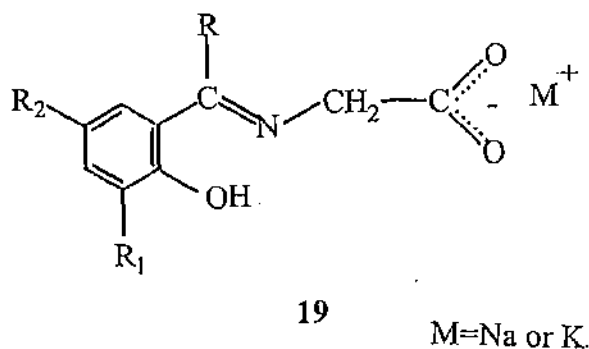


Chapter 3

Chapter 3

3. Conclusion

The present work focuses on the complexation behaviour of 2-[(*E*)-1-(2-hydroxyaryl)alkylidene]amino}acetic acid **20** with organotin(IV) halide, an area almost unexplored systematically in sharp contrast to the established transition metal chemistry. The ligand framework **20** in the form of LHM **19** has been used for the preparation of a great variety of organotin(IV) complexes.

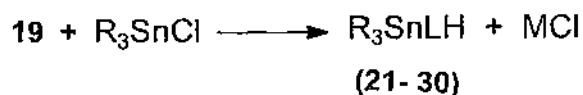


	R	R ₁	R ₂
L ¹ HK	H	H	H
L ² HK	H	H	Cl
L ³ HK	H	H	NO ₂
L ⁴ HK	CH ₃	H	H
L ⁴ HNa	CH ₃	H	H
L ⁵ HK	CH ₃	CH ₃	H
L ⁶ HK	CH ₃	H	CH ₃
L ⁶ HNa	CH ₃	H	CH ₃

The bifunctional tridentate ligand afforded three classes of organotin(IV) complexes; *viz.*, (i) the triorganotin(IV) derivatives of the type R₃SnLH (ii) the diorganotin(IV) derivatives of the type R₂SnL.nH₂O and (iii) the dinuclear organotin(IV) derivatives of the type R₂SnL.R_n'SnCl_{4-n}. The main results are summarized below.

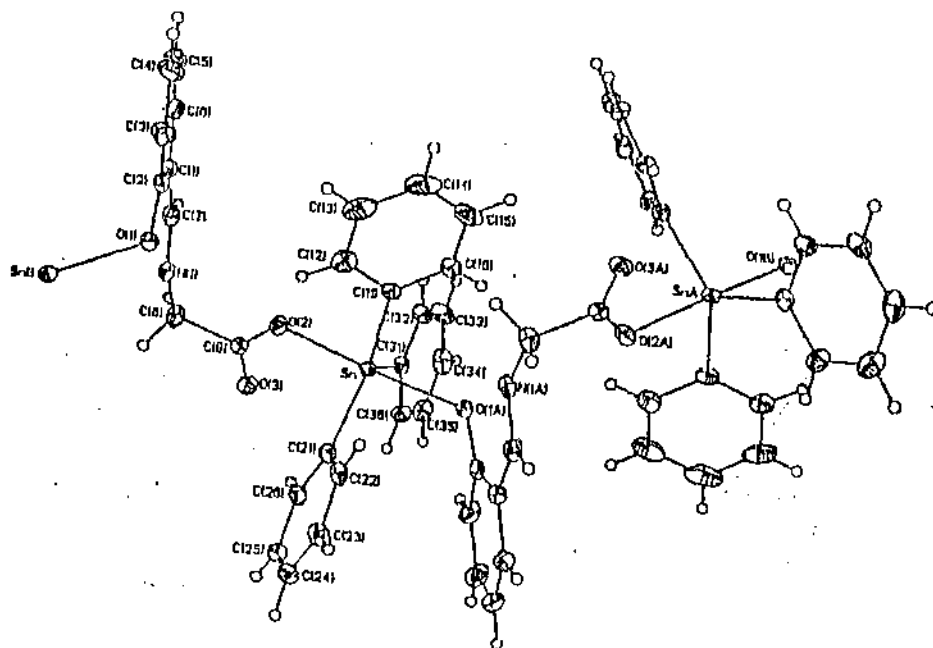
(i) The triorganotin(IV) derivatives of the type R₃SnLH

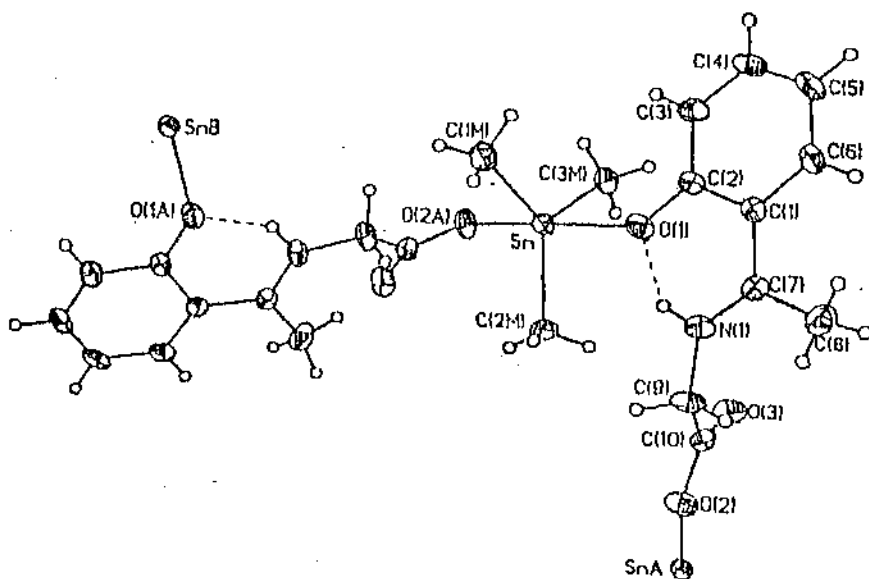
A series of new triorganotin(IV) complexes were synthesized by conventional metathesis reactions of appropriate LHM with R₃SnCl in a suitable organic solvents.



	R	L
21	ⁿ Bu	L ¹
22	Ph	L ¹
23	Ph	L ²
24	Me	L ⁴
25	ⁿ Bu	L ⁴
26	Ph	L ⁴
27	Me	L ⁵
28	Ph	L ⁵
29	ⁿ Bu	L ⁶
30	Ph	L ⁶

The X-ray diffraction, elemental analyses, IR, ¹¹⁹Sn Mössbauer Spectroscopy and multinuclear NMR spectroscopy were applied as characterization methods. The compounds which form the subject of this study, however, have ligands with phenolic groups in close proximity to nitrogen atoms. The resultant zwitterionic forms of the ligands coordinate through monodentate carboxylate groups and the



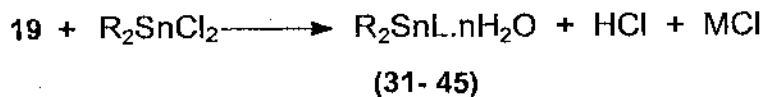


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phenolic oxygen. This series of compounds all exhibit the same polymeric *trans*-O₂SnC₃ trigonal bipyramidal structural motif (as shown in **22** and **24**), namely one with the three R groups occupying the equatorial positions, and the axial positions being occupied by a carboxylate oxygen and the phenolic oxygen of an adjacent molecule. These five-coordinated polymeric complexes dissociate in solution to give monomeric four-coordinate structures as revealed by ¹¹⁹Sn NMR spectroscopy.

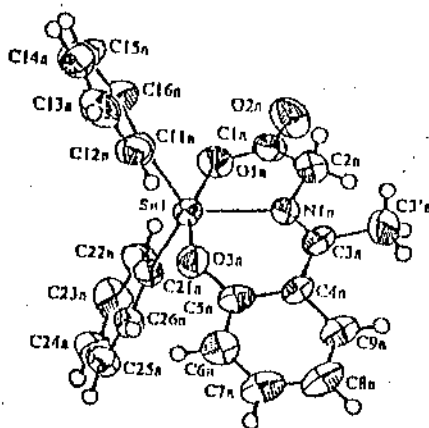
(ii) The diorganotin(IV) derivatives of the type R₂SnL.nH₂O

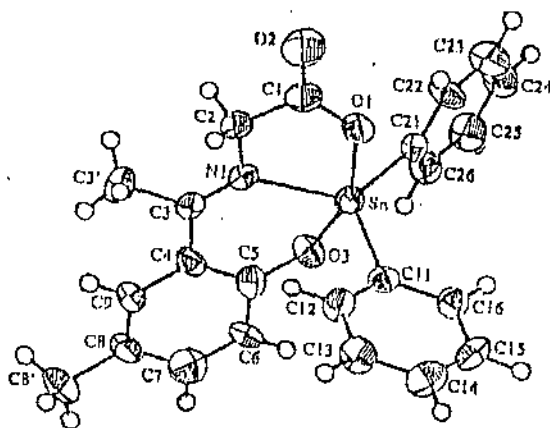
The diorganotin(IV) complexes were prepared by reacting equimolar amounts of appropriate LHM with R₂SnCl₂ either in methanol or methanol-benzene mixture.



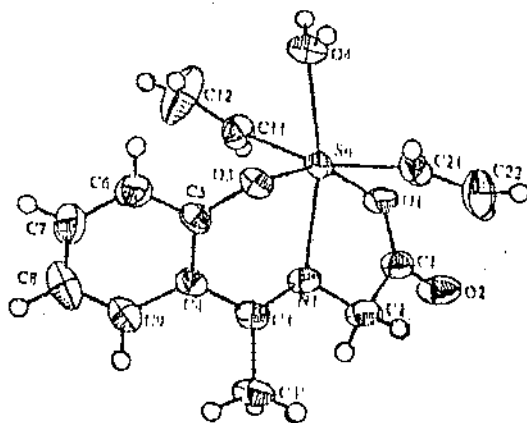
	R	L	n
31	Me	L ¹	1
32	ⁿ Bu	L ¹	1
33	Ph	L ¹	0
34	Me	L ²	1
35	ⁿ Bu	L ²	1
36	Ph	L ²	0
37	Me	L ³	1
38	Ph	L ³	1
39	Me	L ⁴	1
40	ⁿ Bu	L ⁴	0
41	Ph	L ⁴	0
42	Vin	L ⁴	1
43	Ph	L ⁵	0
44	Me	L ⁶	1
45	Ph	L ⁶	0

This class of complexes were obtained either as R₂SnL or R₂SnL.OH₂. A systematic investigation was carried out to ascertain the solid state structures of the complexes by elemental analyses, IR and ¹¹⁹Sn Mössbauer spectroscopy while multinuclear NMR (¹H, ¹³C, ¹¹⁹Sn) spectroscopy has been used to determine the solution state structures. Attempts were also made to obtain single crystals for a range of samples but in most cases, the crystals turned opaque. However, a few complexes provided stable X-ray quality crystals to visualize the suspected molecular structures.





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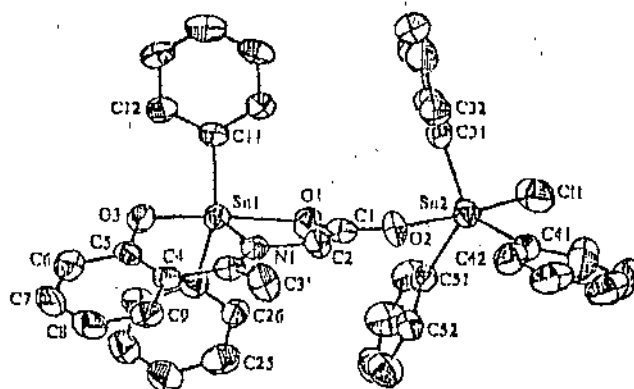
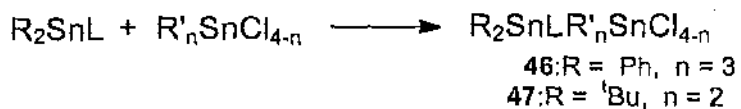


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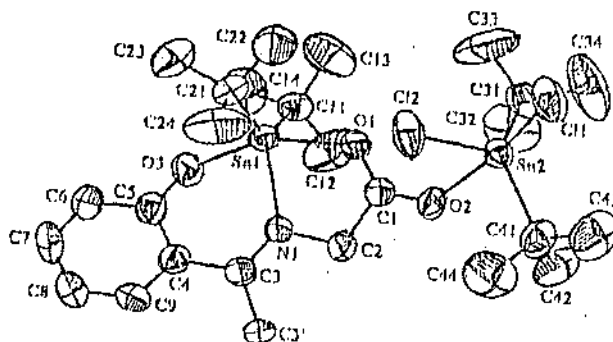
The coordination geometry about the tin atom in **41** and **45** is defined by two phenyl groups, an oxygen (O(1), derived from a unidentate carboxylate group), a phenoxide O(3) atom, and the imino N(1) atom. The arrangement of the donor set is distorted trigonal bipyramidal with the two oxygen atoms defining the axial positions. The confirmation of the structure in $R_2SnL.OH_2$ type complexes is accomplished by X-ray crystal structure analysis on **42**. The six-coordinate structure in the solid state is owing to the coordination of a water molecule. 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. ^{119}Sn NMR results indicated that both types of complexes, *viz.*, R_2SnL and $R_2SnL.OH_2$ exhibit a sharp signal in the range delimited for trigonal bipyramidal geometry in solution.

(iii) The dinuclear organotin(IV) derivatives of the type $R_2SnL.R'_nSnCl_{4-n}$

Reaction of the diorganotin(IV) complexes R_2SnL with R'_nSnCl_{4-n} in benzene at reflux temperature resulted in the smooth formation of dinuclear molecular adduct of composition $R_2SnL.R'_nSnCl_{4-n}$ in which the two tin atoms are joined via the carbonyl atom of the diorganotin complex.



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The monomeric diorganotin(IV) complex possesses additional potentially O-containing coordinating sites. This proved to be sufficiently basic to coordinate a second Sn-containing species, and hence, a thorough investigation of the nature of adduct formation was conducted in non-coordinating solvent employing ^{119}Sn NMR methods and in the solid state by X-ray crystallography. In **46**, the geometry around Sn(1) is trigonal bipyramidal which is consistent with **41**. 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 above the C_3 trigonal plane. This is the first representative of a new type of an unprecedented adduct formation with carbonyl oxygen with Ph_3SnCl which possesses a diorganotin(IV) and triorganotin(IV) moiety connected via a carbonyl oxygen. The examples of such donor-acceptor complexes are rare. Compound **46** has also been investigated in great detail by ^{119}Sn NMR spectroscopy at low temperature down to -95°C . The results indicate extensive adduct formation at low temperature but extensive dissociation at room temperature. A similar structure to **46** is found for **47**. In this case, the adduct involves two diorganotin(IV) centers.

Antitumour screening *in vivo* in Ehrlich ascites carcinoma cells of the complexes **41**, **46**, **47** and L^4HNa is also reported. T/C values showed that neither the organotin complexes nor L^4HNa possess any antitumour properties.

In summary, this work presents the detailed systematic study on organotin(IV) complexes of 2-[[*E*]-1-(2-hydroxyaryl)alkylidene]amino}acetic acid ligand framework. A large structural diversity has been observed in these compounds, which can be rationalised essentially in terms of the steric and/or electronic effects.