

SYNTHESIS AND CHARACTERIZATION OF  
ORGANOTIN(IV) SCHIFF BASE COMPLEXES

A THESIS  
SUBMITTED TO THE  
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FOR THE DEGREE OF  
DOCTOR OF PHILOSOPHY  
(IN CHEMISTRY)

BY  
MRS. M.P. DEGAONKAR

NATIONAL CHEMICAL LABORATORY  
PUNE - 411 008

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## CERTIFICATE

Certified that the work incorporated in the thesis "Synthesis and characterization of organotin(IV) Schiff base complexes." submitted by Mrs. M.P. Degaonkar, M.Sc. was carried out by the candidate at the Inorganic Chemistry Division, National Chemical Laboratory, Pune 411008, under my supervision for the Degree of Doctor of Philosophy in Chemistry, University of Poona. This work was not submitted so far for any other degree.



(Dr. C. Gopinathan)

Research Guide

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Pune

Date

*M.P. Degaonkar*  
(Mrs.M.P. Degaonkar)

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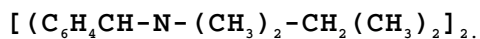
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## CHAPTER 1

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## GENERAL INTRODUCTION

GENERAL INTRODUCTION TO GROUP  
(IV) METALS

Carbon, silicon, germanium, tin and lead, and titanium, zirconium, hafnium and thorium are the elements in the main and transition groups in the Group IV of the Periodic Table. The tendency to form organometallic compounds is much stronger among the elements of the main group than those in the transition group. In fact, it was the accepted view for over a quarter of the present century that transition metals do not as a rule form stable organometallic compounds. The reason lies in the fundamental difference in the atomic structure between the two groups of elements as shown below:

Electronic structure of the atomsMain Group Elements (Gr. IV A)

<u>At. No.</u>	<u>Element</u>	<u>Arrangements of electrons</u>
6	Carbon	He $2s^2 2p^2$
14	Silicon	Ne $3s^2 3p^2 3d^0$
32	Germanium	Ar $3d^{10} 4s^2 4p^2 4d^0$
50	Tin	Kr $4d^{10} 5s^2 5p^2 5d^0$
82	Lead	Xe $5d^{10} 6s^2 6p^2 6d^0$

Transition Group Elements (Gr. IV B)

22	Titanium	Ar $3d^2 4s^2 4p^0$
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40	Zirconium	Kr $4d^2 5s^2 5p^0$
72	Hafnium	Xe $5d^2 6s^2 6p^0$
90	Thorium	Rn $6d^2 7s^2 7p^0$

The possibility of two (+2 and +4) oxidation states, corresponding to the involvement of either two p or all s and p electrons, is suggested by the proximate arrangement of four outermost electrons ( $ns^2 np^2$ ) in the atoms of the main group. The bipoisitive state is stabilized because of the presence of the relatively "inert electron pair" ( $ns^2$ ) of Sidgwick<sup>1</sup>. This situation is, however, seldom found in carbon and silicon because of the tendency of these small atoms to saturate themselves covalently, but it becomes increasingly important with increasing atomic size. The bipoisitive species, common in tin and lead are both known as stable ions in polar solvents. The fact that outermost electronic levels in the atoms of these elements are effectively half filled imparts certain unique properties.

The energy for the removal of the four outermost electrons is high, so Ti(IV) and Sn(IV) compounds tend to be covalent. For Ti(IV) compounds the energies of the 3d, 4s and 4p levels are all within 4 eV of each other and circumstances are favourable for hybridization involving these orbitals, and several such hybrid orbitals are possible<sup>2</sup>. Tetrahedral bonds, for example, would originate from hybridization of either  $d^3s$  or  $sp^3$  atomic

orbitals, both of which are probable with titanium tetrachloride. Raman and infrared studies in titanium tetrachloride<sup>3-5</sup> have shown that the molecule is tetrahedral (point group symmetry  $T_d$ ) with a doublet at  $\nu_3$  like carbon tetrachloride. A quantitative calculation of the constants shows, however, that there is relatively much smaller resistance to deformation without change of the X-Y distance. The relative values of  $k_f / l^2$  (valence force system) and  $k_1$  (central force system), either of which is a measure of the resistance to deformation of the tetrahedral structure are given below for the tetrachlorides of carbon, silicon, titanium and tin for comparison<sup>6</sup>.

	$CCl_4$	$SiCl_4$	$TiCl_4$	$SnCl_4$	
$k_f / l^2$	0.331	0.157	0.100	0.075	) $\times 10^5$ ) dynes/cm
$k_1$	0.79	0.36	0.23	0.15	

A resemblance between Ti(IV) and Sn(IV) is again noticeable in their estimated ionic radii<sup>7</sup> ( $Sn^{4+} = 0.71$ ;  $Ti^{4+} = 0.68 \text{ \AA}$ ) and octahedral covalent radii [ $Sn(IV) = 1.45$ ;  $Ti(IV) = 1.36 \text{ \AA}$ ].

Attainment of higher oxidation states becomes increasingly difficult from carbon to lead with increasing electropositive nature of the element. Regarding Lewis acidity, carbon does not show acceptor properties in its tetravalent state owing to octet limitations; others are weak acceptors towards halide or oxyions. In the tetravalent state, all the elements in this family are characterized by a tetrahedral disposition of four valencies

as already mentioned with titanium. The  $sp^3$  hybridization is facilitated by the proximate presence of the two s and two p electrons in the same valence shell in the atoms of the main group metals.

The metal-carbon bond lengths increase considerably within the elements of the group: C-C 1.54, Si-C 1.94, Ge-C 1.99, Sn-C 2.17 and Pb-C 2.29 Å. The increased bond length for Sn-C explains the increased reactivity and relatively lower thermal stability of the tin alkyls compared to their silicon and germanium counterparts. The Ti-C bond is still longer, being 2.33 to 2.49 Å, and is more reactive than any of the bonds mentioned above. Long bonds, besides being of low strength, lessen the screening effect of the ligands on the central atom, making the latter more accessible to nucleophilic attack. The relationship is also seen clearly in the dissociation energies of the M-C bonds among the metal tetra-alkyls of the main group elements, the mean values being C-C 87, Si-C 70, Ge-C 60, Sn-C 50 and Pb-C 31-37 k.cals. Because of the high atomic weight of tin and relative weakness of the Sn-C bonds, the skeletal vibrations of organotin compounds have low frequencies, generally below  $600\text{ cm}^{-1}$ .

The availability of empty d orbitals in both titanium and tin atoms makes it possible to expand their coordination number to greater than four in many of their organo-derivatives. Donation of electrons by ligands into the empty orbitals is

facilitated for sterical reasons and because of the negligible tendency of any metal-ligand  $d_{\pi} - p_{\pi}$  interaction.

Even as a transition element, the stereochemistry of titanium will be governed like that of the non-transition elements by the tendency of electron pairs to occupy positions of minimum mutual interaction. Only, in the case of transition elements, the additional effect of the non-bonding electrons in the  $(n-1)d$  orbitals must be considered. The non-bonding  $d^0$  configuration of Ti(IV) is symmetrical to both tetrahedral and octahedral ligand fields, so both the regular structures are expected, though the octahedral complexes will be more stable. Compounds of coordination number 5, 7 and 8 have also been reported<sup>7</sup>.

Five coordination is commonly met within  $R_3Sn^{iv}$ , and six coordination in  $R_2Sn^{iv}$  and  $RSn^{iv}$  type compounds. In a number of the latter two types, penta-coordination has also been established<sup>9,10</sup>. Triorganotin acetylacetonate and di-organotin di-oxinate are examples of penta- and hexa- coordination respectively of the tin(IV) atom. Assuming octahedral geometry for the hexa-coordinated complexes, isomers would be expected in suitable cases. However, attempts at resolution of the dialkyl/diaryl tin oxinates resulted in the isolation of only one form believed to be the trans isomer<sup>11</sup>.

Although isotropic molecules of zero dipole moments, both titanium- and tin-tetrachlorides are strong Lewis acids and

addition complexes with ethers, esters and other donor atoms are well known. It would appear, however, that these atoms are easily coordinated either octahedrally, or trigonal bipyramidally to central metal<sup>12</sup>. Also, deviations or slight distortions from totally symmetrical structures are quite probable. Alternative modes of polymerization, linear or cyclic, are common and indeed, form a general structural feature. Thus it appears that, although titanium and tin belong to the groups of transition and non-transition elements, they retain certain chemical similarities, especially in the tetravalent states, with silicon.

Catenation, a dominant characteristic of the carbon atom, is considerably weaker in other elements of the group, falling rapidly in the sequence  $\text{Si} > \text{Ge} > \text{Sn} > \text{Pb}$ . Only a few organotin compounds containing more than two tin atoms are well defined. This property is totally absent in the transition elements Ti, Zr, Hf, and Th. In contrast, the possibilities of hetero-chain organic derivatives, resulting in the formation of polymeric compounds, are diverse and extensive with titanium. Since such hetero-chain skeletons can result not only from combination of elements of different electronegativity but also from the utilization of other bond capacities in large molecules, advantage can be taken of both non-ionogenic and ionogenic bonds. Thus hetero-chain complex compounds can be synthesized containing the transition metal atom, and other organic or

organometalloid compounds having electron donor properties<sup>13</sup>.

The inherent chemical instability of homo-chains (other than of carbon) can be partly corrected in hetero-chain compounds by alternating carefully selected elements in the X-Y- or X-Y-Z chains, selecting elements somewhat more negative than carbon in alternate positions. The compounds thus formed are more resistant to redox processes; and the nearer is the average electronegativity of the hetero-alternates to that of carbon itself, the better is the non-ionogenic character of the bonds formed. The combination of such elements makes it possible to synthesize the interesting poly-organosiloxanes, alumino-organosiloxanes and titano-organosiloxanes. The idea is continually being extended to synthesize polymers with hetero-chains -Al-O-Al-, -Ti-O-Ti-, -Sn-O-Sn-, -Al-O-P-O-Al-, -Ti-O-Si- and others<sup>14</sup>. However, these bonds would be more susceptible to nucleophilic (and electrophilic) attack than the covalent bonds of carbon atoms. The general principles enunciated above formed the basis of our investigation on the nature and type of organic compounds of titanium, with oxygen as the hetero-alternate between titanium and carbon (electronegativity values: Ti 1.32, O 3.5, C 2.5).

In the very rapid development during the last one or two decades of the organic chemistry of titanium and tin, prompted mostly by industrial applications of certain types of its compounds, a lack of systematic build-up of knowledge is

noticeable, even with respect to relatively simple derivatives.

## GENERAL CHEMISTRY OF ORGANOTINS

### a. General preparation of organotin compounds

Organotin compounds ( $R_4Sn$ ,  $R_3SnX$ ,  $R_2SnX_2$  and  $RSnX_3$ ) are prepared by various kinds of synthetic methods such as the Grignard reaction, Wurtz reaction, reactions with organoaluminums and direct reactions. The Grignard reaction, Wurtz reaction and reactions with organoaluminums are generally suitable for the preparation of  $R_4Sn$ , and, on the other hand, direct reactions are suitable for the preparation of  $R_2SnX_2$ .

Hence, the industrial preparation of organotin compounds is not limited to a single method, but several reactions such as Grignards, organoaluminums and direct reactions are applied. Furthermore, the organotin derivatives are prepared by a redistribution reaction (Kocheskov reaction<sup>15</sup>)

### b. Chemistry of organotin compounds

The representative reactions of organotin compounds are hydrostannation, hydrostannolysis, and the Kocheskov reaction. There are some others which include radical reactions, reactions of organostannylenes, transmetalations and condensations.

Recently, studies of organic syntheses with organotin compounds, have rapidly increased, especially in the field of

preparation of hormones, vitamins, coenzymes, antibiotics, terpene hydrocarbons, etc., and many reviews<sup>16-32c</sup> and a book<sup>33</sup> have been published in this field.

Organotin compounds are found in two oxidation states, i.e., tin(II) and tin(IV), and a wide variety of structural types in which the tin atom is two-, three-, four-, five-, six-, and seven-coordinate is assumed<sup>34,35</sup>. The preferred equilibrium solid-state molecular structures for tin are bent, trigonal, tetrahedral, trigonal bipyramidal, octahedral and pentagonal bipyramidal for two- to seven-coordination.

#### c. Applications of organotin compounds

Estimates by the Tin Research Institute, Greenford, put the world production of organotin compounds at 10,000 tons for the year 1968. Later figures are not available. Most of the applications are as polymer stabilizers, insecticides, fungicides and catalysts.

(i) Polymer stabilizers: In the absence of a good stabilizer, polyvinyl chloride gets degraded even at room temperature by ultraviolet light. This is due to dehydrochlorination which, once commenced, appears to proceed automatically causing chain scission.

Compounds of the type  $R_2SnX_2$  are well known stabilizers for PVC, neoprene, chlorinated polyethylenes<sup>36</sup>, vinyl copolymers<sup>36,37</sup>, silicones<sup>38</sup>, polyamides<sup>39</sup> and other polymers. Colorless transparent PVC foils, discs and rigid PVC articles are made



using organotin stabilizers. Dibutyltin-dilaurate<sup>40</sup> and -maleate<sup>41</sup> were the first two compounds to be used, but now a large number of organotin compounds are mentioned in the patent literature. They include derivatives of hydroxy compounds<sup>42</sup>, thioglycollic acid esters, mercaptides and other similar sulphur compounds<sup>36</sup>. Dioctyltin compounds are recommended particularly for PVC sheets or coatings used for food packing, because they are non-toxic<sup>43</sup>.

(ii) Insecticides and fungicides: The notable lack of toxicity of inorganic tin compounds makes organotin fungicides superior to those containing other metals such as Hg, Cu, Cd and Zn. The "biological half-life" of the most of the organotins used as insecticides and fungicides is comparatively short. For example, for triphenyltin acetate it is about 3-4 days only in the open air and 7-8 days under glass. Water and light degrade it to inorganic tin compounds.

Compounds of the type  $R_2SnX_2$  show less fungicidal activity than the  $R_3SnX$  type. The activity is at its maximum when the alkyl groups contain a total of 9-12 carbon atoms<sup>44</sup>. A large number of aliphatic and aromatic organotins have been tested for their activities against various micro-organisms<sup>45-48</sup>. As a rule, aromatic organotins are less phytotoxic than aliphatic ones<sup>49</sup>. Triphenyltin acetate or hydroxide is used to combat fungus diseases in leaves or in root like tobacco, potato and

sugar beet<sup>50,51</sup>. Triphenyltin chloride and tributyltin oxide are added to paints, to impregnate potato sacks (jute), manila ropes, textiles, leather, canvas and nets against attack by moulds, fungi and algae. Triethyltin hydroxide, tributyltin acetate and tributyltin oxide dissolved in mineral oil are recommended as preservatives for wood<sup>52-54</sup>. Tripropyl- and tributyltin fluorides have antiseptic action on non-metallic surfaces<sup>55</sup>. Dibutyltin-dilaurate and -maleate are used in veterinary medicines<sup>56</sup>.

(iii) Catalysts: Organotin compounds such as dibutyltin dilaurate catalyze the reaction of isothiocyanates with alcohols (forming urethanes)<sup>57-60</sup>, and esterification of epoxy resins with fatty acids<sup>61</sup>. Polyurethane foams with improved physical and chemical resistant properties are prepared by using alkyltin halides as catalysts<sup>62</sup>. Organotin compounds are used commercially in Ziegler catalyst systems for polyolefin production<sup>63</sup>, a combination of titanium tetrachloride and organotin hydride gives polymers of high molecular weights under mild conditions. Polymerization of styrene by the use of vanadium oxychloride-tetrapropyltin catalyst has been reported<sup>64</sup>. Tributyltinlithium is an effective catalyst for the solution polymerization of conjugated dienes giving transparent polymers. An organotin ester such as dibutyltin dilaurate is useful in the 'cold curing' of organopolysiloxanes having terminal hydroxy groups<sup>65-69</sup>. These compounds are also used for the production of

polysiloxane elastomers<sup>70-74</sup>, surface coatings, acrylate-silicone copolymers<sup>75</sup> and for hardening epoxy resins<sup>76,77</sup>. Tetraorganotins are useful ballistic additives for solid rocket engine fuels<sup>78</sup>. Hexa-alkyldistannanes are additives for gasoline<sup>79</sup>. They are also used for corrosion prevention of metals, as water-repellents, in paints and varnishes and as a primer for coating glass<sup>80</sup>.

(iv) Industrial uses: The industrial uses of organotin compounds which apply the first characteristic are stabilizers for PVC and the other vinyl polymers, and catalysts. The industrial uses which apply the second characteristic are wood preservatives, antifouling agents, agrochemicals, pharmaceuticals, disinfectants, rodent repellents, protection of masonry and stonework, and slime prevention, etc. The other minor uses of organotin compounds are glass applications and flame retardants, etc.

(v) Other uses: Organotin compounds are often effective in very low concentrations in many applications, which is advantageous from a formulation and cost effectiveness point of view. In addition, there are particularly favourable environmental aspects that often give a decisive advantage over alternative materials<sup>81</sup>.

Organotin compounds are used mainly by applying the following two characteristics. The first is a strong affinity of

the tin atom for a donor ligand atom such as sulphur or oxygen. The second comprises physiological activities such as biocidal activities (e.g., bactericidal, fungicidal, acaridal, insecticidal and molluscidal) and repellent activity against wood-destroying organisms, marine animals, marine plants and rodents etc.

## SUMMARY OF THE PRESENT WORK

This thesis is mainly devoted to the study of organotin(IV) Schiff base complexes. In our endeavor to obtain more knowledge about the coordination chemistry of tin(IV) we have prepared and studied organotin(IV) complexes with Schiff bases. The Schiff bases and their organotin(IV) complexes were characterized by elemental analyses, IR,  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{119}\text{Sn}$  NMR and wherever possible, by mass spectra, and their stereochemistry established beyond doubt.

The Schiff bases [and their abbreviations] used in the study are as follows:

**1) The Schiff bases derived from S-methyl-N-methyldithiocarbamate:**

- i) S-methyl-N-methyl- $\beta$ -N-(2-hydroxyphenyl)methylendithiocarbamate (HSMNMSaD)
- ii) S-methyl-N-methyl- $\beta$ -N-(2-hydroxy-3-methoxyphenyl)methylendithiocarbamate (HSMNMVD)
- iii) S-methyl-N-methyl- $\beta$ -N-(2-hydroxy-1-naphthyl)methylendithiocarbamate (HSMNMND)

**2) The Schiff bases derived from S-methyl/S-benzoyldithiocarbamate:**

- i) S-methyl- $\beta$ -N-(2-hydroxyphenyl)methylendithiocarbamate [H<sub>2</sub>SMSaD]
- ii) S-methyl- $\beta$ -N-(2-hydroxy-3-methoxyphenyl)methylendithiocarbamate [H<sub>2</sub>SMVD]

- iii) S-methyl- $\beta$ -N-(2-hydroxy-1-naphthyl)methylendithiocarbazate  
[H<sub>2</sub>SMND]
- iv) S-benzyl- $\beta$ -N-(2-hydroxyphenyl)methylendithiocarbazate  
[H<sub>2</sub>SBSaD]
- v) S-benzyl- $\beta$ -N-(2-hydroxy-3-methoxyphenyl)methylendithioC  
carbazate [H<sub>2</sub>SBVD]
- vi) S-benzyl- $\beta$ -N-(2-hydroxy-1-naphthyl)methylendithiocarbazate  
[H<sub>2</sub>SBND]

**3) The Schiff bases derived from 2-amino-2-methyl-1-propanol**

- i) 2-N-salicylideneimino-2-methyl-1-propanol [H<sub>2</sub>sa-2m-1p]
- ii) 2-N-chlorosalicylideneimino-2-methyl-1-propanol  
[H<sub>2</sub>Cl.sa-2m-1p]
- iii) 2-N-bromosalicylideneimino-2-methyl-1-propanol  
[H<sub>2</sub>Br.sa-2m-1p]
- iv) 2-N-(2-hydroxy-3-methoxyphenylene)imino-2-methyl-1-propanol  
[H<sub>2</sub>ov-2m-1p]
- v) 2-N-(2-hydroxy-1-naphthaledene)imino-2-methyl-1-propanol  
[H<sub>2</sub>Naph-2m-1p]

**4) The Schiff base derived from malonoyldihydrazone.**

- i) (bis)salicylaldehyde malonoyldihydrazone. [H<sub>4</sub>L]

**1) Molecular addition complexes with the Schiff bases derived from S-methyl-N-methyl-dithiocarbazate:**

Several novel molecular addition complexes of organotin(IV)

chlorides with the Schiff bases such as S-methyl-N-methyl- $\beta$ -N-(2-hydroxyphenyl)methylendithiocarbazate (HSMNMSaD), S-methyl-N-methyl- $\beta$ -N-(2-hydroxy-3-methoxyphenyl)methylendithiocarbazate (HSMNMVD) and S-methyl-N-methyl- $\beta$ -N-(2-hydroxy-1-naphthyl)methylendithiocarbazate (HSMNMND) in 1:1 tin-ligand ratio have been prepared, characterized and reported for the first time.

The Schiff bases used here were prepared by the condensation of N-methyl-S-methylendithiocarbazate with 2-hydroxy benzaldehyde, 2-hydroxy-3-methoxybenzaldehyde or 2-hydroxy-1-naphthaldehyde. These Schiff bases possess five donor atoms, with a potential hydroxyl group which is intramolecularly hydrogen bonded with azomethine nitrogen. The thioenolization of thioketo sulphur is completely absent due to the presence of a  $-\text{CH}_3$  group on the neighbouring nitrogen atom. Hence bonding of the ligand to metal is expected through phenolic oxygen, azomethine nitrogen or thioketo sulphur atoms. These Schiff bases react with organotin chlorides in 1:1 metal-ligand molar ratio in the absence of a base to yield molecular addition complexes as white to yellow solids. These adducts are thermally stable and show sharp melting points. They are soluble in benzene and chloroform.

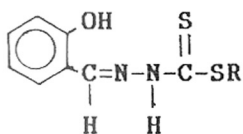
The IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral studies of these adducts reveal that the coordination of the Schiff base occurs through the lone pair of the phenolic oxygen without rupturing the intramolecularly hydrogen bonding. The complexes are assigned to have a trigonal bipyramidal geometry with equatorial disposition

of alkyl/aryl and chlorine groups, and axial alkyl/aryl and Schiff base groups.

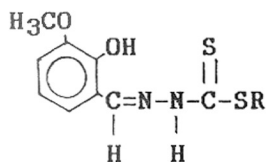
**2) Organotin(IV) complexes with the Schiff bases derived from S-methyl/S-benzyl-dithiocarbamate:**

Several complexes of the type  $R_2SnL$  {where  $R = -CH_2CH_2CO_2CH_3$ ,  $-CH_2CH_2CO_2C_2H_5$  or  $-CH_2CH_2CO_2C_4H_9$ ; and  $L = S$ -methyl/S-benzyl- $\beta$ -N-(2-hydroxyphenyl)methylendithiocarbamate [ $H_2SMSaD/H_2SBSaD$ ], S-methyl/S-benzyl- $\beta$ -N-(2-hydroxy-3-methoxyphenyl)methylendithiocarbamate [ $H_2SMVD/H_2SBVD$ ] or S-methyl/S-benzyl- $\beta$ -N-(2-hydroxy-1-naphthyl)methylendithiocarbamate [ $H_2SMND/H_2SBND$ ]} have been synthesized for the first time.

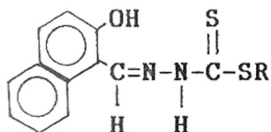
The Schiff bases used for the study are shown as follows:



$H_2SMSaD/H_2SBSaD$



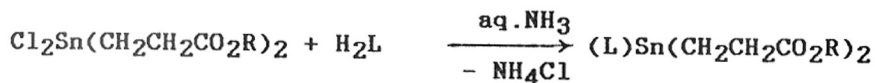
$H_2SMVD/H_2SBVD$



$H_2SMND/H_2SBND$



(The complexes described in this chapter have been synthesized by refluxing diester-tin dichlorides of the general formula  $\text{Cl}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{R})_2$  [where  $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$  or  $\text{C}_4\text{H}_9$ ] with stoichiometric amounts of dibasic Schiff bases [ $\text{H}_2\text{SMSaD}$ ], [ $\text{H}_2\text{SMVD}$ ], [ $\text{H}_2\text{SMND}$ ], [ $\text{H}_2\text{SBSaD}$ ], [ $\text{H}_2\text{SBVD}$ ] and [ $\text{H}_2\text{SBND}$ ] in chloroform using aqueous ammonia as HCl acceptor.)



These complexes are yellow, crystalline, low melting solids soluble in benzene, toluene, chloroform, and methylene chloride and insoluble in hexane. Molecular weight determination by vapour pressure osmometry in toluene at  $45^\circ$ , showed the monomeric nature of the complexes.

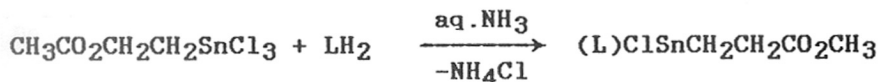
The complexes are characterized by their elemental analyses, molecular weight determination, IR,  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{119}\text{Sn}$  NMR spectra. The values of  $^1\text{J}$  ( $^{119}\text{Sn}$ ,  $^{13}\text{C}$ ) were used for the calculation of C-Sn-C bond angle ( $\theta$ ) which were found to be  $140-143^\circ$ . The spectral data are consistent with an octahedral geometry around tin(IV) in which the Schiff base acted as a dianionic tridentate ligand and the ester groupings as monodentate as well as bidentate moieties.

### 3) The Schiff bases derived from 2-amino-2-methyl-1-propanol

The organotin(IV) Schiff base complexes of the type  $(\text{L})\text{SnR}_2$ ,

(LH)Sn(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> and (L)SnCl(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>) have been prepared for the first time. In the complexes (L)SnR<sub>2</sub> R represents organic groups such as CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub> and ester -CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub> attached to tin and L or LH for the deprotonated Schiff base ligands. The Schiff base ligands used were obtained by condensation of salicylaldehyde and its 5-chloro or 5-bromo derivatives, 2-hydroxy-3-methoxybenzaldehyde and 2-hydroxy-1-naphthaldehyde with the amine, 2-amino-2-methyl-1-propanol.

The complexes have been synthesized by refluxing R<sub>2</sub>SnCl<sub>2</sub> [where R=CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub> or CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>], (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SnCl and (CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>)SnCl<sub>3</sub>, with stoichiometric amounts of dibasic Schiff base, (LH<sub>2</sub>) in chloroform medium using aq. ammonia as HCl acceptor.

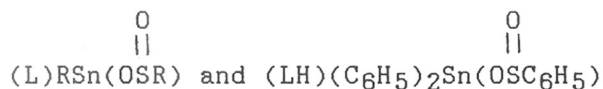


The complexes, (L)Sn(CH<sub>3</sub>)<sub>2</sub> and (LH)Sn(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> were prepared by an alternative procedure in which Me<sub>2</sub>SnO/Ph<sub>3</sub>SnOH was reacted with stoichiometric quantity of Schiff base in refluxing benzene followed by azeotropic removal of eliminated water.

These complexes are yellow crystalline solids soluble in

benzene, chloroform and methylene chloride and insoluble in hexane.

(The ligands and their complexes were characterized on the basis of their elemental analyses, IR,  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{119}\text{Sn}$  NMR spectral studies <sup>and x-ray crystal studies.</sup> In these <sup>dimeric</sup> complexes the Schiff base acts as a dianionic tridentate in diorganotin(IV) complexes of the type  $[(\text{L})\text{SnR}_2]_2$  and monobasic bidentate moiety in  $(\text{LH})\text{Sn}(\text{C}_6\text{H}_5)_3$  by coordinating through alkoxy oxygen, azomethine nitrogen and phenoxy group to tin. Sulphur dioxide inserts into tin-methyl/phenyl bond in the above Schiff base complexes to give mono insertion products which are found to be tin-O-sulphinates of the formula:



#### 4) Organotin(IV) complexes with the Schiff base derived from malonoyldihydrazone.

The Schiff base  $[\text{H}_4\text{L}]$  derived from salicylaldehyde and malonoyldihydrazine reacts with organotin chlorides to yield binuclear complexes of the type  $\text{R}_2\text{Sn}[\text{L}]\text{SnR}_2$  [where  $\text{R} = \text{CH}_3-$ ,  $\text{C}_2\text{H}_5-$ ,  $\text{C}_4\text{H}_9-$ ,  $\text{C}_6\text{H}_5-$ ,  $\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_2-$ ,  $\text{C}_6\text{H}_5\text{CH}_2-$  ].

(Bis)Salicylaldehyde malonoyldihydrazone ( $\text{H}_4\text{L}$ ) is a flexibly bridged binuclear Schiff base which functions as a hexadentate ligand dibasic ligand in the keto form and tetrabasic hexadentate in the enol form under suitable reaction conditions. However, simultaneous involvement of all the donor atoms in coordination

is also possible. In the present study, the reaction of organotin chlorides with  $LH_4$  in a 2:1 molar ratio in benzene medium resulted in the formation of complexes of the type  $(R_2Sn)_2(L)$  [where  $R = CH_3, C_2H_5, C_4H_9, C_6H_5, C_6H_5CH_2$  and  $CH_3COOCH_2CH_2$ ], with the replacement of all the four phenolic and enolic protons from the ligand. Triethylamine was used as HCl acceptor. The complexes are yellow solids and soluble in benzene, chloroform and insoluble in hexane.

The complexes were characterized and the probable structures have been assigned on the basis of their elemental analysis, IR,  $^1H$ ,  $^{13}C$  and  $^{119}Sn$  NMR spectral data, <sup>and x-ray crystal studies.</sup> (In these complexes, the ligand functions as a flexibly bridging tetrabasic hexadentate moiety binding two tin atoms through ONO donor atoms and each half of the molecule acquires trigonal bipyramidal geometry with tin atom at the centre.)

The thesis also incorporates mass spectral studies of Schiff bases, and their organotin(IV) complexes and their probable fragmentation pattern upon electron impact.

## L I T E R A T U R E S U R V E Y

The literature survey presented here covers tin(IV) complexes of Schiff bases containing nitrogen, oxygen and sulphur atoms and the recent work on this line covering papers and articles published in the last few years, relevant to the work reported in this thesis.

This survey is not aimed to cover old literature and hence not comprehensive, however literature appeared in the last 10-15 years has been covered and presented in this thesis.

The molecular structure and the restricted internal rotation about the tin-tin bond in  $[\text{ClSn}(\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{NCH}_3]_2$  and solution isomerism and isomerizations in  $[\text{CH}_3\text{Sn}(\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{NCH}_3]_2$  was determined by Jurkschat et al<sup>82</sup>. In these two five-coordinated compounds the tin centres were bound to each other. The two five-coordinate tin moieties exhibit approximately trigonal-bipyramidal geometry with the chlorine and nitrogen atoms occupying apical positions and the tin-tin and tin-carbon bonds occupying equatorial positions and twisted with respect to one another by about  $120^\circ$  along with tin-tin bond.

The dimethyl-, di-n-butyl-, di-tert-butyl- and diphenyltin(IV) derivatives of 2,6-pyridinedicarboxylic acid were prepared by Marcel et al<sup>83</sup> from the corresponding diorganotin oxide or diacetate and characterized by their Mössbauer, IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR, mass spectroscopy, X-ray diffraction analysis. In diphenyltin(IV) 2,6-pyridinedicarboxylate hydrate complex, tin was

at the centre of a distorted pentagonal bipyramid, the two phenyl groups were in the apical positions. Their *in vitro* activities against p 388, L 1210, p 815 leukemic cells and against B 16 melanoma and lewis lung carcinoma have been detected and were found to be more active than the clinically used antineoplastic agent cis-platin. The most active compound *in vitro* exhibits, however, only a moderate activity against p 388 leukemia *in vivo*.

Holecek et al<sup>84</sup> have studied  $^{13}\text{C}$  and  $^{119}\text{Sn}$  NMR spectra of some divinyltin(IV) complexes of carboxylic acids, such as 8-hydroxyquinoline and N,N'-diethyldithiocarbamate in coordinating and noncoordinating solvents. The results obtained were used to deduce a relation between the chemical shift,  $\delta(^{119}\text{Sn})$  and the coordination number of the central tin atom. Similarly correlation of the coupling constants  $^1J(^{119}\text{Sn}, ^{13}\text{C})$  with C-Sn-C angle is also reported. The complexes are found to be 5 or 6 coordinated on the basis of their  $^{119}\text{Sn}$  chemical shift values. Maji et al<sup>85</sup> have studied organometallic compounds such as triorganostannyl 2-(aryloxy)benzenecarboxylates in relation to the bacterial cell wall. They have shown that these carboxylates have great promise in inhibiting the growth of Gram-positive bacteria. A possible explanation for the structure-activity relationship (SAR) has been discussed through an interaction mechanism. The intercalative binding mechanism finds support from spectral, chemical as well as X-ray computer molecular

modeling evidences. An interpretation of the activity against various microorganisms has also been made in the present investigation.

The complexes of the type  $\text{SnL}_2\text{XCl}$  ( $\text{X} = \text{S}_2\text{COMe}$ ,  $\text{S}_2\text{COCHMe}_2$ ,  $\text{S}_2\text{COBu}$ ;  $\text{HL} = \text{acetylacetone}$ ,  $\text{benzoylacetone}$ ,  $\text{dibenzoylmethane}$ ) were prepared by Sharma et al<sup>86</sup> by the reaction of  $\text{SnCl}_2\text{L}_2$  with  $\text{NaX}$  in acetone under refluxing conditions. The new compounds were characterized by their elemental analyses, molecular weight measurements, IR and NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{119}\text{Sn}$ ) spectral studies and a distorted octahedral geometry was proposed with X as monodentate moiety.

Bozimo et al<sup>87</sup> have prepared 1:1 Lewis acid: Lewis base adducts from the reaction of 2-benzoylpyridine with  $\text{MeSnCl}_3$ ,  $\text{SnCl}_4$  or  $\text{PhSnCl}_3$  and of 2-pyridinecarboxaldehyde with  $\text{PhSnCl}_3$ . The 2-benzoylpyridine and 2-pyridinecarboxaldehyde bind to the organotin Lewis acids through their both N and O atoms. But 2-acetylpyridine reacts in a different manner with the tin(IV) chlorides, giving what appear to be 1:2 adducts with  $\text{MeSnCl}_3$ ,  $\text{SnCl}_4$ ,  $\text{PhSnCl}_3$  and  $\text{Ph}_2\text{SnCl}_2$ . This suggests that, with organotin Lewis acids, 2-acylpyridines with an  $\alpha$ -hydrogen atom on the side-chain reacts differently from 2-acylpyridines without  $\alpha$ -hydrogen in the side-chain.

Complex formation between di- and tri- organotin chlorides and the potentially bidentate ligand p-anisaldehydethiosemicarbazone (abbreviated as PAT) has been

examined by Bangboye<sup>88</sup>. In all the cases, molecular addition complexes of 1:1 stoichiometry are formed. The PAT ligand functions as bidentate N-S donor towards the di-organotin chlorides resulting in octahedral geometries, whereas in the adducts of the tri-organotin chlorides with PAT, the tin atom adopts a trigonal bipyramidal coordination and the PAT acts as monodentate coordinating through its azomethine nitrogen. Elemental analyses confirmed the stoichiometry of the complexes and their solid state configurations have been studied by <sup>119m</sup>Sn Mössbauer and far infrared spectroscopy.

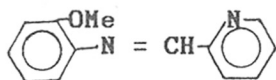
Some of triphenyltin(IV) complexes with semicarbazones and thiosemicarbazones of the general formula  $\text{Ph}_3\text{SnCl}\cdot\text{L}$  (L = semicarbazone or thiosemicarbazone of salicylaldehyde, o-hydroxy naphthaldehyde, 2-methoxybenzaldehyde, 4-methoxybenzaldehyde, furfuraldehyde, o-hydroxyacetophenone, benzyl methyl ketone and benzil) have been synthesized and characterized by Nath et al<sup>89</sup> on the basis of their elemental analyses, conductance measurements, IR, <sup>1</sup>H NMR and electronic spectral studies. An octahedral structure was proposed for all these complexes.

A series of organotin(IV) Schiff base complexes of the type  $(\text{C}_6\text{H}_5)_3\text{SnX}\cdot\text{L}$  (X = Cl, NCS, L = o-HOC<sub>6</sub>H<sub>4</sub>CH:NC<sub>6</sub>H<sub>4</sub>R; 2,3-HO(MeO)C<sub>6</sub>H<sub>3</sub>CH:NC<sub>6</sub>H<sub>4</sub>OMe-4, 2-HOC<sub>10</sub>H<sub>6</sub>CHNC<sub>6</sub>H<sub>4</sub>R, R = CH<sub>3</sub>, OCH<sub>3</sub>) have been synthesized by Khoo et al<sup>90</sup> by the reactions of triphenyltin chloride or isothiocyanate with N-arylsalicylaldenimines and N-



aryl-2-hydroxynaphthylidenimines. The crystal structure of isothiocyanatotriphenyl[1-(4'-methylphenylimino)methyl]-2-naphthol tin(IV), is reported. The complex has a five coordinated distorted trigonal bipyramidal structure, with the Ph groups taking up the equatorial positions around the tin atom. The ligand, which exists in the form of zwitterion in the complex, binds to the tin via the phenolic oxygen atom in one of the axial positions. The other complexes were believed to have structures similar to this.

The reaction between  $\text{Me}_2\text{SnCl}_2$  and the ligand in ethanol



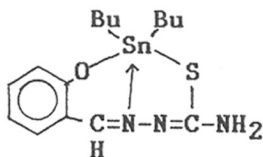
gave the monomeric (1:1) adduct  $\text{Me}_2\text{SnCl}_2 \cdot (2\text{-MeOC}_6\text{H}_4\text{N}:\text{CHC}_5\text{H}_4\text{N}-2)$ . X-Ray diffraction study showed<sup>91</sup> that the tin atom was in a distorted octahedral environment with trans-Me groups. The methoxy oxygen of the ligand remained uncoordinated. The Sn-N bond length was found to be  $> 2.39 \text{ \AA}$ .

The complex formation between  $\text{R}_2\text{SnCl}_2$  (R = Me, Bu, Ph or octyl) and 2-pyridinecarboxaldehyde thiosemicarbazone (PT) has been investigated by Tunde et al<sup>92</sup>. Only with  $\text{Me}_2\text{SnCl}_2$  a substitution reaction was observed, whereas in all other cases, 1:1 addition complexes were formed. The solid state configurations of the complexes have been studied by <sup>119</sup>Sn Mössbauer and far-IR spectroscopy. The chelating ligand

functions as bidentate towards diorganotin chlorides giving octahedral coordination geometry around the tin atom.

Saxena et al<sup>93</sup> have reacted  $\text{Sn}(\text{OAc})_4$  with Schiff base semicarbazones of the type  $\text{HOC}_6\text{H}_4\text{CH}=\text{N}-\text{NH}-\text{CO}-\text{NH}_2$ ,  $\text{HOC}_{10}\text{H}_5\text{CH}=\text{N}-\text{NH}-\text{CO}-\text{NH}_2$  or  $\text{HOC}_6\text{H}_4\text{CCH}_3=\text{N}-\text{NH}-\text{CO}-\text{NH}_2$ , (abbreviated as  $\text{SCzH}_2$ ) in toluene in 1:1 and 1:2 molar ratios to obtain complexes of type  $\text{Sn}(\text{OAc})_{4-2n}(\text{SCz})_n$ , (where  $n = 1, 2$  and  $\text{SCz}^{-2}$  represents the anion of semicarbazone). Compounds are characterized by X-ray, electronic, IR, and Mössbauer spectral studies. In the compound  $\text{Sn}(\text{sal semicarbazate})_2$  tin atom is in (IV) oxidation state in a symmetrical octahedral field and adopts an orthorhombic lattice with  $a = 6.72 \text{ \AA}$ ,  $b = 23.45 \text{ \AA}$  and  $c = 21.62 \text{ \AA}$ . The IR spectra have given evidence for the tridentate ligation of ligands,

Some five- and six-coordinated di- and tri- butyltin(IV) semi- and thiosemicarbazates were synthesized by Saxena et al<sup>94</sup>.

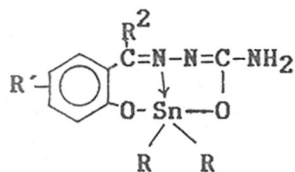


The characterization of these complexes by IR, NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{119}\text{Sn}$ ),  $^{119}\text{Sn}$  Mössbauer and mass spectroscopies along with X-ray diffraction, revealed that tin(IV) complexes of the type  $\text{Bu}_2\text{SnL}$  containing dibasic ligand anion were five coordinated having trigonal bipyramidal geometry. X-Ray structural studies on compound showed that it crystallized in a monoclinic lattice with

$a = 16.90 \text{ \AA}$ ,  $b = 9.71 \text{ \AA}$ ,  $c = .60 \text{ \AA}$ , and  $\beta = 103^\circ 45'$ . However, complexes of the type  $\text{Bu}_2\text{SnL}_2$  containing monoionic ligands were six-coordinated in a distorted cis-octahedral geometry and  $\text{Bu}_3\text{SnL}$  were five coordinated with a trigonal bipyramidal structure.

Several chlorine substitution products of  $\text{Me}_2\text{SnCl}_2$  with biologically active Schiff bases derived by the condensation of furfuraldehyde, thiophene-2-aldehyde, indole-3-carboxaldehyde and cinnamaldehyde with thiosemicarbazide and having the general formulae,  $\text{Me}_2\text{Sn}(\text{TSCZ})$  and  $\text{Me}_2\text{Sn}(\text{TSCZ})_2$  (where  $\text{TSCZ}^-$  = anion of Schiff base) have been synthesized by Kiran et al<sup>95</sup>. These complexes have been characterized by elemental analyses, molecular weight determinations and conductivity measurements. The IR and NMR spectra of the complexes showed that the ligand bonded through O, S and azomethine nitrogen to the tin atom.

Some semicarbazone derivatives of dibutyltin (IV) and



( $R = \text{Ph, Bu}$ ;  $R' = \text{H, 5,6-benzeneno}$ ;  $R^2 = \text{H, Me}$ )

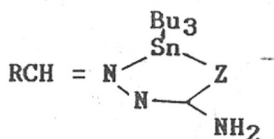
diphenyltin(IV) compounds of have been prepared and characterized by Srivastav et al<sup>96</sup>. A trigonal bipyramidal geometry is assigned for the above complexes on the basis of elemental analysis, conductance, IR and  $^1\text{H}$  NMR spectral data, having two oxygen atoms in axial positions and two phenyl/butyl groups in

equatorial positions.

Dixit et al<sup>97</sup> have condensed benzoin and acetoin with semicarbazide hydrochloride and thiosemicarbazide, which gave corresponding Schiff bases. These carbazones when reacted with  $\text{Me}_2\text{SnCl}_2$  and  $\text{Bu}_2\text{SnO}$  gave substitution products of the type  $\text{R}_2\text{SnL}$  ( $\text{R} = \text{Me, Bu}$ ;  $\text{LH}_2 = \text{ligand mol}$ ). The resulting complexes were characterized by elemental analysis, molecular weight determination and conductance measurements. Ligand-metal bonding was deduced and a penta-coordinated trigonal bipyramidal structure was assigned for the complex on the basis of IR,  $^1\text{H}$  NMR and electronic spectral studies. All the ligands studied behave as bifunctional tridentate ONS donors.

Synthesis and structural features of some trigonal bipyramidal and octahedral semicarbazonato complexes of organotin(IV) of the types  $\text{Me}_2\text{Sn}(\text{SCZ})\text{Cl}$  and  $\text{Me}_2\text{Sn}(\text{SCZ})_2$  ( $\text{SCZ}^{-1} = \text{e.g., furfuraldehyde semicarbazone anion}$ ) have been prepared from  $\text{Me}_2\text{SnCl}_2$  and characterized by elemental analyses, conductance measurements, molecular weight determinations and electronic, IR,  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{119}\text{Sn}$  NMR spectral studies by Singh et al<sup>98</sup>. The fungitoxicity these semicarbazones and their corresponding 1:1 and 1:2 tin complexes was ascertained on pathogenic fungi.

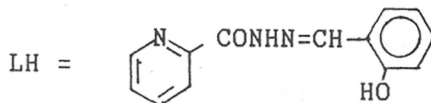
Reaction of the ligands  $\text{RCH:NNHC(Z)NH}_2$  ( $\text{R} = 2\text{-furyl, 2-thienyl, 3-indolyl}$ ;  $\text{Z} = \text{O, S}$ ) with  $(\text{Bu}_3\text{Sn})_2\text{O}$  in 2:1 molar ratio in refluxing benzene gave cyclic complexes<sup>99</sup>. The IR and NMR



spectra of the complexes indicate the participation of ketonic sulphur/oxygen in bond formation and non-involvement of  $\text{NH}_2$  in the complexation reaction. The  $^{119}\text{Sn}$  Mössbauer spectra suggest trigonal bipyramidal co-ordination around tin. The  $^{119}\text{Sn}$  NMR spectral data are in accordance with the proposed five-coordinated structure.

Some triorganotin(IV) complexes with general formula,  $\text{Ph}_3\text{SnL}$  [where LH = semi- and thiosemicarbazones of 2-acetylthiophene, 2-acetylfuran and 2-acetylnaphthalene] have been prepared and characterized by Kumari et al<sup>100</sup> on the basis of their elemental analyses, molecular weight, conductivity, and IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data. The IR and  $^1\text{H}$  NMR spectral data suggest that the ligands acted in monofunctional bidentate manner coordinating through nitrogen and sulphur donor atoms. A pentacoordinated trigonal-bipyramidal structure was tentatively proposed for the complexes.

Complexes of the type  $\text{SnX}_4 \cdot \text{LH}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{iodo}$ ),  $\text{RSnCl}_3 \cdot \text{LH}$  ( $\text{R} = \text{Bu}, \text{Ph}$ )  $\text{PhSnCl}_2 \cdot \text{L}$  and  $\text{PhSn}(\text{NCS})_2 \cdot \text{L}$  were prepared<sup>101</sup> by treating LH with Sn(IV) compound.



The complexes have been characterized by elemental analyses, molar conductivity, IR, electronic and PMR spectral measurements. From molar conductance values all the complexes are found to be non-ionic in nature. A negative shift in amide-I, band and positive shift in amide II and amide III bands in the IR spectra of the adducts compared to the solution of the amide group. The involvement of the oxygen of the amide group. The involvement of the azomethine nitrogen in the complexes is indicated by a positive shift in  $\nu(\text{N-N})$  and a negative shift in  $\nu(\text{C=N})$  vibrations of the ligand. The cis octahedral geometry is assigned for all the chloride complexes as  $\nu(\text{Sn-Cl})$  mode appearing as a strong and broad band in the region  $280\text{-}328\text{ cm}^{-1}$  in chloride complexes. These octahedral complexes are examples for hexacoordination around tin(IV).

Singh et al<sup>102</sup> have reported studies on organotin(IV) derivatives of diethylaminomethyl ester of 2-amino-1-cyclopentene-1-carbodithioic acid,  $\text{H}_2\text{NCCH}_2\text{CH}_2\text{CH}_2\text{CC}(\text{S})\text{SCH}_2\text{N}(\text{C}_2\text{H}_5)$   $[(\text{LH})_2]$  with  $\text{Bu}_2\text{SnCl}_2$ ,  $\text{Ph}_2\text{SnCl}_2$  and  $\text{BuSnCl}_3$  and have proposed composition  $(\text{L})_x\text{SnR}_n\text{Cl}_{4-n-x}$  to the compound formed (L = ester anion; R = Bu, n = 3, x = 1; R = Bu, Ph, n = 2, x = 1; R = Bu, n = 1, x = 1). Similarly, treating  $\text{Me}_2\text{Sn}(\text{OCHMe}_2)_2$  with above ester gave  $\text{Me}_2\text{Sn}(\text{OCHMe}_2)_{2-n}(\text{L})_n$  (n = 1, 2).

Ghosh et al<sup>103</sup> have isolated crystalline triorganotin(IV) and diorganotin(IV) derivatives of dithizone ( $\text{H}_2\text{Dz}$ ) and characterized by visible, IR and  $^1\text{H}$  NMR spectroscopy. The triorganotin

derivatives such as  $R_3Sn(HDz)$  (where  $R = Bu$  or  $Ph$ ) are possibly penta-coordinated and those of diorganotin derivatives,  $R_2Sn(HDz)_2$  (where  $R = Me, Pr, Bu, Ph, p\text{-tolyl}$  or  $benzyl$ ) are hexacoordinated. For dimethyltin bis-dithizonate, a trans arrangement of methyl groups has been suggested.

Varshney et al<sup>104</sup> have made Schiff bases by condensation of salicylaldehyde with sulphisoxazole, sulphapyridine and sulphanilamide with general formula LH. These monoionic Schiff bases reacted with  $Bu_2SnO$  and  $(Bu_3Sn)_2O$  to give six- and five-coordinated tin(IV) complexes respectively of the type  $Bu_2SnL_2$  and  $Bu_3SnL$  respectively. The complexes are characterized by UV, IR, NMR ( $^1H$ ,  $^{119}Sn$ ), and  $^{119}Sn$  Mössbauer spectral studies.

Weng et al<sup>105</sup> have carried out crystal structure studies of bis(2-carbomethoxyethyl)bis(N,N-dimethyldithiocarbamato)tin(IV),  $[MeOC(O)CH_2CH_2]_2Sn[SC(S)NMe_2]_2$ . The compound is monomeric and the tin atom is seven coordinated in a distorted pentagonal bipyramid with the organic groups in apical positions; the pentagonal girdle is made up of the four sulphur atoms of the ansibidentate dithiocarbamato ligands and the carbonyl oxygen atom of a bent apical organic group. The oxygen atom and one sulphur atom are displaced equally but oppositely by  $0.24 \text{ \AA}$  from the pentagonal least-squares plane, and the tin atom by  $0.054 \text{ \AA}$ . The compound is six-coordinate in  $CDCl_3$  solution, as shown by  $^{13}C$  NMR data; the one-bond coupling constant,  $^1J(^{119}Sn-^{13}C)$ , has the

value 794.2 Hz, consistent with the lower coordination state. There is some evidence, however, of retention of the seven coordination in pyridine solution.

The coordination behaviour of Schiff bases ( $H_2L$ ) derived from salicylaldehyde and some well known sulpha drugs, viz., sulphathiazole, sulphaphenazole, sulphadiazine, sulphaguanidine and 2-(p-aminobenzenesulphonamido)-4,5-dimethyloxole, was systematically studied by Varshney et al<sup>106</sup> with  $Sn(OAc)_4$  in 1:1 and 2:1 molar ratio. An attempt was made to probe into the structures of their metal complexes by elemental analyses, molecular weight determinations, conductivity measurements as well as UV, IR,  $^1H$  NMR and  $^{119}Sn$  Mössbauer spectral studies. On the basis of these studies, a trigonal bipyramidal and square bipyramidal geometry is assigned for 1:1 and 1:2 complexes respectively.

Ten complexes formulated as  $Ph_2SnL$ , where L was  $RC_6H_4C(O)N_2CHC_6H_4O$  with R = H, p- $NO_2$ , p-Cl, p-Br, p- $CH_3$ , p- $OCH_3$ , o- $NO_2$ , m- $OCH_3$  and 3,5-dinitro, have been prepared and were characterized<sup>107</sup> by  $^1H$  NMR, IR and mass spectroscopy and elemental analyses. A single crystal X-ray diffraction study of the complex with R = o- $NH_2$  confirms that the tin atom has a distorted trigonal bipyramidal coordination. The 2 Sn-O bands of 2.073 and 2.116 Å respectively and one Sn-N bond [of 2.143 Å] are shorter than those found in related complexes. A comparison of IR spectra of the ligands with those of the corresponding complexes,



reveals that the disappearance of the bonds assigned to carbonyl unambiguously confirm that the ligands coordinate with the tin in the enol form.

Schiff bases (L), derived from the condensation of salicylaldehyde, 2-(p-aminobenzene sulphonamide)-4,5-dimethyloxazole, sulphisoxazole and sulphapyridine, reacted with  $\text{Me}_2\text{SnCl}_2$  to give tin complexes  $\text{Me}_2\text{SnL}$ , which were characterized by Varshney et al<sup>108</sup> by Mössbauer, NMR and IR spectroscopic studies.

Podesta et al<sup>109</sup> have reported free radical hydrostannation of methyl 3,4-dihydronaphthalene-1-carboxylate (I), 3,4-dihydronaphthalene-2-carboxylate (III) and methyl 1,4-dihydronaphthalene-1-carboxylate (V) with  $\text{R}_3\text{SnH}$  (R = Me, Bu, Ph). The energetically unfavourable cis- products, 2-triorganostannyl-1,2,3,4-tetrahydronaphthalene-2-carboxylate(II) 1-triorganostannyl-1, 1,2,3,4-tetrahydronaphthalene-2-carboxylate (IV) and 3-triorganostannyl-1,2,3,4-tetrahydronaphthalene-2-carboxylate(VI) respectively were obtained in high yields, via a trans addition of the tin hydrides. The hydride abstraction by the intermediate 2-,1-,3-triorganostannyl-1,2,3,4-tetrahydronaphthyl radicals (XI, XII and XIII respectively) take place stereospecifically and exclusively from the less-hindered ring side. The structures of the isomers II, IV, VI were established by their transformation into the corresponding

chlorodiorganostannyl derivatives VIII, IX and X which were shown spectroscopically to have cis stereochemistries by intramolecular complexation of the ester group, and by their NMR data. Full  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{119}\text{Sn}$  NMR data was reported.

The Mössbauer parameters have reported by Jurksat et al<sup>110</sup> on 25 tetra-, penta-, and hexacoordinated organotin compounds of the general types  $\text{RSn}(\text{CH}_2\text{CH}_2\text{CH}_2)_3\text{N}$  ( $\text{R} = \text{Cl}, \text{Me}$ ),  $\text{RR}'\text{Sn}(\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{E}$  ( $\text{R} = \text{Cl}, \text{Me}$ ;  $\text{R}' = \text{Cl}, \text{Me}$ ;  $\text{E} = \text{NMe}, \text{O}$ ),  $\text{Me}_2\text{ClSnCH}_2\text{CH}_2\text{CH}_2\text{E}$  ( $\text{E} = \text{NMe}_2, \text{PPhBu}^t, \text{MeNCH}_2\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{CH}_2\text{SnMe}_2\text{Cl}$ ),  $\text{RR}'\text{Sn}[\text{CH}_2\text{CH}_2\text{CH}_2\text{N}(\text{Me})\text{CH}_2]_2$  ( $\text{R} = \text{R}' = \text{Cl}, \text{Br}, \text{I}, \text{SPh}$ ;  $\text{R} = \text{Me}, \text{R}' = \text{Cl}$ ),  $\{\text{SSn}[\text{CH}_2\text{CH}_2\text{CH}_2\text{N}(\text{Me})\text{CH}_2]_2\}_2$ ,  $\text{Cl}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)_2$ ,  $\text{S}(\text{CH}_2\text{CH}_2\text{CH}_2\text{SnMe}_{(3-n)}\text{Cl}_n)_2$  ( $n = 1, 2$ )  $\text{Et}_{(3-n)}\text{X}_n\text{SnCH}_2\text{CH}_2\text{E}$  ( $n = 0, \text{E} = \text{P}(\text{O})(\text{OEt})\text{Ph}, \text{P}(\text{O})\text{Bu}_2$ ;  $n = 1, \text{X} = \text{Br}, \text{E} = \text{P}(\text{O})(\text{OEt})\text{Ph}, \text{P}(\text{O})\text{Bu}_2, \text{Me}_2\text{ClSnCH}_2\text{CH}_2\text{PPh}_2$ , and  $\text{Ph}(\text{O})\text{P}(\text{CH}_2\text{CH}_2\text{SnClMe}_2)_2$ ). The pentacoordinated derivatives show a big difference between  $\text{QS}_{\text{calc}}$  and  $\text{QS}_{\text{exp}}$  suggesting substantial distortions from ideal geometry. The monocyclic derivatives  $\text{Me}_2\text{ClSnCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2$  and  $\text{Me}_2\text{ClSnCH}_2\text{CH}_2\text{CH}_2\text{PPhBu}^t$  exhibit remarkable similar QS values, although trivalent phosphorus is known to be a poor donor towards tin(IV) as compared with trivalent nitrogen. Obviously, this difference in donor capacity is much more expressed in their different IS values. Some organostannoxy complexes of NO donor Schiff bases derived from heterocyclic ketones were reported by Dixit et al<sup>111</sup>. The isolated products were characterized by various physicochemical methods and

spectroscopic studies viz. IR,  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{119}\text{Sn}$  NMR and X-ray powder diffraction. The metal derivatives as well as the chelating agents were screened on the male albino rats and an effort was made to evaluate their effects on the motility of sperms as well as the the numbers of counts of sperms. A study of the fungicidal activity of these compounds has been carried out.

The synthesis and investigation of the anti-tumor activity of series of six new diorganotin dichloride complexes  $\text{Ar}_2\text{SnCl}_2\text{L}_2$ , where Ar = 2-thienyl, 2,4-dimethoxyphenyl, 4-methoxyphenyl, 4-methoxyphenyl or 4-trifluoromethylphenyl, and  $\text{L}_2$  = 2-(2-pyridyl)benzimidazole (PBI) or 2-aminomethylpyridine, were reported by Biddle et al<sup>112</sup>. One of the complexes was found to be active against P 388 lymphocytic leukemia in mice. The activity of the diaryltin dichloride complexes was found to be dependent on the electronic effect of the aromatic group. The use of PBI as a ligand, however, shows no advantage over other ligands used in the series investigated.

The electrochemical oxidation of anodic tin in acetonitrile solutions in the Schiff bases derived from the required salicylaldehyde and bis(2-aminophenyl)disulphide ( $\text{L}_2\text{H}_2$ ) yielded compounds of formulae  $\text{SnL}_2$ . The crystal structure of bis{2-(2-mercaptophenyl)imino-4,6-dimethoxyphenoxy}tin(IV) [ $\text{SnL}_2'$ ] was determined by Elena et al<sup>113</sup>. The tin atom had an octahedral

geometry with a meridinal ligand occupancy the average Sn-N, Sn-O and Sn-S bond lengths were 2.17, 2.07 and 2.47 Å respectively.

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## CHAPTER 2

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STUDY ON MOLECULAR ADDITION COMPLEXES OF ORGANOTIN(IV) WITH  
S-METHYL-N-METHYLDITHIOCARBAZATE SCHIFF BASES.

S U M M A R Y

Several novel molecular addition complexes of organotin(IV) chlorides with the Schiff bases, S-methyl-N-methyl- $\beta$ -N-(2-hydroxyphenyl)methylendithiocarbazate (HSMNMSaD), S-methyl-N-methyl- $\beta$ -N-(2-hydroxy-3-methoxyphenyl)methylendithiocarbazate (HSMNMVD) and S-methyl-N-methyl- $\beta$ -N-(2-hydroxy-1-naphthyl)methylendithiocarbazate (HSMNMND) in 1:1 tin-ligand ratio have been prepared and characterized. The IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral studies of these adducts reveal that the coordination of the Schiff base occurs through the hydrogen bonded phenolic oxygen without rupturing the hydrogen bonded ring. The complexes are assigned to have a trigonal bipyramidal geometry with equatorial disposition of alkyl/aryl groups and a chlorine atom, and axial chlorine and Schiff base groups.

I N T R O D U C T I O N

The study of organotin complexes of dithiocarbazic acid,  $\text{H}_2\text{N}-\text{NH}-\text{C}(\text{S})\text{SH}$ , and its Schiff base derivatives is currently drawing considerable attention because of their interesting ligating properties and potential biological activities.

Akbar Ali et al<sup>1</sup> have prepared hydrated complexes, such as  $\text{Cr}(\text{H}_2\text{NNHCS}_2)_3 \cdot 2\text{H}_2\text{O}$ ,  $\text{Ni}(\text{H}_2\text{NNHCS}_2)_2 \cdot \text{H}_2\text{O}$  and anhydrous complexes such as  $\text{M}(\text{H}_2\text{NNHCS}_2)_2$  where  $\text{M} = \text{Pd}, \text{Pt}, \text{Zn}, \text{Cd}$  and  $\text{Pb}$ , by the reaction of dithiocarbazic acid with the appropriate metal salt, in which ligand is coordinated via nitrogen and sulphur atoms.

The ligand behaviour of methyl esters of dithiocarbazic acid,  $[\text{NH}_2\text{NHC}(=\text{S})\text{SMe}]$  and 2-methyldithiocarbazic acid  $[\text{NH}_2\text{NMeC}(=\text{S})\text{SMe}]$ , in the cobalt complexes has been investigated by Monoci et al<sup>2</sup>. The nickel complexes<sup>3</sup> of the type  $[\text{NiL}_3]\text{X}_2$  with methyl/butyl/phenyl esters of dithiocarbazic acid,  $\text{NH}_2\text{NMeC}(=\text{S})\text{SR}$  (where  $\text{R} = \text{H}, \text{Me}, \text{Bu}$  or  $\text{Ph}$ ) have been prepared by the reaction of  $\text{NiX}_2$  (where  $\text{X} = \text{Cl}, \text{Br}$  or  $\text{I}$ ) with the ligand in 1:3 molar ratio. These complexes are assigned to have an octahedral geometry on the basis of their electronic and IR spectra.

$\text{Cr}(\text{III})$ ,  $\text{Mn}(\text{II})$  and  $\text{Ni}(\text{II})$  halides form molecular addition complexes with the Schiff base,  $\alpha$ -N-methyl-S-methyl- $\beta$ -N-(2-pyridyl)methylendithiocarbazate (L). In these complexes the ligand behaves as a neutral tridentate moiety forming complexes of the type  $\text{Cr}(\text{L})\text{Cl}_3$ ,  $\text{Mn}(\text{L})\text{X}_2$  ( $\text{X} = \text{Cl}, \text{NCS}$ ) and  $\text{M}(\text{L})\text{X}_2$  ( $\text{M} = \text{Ni}, \text{Cu}$ ). A monomeric octahedral configuration is assigned for  $\text{Cr}(\text{III})$  complexes on the basis of conductivity and spectral data, whereas the manganese and nickel complexes are probably halogen-bridged, binuclear and octahedral in structure. The bis-ligand complexes of type  $[\text{M}(\text{L})_2](\text{ClO}_4)_2$  ( $\text{M} = \text{Fe}, \text{Co}, \text{Ni}$ ),  $[\text{Ni}(\text{L})_2](\text{BF}_4)_2 \cdot 2\text{H}_2\text{O}$ ,

and  $[M(L)_2][MX_4]$  ( $M = Fe, Co; X = Cl, Br, I, NCS$ ) were also reported<sup>4</sup>. In these complexes the Fe(II) cation is low spin and diamagnetic but Co(II) cation is high-spin.

Ali et al<sup>5</sup> have prepared novel Schiff base ligands by the condensation of 2-methoxybenzaldehyde/2-4-dimethoxybenzaldehyde and N-methyl-S-alkyldithiocarbazates, and synthesized their Ni(II) and Cu(II) complexes. In these complexes, the Schiff bases behave as neutral tridentate chelating agents coordinating through ONS donor atoms and forming stable complexes of the type  $NiLX_2.nC_2H_5OH$  and  $CuLCl_2$ . On the basis of conductivity, magnetic and spectral data, these complexes are assigned to have a pseudo octahedral structure.

Pandey et al<sup>6</sup> have carried out the reactions of chromium (0)- and molybdenum (0)- hexacarbonyls with bidentate thio-Schiff bases (TSB), derived by the condensation of S-methyldithiocarbamate with benzaldehyde, salicylaldehyde, acetophenone and furfuraldehyde in dry benzene under refluxing condition. The products isolated were of the type  $[M(CO)_4(TSB)]$  ( $M = Cr$  or  $Mo$ ) and have been characterized by their elemental analysis, electrical conductance, magnetic susceptibility measurements and infrared spectral data. IR spectrum reveals that the Schiff base is coordinated to metal through its thioketo sulphur and azomethine nitrogen and two carbonyls are situated *trans* to each other while other two are in *cis* position forming an octahedral complex.



Complexes with general formula  $M(N-SBz)_2X_2$ , where  $M = Ni(II)$ ,  $Cu(II)$ ,  $X = NO_3, 0.5 SO_4$ ;  $M = Cd(II)$ ;  $X = NO_3, 0.5 SO_4$ ; and  $M(N-SBz)X_2$ , [ $M = Cu(II)$ ,  $X = Cl, Br$ ;  $M = Cd(II)$ ,  $X = Cl$ ;  $N-SBz = N$ -methyl-S-benzylthiocarbamate] have been synthesized and characterized by Raheman et al<sup>7</sup>. The  $Ni(II)$  complexes are of high spin and octahedral in structure. The  $Cu(II)$  complexes,  $Cu(N-SBz)X_2$ , reported to have magnetic moments of 1.78-1.81 B.M. at room temperature. The electronic and ESR spectroscopic data support polymeric tetragonal structures for these complexes. Some of the complexes have been tested for their antifungal activities against three pathogenic fungi; viz. *alternaria solani*, *curvularia geniculata* and *colletotrichum capsici*. The results show that both the ligand and its complexes are fungitoxic. Among the metal complexes, those having copper(II) as the central metal ion, display more toxicity toward the test fungi than the other complexes.

$Ni(II)$ ,  $Cu(II)$  and  $Pd(II)$  complexes of the Schiff bases  $\alpha$ -N-methyl-S-methyl- $\beta$ -N-(2-hydroxyphenyl)methylendithiocarbamate (HL), have been prepared by Akbar Ali et al<sup>8</sup>. In these complexes the ligand behave as monobasic tridentate moiety. The complexes  $Ni(L)X$  ( $X = Cl, Br, NCS$ ) are diamagnetic and square-planar, while the complex  $Ni(L)_2$  is paramagnetic and octahedral. The palladium complex  $Pd(L)Cl$  having a square planar monomeric structure is also isolated. The copper complexes,  $Cu(L)NO_3$  and

[Cu(L)Py]ClO<sub>4</sub>, display normal magnetic behaviour. Both of these complexes have square-planar configuration. The compound Cu(L)BF<sub>4</sub> has an anomalously low magnetic moment. The oxygen-bridged binuclear structure is assigned for this complex. The complex Cu<sub>2</sub>(L)Cl<sub>3</sub> also displays antiferromagnetic interaction between the two copper atoms of the dimer. The complex Cu<sub>3</sub>(L)<sub>2</sub>Cl<sub>4</sub> has, most likely, a linear trimeric structure.

Akbar Ali et al<sup>9</sup> have conducted magnetic and spectral studies on copper(II) complexes of a similar Schiff base formed by condensation of 2-hydroxybenzaldehyde with N-methyl-S-benzylidithiocarbamate. The complexes have been characterized by the IR and electronic spectroscopic techniques and variable-temperature magnetic susceptibility measurements. The complex Cu(Sal-SBz)ClO<sub>4</sub> (Sal-SBz is the anionic form of the Schiff base) exhibits an anomalously low magnetic moment of 0.43 B.M. at room temperature. Magnetic and IR spectral data support an oxygen-bridged binuclear structure for the complex. The Cu<sub>3</sub>(sal-SBz)<sub>2</sub>Cl<sub>4</sub> complex is thought to possess a trimeric structure. The complexes having the general formula, [Cu(sal-SBz)X] (X = Br<sup>-</sup>, OH<sup>-</sup>) were also isolated. variable temperature magnetic susceptibility data and spectral evidences are in accordance with a square-planar structure for these complexes.

Surprisingly, there is no mention in the literature about molecular addition complexes of organotin chlorides with the above type of Schiff bases. We herein report the preparation and

characterization of the molecular addition complexes of the Schiff bases HSMNMSaD, HSMNMVD and HSMNMND with some organotin chlorides.

## EXPERIMENTAL

The organic solvents were purified, dried and distilled before use. Methyl iodide, carbon disulphide, tin tetrachloride and potassium hydroxide (Loba Chemie, India, G.R.grade) were used as such. 2-Hydroxy-3-methoxybenzaldehyde and 2-hydroxy-1-naphthaldehyde were purchased from Aldrich Chemical Co., U.S.A. Organotin chlorides were products of Alfa Inorganics, U.S.A.

The Schiff bases S-methyl-N-methyl- $\beta$ -N(2-hydroxyphenyl)C-methylendithiocarbamate (HSMNMSaD) and S-methyl-N-methyl- $\beta$ -N(2-hydroxy-1-naphthyl)methylendithiocarbamate (HSMNMND) were prepared by the reported procedure<sup>10</sup>.

The IR spectra of the adducts were recorded on a Perkin-Elmer 1620 FTIR spectrophotometer as KBr pellets, CH<sub>2</sub>Cl<sub>2</sub> solution or nujol mulls. The <sup>1</sup>H NMR spectra were recorded on a Varian FT-80 A or Bruker WH-90 spectrophotometer using TMS as internal standard. The <sup>13</sup>C NMR spectrum of Me<sub>2</sub>SnCl<sub>2</sub>.HSMNMSaD was measured with a Bruker MSL 300 spectrometer at 75.47 MHz. The spectrum was recorded in CDCl<sub>3</sub> solution at ambient temperature. The <sup>13</sup>C chemical shift is related to CDCl<sub>3</sub> signal (<sup>13</sup>C CDCl<sub>3</sub> = 76.9 ppm).

The following Schiff bases and their molecular addition complexes of organotin(IV) chlorides have been prepared. The elemental analyses, m.p. and colour etc. have been presented in Table 2.1.

**Preparation of S-methyl-N-methyl- $\beta$ -N-(2-hydroxyphenyl)methylenedithiocarbazate (HSMNMSaD) [1]**

S-Methyl-N-methyldithiocarbazate (2.72 g; 0.02 mol) in ethanol (50 ml) and salicylaldehyde (2.44 g; 0.02 mol) in ethanol (50 ml) were mixed and refluxed for 3 hr. Upon cooling the white crystals separated, were filtered and air dried; Yield 4.44 g (86%); m.p. 125°.

**Preparation of S-methyl-N-methyl- $\beta$ -N-(2-hydroxy-3-methoxyphenyl)methylenedithiocarbazate (HSMNMVD) [2]**

S-Methyl-N-methyldithiocarbazate (2.72 g; 0.02 mol) was dissolved in ethanol (50 ml) and to this solution 2-hydroxy-3-methoxybenzaldehyde (3.04 g; 0.02 mol) was added and refluxed for 3 h. The resulting solution upon cooling deposited a white crystalline solid which was collected and dried in air; Yield 3.84 g (80%); m.p. 138°.

**Preparation of S-methyl-N-methyl- $\beta$ -N-(2-hydroxy-1-naphthyl)methylenedithiocarbazate (HSMNMND) [3]**

S-Methyl-N-methyldithiocarbazate (2.72 g; 0.02 mol) was dissolved in ethanol (75 ml) and mixed with 2-hydroxy-1-naphthaldehyde (3.48 g; 0.02 mol) and the contents refluxed for 3 h. On cooling the yellow crystals separated were filtered and

recrystallised from benzene; Yield 5.27 g (85%); m.p. 185<sup>o</sup>.

#### Preparation of Me<sub>2</sub>SnCl<sub>2</sub>.HSMNMSaD [4]

A solution of Me<sub>2</sub>SnCl<sub>2</sub> (0.22 g; 0.001 mol) in benzene (25 ml) was added to a solution of HSMNMSaD (0.24 g; 0.001 mol) in 10 ml of the same solvent and refluxed for 3 h. The clear yellow solution upon concentration under reduced pressure gave a crystalline yellow solid, which after recrystallization from a small volume of hexane gave the pure addition compound; Yield 0.30 g (65%); m.p. 98<sup>o</sup>.

#### Preparation of Me<sub>2</sub>SnCl<sub>2</sub>.HSMNMVD [5]

To a benzene solution of Me<sub>2</sub>SnCl<sub>2</sub> (0.22 g; 0.001 mol) (10 ml) the benzene solution (10 ml) of the ligand HSMNMVD (0.27 g; 0.001 mol) was added and the mixture was refluxed for 3 h. The resulting solution was concentrated to a small volume. The white crystals separated were filtered, washed with hexane and dried in vacuo. Yield 0.35 g (71%); m.p. 112<sup>o</sup>.

#### Preparation of Et<sub>2</sub>SnCl<sub>2</sub>.HSMNMVD [6]

The addition complex Et<sub>2</sub>SnCl<sub>2</sub>.HSMNMVD was prepared by adding a solution of the Et<sub>2</sub>SnCl<sub>2</sub> (0.25 g; 0.001 mol in 10 ml benzene) to a solution of the Schiff base HSMNMVD (0.27 g; 0.001 mol in 15 ml benzene) and refluxing for 2 h. Precipitation was effected by addition of 2-3 drops of hexane to the reaction mixture. The complex thus obtained was filtered, washed with hexane and dried in vacuo to get white crystals. Yield 0.39 g (74%); m.p. 132<sup>o</sup>.

**Preparation of  $\text{Bu}_2\text{SnCl}_2 \cdot \text{HSMNMVD}$  [7]**

The Schiff base HSMNMVD (0.27 g; 0.001 mol) and  $\text{Bu}_2\text{SnCl}_2$  (0.31g; 0.001 mol) were dissolved in 25 ml benzene. The solution was refluxed for 3 h. Upon cooling, a yellow crystalline solid slowly precipitated from the solution. This was separated by filtration, and washed with hexane. Yield 0.44 g (76%); m.p.  $130^\circ$ .

**Preparation of  $\text{Ph}_3\text{SnCl} \cdot \text{HSMNMVD}$  [8]**

To a solution of  $\text{Ph}_3\text{SnCl}$  (0.39 g; 0.001 mol) in 20 ml benzene was added the Schiff base, HSMNMVD (0.27 g; 0.001 mol). The reaction mixture was refluxed for 2 h, and the clear solution was concentrated to ~ 10 ml. About 20 ml of hexane was added to separate a white solid. Yield 0.48 g (73%); m.p.  $92^\circ$ .

**Preparation of  $\text{Me}_2\text{SnCl}_2 \cdot \text{HSMNMND}$  [9]**

A solution  $\text{Me}_2\text{SnCl}_2$  (0.24 g; 0.001 mol) in 15 ml of benzene was slowly added to a clear solution of the HSMNMND (0.29 g; 0.001 mol) in 15 ml of benzene with constant stirring. The reaction mixture was refluxed for 3 h. and allowed to stand overnight. The yellow crystals obtained were filtered, washed with hexane and dried in vacuum; Yield 0.37 g (69%); m.p.  $179^\circ$ .

**Preparation of  $\text{Et}_2\text{SnCl}_2 \cdot \text{HSMNMND}$  [10]**

$\text{Et}_2\text{SnCl}_2$  (0.25 g; 0.001 mol) and Schiff base HSMNMND (0.29 g; 0.001 mol) were dissolved in benzene and refluxed for 3 h. The solvent was removed under reduced pressure and upon addition of hexane (~ 10 ml) yielded a yellow product. Yield 0.38 g

(70%); m.p. 185<sup>o</sup>.

#### Preparation of Bu<sub>2</sub>SnCl<sub>2</sub>.HSMNMND [11]

A solution of Bu<sub>2</sub>SnCl<sub>2</sub> (0.31 g; 0.001 mol in 20 ml benzene) was mixed with a benzene solution of HSMNMND (0.29 g; 0.001 mol). The reaction mixture was refluxed for 3 h. After the completion of the reaction, excess solvent was removed under vacuum and the compound obtained was recrystallised from benzene/hexane mixture, to yield a yellow solid. Yield 0.41 g (68%); m.p. 182<sup>o</sup>.

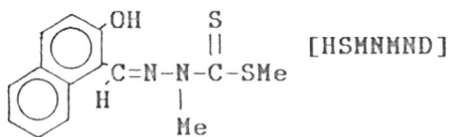
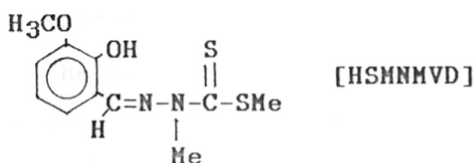
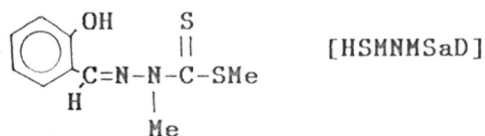
#### Preparation of Ph<sub>3</sub>SnCl.HSMNMND [12]

A mixture of Ph<sub>3</sub>SnCl (0.39 g; 0.001 mol in 20 ml benzene) and the Schiff base HSMNMND (0.29 g; 0.001 mol) in 20 ml benzene was refluxed for 3 h. The mixture was cooled to room temperature and kept in refrigerator overnight. The yellow crystalline compound precipitated was separated by filtration, washed several times with hexane, and finally recrystallized from a methylene chloride/ hexane mixture. Yield 0.48 g (71%); m.p. 170<sup>o</sup>.

## R E S U L T S   A N D   D I S C U S S I O N

The Schiff bases reported here have been derived from the condensation of N-methyl-S-methyldithiocarbamate with 2-hydroxy aromatic aldehydes such as 2-hydroxy benzaldehyde, 2-hydroxy-3-methoxybenzaldehyde and 2-hydroxy-1-naphthaldehyde and they contain phenolic hydroxyl (O-H), thiocarbonyl (C=S) and

azomethine (C=N) groups as represented below with abbreviation in parenthesis.



These Schiff bases react with organotin chlorides in 1:1 metal-ligand molar ratio in the absence of a base to yield molecular addition complexes as white to yellow solids. These adducts are thermally stable and show sharp melting points. They are soluble in benzene and chloroform. Analytical data are given in Table 2.1.



**IR spectral data of the Schiff bases, HSMNMSaD, HSMNMVD & HSMNMND and its molecular addition complexes**

The IR spectra of the Schiff bases, HSMNMSaD, HSMNMVD and HSMNMND, in solid state, [Table 2.2] exhibit weak to medium intensity bands at 3154, 3260 and 3170  $\text{cm}^{-1}$  respectively attributable to hydrogen bonded  $\nu(\text{OH})$ . The bands appearing between 1617 to 1595 and 1601 to 1575  $\text{cm}^{-1}$  are assigned to the coupled vibration of  $\nu(\text{C}=\text{N})$  and  $\nu(\text{C}=\text{C})$  respectively of the Schiff bases. The phenolic  $\nu(\text{C}-\text{O})$  is observed at  $\sim 1210 - 1267 \text{ cm}^{-1}$  respectively. The bands at  $\sim 1020 \text{ cm}^{-1}$  is assigned to  $\nu(\text{C}=\text{S})$  and the  $\nu(\text{N}-\text{N})$  stretching frequency is observed between 944 and 965  $\text{cm}^{-1}$  in these ligands.

The IR spectrum of adduct,  $\text{Me}_2\text{SnCl}_2 \cdot \text{HSMNMSaD}$ , [fig. 2.2] exhibits a broad band at 3148  $\text{cm}^{-1}$  attributable to hydrogen bonded  $\nu(\text{OH})$ . The adducts with Schiff bases HSMNMVD and HSMNMND also show  $\nu(\text{OH})$  in the region 3060-3180  $\text{cm}^{-1}$ . The shift of the  $\nu(\text{OH})$  band to lower frequency region in the adducts is suggested to be due to coordination of the lone pair on the oxygen of the hydrogen bonded OH group to the tin atom. Further, coordination of the oxygen atom would result in the weakening of the hydrogen bond of the OH group and strengthening of the  $>\text{C}=\text{N} \dots \text{H}$  bond<sup>11-14</sup>. The  $\nu(\text{C}=\text{N})$  frequency appears almost at the same position as that of the Schiff bases which indicates non-involvement of nitrogen lone pair in the coordination to tin atom. The bands due to  $\nu(\text{C}=\text{S})$  and  $\nu(\text{N}-\text{N})$  in the adducts remain unchanged

suggesting the non-involvement of these groups in the bonding. The complex  $\text{Me}_2\text{SnCl}_2 \cdot \text{HSMNMSa}$  shows an additional band at  $471 \text{ cm}^{-1}$ , assignable to  $\nu(\text{Sn-O})$  which again confirms the mode of ligand bonding to tin. Other molecular addition complexes also show Sn-O stretching band in the region  $445\text{-}480 \text{ cm}^{-1}$ . Two medium intensity bands are discernible due to  $\nu(\text{Sn-C})$  at  $519$  and  $480 \text{ cm}^{-1}$  in the complex  $\text{Me}_2\text{SnCl}_2 \cdot \text{HSMNMSa}$  which suggest equatorial arrangement of methyl groups.

**$^1\text{H}$  NMR spectral data of the Schiff bases, HSMNMSaD, HSMNMVD & HSMNMND and its molecular addition complexes**

The  $^1\text{H}$  NMR spectral studies [Table 2.3] of the adducts,  $\text{Me}_2\text{SnCl}_2 \cdot \text{HSMNMSaD}$  [fig. 2.3],  $\text{Me}_2\text{SnCl}_2 \cdot \text{HSMNMVD}$  and  $\text{Me}_2\text{SnCl}_2 \cdot \text{HSMNMND}$ , show resonances due to  $\text{CH}_3$  protons attached to the tin at 1.18, 1.20 and 1.14 ppm respectively. In  $\text{Et}_2\text{SnCl}_2 \cdot \text{HSMNMVD}$  and  $\text{Et}_2\text{SnCl}_2 \cdot \text{HSMNMND}$ , the ethyl protons resonate at 1.10-1.80 ppm and 1.11-1.64 ppm respectively. Similarly  $\text{Bu}_2\text{SnCl}_2 \cdot \text{HSMNMVD}$  and  $\text{Bu}_2\text{SnCl}_2 \cdot \text{HSMNMND}$  show clusture of signals for butyl group in the region 0.95-1.79 and 0.94-1.76 ppm respectively. The S- $\text{CH}_3$  and N- $\text{CH}_3$  protons in the complexes resonate almost at same position as that of starting Schiff bases at 2.6 and 3.9 ppm respectively. The sharp signal due to azomethine proton found at 8.00 ppm in the ligands remains unchanged indicating non-involvement of azomethine nitrogen in the bond formation. The phenolic hydrogen bonded OH proton found

at 10.21, 10.13 and 11.26 ppm in these Schiff base ligands shows downfield shifts in the adducts. However these signals are somewhat broadened probably due to bond formation between the oxygen atom and the tin without rupturing the hydrogen bonded ring system<sup>15</sup>. The hydrogen bonded nature is further confirmed by D<sub>2</sub>O exchange studies.

**<sup>13</sup>C NMR data of the Schiff base, HSMNMSAD and Me<sub>2</sub>SnCl<sub>2</sub>. HSMNMSaD**

<sup>13</sup>C NMR spectrum of the ligand HSMNMSaD [fig. 2.4] shows signals at 19.41 and 34.86 ppm attributable to N-CH<sub>3</sub> and S-CH<sub>3</sub> carbons respectively. The azomethine CH, phenolic C-O and thioketo C=S carbons resonate at 144.80, 157.13 and 199.20 ppm respectively. The assignments of quarternary carbons were done using distortionless enhancement by polarization transfer (DEPT) technique.

In the molecular addition complex, Me<sub>2</sub>SnCl<sub>2</sub>.HSMNMSa [fig. 2.5] the resonances due to S-CH<sub>3</sub>, N-CH<sub>3</sub> and C=S carbons are observed at 19.58, 35.11 and 199.79 ppm respectively, which suggests non-bonding nature of thioketo group. Similarly the azomethine (C=N) also remains almost in the same position confirming its hydrogen bonded nature. The phenolic carbon signal has been shifted to lower magnetic field by 2.4 ppm which is consistent with the coordination of phenolic oxygen to tin. The methyl carbons attached to tin resonate at 6.33 ppm with well separated <sup>117</sup>Sn and <sup>119</sup>Sn satellite signals having <sup>1</sup>J(<sup>117</sup>Sn, <sup>13</sup>C) = 553 Hz and <sup>1</sup>J(<sup>119</sup>Sn, <sup>13</sup>C) = 573 Hz. The Me-Sn-Me angle  $\theta$ ,

calculated from the observed tin-carbon coupling constant, is  $127^\circ$ , which suggests equatorial disposition of methyl groups in the trigonal plane. All these data are consistent with a trigonal bipyramidal geometry for the 1:1 addition complexes with the Schiff base occupying one of the axial positions as shown in fig. 2.1.

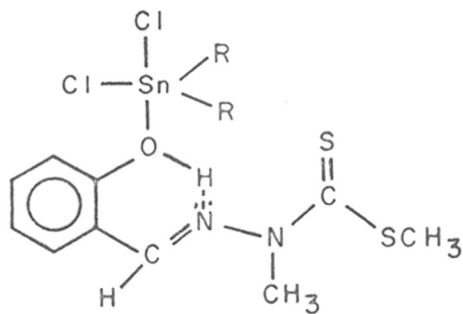


FIG. 2.1

Table 2.1. Analytical data of molecular addition complexes of organotin(IV) chlorides with HSMNMSaD, HSMNMVD and HSMNMND.

No. Ligand/Complex	Colour	m.p. (°C)	Ele. Anal. (%) found (calc)			
			Sn	C	H	Cl
1 HSMNMSaD (L) C <sub>10</sub> H <sub>12</sub> N <sub>2</sub> OS <sub>2</sub>	white	125	-	48.81 (49.97)	5.10 (5.03)	-
2 HSMNMVD (L') C <sub>11</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub> S <sub>2</sub>	white	138	-	48.67 (48.86)	5.02 (5.22)	-
3 HSMNMND(L'') C <sub>14</sub> H <sub>14</sub> N <sub>2</sub> OS <sub>2</sub>	Yellow	185	-	57.68 (57.90)	4.91 (4.86)	-
4 Me <sub>2</sub> SnCl <sub>2</sub> .L SnC <sub>12</sub> H <sub>18</sub> N <sub>2</sub> OS <sub>2</sub> Cl <sub>2</sub>	white	98	25.77 (25.80)	31.12 (31.33)	3.85 (3.94)	15.49 (15.41)
5 Me <sub>2</sub> SnCl <sub>2</sub> .L' SnC <sub>13</sub> H <sub>20</sub> N <sub>2</sub> O <sub>2</sub> S <sub>2</sub> Cl <sub>2</sub>	white	112	24.18 (24.22)	31.97 (31.86)	4.21 (4.11)	14.29 (14.47)
6 Et <sub>2</sub> SnCl <sub>2</sub> .L' SnC <sub>15</sub> H <sub>24</sub> N <sub>2</sub> O <sub>2</sub> S <sub>2</sub> Cl <sub>2</sub>	White	132	22.99 (22.91)	34.65 (34.77)	4.82 (4.67)	13.54 (13.69)
7 Bu <sub>2</sub> SnCl <sub>2</sub> .L' SnC <sub>19</sub> H <sub>32</sub> N <sub>2</sub> O <sub>2</sub> S <sub>2</sub> Cl <sub>2</sub>	Yellow	130	20.85 (20.67)	39.56 (39.74)	5.78 (5.62)	12.21 (12.35)
8 Ph <sub>3</sub> SnCl.L' SnC <sub>29</sub> H <sub>29</sub> N <sub>2</sub> O <sub>2</sub> S <sub>2</sub> Cl <sub>2</sub>	White	92	18.21 (18.10)	52.99 (53.11)	4.33 (4.76)	5.60 (5.41)
9 Me <sub>2</sub> SnCl <sub>2</sub> .L'' Sn <sub>16</sub> H <sub>20</sub> N <sub>2</sub> OS <sub>2</sub> Cl <sub>2</sub>	Yellow	179	23.29 (23.27)	37.73 (37.67)	3.83 (3.95)	13.79 (13.90)
10 Et <sub>2</sub> SnCl <sub>2</sub> .L'' SnC <sub>18</sub> H <sub>24</sub> N <sub>2</sub> OS <sub>2</sub> Cl <sub>2</sub>	Yellow	185	21.97 (22.06)	40.28 (40.17)	4.62 (4.50)	13.07 (13.18)
11 Bu <sub>2</sub> SnCl <sub>2</sub> .L'' SnC <sub>22</sub> H <sub>32</sub> N <sub>2</sub> OS <sub>2</sub> Cl <sub>2</sub>	Yellow	182	19.82 (19.97)	44.52 (44.47)	5.35 (5.43)	11.99 (11.93)
12 Ph <sub>3</sub> SnCl.L'' SnC <sub>32</sub> H <sub>29</sub> N <sub>2</sub> OS <sub>2</sub> Cl <sub>2</sub>	Yellow	170	17.61 (17.56)	56.61 (56.87)	4.39 (4.33)	5.17 (5.25)

Table 2.2. Characteristic IR spectral bands ( $\nu$ , in  $\text{cm}^{-1}$ ) of molecular addition complexes of organotin(IV) chlorides with HSMNMSaD, HSMNMVD and HSMNMND.

No.	C=C / C=N	C-O	C-S	N-N	O-H	Sn-O	Sn-Cl
HSMNMSaD	1617,1601	1267	1015	965,944	3154	-	-
1	1617,1601	1275	1015	967,947	3148	471	310,285
HSMNMVD	1595 1575	1235	1020	980,965	3260	-	-
2	1585 1560	1240	1020	970,960	3180	480	315,310
3	1600 1570	1240	1025	990,960	3070	455	300,280
4	1590 1565	1240	1020	975,950	3120	485	310,300
5	1600 1575	1245	1005	965,940	3120	455	310,270
HSMNMND	1610 1585	1210	1020	950	3170	-	-
6	1615 1595	1225	1015	955,920	3160	465	310,280
7	1620 1595	1225	1015	945	3060	445	300,260
8	1620 1590	1220	1025	960	3070	-	300,280
9	1620 1590	1220	1025	960,920	3070	450	310,270

Table 2.3.  $^1\text{H}$  NMR Spectral data ( $\delta$ , ppm) of molecular addition complexes of organotin(IV) chlorides with HSMNMSaD, HSMNMVD and HSMNMND.

No.	Aliphatic	.SCH <sub>3</sub>	NCH <sub>3</sub>	OCH <sub>3</sub>	CH	OH	Aromatic protons
HSMNMSaD	-	2.59(s)	3.95(s)	-	7.92(s)	10.21(s)	6.72-7.32(m)
1	1.18(s)	2.60(s)	3.93(s)	-	7.90(s)	10.24(s)	6.76-7.36(m)
HSMNMVD	-	2.60(s)	3.90(s)	3.96(s)	7.95(s)	10.13(s)	6.83-7.20(m)
2	1.20(s)	2.64(s)	3.90(s)	3.96(s)	7.98(s)	10.14(s)	6.79-7.20(m)
3	1.10-1.80(m)	2.59(s)	3.86(s)	3.95(s)	7.95(s)	10.14(s)	6.80-7.29(m)
4	0.95-1.79(m)	2.58(s)	3.88(s)	3.96(s)	7.95(s)	10.15(s)	6.85-7.30(m)
5	-	2.59(s)	3.87(s)	3.89(s)	7.90(s)	10.17(s)	6.80-7.61(m)
HSMNMND	-	2.60(s)	4.00(s)	-	8.66(s)	11.26(s)	7.00-7.86(m)
6	1.14(s)	2.58(s)	4.05(s)	-	8.78(s)	11.44(s)	7.07-7.97(m)
7	1.11-1.64(m)	2.67(s)	4.01(s)	-	8.79(s)	11.44(s)	7.16-8.02(m)
8	0.94-1.76(m)	2.60(s)	4.02(s)	-	8.76(s)	11.37(s)	7.08-7.95(m)
9	-	2.64(s)	4.05(s)	-	8.75(s)	11.39(s)	7.05-7.95(m)

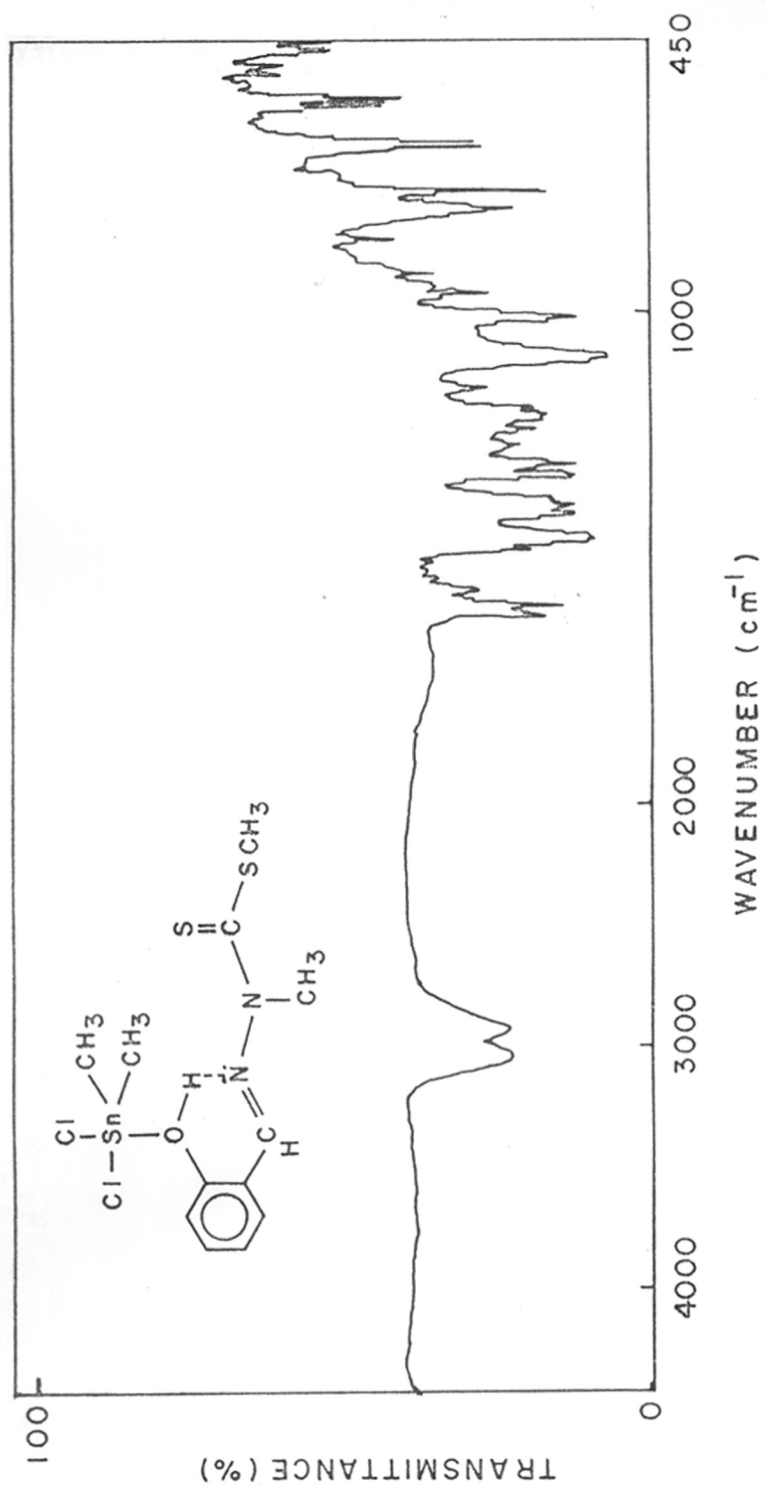


FIG. 2.2: IR SPECTRUM OF Me<sub>2</sub>SnCl<sub>2</sub> · HSMNMSa IN NUJOL.



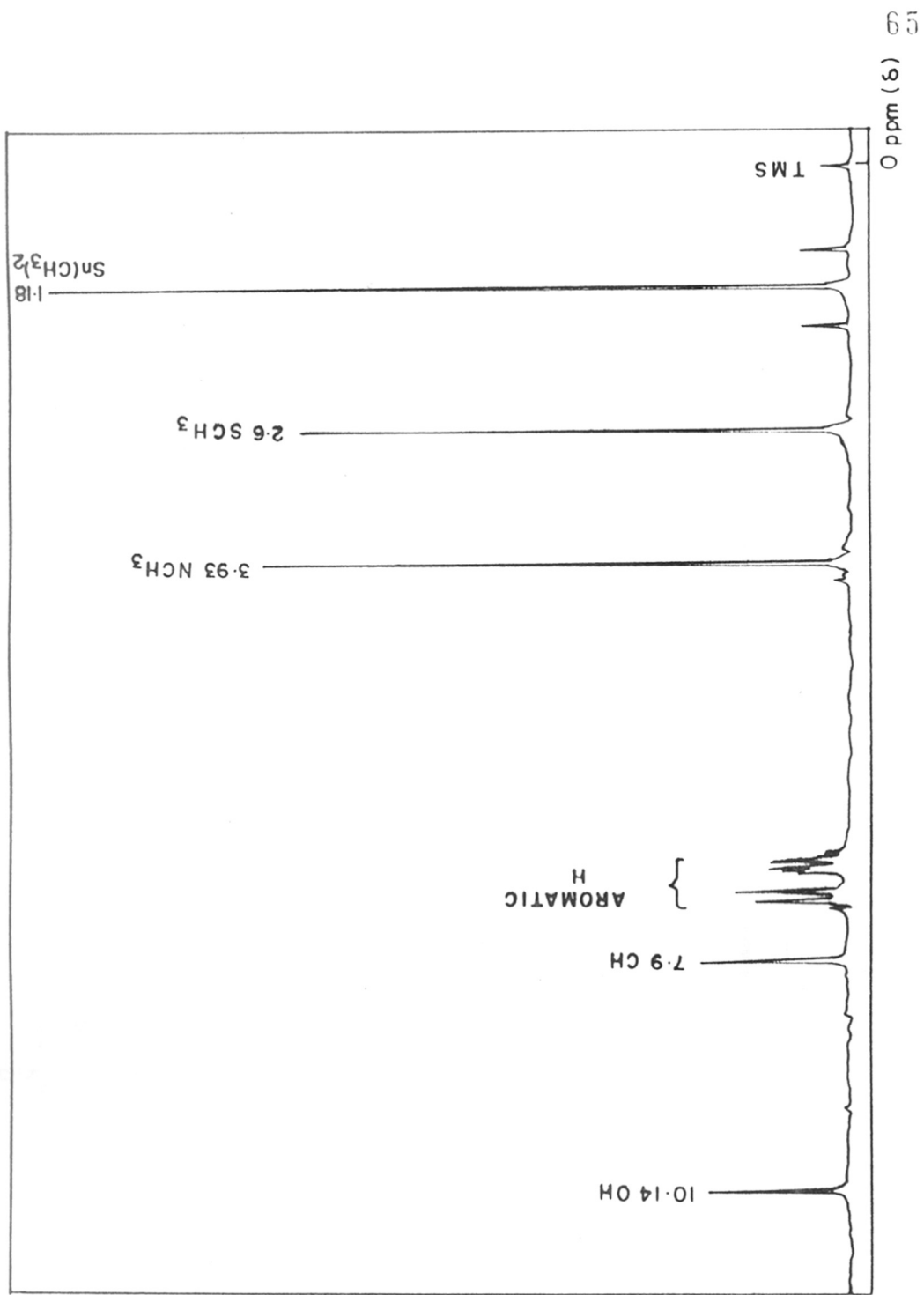


FIG. 2.3 : <sup>1</sup>H NMR SPECTRUM OF Me<sub>2</sub>SnCl<sub>2</sub> · HSMNMSa IN CDCl<sub>3</sub>

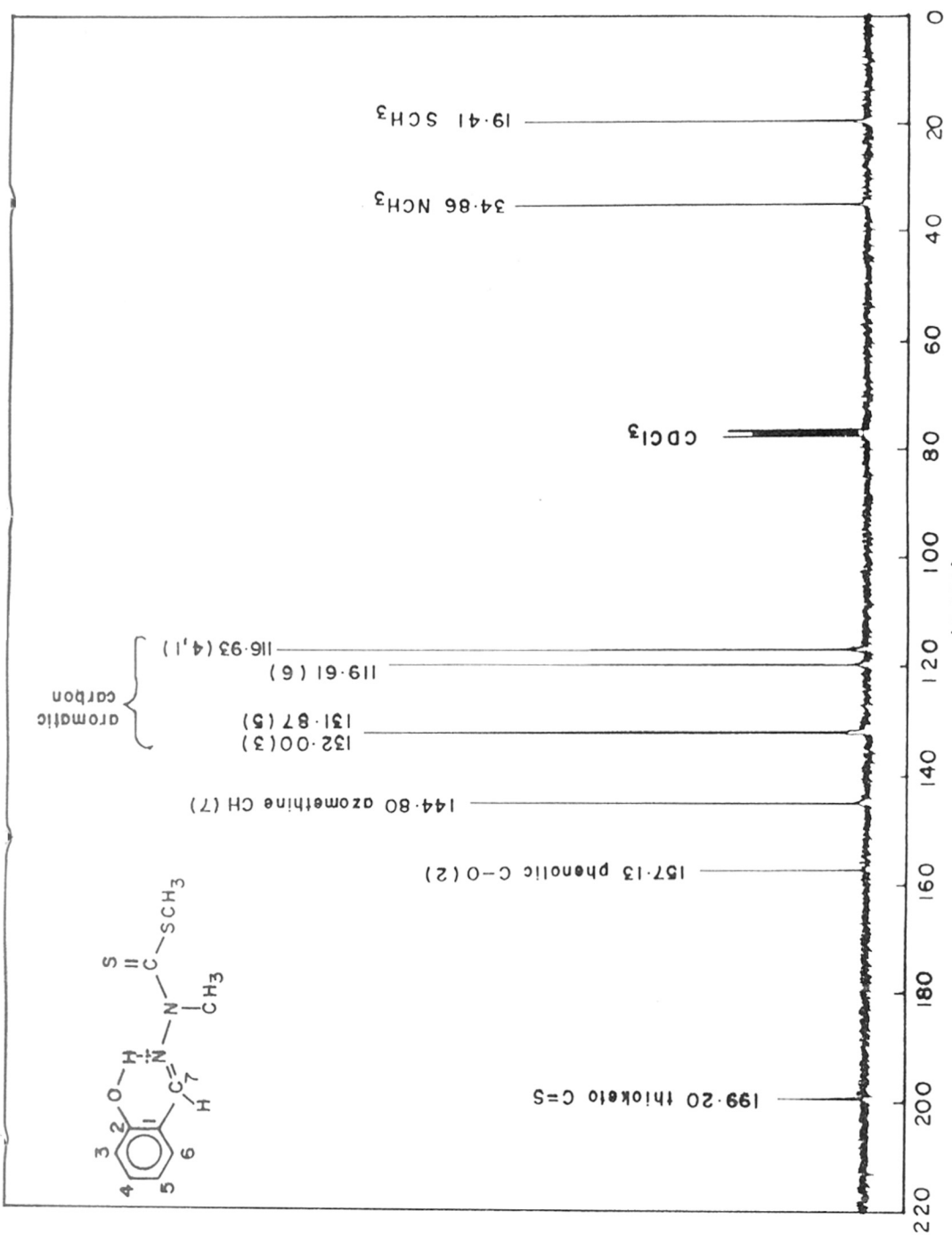


FIG. 2.4 : <sup>13</sup>C NMR SPECTRUM OF HSMMSa IN CDCl<sub>3</sub>

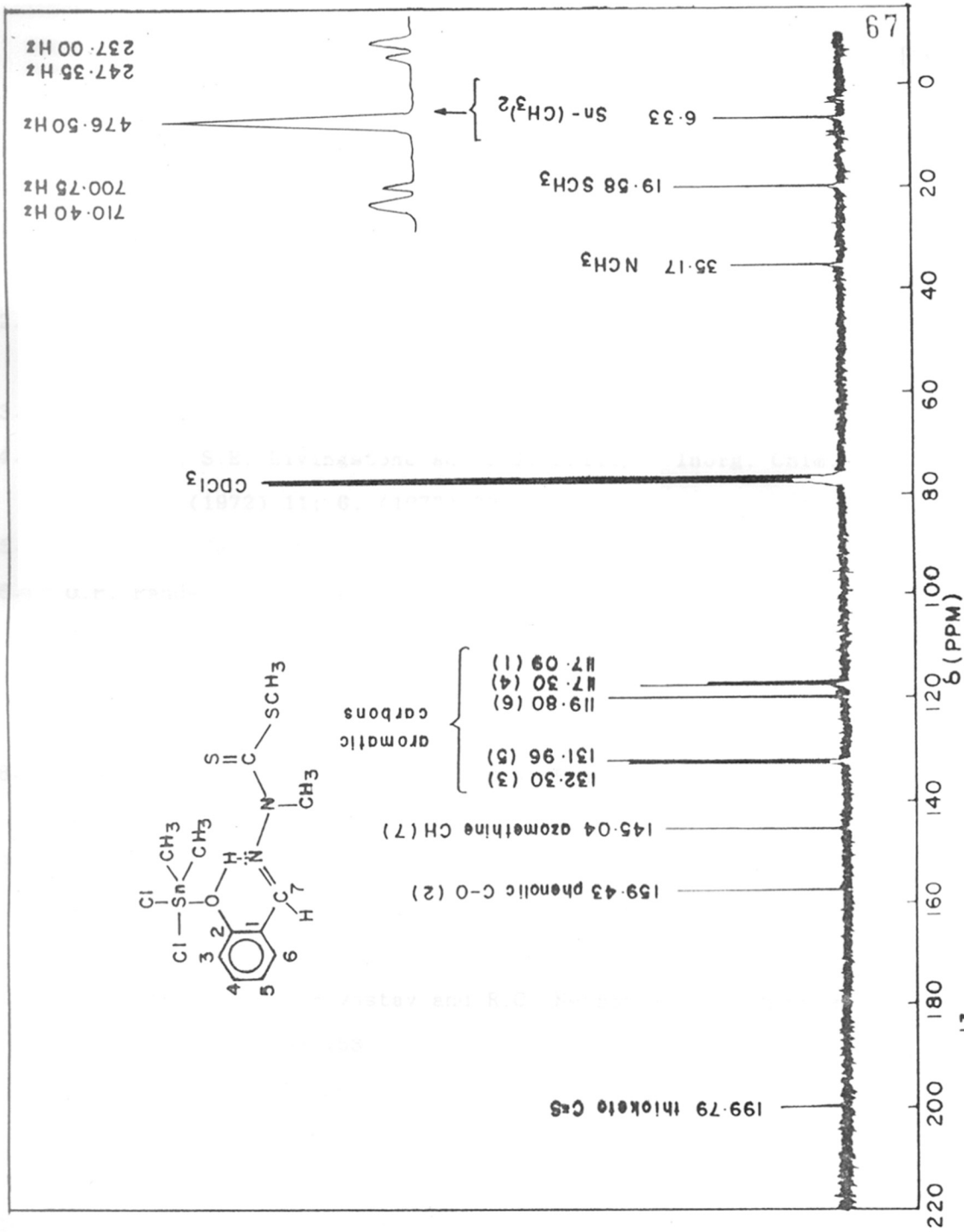


FIG. 2.5: <sup>13</sup>C NMR SPECTRUM OF Me<sub>2</sub>SnCl<sub>2</sub>.HSMNSa IN CDCl<sub>3</sub>

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CHAPTER 3
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STUDIES ON SOME NEW CHELATED COMPLEXES OF BIS- $\beta$ -CARBOALKOXYTIN(IV)  
DICHLORIDE WITH S-METHYL/S-BENZYL-DITHIOCARBAZATE SCHIFF BASES.

S U M M A R Y

Several complexes of the type  $R_2SnL$  {where  $R = -CH_2CH_2CO_2CH_3$ ,  $-CH_2CH_2CO_2C_2H_5$  or  $-CH_2CH_2CO_2C_4H_9$ ; and  $H_2L = S$ -methyl/ $S$ -benzyl- $\beta$ -N-(2-hydroxyphenyl)methylendithiocarbazate [ $H_2SMSaD/H_2SBSaD$ ],  $S$ -methyl/ $S$ -benzyl- $\beta$ -N-(2-hydroxy-3-methoxyphenyl)methylendithiocarbazate [ $H_2SMVD/H_2SBVD$ ] or  $S$ -methyl/ $S$ -benzyl- $\beta$ -N-(2-hydroxy-1-naphthyl)methylendithiocarbazate [ $H_2SMND/H_2SBND$ ]} have been synthesized for the first time and characterized by their elemental analyses, molecular weight determination, IR,  $^1H$ ,  $^{13}C$  and  $^{119}Sn$  NMR spectral studies. The values of coupling constants,  $^1J(^{119}Sn, ^{13}C)$ , were used for the calculation of C-Sn-C angles ( $\theta$ ) which were found to be in the range of  $140-143^\circ$ . The spectral data are consistent with an octahedral geometry around tin(IV) with trans ester groupings and equatorial disposition of Schiff base residue.

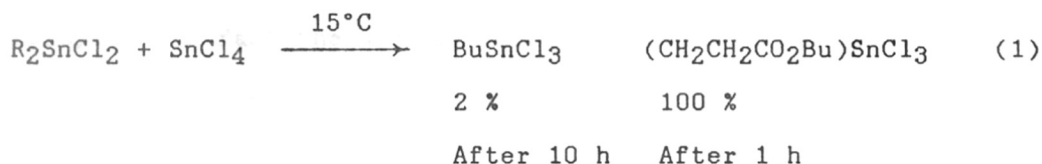
I N T R O D U C T I O N

Diestertin(IV) compounds have attracted considerable attention because of their applicability as nontoxic PVC stabilizers and also because of their structure involving

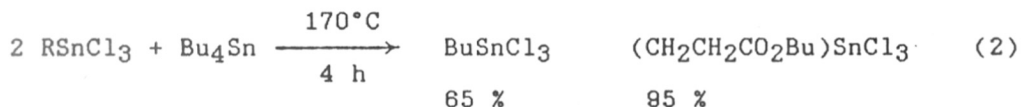
potential intramolecular carbonyl coordination to tin. Lanigan et al<sup>1</sup> have described the evaluation of first generation estertin stabilizers in the major applications in the areas of extrusion, calendering, injection molding, blow molding, plastisol coating and rotational casting. Comparisons were made with octyl-, butyl- and methyl-tin stabilizers as well as barium-cadmium-zinc and cadmium-zinc stabilizer systems. Estertins are a new class of organotin stabilizers for the use in PVC. The unique structure of estertins, compared to alkyltins, gives low volatility and extra activity while retaining all the virtues of conventional alkyltin compounds. eg., excellent heat stability and clarity. The results showed that the performance of estertins was equivalent to or better than the available commercial alkyltin stabilizers in all applications tested.

Hutton et al<sup>2</sup> have compared reactivity of estertin chlorides with alkyltin chlorides. They found that the chemical properties of functionally substituted alkyltin halides show some interesting differences from conventional alkyltins. For example, in disproportion reactions, the functionally substituted alkyltin halides are much more labile (reactions 1 and 2).

#### Yield







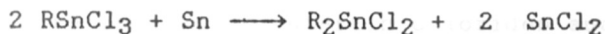
R = Bu or  $\text{CH}_2\text{CH}_2\text{CO}_2\text{Bu}$

The reaction (1) to give an organotin trichloride from an organotin dichloride shows high reactivity in the case of bis( $\beta$ -carboboxyethyl)tin dichloride compared with dibutyltin-dichloride. Similarly, higher reactivity is shown in the second reaction with ( $\beta$ -carboboxyethyl)tin trichloride compared to butyltin trichloride. The increased reactivity of the functionally substituted alkyltins in these reactions may be caused by coordination of the carbonyl group to tin. The products have industrial potential as intermediates for PVC stabilizers.

Hutton et al<sup>3</sup> have reacted  $\text{HSnCl}_3(\text{Et}_2\text{O})_2$  with a variety of  $\alpha, \beta$ -unsaturated carbonyl compounds to get high yields of  $\beta$ -substituted organotin chlorides. eg., addition of methyl acrylate to a suspension of  $\text{HSnCl}_3(\text{Et}_2\text{O})_2$  in ether or solutions of  $\text{HSnCl}_3$  in solvents such as ether, THF, dimethyl ether, ethyl acetate or methanol. In each case gave good yields of  $\text{Cl}_3\text{SnCH}_2\text{CH}_2\text{CO}_2\text{Me}$ . The hydrostannation proceeds under a wide variety of conditions. Temperatures between approximately  $-30$  and  $120^\circ\text{C}$  are employed. In fact the solvent can be dispensed with if an excess of appropriate monomer is employed, since monomer salvation of  $\text{HSnCl}_3(\text{M} \rightarrow \text{HSnCl}_3)$  can occur in non-ethereal media.

Intramolecular carbonyl coordination to tin occurs in these  $\beta$  - substituted organotin compounds.

Burley et al<sup>4</sup> have reacted hydrogen halides, tin and  $\alpha, \beta$ -unsaturated carbonyl compounds under mild conditions to give mixtures of  $\beta$ -substituted alkyltin trihalides and bis( $\beta$ -substituted alkyl)tin dihalides. Spectroscopic data for a number of pure functionally substituted dialkyl compounds are presented. The  $\beta$ -substituted alkyltin trihalides are prepared by the in situ reaction of hydrogen halides, stannous halide and  $\alpha, \beta$ -unsaturated carbonyl compounds, and similarly bis( $\beta$ -substituted alkyl)tin dihalides are prepared in good yields by the reactions between hydrogen halide, tin and the same  $\alpha, \beta$ -unsaturated carbonyl compounds in an oxygenated solvent. Several possible mechanisms are discussed for the formation of the dialkyltin compounds. The functionally substituted monoalkyltin chlorides react with tin to give the corresponding dialkyltin compounds and stannous chloride.



Cheng et al<sup>5</sup> have prepared bis(2-alkoxycarbonylethyl)tin dichlorides,  $(\text{ROCOCH}_2\text{CH}_2)_2\text{SnCl}_2$ , with various R groups, by using acid or base catalysts, in high yield by alcoholysis of the bis( $\alpha$ -carbomethoxyethyl)tin dichloride,  $(\text{CH}_3\text{OCOCH}_2\text{CH}_2)_2\text{SnCl}_2$  in various alcohols, such as ethyl, butyl, isobutyl, amyl, benzyl or  $\text{C}_4\text{H}_9\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2$  alcohol. They have found that, in general,

conversion by alcoholysis increases with increasing boiling point of the alcohol, but decreases with an increase in branching of the alcohol, ie primary alcohol > secondary alcohol >> tertiary alcohol. e.g., the conversion of  $(\text{CH}_3\text{OCOCH}_2\text{CH}_2)_2\text{SnCl}_2$  to  $(t\text{-C}_4\text{H}_9\text{OCOCH}_2\text{CH}_2)_2\text{SnCl}_2$  was less than 10 percent. Steric effects were certainly responsible for the poor yield.

Haigh et al<sup>6</sup> have studied the properties of the  $\beta$ -carbonylalkyltin chlorides and obtained the evidence for intramolecular coordination of CO group. The Mossbauer spectra and the solvent effect on the  $^1\text{H}$  NMR spectra support the conclusions drawn from infrared studies that the compounds  $\text{Cl}_3\text{SnCR}_2\text{CRHCOX}$  and the  $\text{Cl}_2\text{Sn}(\text{CR}_2\text{CRHCOX})_2$  ( $\text{R} = \text{Me}$  or  $\text{H}$ ;  $\text{X} = \text{Me}$ ,  $\text{OH}$  or  $\text{O-alkyl}$ ) are intramolecularly coordinated in both the solid state and in solution. The compounds  $\text{Cl}_3\text{SnCR}_2\text{CRHCOX}$  ( $\text{X} = \text{OH}$  or  $\text{O-alkyl}$ ) react with *t*-butoxyl radicals in solution to show the ESR spectra of the displaced radicals  $\cdot\text{CR}_2\text{CRHCOX}$ .

Harrison and co-workers<sup>7</sup> have done crystal and molecular structure studies of estertin chlorides such as  $\text{Cl}_3\text{SnCH}_2\text{CH}_2\text{CO}_2\text{Me}$ ,  $\text{Cl}_2\text{Sn}[\text{CH}_2\text{CH}_2\text{CO}_2\text{Me}]_2$  and  $\text{Cl}_2\text{Sn}[\text{CH}_2\text{CH}_2\text{CO}_2\text{NH}_2]$ . The crystal structure of first compound is orthorhombic whereas latter two compounds are monoclinic. The crystals of  $\text{Cl}_3\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{Me})$  and  $\text{Cl}_2\text{Sn}[\text{CH}_2\text{CH}_2\text{CO}_2\text{Me}]_2$  consist of discrete molecules; however extensive intermolecular hydrogen-bonding is found in crystals of  $\text{Cl}_2\text{Sn}[\text{CH}_2\text{CH}_2\text{CONH}_2]_2$ . Intramolecular carbonyl oxygen-to-tin

coordination occurred in all the three compounds. Vibrational and mass spectra are assigned in accordance with the determined structures. Tin-119 Mössbauer studies demonstrated that it is possible to investigate the nature of organotin additives to PVC by this method.

Jung et al<sup>8</sup> have synthesized and studied the properties of organotin(IV) complexes of the type  $\text{CH}_3\text{OOCCH}_2\text{CH}_2\text{Sn}(\text{S}_2\text{CNMe}_2)_x\text{Cl}_{3-x}$  ( $x = 1-3$ ). The crystal structure of  $(\text{CH}_3\text{OOCCH}_2)\text{Sn}(\text{S}_2\text{CNMe}_2)\text{Cl}_2$  showed that the tin atom adopts a distorted octahedral geometry via the chelating dithiocarbamate ligand and intramolecularly bonded ester group through ester CO to tin. Infrared and  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{119}\text{Sn}$  NMR spectral studies along with the cryoscopic data indicated that the complex has the same molecular structure both in the solid state and in solution.

Blunden et al<sup>9</sup> have investigated the structures of the alkyltin isooctyl thioglycollates,  $\text{R}_2\text{SnCl}_n(\text{IOTG})_{2-n}$  ( $n = 0,1$ ) and  $\text{RSnCl}_n(\text{IOTG})_{3-n}$  ( $n = 0,1,2$  and  $\text{R} = \text{Me-}$  or  $\text{BuOCOCH}_2\text{CH}_2$ ) by IR,  $^1\text{H}$  NMR and  $^{119}\text{Sn}$  NMR spectroscopy. The  $^{119}\text{Sn}$  NMR technique has been used to study the redistribution of the ligands Cl and IOTG between dialkyltin and monoalkyltin centres which proceeds to maximize the degree of ligand mixing and stabilization due to chelation by the groups  $\text{BuOCOCH}_2\text{CH}_2$  and  $\text{SCH}_2\text{CO}_2\text{Oct}^1$ . These reactions are relevant to those which occur in a PVC matrix when mixtures of mono- and di-alkyltin isooctyl thioglycollates are incorporated as synergistic stabilizers. The authors have

concluded from H redistribution reactions that rapid exchange occurs at room temperature between the chloro and IOTG ligands to maximize the possible degree of mixing at the two tin centres. One IOTG and 4 Cl ligands distribute themselves between  $R_2Sn$  and  $R_2SnCl_2$  to give  $R_2SnCl_2(IOTG)$  probably because, it is stabilized by chelation.

$\beta$ -Alkoxy-carbonylethyltin chlorides form stable coordination complexes with bidentate ligands like oxine and substituted oxines. A number of complexes of the types,  $R_2SnL_2$ ,  $R_2SnLX$ ,  $R_2SnL_2X$  and  $R_2SnL_3$  where  $R = CH_3CO_2CH_2CH_2$ ,  $C_4H_9CO_2CH_2CH_2$ ,  $CH_3CO_2CH(CH_3)CH_2$  or  $CH_3COCH_2C(CH_3)_2$ ,  $X = Cl$  or  $SCN$  and  $L =$  oxine, 5,7-dichloro oxine or 5,7-dibromo oxine, have been studied by Deb et al<sup>10</sup>. On the basis of IR, NMR and electronic spectral data, a penta-coordinated trigonal bipyramidal structure is assigned for  $(CH_3CO_2CH_2CH_2)_2Sn(oxine)(SCN)$  complex and a hexa-coordinated distorted octahedral geometry is suggested for  $R_2SnL_2$  ( $R = CH_3CO_2CH_2CH_2$ ) and  $R_2SnXL_2$  ( $R = CH_3CO_2CH_2CH_2$ ,  $C_4H_9CO_2CH_2CH_2$  or  $CH_3CO_2CH(CH_3)CH_2$ ) complexes.

Maughan et al<sup>11</sup> have investigated the Lewis acidity of  $Cl_3SnCH_2CH_2CO_2R$  ( $R = Me, Pr^i, Ph$  and  $H$ ) and  $Cl_2Sn(CH_2CH_2CO_2R)_2$  ( $R = Me$  and  $Pr^i$ ) towards Py and compared with that of  $R_2SnCl_3$  and  $R_2SnCl_2$ . It has been found that  $Me_2SnCl_2$  is ~ 200 times more acidic than  $Cl_2Sn(CH_2CH_2-CO_2Pr^i)_2$  towards pyridine. Stability constants for adducts of these Lewis acids with nitrogen donors,

e.g., D = bipy, phen, py, quinoline and aniline, have been determined in methylene chloride solution at 25° by UV and IR spectral data. From comparisons of stability constants, the following conclusions can be made: i)  $\text{Cl}_3\text{SnCH}_2\text{CH}_2\text{CO}_2\text{Me}$  appears as strong Lewis acid as  $\text{MeSnCl}_3$  towards bidentate ligands and pyridine and bipyridyl ligands (from  $k_1$  values); ii)  $\text{Cl}_3\text{SnCH}_2\text{CH}_2\text{CO}_2\text{Me}\cdot\text{D}$  (D = monodentate ligand) is a poorer acceptor than  $\text{MeSnCl}_3\cdot\text{D}$  but comparable to  $\text{Me}_2\text{SnCl}_2$  (using  $k_2$  and  $k_3$  values) towards D, and iii)  $\text{Cl}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{R})_2$  is a weaker acceptor than  $\text{Cl}_2\text{SnMe}_2$  towards phen and bipy (from  $k_3$  values).

Kumar Das et al<sup>12</sup> have prepared and carried out spectroscopic studies on complexes of the type  $(\text{MeOCOCH}_2\text{CH}_2)_2\text{SnCl}_2\text{L}_2$ ,  $(\text{MeOCOCH}_2\text{CH}_2)_2\text{SnL}'_2$  and  $(\text{MeOCOCH}_2\text{CH}_2)_2\text{SnCl}(\text{oxine})$  (where  $\text{L}_2 = 2\text{Ph}_3\text{AsO}$ , phen, bipy and  $\text{L}' = \text{oxine}$ ,  $-\text{SC}(\text{S})\text{NR}_2$ ) derived from  $(\text{MeOCOCH}_2\text{CH}_2)_2\text{SnCl}_2$ . However the diastertin dichloride exhibits weaker acceptor properties towards other ligands including phosphine oxides. Structural features of the isolated complexes both in the solid state and in solution are discussed on the basis of their IR, UV, NMR, Mössbauer spectral evidences. Except for the phosphine oxide complexes, an octahedral *trans*- or *cis*-  $\text{R}_2\text{Sn}$  and trigonal bipyramidal with equatorial  $-\text{R}_2\text{Sn}$  stereochemistry are proposed, whereas for the phosphine oxide complexes, a distorted octahedral configuration with *cis*-disposition of the halogens and  $\text{CSnC}$  angle of 144° is suggested.

The synthesis and replacement reactions of  $\beta$ -carboboxyethyltin trichloride are reported by Garad et al<sup>13</sup>. The bidentate ligands used for replacement were acetylacetone, salicylaldehyde, dibenzoylmethane, 2-hydroxy-4-methoxybenzophenone, 8-hydroxyquinone, benzoylphenylhydroxylamine and salazine. The stepwise replacement reactions of  $\beta$ -carboboxyethyltin trichloride were also carried out. In the complexes the coordination due to ester carbonyl is broken and C=N or C=O of the ligand coordinated to give a hexacoordinated structure to tin. These complexes are monomeric in boiling benzene.

Ghosh et al<sup>14</sup> have prepared a number of  $\beta$ -alkoxycarbonyl ethyltin chelates of the types  $R_2SnL_2$ ,  $R_2SnLX$ ,  $RSnL_2X$  and  $(MeOCOCH_2CH_2)_2SnL'Cl$  (where  $R = CH_3OCOCH_2CH_2-$ ,  $C_4H_9OCOCH_2CH_2-$  and  $CH_3OCOCH(CH_3)CH_2-$ ;  $X = Cl, SCN$  and  $L =$  dithizone (1,5-diphenyl thiocarbazono) and  $L' =$  diphenylcarbazono and the complex  $(CH_3OCOCH_2CH_2)_2SnL'Cl$ , and characterized by spectroscopic methods. The complexes of the types  $R_2SnLX$  and  $RSnL_2X$  are assigned to have distorted octahedral geometry whereas in  $R_2SnL_2X$  complexes, the arrangement of groups around tin atom may possibly be a trigonal bipyramidal one. Preliminary evaluation of the complex,  $(CH_3OCOCH_2CH_2)Sn(HDz)_2$  as a PVC stabilizer suggests that this complex is comparable to that of dibutyltin glycolate.

Estertin(IV) sulphides  $[MeO_2CCH_2CH_2(L)SnS]_n$  (1a:  $L = Me_2NCS_2-$ ,  $n = 2$ ; 1b:  $L = Et_2NCS_2-$ ,  $n = 2$ ; 2:  $MeO_2CCH_2CH_2-$ ,  $n = 3$ ) are

reported by Jung et al<sup>15</sup>. The crystal structures of (1a) is a centrosymmetric four membered dimer in which the dithiocarbamate ligand is anisobidentate and each tin atom is pentacoordinated with local geometry of distorted trigonal bipyramidal whereas structure (2) shows a six-membered trimer in the boat conformation with tetracoordinated tin atoms. Spectral data from IR and <sup>1</sup>H, <sup>13</sup>C and <sup>119</sup> Sn NMR along with the cryoscopic data indicate that the complexes have the same structure in the solid state and in solution.

S-Benzyl-β-N-(2-hydroxyphenyl)methylendithiocarbamate (LH<sub>2</sub>) forms a stable tin derivative such as LSnCl<sub>2</sub>, from stannic chloride and the sodio-derivative of the ligand. Organotin oxide/hydroxide reacts with the ligand giving organotin chelated derivatives<sup>16</sup>.

S-Benzyl-β-N-(2-hydroxyphenyl)methylendithiocarbamate (LH<sub>2</sub>) forms<sup>17</sup> stable derivatives of the type LTiCl<sub>2</sub>, L<sub>2</sub>Ti or LTi, when reacted with titanium tetrachloride, tetraisopropyl titanate or bis-chelated diisopropoxytitanium with LH<sub>2</sub> in 1:1 or 1:2 molar ratio. Salicylaldehyde, benzoyl acetone, benzoylphenylhydroxylamine and salicylaldehyde are the chelating ligands used in formation of bis-chelated diisopropoxy titanium. LSnCl<sub>2</sub> has been prepared from stannic chloride and the sodio-derivative of the ligand. Organotin oxide/hydroxide reacts with the Schiff base giving organotin derivatives. Synthesis and structure of these compounds have been discussed based on their molecular weights,



infrared, PMR and ultraviolet spectral data. In these complexes the ligand coordinates through ONS atoms. The structure of 1:1 complexes may be trigonal bipyramidal and 1:2 complexes might have distorted octahedral geometry from IR and NMR spectral studies. The complexes are found to be nonelectrolytic and monomeric in solution.

Penta- (trigonal bipyramidal) and hexa- (octahedral) coordinated compounds of Ti(IV) and Sn(IV) with Schiff bases, derived by the condensation of S-benzylidithiocarbamate and o-hydroxyacetophenone, 5-chlorosalicylaldehyde, or 5-bromosalicylaldehyde have been prepared and characterized by Pandit et al<sup>18</sup>. The complexes are obtained by reacting Schiff bases with  $TiCl_4$ ,  $Ti(OPr^i)_4$ ,  $SnCl_4$ ,  $Me_2SnO$ ,  $Bu_2SnO$ ,  $Oct_2SnO$  or  $Ph_3SnOH$  in 1:1 ratio.

Synthesis, characterization and geometrical feature of pentacoordinated dibutyltin(IV) dithiocarbamate complexes of the type  $n-Bu_2SnL$  [where L = dianion of S-methyl- $\beta$ -N-(2-hydroxyphenyl)methylendithiocarbamate and S-methyl- $\beta$ -N-(2-hydroxy-acetylphenyl)methylen dithiocarbamate] are described by Saxena et al<sup>19</sup>. These are obtained as viscous oils from the reactions of  $n-Bu_2SnO$  with equimolar proportions of the ligands in benzene. On the basis of UV, IR, NMR ( $^1H$ ,  $^{13}C$ ,  $^{119}Sn$ ) spectra along with the mass spectral fragmentation pattern a trigonal bipyramidal geometry is proposed for the complexes. The N atom probably occupies the axial site, while remaining donor atoms O and S and the dibutyl

groups occupy in an equatorial plane. These complexes are active against p.388 Lymphocyte leukemia system.

Raizada<sup>20</sup> has synthesized and characterized some five- and six-coordinated di- and tri-n-butyltin(IV) dithiocarbazates by reacting  $\text{Bu}_2\text{SnO}$  or  $(\text{Bu}_3\text{Sn})_2\text{O}$  with respective dithiocarbazate Schiff base in 1:1 and 1:2 metal to ligand ratios respectively. The ligands are prepared by the condensation of S-benzyl dithiocarbazate with benzaldehyde, salicylaldehyde, p-hydroxybenzaldehyde, acetophenone, o-hydroxyacetophenone and p-hydroxyacetophenone in 1:1 ratio. The ligands act as a bidentate ( $\text{L}^{\text{II}}$ ) or tridentate ( $\text{L}^{\text{III}}$ ) chelating agents. Spectral data support a five coordinate, presumably trigonal bipyramidal geometry for complexes of the type  $\text{Bu}_2\text{SnL}^{\text{III}}$  whereas, complexes of the type  $\text{Bu}_2\text{Sn}(\text{L}^{\text{II}})$  are six-coordinated with a distorted octahedral geometry and  $\text{Bu}_3\text{SnL}^{\text{II}}$  are five-coordinated with a trigonal bipyramidal structure. The mode of bonding of all the Schiff bases in the complex is via the azomethine nitrogen, thiolosulphur and the phenolic oxygen atom as revealed by IR and NMR spectra.

Nath et al<sup>21</sup> have synthesized and studied structural features of S-benzyl dithiocarbazate Schiff base complexes of organotin(IV). The complexes with Schiff bases derived from aromatic aldehydes/ ketones and S-benzyl dithiocarbazate, such as S-benzyl- $\beta$ -N-(2-hydroxyphenyl)methyl dithiocarbazate, S-benzyl- $\beta$ -

N-(2-hydroxy-1-naphthyl)methylenedithiocarbazate, S-benzyl- $\beta$ -N-(4-methoxyphenyl)methylenedithiocarbazate, S-benzyl- $\beta$ -N-(2-furanyl)methylenedithiocarbazate, S-benzyl- $\beta$ -N-(2-benzoylphenyl)methylenedithiocarbazate, formulated as  $R_nSnL$  ( $n = 2$ ,  $R = Ph$ ,  $L =$  dibasic thio Schiff base;  $n = 0$ ,  $R = Me, Ph$ ;  $L =$  monobasic thio-Schiff base) were prepared and characterized on the basis of elemental analyses, conductivity measurements and IR, far-IR, electronic and NMR spectral studies. IR spectral studies indicate that thio-Schiff bases behave as bidentate (NS) or tridentate (ONS) ligands and form chelate rings through the thiolo S, the azomethine N and the phenolic O. On the basis of the spectral data a distorted trigonal bipyramidal geometry around tin atom is suggested for the complexes.

Four new tin(IV) complexes of tridentate dithiocarbazate Schiff bases have been synthesized and characterized<sup>22</sup> by their elemental analysis, UV,  $^1H$  NMR spectra, Mössbauer spectroscopic studies and X-ray powder diffraction. Complexes having the general formula,  $Sn(OCOCH_3)_2L$ , where  $L =$  dianion of S-benzyl- $\beta$ -N-(2-hydroxyphenyl)methylen and methyl dithiocarbazate. The complexes are prepared by the reactions of tin tetraacetate with ligands. During the reaction the eliminated acetic acid was removed azeotropically with toluene. The complexes are five coordinated having distorted trigonal bipyramidal geometry, whereas complexes of the type  $SnL_2$  show hexa-coordination about the tin atom which is arranged in a distorted octahedral geometry

with an orthorhombic lattice.

Five and six coordinated complexes of triorganotin(IV) complexes with Schiff bases derived from S-methyl- or benzyl-dithiocarbamate and a ketone (such as acetyl acetone, ethyl acetone or benzoyl acetone) or pyridine-2-carboxaldehyde respectively, have been synthesized by Srivastava<sup>23</sup> and characterized by their elemental analyses, molar conductance, molecular weight determination and ultraviolet and infrared spectroscopy. It may be concluded that the Schiff bases derived from pyridine-2-carboxaldehyde behave as mono-anionic, tridentate ligands resulting in a six coordinated octahedral environment around the tin atom. On the other hand, the ketone Schiff bases under similar conditions act as mono anionic, bidentate ligands. The interaction with triorganotin(IV) moieties, thus yield pentacoordinated trigonal bipyramidal complexes. The complexes are nonelectrolytes and monomeric in solution.

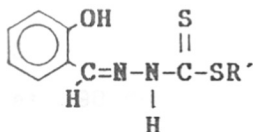
Our earlier work describes synthesis and characterization of organo-titanium(IV), -tin(IV) and -lead(IV) complexes of the Schiff bases derived from S-methyl-<sup>24</sup>/S-benzyl-<sup>25</sup> dithiocarbamate. The Schiff bases H<sub>2</sub>L, derived from S-methyl-/S-benzyl-dithiocarbamate and 2-hydroxy-3-methoxybenzaldehyde or 2-hydroxy-1-naphthaldehyde, react with titanium tetrachloride, titanium alkoxides, decyclopentadienyltitanium dichloride, organotin chlorides/ oxides/ hydroxides and di-/tri- phenyllead chlorides

in 1:1 molar proportion to yield neutral penta-coordinated complexes of the type  $X_2M(L)$  [  $M = Ti$  or  $Sn$  and  $X = Cl, OPr^i, OBu^n, Me, Et$  or  $Ph$  ] and  $Ph_3M(HL)$  ( $M = Sn$  or  $Pb$ ). The complexes are characterized on the basis of IR,  $^1H$  NMR and electronic spectral studies. In the former complexes the Schiff base acts as dibasic tridentate O, N, S coordinator, whereas in the latter complexes the Schiff base behaves as monobasic bidentate with O, N coordination. The spectral data suggest a trigonal bipyramidal geometry with *cis* chlorides or alkyl/phenyl group for these pentacoordinated metal complexes.

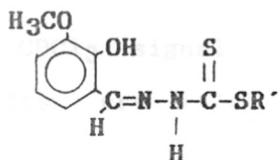
In the present chapter the syntheses and characterization of several new bis- $\beta$ -carboalkoxytin(IV) Schiff base complexes have been reported for the first time. The 'estertin' compounds containing various alkoxy groups such as  $O-CH_3, OC_2H_5$  and  $OC_4H_9$  have been used as the source of organotin compound and the Schiff base ligands  $H_2SMSaD, H_2SBSaD, H_2SMVD, H_2SBVD, H_2SMND$  and  $H_2SBND$ , were obtained by the condensation of S-methyl/S-benzyl dithiocarbamate and aldehydes such as salicylaldehyde, 2-hydroxy-3-methoxybenzaldehyde and 2-hydroxy-1-naphthaldehyde. These Schiff bases containing ONS donor atoms acted as tridentate chelating moieties. The complexes isolated were of  $R_2SnL$  type where R was an ester residue, either non-chelated through ester carbonyl or chelated and acted as mono/bidentate moieties and L was the Schiff base bonding to metal through their ONS donor atoms.

The Schiff bases used in the present study are shown as

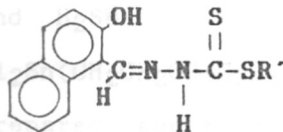
follows:



[H<sub>2</sub>SMSaD/H<sub>2</sub>SBSaD]



[H<sub>2</sub>SMVD/H<sub>2</sub>SBVD]



[H<sub>2</sub>SMND/H<sub>2</sub>SBND]

where R' = CH<sub>3</sub> or CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>.

## EXPERIMENTAL

The starting materials were of reagent or analytical reagent grade. Solvents were dried and distilled before use. Infrared spectra of the complexes were recorded as nujol mull, on a Perkin-Elmer Model 1620 FT-IR spectrophotometer. The electronic

spectra were recorded on Shimadzu Model UV-2101PC spectrophotometer. The proton NMR spectra of the complexes in  $\text{CDCl}_3$  solutions, were recorded at 80 MHz using a Varian FT-80 A or at 90 MHz using a Bruker WH-90 spectrometer. The  $^{13}\text{C}$  and  $^{119}\text{Sn}$  NMR spectra of the complexes recorded in  $\text{CDCl}_3$  solutions at ambient temperature with a Bruker MSL 300 spectrometer at 75.47 and 111.89 MHz, respectively. The  $^{13}\text{C}$  chemical shifts are related to  $\text{CDCl}_3$  signal ( $^{13}\text{C}$   $\text{CDCl}_3 = 76.9$  ppm) and ( $^{119}\text{Sn}$ ) chemical shifts are relative to external neat tetramethylstannane. Molecular weight was determined using a Knauer Vapour Pressure Osmometer.

The ligands,  $\text{H}_2\text{SMSaD}$ ,  $\text{H}_2\text{SMVD}$ <sup>26</sup>,  $\text{H}_2\text{SMND}$ <sup>27</sup>,  $\text{H}_2\text{SBSaD}$ <sup>28</sup>,  $\text{H}_2\text{SBVD}$ <sup>29</sup> and  $\text{H}_2\text{SBND}$ <sup>28</sup> and the ester-tin compounds  $\text{Cl}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3)_2$ <sup>30</sup>,  $\text{Cl}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5)_2$ <sup>30</sup>, and  $\text{Cl}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{C}_4\text{H}_9)_2$ <sup>30</sup> were prepared according to methods reported in the literature.

#### Preparation of $(\text{SMSaD})\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3)_2$ [13]

A solution of  $\text{H}_2\text{SMSaD}$  (0.23 g; 1 mmol) in chloroform (20 ml) was added slowly with vigorous stirring to a solution of  $\text{Cl}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3)_2$  (0.36 g; 1 mmol) in chloroform (20 ml). After the addition was complete, the reaction mixture was refluxed for ten minutes and then cooled. Ammonia solution was added dropwise to neutralize the liberated acid and the ammonium chloride formed was removed by filtration. The filtrate was further refluxed for about 2h, and the removal of solvent in

vacuo gave a yellow solid. The solid was dissolved in methylene chloride (20 ml) and the solution cooled to  $-24^{\circ}$ . Precipitation of the product was effected by layering n-hexane over the cooled solution. The yellow crystalline solid thus separated, was filtered, washed with n-hexane, and dried in vacuo. Yield 0.37 g (71%); m.p.  $57^{\circ}$ .

#### Preparation of $(\text{SMSaD})\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5)_2$ [14]

A solution of  $\text{H}_2\text{SMSaD}$  (0.23 g; 1 mmol) in chloroform (20 ml) was added slowly with vigorous stirring to a solution of  $\text{Cl}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5)_2$  (0.39 g; 1 mmol) in chloroform (20 ml). After the addition was complete, the reaction mixture was refluxed for ten minutes and then cooled. Ammonia solution was added dropwise to neutralize the liberated acid and the ammonium chloride formed was removed by filtration. The filtrate was further treated as in [13] to give yellow crystalline solid. Yield 0.34 g (63%); m.p.  $61^{\circ}$ .

#### Preparation of $(\text{SMSaD})\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{C}_4\text{H}_9)_2$ [15]

A mixture of  $\text{Cl}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{C}_4\text{H}_9)_2$  (0.41 g; 1 mmol) and ligand  $\text{H}_2\text{SMSaD}$  (0.23 g; 1 mmol) in chloroform (50 ml) was refluxed on a water bath for 10 min. A few drops of ammonia solution were added dropwise to neutralize the liberated acid and the ammonium chloride formed was removed by filtration. The filtrate was further refluxed for about two hours and evaporated to dryness under reduced pressure and the resulting solid was dissolved in methylene chloride (5 ml), cooled and n-hexane was



then added. Any solid which separated was filtered off and the filtrate was concentrated in vacuo to yield the complex. Yield 0.37 g (62 %).

#### Preparation of (SMVD)Sn(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>)<sub>2</sub> [16]

A solution of Schiff base (H<sub>2</sub>SMVD) (0.26 g; 1 mol) and the ester, Cl<sub>2</sub>Sn(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>, (0.36 g; 1 mol) were reacted in chloroform (20 ml). The reaction mixture was refluxed for ten minutes and then cooled. Dilute ammonia solution was added dropwise to neutralize the liberated acid and the ammonium chloride formed was removed by filtration. The filtrate was further refluxed for about 2 h, and the removal of solvent, gave a brown sticky mass. This was dissolved in 10 ml methylene chloride cooled in ice-salt mixture bath and layering n-hexane over the well cooled solution. Any solid separated was filtered off. The orange low melting substance obtained after concentration of the filtrate was washed with n-hexane and dried in vacuo. Yield 0.35 g (64%).

#### Preparation of (SMVD)Sn(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> [17]

A solution of Schiff base H<sub>2</sub>SMVD (0.26 g; 1 mol) in chloroform (20 ml) was added dropwise to a stirred solution of the ester, Cl<sub>2</sub>Sn(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>, (0.39 g; 0.001 mol) in chloroform (20 ml). After the addition was complete, the reaction mixture was refluxed for ten minutes and then cooled. Dilute ammonia solution was added dropwise to neutralize the liberated

acid and the ammonium chloride formed was removed by filtration. The filtrate was further refluxed for about 2 h, and the removal of solvent in vacuo gave a brown sticky mass. The complex was isolated dissolving the brown mass in methylene chloride-hexane mixture (1:1) using the same technique as described above. Yield 0.37 g (65%).

#### Preparation of (SMVD)Sn(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>C<sub>4</sub>H<sub>9</sub>)<sub>2</sub> [18]

To the chloroform solution of Cl<sub>2</sub>Sn(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>C<sub>4</sub>H<sub>9</sub>)<sub>2</sub> (0.41 g; 1 mmol) a chloroform solution of ligand (0.26 g; 1 mmol) (10 ml) was added. The clear solution obtained was refluxed for 10 min. and cooled. The pH of the reaction mixture was raised to 7 by adding aq. ammonia drop by drop with constant stirring. About 4-5 drops of ammonia solution were required to attain the desired pH. The ammonium chloride formed was filtered off and the filtrate was further refluxed for 2 h, then concentrated to dryness to get low melting solid. This was dissolved in minimum quantity of methylene chloride + hexane mixture was added. The solid separated was removed and the filtrate concentrated in vacuo. Yield 0.38 g (60%).

#### Preparation of (SMND)Sn(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>)<sub>2</sub> [19]

To a solution of H<sub>2</sub>SMVD (0.28 g; 0.001 mol) in CHCl<sub>3</sub> (10 ml), a equimolar amount of the ester, Cl<sub>2</sub>Sn(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>)<sub>2</sub> (0.36 g; 0.001 mol) in 20 ml chloroform was added with stirring. The mixture was refluxed for 15 min. and the pH was adjusted by addition of ammonia solution. The precipitated ammonium chloride

was filtered off and the filtrate was refluxed for 3 h. The complex was obtained by concentration of the filtrate in vacuo. Yield 0.36 g (63%).

#### Preparation of (SMND)Sn(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> [20]

A solution of ligand (0.28 g; 1 mmol) in chloroform was added to a well stirred solution of Cl<sub>2</sub>Sn(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> (0.39 g; 1 mmol) in chloroform. The resulting solution was heated on a water bath, a few drops of ammonia solution were added and the solid NH<sub>4</sub>Cl formed filtered. The filtrate was further refluxed for 1 h., concentrated, and cooled. The brown product obtained was processed adopting same procedure as in [15]. Yield 0.35 g (62%).

#### Preparation of (SMND)Sn(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>C<sub>4</sub>H<sub>9</sub>)<sub>2</sub> [21]

Cl<sub>2</sub>Sn(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>C<sub>4</sub>H<sub>9</sub>)<sub>2</sub> (0.41 g; 1 mmol) and the ligand (0.28 g; 1 mmol) were dissolved separately in minimum volume of chloroform and then mixed with stirring. The mixed solution was heated on water bath for ten minutes and ammonia solution added until the liberated acid was neutralized. The NH<sub>4</sub>Cl formed was filtered and the filtrate refluxed for 2 h., and treated as above to get the pure compound. Yield 0.40 g (62%).

#### Preparation of (SBSaD)Sn(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>)<sub>2</sub> [22]

A solution of H<sub>2</sub>SBSaD (0.30 g, 1 mmol) in chloroform (20 ml) was added slowly to a well stirred solution of Cl<sub>2</sub>Sn(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>)<sub>2</sub> (0.36 g, 1 mmol) in chloroform (20 ml).

After the addition was complete, the reaction mixture was refluxed for ten minutes and then cooled. Ammonia solution was added dropwise to neutralize the liberated acid and the ammonium chloride formed was removed by filtration. The filtrate was further refluxed for about 2h, and the removal of solvent in vacuo gave a low melting solid. The solid was dissolved in methylene chloride (20 ml) and the solution cooled to  $-24^{\circ}$ . Precipitation of the product was effected by layering n-hexane over the cooled solution. The yellow crystalline solid that separated, was filtered, washed with n-hexane, and dried in vacuo. Yield 0.36 g (61%),

#### Preparation of $(\text{SBSaD})\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5)_2$ [23]

A solution of  $\text{H}_2\text{SBSaD}$  (0.30 g; 1 mmol) in chloroform (20 ml) was slowly added to a vigorously stirred solution of  $\text{Cl}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5)_2$  (0.39 g; 1 mmol) in chloroform (20 ml). After the addition was complete, the reaction mixture was refluxed for ten minutes and then cooled. Ammonia solution was added dropwise to neutralize the liberated acid and the ammonium chloride formed was removed by filtration. The filtrate was further treated in same manner as in [13] which gave yellow crystalline solid. Yield 0.37 g (59%).

#### Preparation of $(\text{SBSaD})\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{C}_4\text{H}_9)_2$ [24]

A mixture of  $\text{Cl}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{C}_4\text{H}_9)_2$  (0.41 g; 1 mmol) and ligand  $\text{H}_2\text{SBSaD}$  (0.30 g; 1 mmol) in chloroform (50 ml) was refluxed on a water bath for 10 min. A few drops of ammonia

solution were added dropwise to neutralize the liberated acid and the ammonium chloride formed was removed by filtration. The filtrate was further refluxed for about two hours and evaporated to dryness under reduced pressure and the resulting solid was dissolved in methylene chloride (5 ml), cooled and n-hexane was added. The solid which separated was filtered off and the filtrate concentrated in vacuo to yield the desired complex. Yield 0.41 g (60 %).

#### Preparation of (SBVD)Sn(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>)<sub>2</sub> [25]

A solution of Schiff base (LH<sub>2</sub>) (0.33 g; 1 mmol) and the ester tin chloride, Cl<sub>2</sub>Sn(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>, (0.36 g; 1 mmol) were reacted in chloroform (20 ml). The reaction mixture was refluxed for ten minutes and then cooled. Dilute ammonia solution was added dropwise to neutralize the liberated acid and the ammonium chloride formed was removed by filtration. The filtrate was further refluxed for about 2 h., and removal of solvent gave a brown sticky mass. This was dissolved in 10 ml methylene chloride cooled in ice-salt mixture bath and layered n-hexane over the well cooled solution. The solid separated was filtered off and the orange low melting substance obtained after concentration of this filtrate was washed with n-hexane and dried in vacuo. Yield 0.39 g (62%).

#### Preparation of (SBVD)Sn(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> [26]

A solution of Schiff base [LH<sub>2</sub>] (0.33 g; 1 mol) in chloroform

(20 ml) was added dropwise to a stirred solution of the ester tin chloride,  $\text{Cl}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5)_2$ , (0.39 g; 0.001 mol) in  $\text{CHCl}_3$  (20 ml). After the addition was complete, the reaction mixture was refluxed for ten minutes and then cooled. Dilute ammonia solution was added dropwise to neutralize the liberated acid and the ammonium chloride formed was removed by filtration. The filtrate was further refluxed for about 2 h, and the removal of solvent in vacuo gave a brown sticky mass. The complex was isolated by dissolving the brown sticky mass in methylene chloride hexane mixture using the same technique as described above. Yield 0.36 g (61%).

#### Preparation of $(\text{SBVD})\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{C}_4\text{H}_9)_2$ [27]

To the chloroform solution of  $\text{Cl}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{C}_4\text{H}_9)_2$  (0.41 g; 1 mmol) a chloroform solution (10 ml) of ligand (0.33 g; 1 mmol) was added. The clear solution obtained was refluxed for 10 min. and cooled. The pH of the reaction mixture was raised to 7 by adding aq. ammonia drop by drop with constant stirring. About 4-5 drops of ammonia solution were required to attain the desired pH. The ammonium chloride formed was filtered off. Filtrate was further refluxed for 2 h and then concentrated to yield low melting solid. This was dissolved in minimum quantity of methylene chloride and hexane was added. The first formed solid was removed by filtration and filtrate was concentrated in vacuo. Yield 0.45 g (63%).

**Preparation of (SBND)Sn(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>)<sub>2</sub> [28]**

To a solution of H<sub>2</sub>SBND (0.35 g; 0.001 mol) in chloroform (10 ml), a equimolar amount of the ester, Cl<sub>2</sub>Sn(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>)<sub>2</sub> (0.36 g; 1 mmol) in 20 ml chloroform was added with stirring. The mixture was refluxed for 15 min. and the pH was adjusted by addition of ammonia solution. The precipitated ammonium chloride was filtered off and the filtrate was refluxed for 3 h. The reaction mixture was then treated in same manner as above. Yield 0.37 g (58%)

**Preparation of (SBND)Sn(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> [29]**

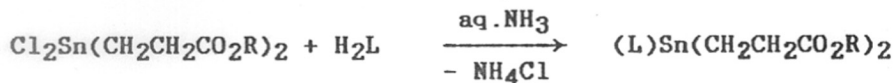
A solution of ligand (0.35 g; 1 mmol) in chloroform was added to a stirred solution of Cl<sub>2</sub>Sn(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> (0.39 g; 1 mmol) in CHCl<sub>3</sub>. The resulting solution was heated on a water bath, a few drops of ammonia solution were added and the solid NH<sub>4</sub>Cl formed was filtered. The filtrate was refluxed for 1 h., concentrated, and cooled. The brown product obtained was processed adopting same procedure as in [24] Yield 0.42 g (62%).

**Preparation of (SBND)Sn(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>C<sub>4</sub>H<sub>9</sub>)<sub>2</sub> [30]**

Cl<sub>2</sub>Sn(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>C<sub>4</sub>H<sub>9</sub>)<sub>2</sub> (0.41 g; 1 mmol) and the ligand (0.35 g; 1 mmol) were dissolved separately in minimum volume of chloroform and mixed with shaking. The mixed solution was heated on water bath for ten minutes and ammonia solution was added to neutralize the liberated acid. The NH<sub>4</sub>Cl formed was filtered and the filtrate refluxed for 2 h., and treated as above to get pure compound. Yield 0.44 g (61%).

## RESULTS AND DISCUSSION

The complexes described in this chapter have been synthesized by refluxing diester-tin dichlorides of the general formula  $\text{Cl}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{R})_2$  [where  $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$  or  $\text{C}_4\text{H}_9$ ] with stoichiometric amounts of dibasic Schiff bases  $[\text{H}_2\text{SMSaD}]$ ,  $[\text{H}_2\text{SMVD}]$ ,  $[\text{H}_2\text{SMND}]$ ,  $[\text{H}_2\text{SBSaD}]$ ,  $[\text{H}_2\text{SBVD}]$  and  $[\text{H}_2\text{SBND}]$  in chloroform using aqueous ammonia as HCl acceptor.



These complexes are yellow, crystalline, low melting solids soluble in benzene, toluene, chloroform, and methylene chloride and insoluble in hexane. The molecular weight determination by vapour pressure osmometry in toluene at  $45^\circ$ , shows monomeric nature of the complexes. The complexes are listed together with their analytical and molecular weight data in Table 3.1.

### IR Spectral data of bis-( $\beta$ -carboalkoxyethyl)tin(IV) S-methyl $\odot$ dithiocarbazate Schiff base complexes.

The IR spectra of the complexes recorded as Nujol mulls [Table 3.2] show vibrational modes due to ester-tin and Schiff base groupings. The IR spectra of bis( $\beta$ -carboalkoxyethyl) $\odot$  tin dichloride abbreviated as (estertin) show one band due to the intramolecularly coordinated C=O stretching at  $1660\text{-}1680 \text{ cm}^{-1}$ .



In the complex two bands were found due to the ester C=O stretch at  $\sim 1700$  and  $1680 \text{ cm}^{-1}$ , indicating the presence of both free and coordinated ester groupings in these complexes. Further alkoxy  $\nu(\text{C-O})$ , which occurs at  $\sim 1230 \text{ cm}^{-1}$  in  $(\text{ester})\text{SnCl}_2^{31}$  is observed as a split band in the complexes at  $\sim 1220$  and  $1200 \text{ cm}^{-1}$ . The low-frequency band could be due to the non-coordinated ester carboxyl groups.

The Schiff base ligands show the characteristic band due to N-H stretching vibrations at  $\sim 3200 \text{ cm}^{-1}$  as a sharp medium intensity peak and the band due to phenolic OH was seen  $\sim 3400 \text{ cm}^{-1}$  in dilute  $\text{CHCl}_3$  solution. The  $\nu(\text{C=N})$  and  $\nu(\text{C=S})$  bands are observed at  $\sim 1610$  and  $\sim 1040 \text{ cm}^{-1}$ , respectively. The phenolic ( $\nu\text{CO} + \delta \text{OH}$ ) band appears at  $1280\text{-}1300 \text{ cm}^{-1}$ . The bands at  $\sim 1020$  may be due to  $\nu(\text{C-S})$  and bands at  $980\text{-}950 \text{ cm}^{-1}$  due to  $\nu(\text{N-N})$  group.

In the complexes the  $\nu(\text{C=N})$  band shifts to lower frequency ( $\sim 1580 \text{ cm}^{-1}$ ) suggesting nitrogen lone-pair coordination to tin. The hydrogen bonded  $\nu(\text{OH})(\text{phenolic})$  of the ligand at  $\sim 3400 \text{ cm}^{-1}$  is absent in the complexes. The phenolic  $\nu(\text{C-O})$  band, which occurs in the ligands at  $\sim 1270 \text{ cm}^{-1}$  is shifted to  $\sim 1310 \text{ cm}^{-1}$  in the complexes due to chelate ring formation through deprotonated oxygen and azomethine nitrogen<sup>32</sup>. Further, the absence of  $\nu(\text{N-H})$  and the lowering of the  $\nu(\text{C=S})$  stretching frequencies suggest thioenolization followed by proton replacement by tin. The N-N stretching vibration is moved slightly to higher frequency region

due to increased N-N bond order in the chelated structure. In the lower frequency region the band at  $560\text{ cm}^{-1}$  is attributed to  $\nu(\text{Sn-C})$ . These findings suggest that the Schiff base binds to tin as a dianionic tridentate moiety.

**$^1\text{H}$  NMR Spectral data of bis-( $\beta$ -carboalkoxyethyl)tin(IV) S-methyl dithiocarbazate Schiff base complexes.**

$^1\text{H}$  NMR spectra [Table 3.3] of the bis( $\beta$ -carboalkoxyethyl)tin Schiff base complexes show two triplets at  $\sim 1.7$  and  $2.75$  ppm due to  $\alpha$ - $\text{CH}_2$  and  $\beta$ - $\text{CH}_2$  protons, respectively, compared to the corresponding resonances at  $\sim 1.89$  and  $2.90$  ppm in estertin-dichlorides. The shielding may be attributed to the replacement of electronegative chlorine atoms by a strongly coordinating Schiff base. Similar shielding was observed in the case of estertin oxinate complexes as reported by Ghosh et al<sup>10</sup>. The greater shielding observed for the  $\alpha$ - $\text{CH}_2$  protons of  $(\text{SMND})\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{R})_2$  is consistent with the increased basicity of the Schiff base  $\text{H}_2\text{SMND}$  compared to  $\text{H}_2\text{SMSaD}$  or  $\text{H}_2\text{SMVD}$ . Further the presence of only one singlet due to ester  $\text{OCH}_2/\text{OCH}_3$  protons suggests magnetic equivalence of the coordinated and uncoordinated ester groupings due to fast exchange.

The Schiff bases show resonances due to S- $\text{CH}_3$ , aldehydic  $=\text{CH}$ , NH and OH protons at  $\sim 2.65$ ,  $\sim 8.00$ ,  $\sim 9.10$  and  $\sim 10.10$  ppm respectively. In the complexes both NH and OH proton signals are absent. The aldehydic proton is deshielded as a result of the

azomethine nitrogen lone pair coordination to tin. The singlet due to S-CH<sub>3</sub> resonance moves to ~ 2.50 ppm which confirms coordination of thiolate ion.

**<sup>13</sup>C NMR Spectral data of bis-(β-carboalkoxyethyl)tin(IV) S-methyl dithiocarbazate Schiff base complexes.**

High resolution <sup>13</sup>C NMR spectra of the diester-tin Schiff base complexes show sharp signals for α-CH<sub>2</sub>, β-CH<sub>2</sub>, phenolic C-O and ester C=O carbon resonances coupled with the two tin isotopes <sup>117</sup>Sn and <sup>119</sup>Sn giving rise to well-separated satellite signals. The <sup>13</sup>C NMR chemical shift values [Table 3.4] for α-CH<sub>2</sub>, β-CH<sub>2</sub>, OCH<sub>3</sub> and C=O carbon resonances are at ~ 21, ~ 29, ~ 52 and ~ 176 ppm, respectively. The hexa-coordinated diester-tin dichloride, Cl<sub>2</sub>Sn(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>Me)<sub>2</sub>, shows the corresponding resonances at 24.15, 28.8, 53.7 and 181.1, ppm respectively. A high field shift of ~ 5 ppm for the ester carbonyl carbon indicates increased electron density at that carbon, and the appearance of a single signal at 176 ppm due to ester C=O carbon suggests fast exchange of metal-bonded and non-bonded carbonyl groups which leads to magnetic equivalence of the ester groupings<sup>33</sup>. The free Schiff bases show S-CH<sub>3</sub>, =CH and C=S carbon resonances at ~ 18, ~ 147 and ~ 199 ppm, respectively. The S-CH<sub>3</sub> and C=S carbons are shielded by ~ 3 and ~ 26 ppm, respectively, in the complexes suggesting metal-complex formation. Further, the large shielding observed for the thioketo carbon indicates thiolate ion formation. The aldehydic

carbon is deshielded by ~ 19 ppm due to azomethine nitrogen lone-pair coordination to tin.

**$^{119}\text{Sn}$  NMR Spectral data of bis-( $\beta$ -carboalkoxyethyl)tin(IV)  $\subset$  S-methyldithiocarbazate Schiff base complexes.**

For the determination of the structure of diester-tin(IV) Schiff base complexes,  $\delta(^{119}\text{Sn})$  and  $^1J(^{119}\text{Sn}, ^{13}\text{C})$  are the most important parameters and are given in Table 3.5. The values of the chemical shifts,  $\delta(^{119}\text{Sn})$ , fall between -180 and -183 ppm, whereas the pentacoordinated dimethyltin Schiff base complex (SMSaD)Sn(CH<sub>3</sub>)<sub>2</sub> has  $\delta(^{119}\text{Sn})$  at -110 ppm. The upfield shift observed for the former complexes suggests an increased coordination number for tin<sup>34</sup>.

The coupling constants  $^1J(^{119}\text{Sn}, ^{13}\text{C})$  are directly linked to the values of the C-Sn-C angle ( $\theta$ ) according to the equation<sup>35</sup>.

$$|^1J(^{119}\text{Sn}, ^{13}\text{C})| = 11.4 (\theta) - 875$$

The coupling constants  $^1J(^{119}\text{Sn}, ^{13}\text{C})$  for the diester Schiff base complexes fall between 725 and 752 Hz, corresponding to C-Sn-C angles ( $\theta$ ) between 140 and 143°. The well characterized octahedral complexes Cl<sub>2</sub>Sn(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>Sn(acac)<sub>2</sub><sup>36</sup> and (CH<sub>3</sub>)<sub>2</sub>Sn(koj)<sub>2</sub><sup>37</sup> in CDCl<sub>3</sub> give the  $\theta$  values 144<sup>38</sup>, 180 and 142° respectively.

The  $^2J(^{119}\text{Sn}, ^{13}\text{C})$  values are found to be always smaller than the  $^3J(^{119}\text{Sn}, ^{13}\text{C})$  coupling constants<sup>39</sup>. The observed tin-

ester carbonyl carbon coupling constant of  $\sim 60$  Hz [Table 3.5] can also be interpreted in terms of a two-bond coupling through the hetero atom oxygen, in these chelates.

The above data are consistent with a distorted octahedral geometry at tin, with *trans* ethyl carboalkoxy groups for the Schiff base complexes as shown in fig 3.1.

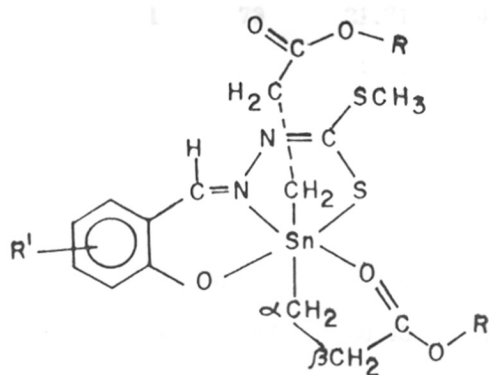


FIG. 3.1

$35\text{H}_2\text{S}_2\text{Sn}$	melting	20.58	44.12	1.0
		(20.93)	(44.47)	

**Table 3.1. Analytical data for bis(β-carboalkoxyethyl)tin(IV)  
S-methyldithiocarbazate Schiff base complexes.**

No. Compound	m.p. (°C)	Yield %	Ele. anal. [found(cal.)(%)]				Mol. wt. [found (cal)]
			Sn	C	H	N	
13 (SMSaD)Sn(CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> C <sub>17</sub> H <sub>22</sub> O <sub>5</sub> N <sub>2</sub> S <sub>2</sub> Sn	57	71	22.59 (22.95)	39.50 (39.48)	4.12 (4.30)	5.19 (5.42)	510 (517)
14 (SMSaD)Sn(CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> C <sub>19</sub> H <sub>26</sub> O <sub>5</sub> N <sub>2</sub> S <sub>2</sub> Sn	61	73	21.71 (21.77)	41.61 (41.86)	4.58 (4.82)	4.95 (5.14)	539 (545)
15 (SMSaD)Sn(CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> C <sub>23</sub> H <sub>34</sub> O <sub>5</sub> N <sub>2</sub> S <sub>2</sub> Sn	low melting	65	18.48 (19.74)	45.59 (45.94)	5.39 (5.71)	4.68 (4.68)	594 (601)
16 (SMVD)Sn(CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> C <sub>18</sub> H <sub>24</sub> O <sub>6</sub> N <sub>2</sub> S <sub>2</sub> Sn	low melting	69	21.33 (21.69)	39.33 (39.51)	4.21 (4.43)	5.15 (5.12)	550 (547)
17 (SMVD)Sn(CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> C <sub>20</sub> H <sub>28</sub> O <sub>6</sub> N <sub>2</sub> S <sub>2</sub> Sn	low melting	67	20.45 (20.64)	41.43 (41.76)	4.55 (4.92)	4.49 (4.87)	567 (575)
18 (SMVD)Sn(CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> C <sub>24</sub> H <sub>38</sub> O <sub>6</sub> N <sub>2</sub> S <sub>2</sub> Sn	low melting	66	18.71 (18.80)	45.35 (45.66)	5.61 (5.76)	4.11 (4.44)	619 (631)
19 (SMND)Sn(CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> C <sub>21</sub> H <sub>24</sub> O <sub>5</sub> N <sub>2</sub> S <sub>2</sub> Sn	low melting	68	20.58 (20.93)	44.12 (44.47)	4.08 (4.27)	4.63 (4.94)	553 (567)
20 (SMND)Sn(CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> C <sub>23</sub> H <sub>28</sub> O <sub>5</sub> N <sub>2</sub> S <sub>2</sub> Sn	low melting	70	19.66 (19.94)	46.55 (46.40)	4.52 (4.75)	4.36 (4.71)	598 (595)
21 (SMND)Sn(CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> C <sub>27</sub> H <sub>38</sub> O <sub>5</sub> N <sub>2</sub> S <sub>2</sub> Sn	low melting	64	18.01 (18.22)	49.32 (49.79)	5.34 (5.58)	4.18 (4.30)	643 (651)

Table 3.2. IR data for bis( $\beta$ -carboalkoxyethyl)tin(IV) S-methyl dithiocarbazate Schiff base complexes ( $\nu$ ,  $\text{cm}^{-1}$ ).

No.	(C=O)	(C-O) (ester)	(C=N)+(C=C)	(C-O)*	(C-S)	(N-N)
13	1700,1690	1230,1200	1590,1520	1300	1020	980,950
14	1690,1680	1220,1200	1600,1530	1300	1030	970
15	1695,1690	1220,1200	1580,1530	1290	1035	975,965
16	1710,1695	1235,1200	1590,1530	1310	1020	965
17	1710,1670	1220,1200	1590,1550	1270	1020	975
18	1735,1695	1225,1200	1590,1560	1320	1020	980
19	1715,1690	1210,1190	1590,1530	1300	1010	970,950
20	1715,1690	1220,1200	1600,1540	1295	1020	975
21	1728,1695	1218,1192	1598,1538	1298	1020	961,944

\* (C-O) of Schiff bases.

Table 3.3.  $^1\text{H}$  NMR Data for bis(  $\beta$ -carboalkoxyethyl)tin(IV) S-methyl dithiocarbazate Schiff base complexes ( $\delta$ , ppm).

No.	Chemical shifts ( $\delta$ , ppm in $\text{CDCl}_3$ )							Aromatic protons
	$\alpha$ - $\text{CH}_2$	$\beta$ - $\text{CH}_2$	$\text{OCH}_2/\text{OCH}_3$ (ester)	$\text{CH}_3$ (ester)	$\text{SCH}_3$	$\text{OCH}_3^*$	CH	
13	1.70	2.75	3.65	-	2.53	-	8.60	6.50 - 7.30
14	1.69	2.69	4.02	1.22	2.52	-	8.40	6.58 - 7.39
15	1.59	2.78	4.03	1.22	2.54	-	8.79	6.82 - 7.44
16	1.68	2.69	3.56	-	2.47	3.72	8.56	6.44 - 7.20
17	1.73	2.80	4.11	1.31	2.53	3.80	8.62	6.51 - 7.27
18	1.73	2.74	4.03	0.90	2.53	3.80	8.81	6.50 - 7.33
19	1.62	2.62	3.54	-	2.46	-	9.40	6.68 - 7.88
20	1.71	2.74	4.14	1.23	2.58	-	9.49	6.78 - 7.98
21	1.72	2.75	4.05	0.90	2.63	-	9.50	6.80 - 8.11

\*  $\text{OCH}_3$  of the Schiff base  $\text{H}_2\text{SMVD}$ .



Table 3.4.  $^{13}\text{C}$  NMR Chemical Shift Data for Bis(  $\beta$ -carbomethoxyethyl) tin(IV) S-methyl dithiocarbazate Schiff base complexes (  $\delta$ , ppm).

Compound	S-CH <sub>3</sub>	$\alpha$ -CH <sub>2</sub>	$\beta$ -CH <sub>2</sub>	OCH <sub>3</sub> (ester)	=CH	C=S	C=O (ester)
$\text{Cl}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3)_2$	-	24.15	28.38	53.68	-	-	181.13
(SMSaD)Sn(CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	14.98	21.02	29.12	52.08	165.00	167.70	176.62
(SMVD)Sn(CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	14.99	20.98	28.97	51.99	164.90	173.53	176.70
(SMND)Sn(CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	15.06	20.25	29.11	52.05	160.02	170.22	176.59

OCH<sub>3</sub> of (SMVD)Sn(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>)<sub>2</sub> = 55.93

Table 3.5.  $^{119}\text{Sn}$  NMR Chemical Shift and Coupling Constants for Bis( $\beta$ -carboalkoxyethyl)tin(IV) S-methyl dithiocarbazate Schiff Base Complexes.

No.	$^{119}\text{Sn}$ ( $\delta$ , ppm)	$^1J(^{119}\text{Sn}, ^{13}\text{C})$ (Hz) $\alpha\text{-CH}_2$	$^1J(^{117}\text{Sn}, ^{13}\text{C})$ (Hz) $\alpha\text{-CH}_2$	$^2J(^{119}\text{Sn}, ^{13}\text{C})$ (Hz) $\beta\text{-CH}_2$	$^2J(^{119}\text{Sn}, ^{13}\text{C})$ (Hz) Phenolic C-O	$^3J(^{119}\text{Sn}, ^{13}\text{C})$ (Hz) C=O (ester)	C-Sn-C ( $^\circ$ )
1.	-66.40	-	-	-	-	-	-
2.	-110.19	565	530.12	-	-	-	126.32
3.	-180.34	725	692.40	40.5	31.11	60	140.35
4.	-181.17	731	699.30	53.61	29.23	63	140.87
5.	-181.68	752	689.61	70.79	33.44	60	142.71
6.	-183.32	730	690.44	51.45	28.94	61	140.79

1.  $\text{Cl}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3)_2$
2.  $(\text{SMSaD})\text{Sn}(\text{CH}_3)_2$
3.  $(\text{SMSaD})\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3)_2$
4.  $(\text{SMVD})\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3)_2$
5.  $(\text{SMND})\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3)_2$
6.  $(\text{SMSaD})\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5)_2$

**Bis-( $\beta$ -carboalkoxyethyl)tin(IV) S-benzyl dithiocarbazate Schiff base complexes.**

The Schiff base complexes which were oils at room temperature solidified on cooling below  $\sim -20^{\circ}$ . They were characterized by elemental analysis and their IR, NMR spectral studies. The complex (SBSaD)Sn(CH<sub>3</sub>)<sub>2</sub> was prepared by azeotropic dehydration of a mixture of dimethyltin oxide and H<sub>2</sub>SBSaD in benzene.

**IR Spectral data of bis-( $\beta$ -carboalkoxyethyl)tin(IV) S-benzyl dithiocarbazate Schiff base complexes.**

In the spectra of diestertin Schiff base complexes, [Table 3.7] two strong bands are observed at  $\sim 1700$  and  $\sim 1730$  cm<sup>-1</sup> due to  $\nu$ (C=O) of carboxylic group, which suggests coordinated and free ester groupings in the complexes. The  $\nu$ (C-OR) band, found at  $\sim 1220$  cm<sup>-1</sup> in the ester tin dichloride, is observed as a split band in the complexes, one at  $\sim 1260$  cm<sup>-1</sup> and other at  $\sim 1205$  cm<sup>-1</sup>. The low frequency shift could be due to the non-involvement of one of the ester groupings in coordination to tin to give a -C=O  $\rightarrow$  Sn band.

The IR spectra of the Schiff base ligands in Nujol mull, show  $\nu$ (NH) at  $\sim 3085$  cm<sup>-1</sup>. Intramolecularly hydrogen bonded  $\nu$ (OH) is discernible at  $\sim 3400$  cm<sup>-1</sup> in their dilute chloroform solutions. The  $\nu$ (C=N) frequency is observed at  $\sim 1600$  cm<sup>-1</sup> and  $\nu$ (C=S) at  $\sim 1030$  cm<sup>-1</sup>. The shift of  $\nu$ (C=N) band to  $\sim 1585$  cm<sup>-1</sup> in the complexes suggests coordination of the lone pair of electrons

on nitrogen to tin. The phenolic  $\nu(\text{C-O})$  of the ligands observed at  $\sim 1240 \text{ cm}^{-1}$  has been shifted to higher wave numbers  $\sim 1310 \text{ cm}^{-1}$  due to increased C-O bond order as a result of proton replacement with tin<sup>23</sup>. The absence of  $\nu(\text{NH})$  and lowering of  $\nu(\text{C=S})$  bands suggest thioenolization followed by complex formation. Hence the Schiff bases act as dianionic tridentate ligands. The  $\nu(\text{Sn-C})$  is observed at  $\sim 560 \text{ cm}^{-1}$  in all the complexes.

**<sup>1</sup>H NMR Spectral data of bis-( $\beta$ -carboalkoxyethyl)tin(IV) S-benzyl dithiocarbazate Schiff base complexes.**

<sup>1</sup>H NMR spectra of bis-( $\beta$ -carboalkoxyethyl)tin dichlorides show two triplets centered at  $\sim 1.89$  and  $\sim 2.90$  ppm due to  $\alpha\text{-CH}_2$  and  $\beta\text{-CH}_2$  proton respectively. These resonances are shifted to higher magnetic field in the Schiff base complexes [Table 3.8]. The shielding may be attributed to the replacement of electronegative chlorine atom by donor atoms O, N and S of the Schiff base. Marginal shielding is also observed for  $\text{OCH}_3/\text{OCH}_2$  protons of ester groupings. Furthermore the presence of only one singlet due to  $-\text{OCH}_3$  protons in  $(\text{SBSaD})\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3)_2$  complex suggests magnetic equivalence of both the ester groupings, presumably due to a rapid exchange of coordinated and noncoordinated carbonyl groups in solution leading to equivalence of both the ester moieties<sup>32</sup>. The complex  $(\text{SBSaD})\text{Sn}(\text{CH}_3)_2$  shows a singlet at 0.93 ppm due to methyl resonances with two satellite signals having the coupling constants  $^2J(^{119}\text{Sn}, ^1\text{H})$  69

and  $^2J(^{117}\text{Sn}, ^1\text{H})$  72 Hz.

The Schiff bases display signals at  $\sim 4.55$ ,  $\sim 8.50$ ,  $\sim 10.50$  and  $\sim 12.00$  ppm assignable to  $\text{SCH}_2^-$ ,  $=\text{CH}$  (aldehydic), NH and OH protons respectively. In the complexes both NH and OH proton resonances are absent. The aldehydic proton gets deshielded in the complexes as expected, whereas benzyl the  $\text{SCH}_2^-$  signal shifts to higher magnetic field.

**$^{13}\text{C}$  NMR Spectral data of bis-( $\beta$ -carboalkoxyethyl)tin(IV) S-benzyl dithiocarbazate Schiff base complexes.**

The high resolution  $^{13}\text{C}$  NMR spectra of the estertin complexes [Table 3.9] show sharp signals due to  $\alpha$ - $\text{CH}_2$ ,  $\beta$ - $\text{CH}_2$  and C=O (ester) resonances along with well separated  $^{119}\text{Sn}$  satellite signals. An upfield shift has been observed for the  $\alpha$ - $\text{CH}_2$  and alkoxy carbon resonances in the complexes, compared to those of  $\text{Cl}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3)_2$  which suggests breaking or weakening of intramolecular ester coordination to tin. The ester carbonyl carbon (C=O) suffers a high field shift of  $\sim 5$  ppm indicating increased electron density and the appearance of a single signal at  $\sim 176$  ppm also may suggest fast exchange of metal bonded and non-bonded carbonyl groups leading to magnetic equivalence of the ester groupings<sup>33</sup>.

Because of the limited solubility,  $^{13}\text{C}$  NMR spectra of the free Schiff bases are taken in the solid state. The spectra show resonances due to C=S, CH (aldehydic), phenolic C-O and  $\text{SCH}_2^-$

at ~ 198, ~ 148, ~ 159 and ~ 40.5 ppm respectively. In the complexes large shielding has been observed for the thioketo carbon which indicates thiolate ion formation. The azomethine and phenolic carbons are deshielded due to coordination of these groups to tin.

Tin-carbon coupling has been observed for  $\alpha$ -CH<sub>2</sub>,  $\beta$ -CH<sub>2</sub>, ester C=O and phenolic C-O groups [Fig 3.5]. The coupling constants  $^1J(^{119}\text{Sn}, ^{13}\text{C})$  [Table 3.10] are in the range 720-730 Hz for complex nos. 3,4 and 5. This coupling constant,  $^1J$  (coupling constant) is directly linked to the values of C-Sn-C bond angle ( $\theta$ ) according to the equation<sup>35</sup>.

$$|^1J(^{119}\text{Sn}, ^{13}\text{C})| = 11.4 (\theta) - 875$$

The values of  $\theta$  calculated for the above complexes are between 140-141°. The corresponding values calculated for the complex, (no. 2) (SBSaD)Sn(CH<sub>3</sub>)<sub>2</sub> having a coupling constant of  $^1J(^{119}\text{Sn}, ^{13}\text{C})$  596 Hz is 129°. The well characterized octahedral complex Me<sub>2</sub>Sn(koj)<sup>37</sup> [koj = 5-oxy-2-(hydroxymethyl)-4H pyran-4-one] with trans methyl groups has a  $\theta$  values of 142°. For the complex nos. 3, 4 and 5  $^2J(^{119}\text{Sn}, ^{13}\text{C})$  for  $\beta$ -CH<sub>2</sub> grouping is ~ 42 Hz. The tin satellite signals observed for phenolic C-O and ester carbonyl carbons may be attributed to tin-carbon coupling through oxygen. The tin-carbon coupling constant value for phenolic C-O is ~ 30 Hz whereas for ester carbonyl carbon it is ~ 53 Hz.

$^{119}\text{Sn}$  NMR spectral data of bis-( $\beta$ -carboalkoxyethyl)tin(IV)

S-benzylthiocarbamate Schiff base complexes.

It is to be noted that tin chemical shift ( $^{119}\text{Sn}$ ) values reflect the nature of donor atoms to which tin is bonded. The  $\delta(^{119}\text{Sn})$  observed for  $\text{Cl}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3)_2$  is at -66.4 ppm [Table 3.10]. The tin atom in the complex  $(\text{SBSaD})\text{Sn}(\text{CH}_3)_2$  resonates at -111 ppm which suggests the metal atom to be in a pentacoordinated environment as reported in the literature<sup>34</sup>. The increased shielding is attributed to the presence of nitrogen, oxygen and sulphur donors in place of electron withdrawing chlorine atoms. The  $^{119}\text{Sn}$  chemical shift values of diestertin Schiff base complexes fall in the range 182 to 183 ppm. The cause of increased shielding has been related to higher coordination number at tin. All these spectral data are consistent with a distorted octahedral geometry for the complexes with trans ester groupings. The structure of the complexes is similar as shown in fig 3.2.

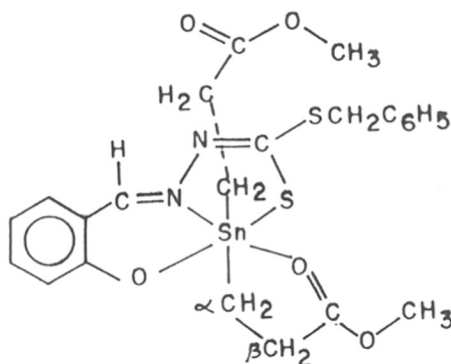


FIG. 3.2

## ELECTRONIC SPECTRA

The electronic spectra of the Schiff bases and their ester tin complexes have been studied in chloroform solution. [Table 3.11] The spectra of the Schiff bases show high intensity bands between 300-380 nm. In the higher wavelength region the ligands H<sub>2</sub>SBSaD, H<sub>2</sub>SBVD and H<sub>2</sub>SBND show absorption maxima at 348, 338 and 400 nm respectively. In the complexes these bands suffer blue shift with reduced intensities as a result of chelate formation. An additional band of medium intensity has been observed between 416-444 nm in the complexes which may be attributed to the ligand-to-metal charge transfer band<sup>40</sup> and this is a clear indication of stable complex formation.



Table 3.6. Analytical data for bis( $\beta$ -carboalkoxyethyl)tin(IV)  
S-benzylthiocarbazate Schiff base complexes.

No.	Compound	Elemental analysis found (cal.) %				Mol.wt. found(cal.)
		Sn	C	H	N	
22	(SBSaD)Sn(CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> C <sub>23</sub> H <sub>26</sub> O <sub>5</sub> N <sub>2</sub> S <sub>2</sub> Sn	19.88 (20.01)	46.29 (46.56)	4.45 (4.42)	4.66 (4.72)	585.33 (593.27)
23	(SBSaD)Sn(CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> C <sub>25</sub> H <sub>30</sub> O <sub>5</sub> N <sub>2</sub> S <sub>2</sub> Sn	19.25 (19.10)	48.47 (48.32)	4.52 (4.87)	4.41 (4.51)	610.15 (621.32)
24	(SBSaD)Sn(CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> C <sub>29</sub> H <sub>38</sub> O <sub>5</sub> N <sub>2</sub> S <sub>2</sub> Sn	17.37 (17.52)	51.18 (51.41)	5.73 (5.65)	4.19 (4.34)	661.45 (677.43)
25	(SBVD)Sn(CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> C <sub>24</sub> H <sub>28</sub> O <sub>6</sub> N <sub>2</sub> S <sub>2</sub> Sn	19.21 (19.05)	46.36 (46.24)	4.19 (4.53)	4.23 (4.49)	618.41 (623.30)
26	(SBVD)Sn(CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> C <sub>26</sub> H <sub>32</sub> O <sub>6</sub> N <sub>2</sub> S <sub>2</sub> Sn	18.13 (18.22)	47.62 (47.94)	4.61 (4.95)	4.41 (4.30)	633.87 (651.35)
27	(SBVD)Sn(CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> C <sub>30</sub> H <sub>40</sub> O <sub>6</sub> N <sub>2</sub> S <sub>2</sub> Sn	18.52 (18.78)	50.63 (50.93)	5.35 (5.70)	3.72 (3.98)	710.66 (707.45)
28	(SBND)Sn(CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> C <sub>27</sub> H <sub>28</sub> O <sub>5</sub> N <sub>2</sub> S <sub>2</sub> Sn	18.57 (18.45)	50.23 (50.41)	4.57 (4.39)	4.22 (4.35)	629.23 (643.33)
29	(SBND)Sn(CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> C <sub>29</sub> H <sub>32</sub> O <sub>5</sub> N <sub>2</sub> S <sub>2</sub> Sn	17.32 (17.68)	51.91 (51.88)	4.59 (4.80)	4.28 (4.17)	654.34 (671.38)
30	(SBND)Sn(CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> C <sub>33</sub> H <sub>40</sub> O <sub>5</sub> N <sub>2</sub> S <sub>2</sub> Sn	16.18 (16.32)	54.37 (54.48)	5.41 (5.54)	3.72 (3.85)	730.11 (727.48)

Table 3.7. IR data ( in  $\text{cm}^{-1}$ ) for bis( $\beta$ -carboalkoxyethyl)tin(IV)  
S-benzylidithiocarbazate Schiff base complexes ( $\nu$ ,  $\text{cm}^{-1}$ ).

No.	(C=O)	(C-O)(ester)	(C=N)(C=C)	(C-O)(L)*	(C-S)	(N-N)
22	1732,1707	1283,1219	1582,1536	1311	1026	959
23	1730,1705	1260,1205	1585,1538	1310	1024	960,925
24	1731,1711	1264,1218	1586,1540	1302	1028	966,937,917
25	1727,1712	1246,1213	1582,1549	1316	1026	962
26	1727,1701	1247,1211	1584,1548	1342	1015	960,917
27	1726,1672	1250,1215	1586,1547	1313	1028	966,915
28	1730,1713	1253,1191	1598,1536	1301	1024	985,962,943
29	1725,1704	1256,1204	1598,1536	1300	1024	987,960,942
30	1728,1676	1260,1193	1598,1538	1301	1029	989,963,944

\* of Schiff bases.

Table 3.8.  $^1\text{H}$  NMR data for bis( $\beta$ -carboalkoxyethyl)tin(IV) S-benzyl dithiocarbazate Schiff base complexes ( $\delta$ , ppm).

No.	Chemical shifts( $\delta$ , ppm in $\text{CDCl}_3$ )							Aromatic protons
	$\alpha$ - $\text{CH}_2$	$\beta$ - $\text{CH}_2$	$\text{OCH}_2/\text{OCH}_3$ (ester)	$\text{CH}_3$ (ester)	$\text{SCH}_2$	$\text{OCH}_3$ (L)	CH	
22	1.64	2.69	3.58	-	4.33	-	8.60	6.60 - 7.36
23	1.63	2.64	4.12	1.20	4.34	-	8.61	6.58 - 7.41
24	1.77	2.70	4.02	0.87	4.35	-	8.59	6.50 - 7.38
25	1.76	2.76	3.64	-	4.40	3.82	8.64	6.53 - 7.42
26	1.70	2.71	4.10	1.25	4.35	3.80	8.60	6.55 - 7.50
27	1.73	2.70	3.77	0.90	4.33	3.80	8.70	6.53 - 7.46
28	1.69	2.72	3.60	-	4.38	-	9.42	6.80 - 7.92
29	1.63	2.66	4.00	1.15	4.33	-	9.38	6.55 - 8.00
30	1.80	2.77	4.03	0.88	4.40	-	9.60	6.78 - 8.00

$\text{OCH}_3$  (L) =  $\text{OCH}_3$  of the Schiff base  $\text{H}_2\text{SBVD}$ .

Table 3.9.  $^{13}\text{C}$  NMR data for bis(  $\beta$ -carboalkoxyethyl)tin(IV)  
S-benzylthiocarbamate Schiff base complexes (ppm).

No.	$\alpha$ -CH <sub>2</sub>	$\beta$ -CH <sub>2</sub>	SCH <sub>2</sub> -	OCH <sub>3</sub> (est)	=CH	C-O	C=S	C=O(est)
1	-	-	40.54	-	148.21	172.42	198.88	-
2	-	-	41.32	56.05	149.05	169.78	197.09	-
3	-	-	46.19	-	128.59	173.95	210.73	-
4	24.15	28.39	-	53.68	-	-	-	181.13
5	-	-	36.00	-	185.84	167.50	173.17	-
6	21.07	29.12	36.09	52.07	165.05	167.78	172.73	176.65
7	21.03	28.98	36.13	52.04	165.04	158.50	172.58	178.74
8	20.32	29.13	36.28	52.11	160.00	170.33	170.06	176.65

1. H<sub>2</sub>SBSaD\*

2. H<sub>2</sub>SBVD\*

3. H<sub>2</sub>SBND\*

4. Cl<sub>2</sub>Sn(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>

5. (SBSaD)Sn(CH<sub>3</sub>)<sub>2</sub>

6. (SBSaD)Sn(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>

7. (SBVD)Sn(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>

8. (SBND)Sn(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>

CH<sub>3</sub> in (SBSaD)Sn(CH<sub>3</sub>)<sub>2</sub> = 6.27 ppm

OCH<sub>3</sub> in (SBVD)Sn(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>)<sub>2</sub> = 55.97 ppm

\* (1-3) Recorded in solid state;  
(4-8) Recorded in CDCl<sub>3</sub> solution.

Table 3.10.  $^{119}\text{Sn}$  NMR data and tin-carbon coupling constants for bis( $\beta$ -carbomethoxyethyl) tin(IV) S-benzyl dithiocarbazate Schiff base complexes.

No.	$^{119}\text{Sn}$ ( $\delta$ , ppm)	$^1J(^{119}\text{Sn}, ^{13}\text{C})$ (Hz) $\alpha\text{-CH}_2$	$^1J(^{117}\text{Sn}, ^{13}\text{C})$ (Hz) $\alpha\text{-CH}_2$	$^2J(^{119}\text{Sn}, ^{13}\text{C})$ (Hz) $\beta\text{-CH}_2$	$^2J(^{117}\text{Sn}, ^{13}\text{C})$ (Hz) Phenolic C-O	$^3J(^{119}\text{Sn}, ^{13}\text{C})$ (Hz) C=O (ester)	C-Sn-C ( $^\circ$ )
1	-66.40	-	-	-	-	-	-
2	-110.94	596.39	571.09	-	30.31	-	129.07
3	-181.74	723.82	692.80	42.14	30.58	59.46	140.25
4	-182.70	731.53	699.50	41.77	28.29	52.95	140.92
5	-183.00	720.73	689.03	42.00	27.88	51.11	139.98

1.  $\text{Cl}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3)_2$
2.  $(\text{SBSaD})\text{Sn}(\text{CH}_3)_2$
3.  $(\text{SBSaD})\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3)_2$
4.  $(\text{SBVD})\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3)_2$
5.  $(\text{SBND})\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3)_2$

Table 3.11. UV spectral data for S-benzyl dithiocarbazate Schiff base ligands and their bis(β-carboalkoxyethyl)tin(IV) complexes.

No. Schiff base/compound	$\lambda_{\max}$ ( $\epsilon_{\max}$ )
H <sub>2</sub> SBSaD	280(18600), 306(19200), 318(36000), 348(28600)
1 (SBSaD)Sn(CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	298(8000), 342(7600), 416(6800)
H <sub>2</sub> SBVD	237(15780), 338(31100)
2 (SBVD)Sn(CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	245(11020), 348(10060), 431(5580)
3 (SBVD)Sn(CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	245(11820), 307(8430), 345(11410), 431(6080)
4 (SBVD)Sn(CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub>	243(11400), 344(12660), 424(5120)
H <sub>2</sub> SBND	268(14400), 336(14600), 382(22000), 400(19800)
5 (SBND)Sn(CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	334(10440), 348(1992), 444(16271)

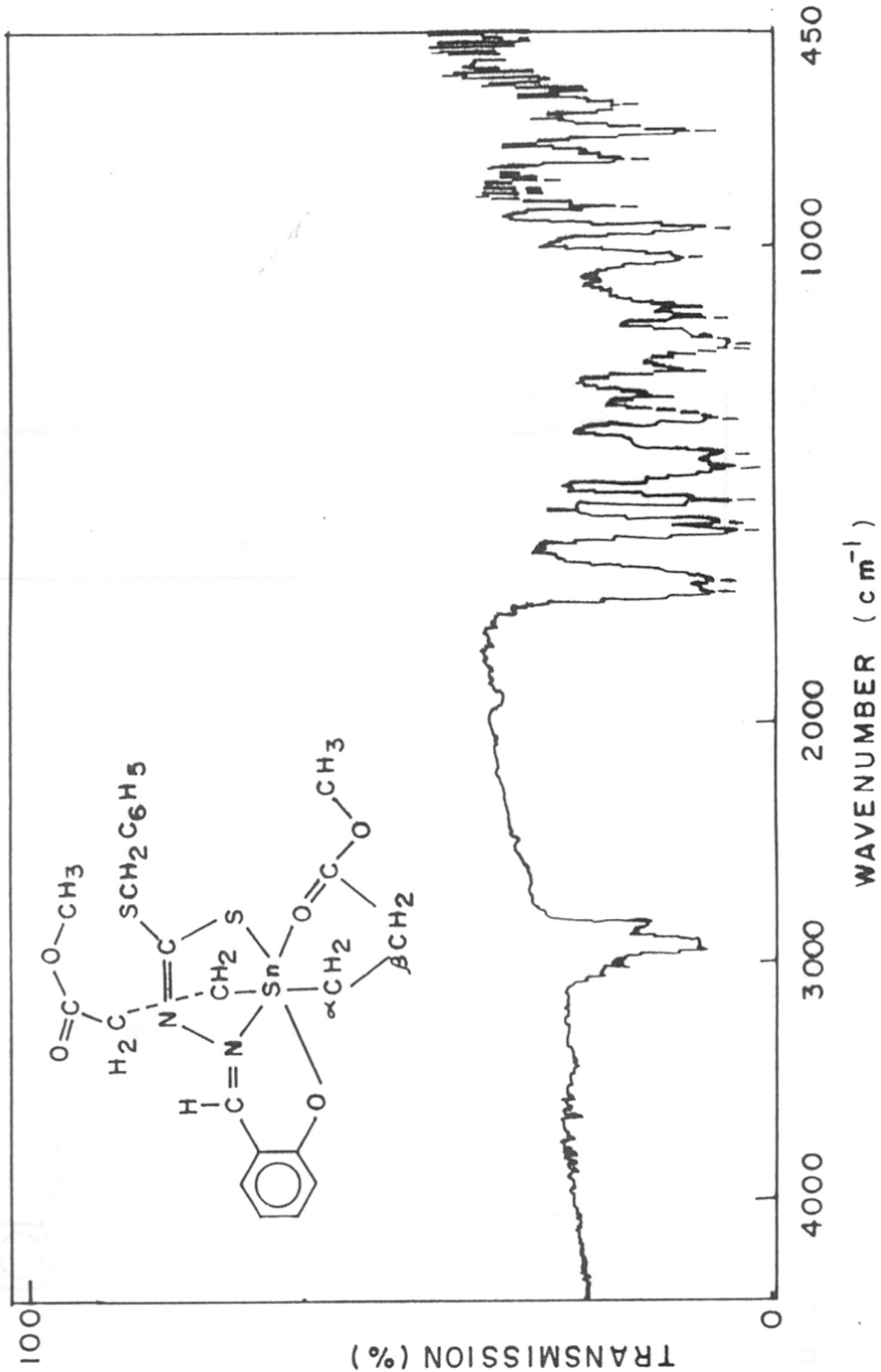
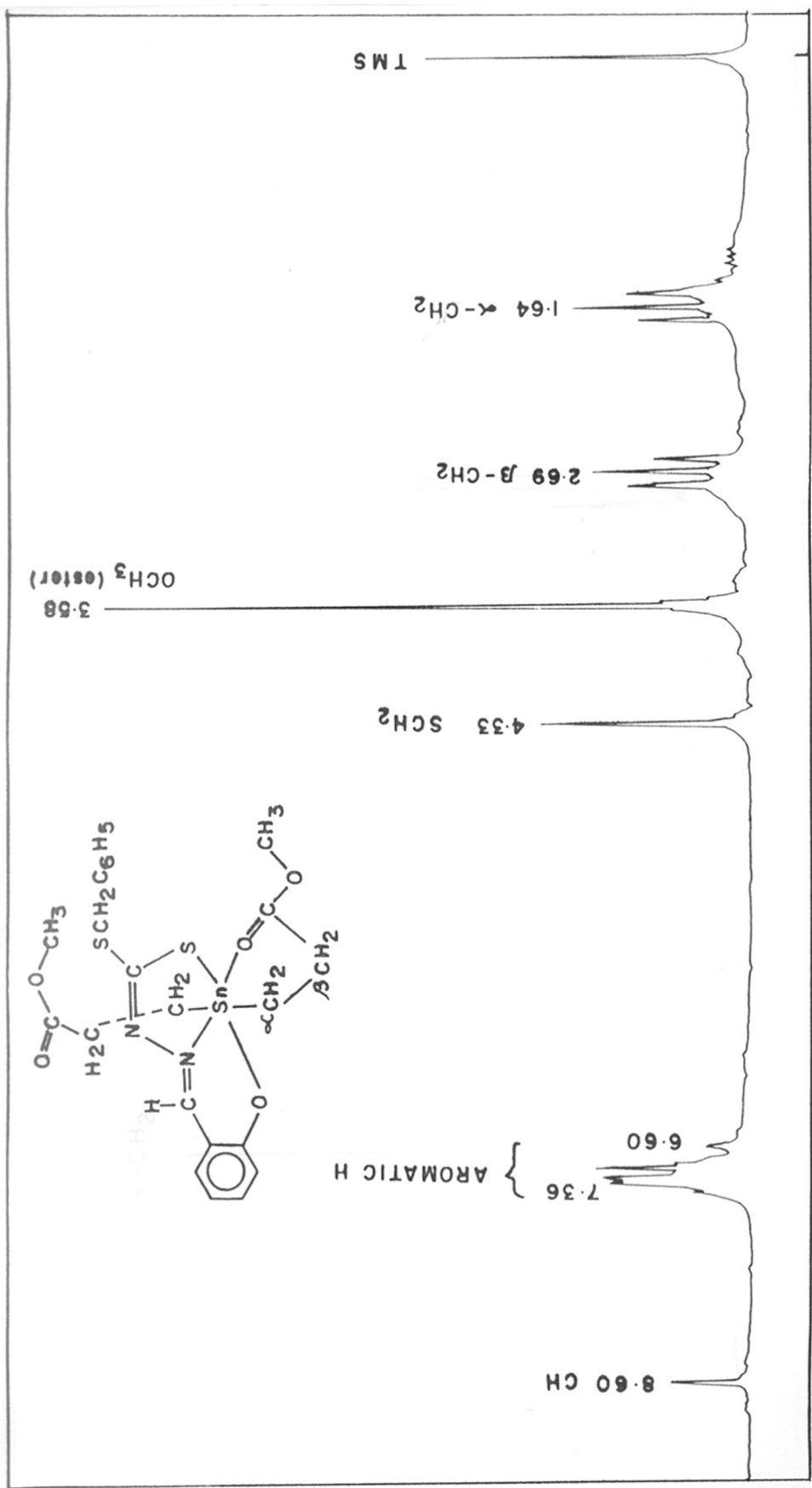
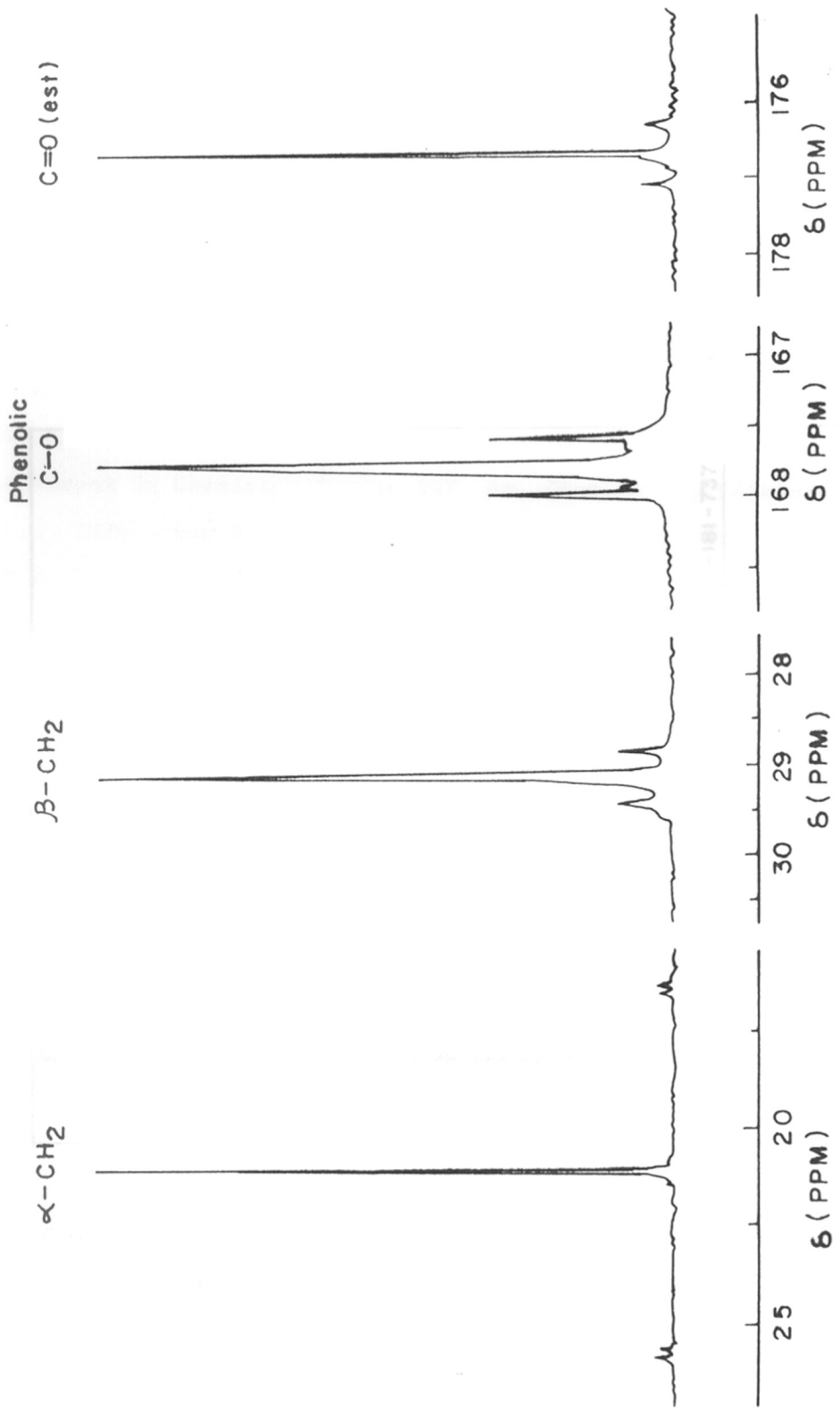


FIG. 3.3 : IR SPECTRUM OF (SBSad) Sn (CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>)<sub>2</sub> IN NUJOL

FIG. 3.4: <sup>1</sup>H NMR SPECTRUM OF (SBS<sub>0</sub>D) Sn (CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>)<sub>2</sub> IN CDCl<sub>3</sub>.







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FIG.3.5: <sup>13</sup>C NMR SPECTRUM AND TIN - CARBON COUPLING CONSTANTS OBSERVED FOR THE COMPLEX (SBSad) Sn (CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>)<sub>2</sub> IN CDCl<sub>3</sub>

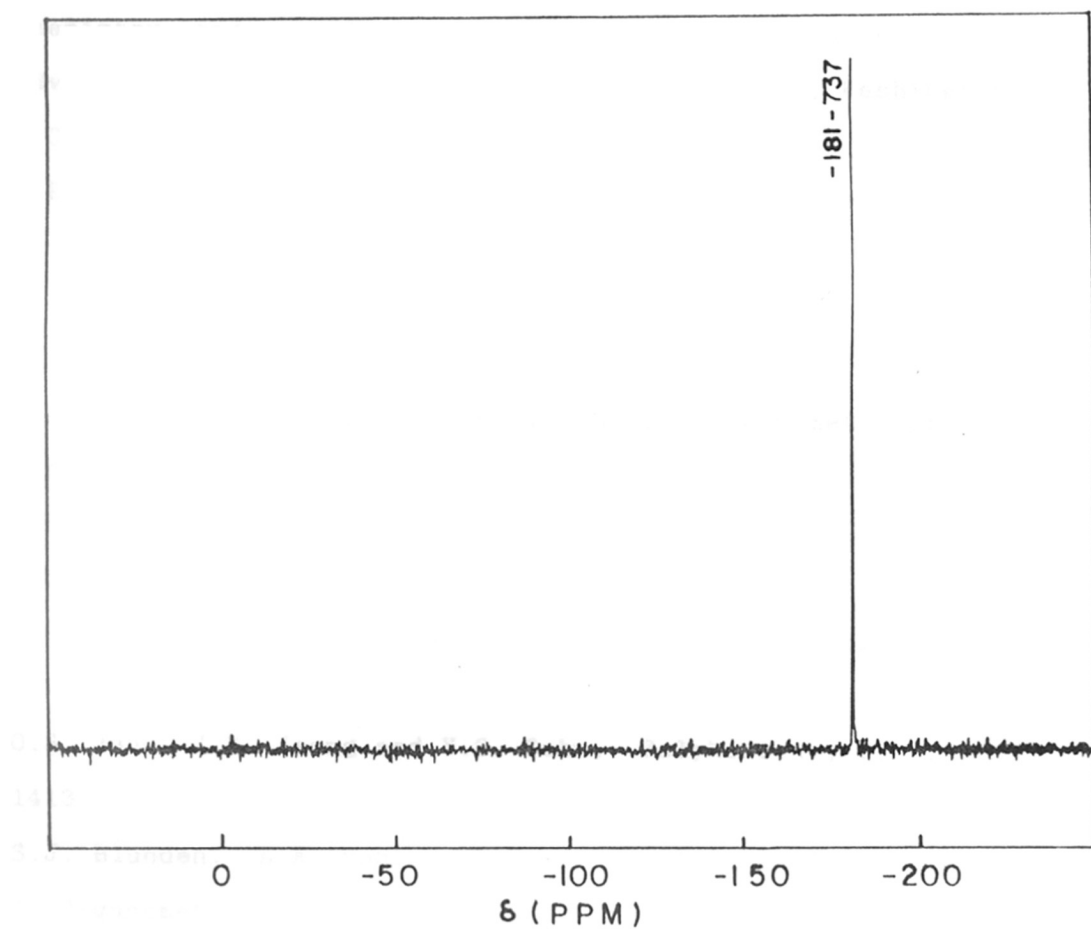


FIG. 3.6 :  $^{119}\text{Sn}$  NMR SPECTRUM OF (SBSaD)  $\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3)$   
IN  $\text{CDCl}_3$

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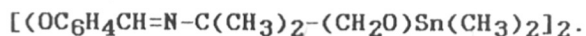
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leptons) **CHAPTER 4** (of the **Standard Model**)

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STUDIES ON ORGANOTIN(IV) COMPLEXES OF N-(HYDROXYPROPYL)  
SALICYLIDENEIMINES AND X-RAY CRYSTAL STUDY OF THE COMPLEX



S U M M A R Y

In this chapter, synthesis and spectral studies of a series of novel organotin(IV) complexes with Schiff bases derived from salicylaldehyde or substituted salicylaldehyde and 2-amino-2-methyl-1-propanol, are described.

The above Schiff base (LH<sub>2</sub>) forms stable organotin(IV) complexes of the type (L)SnR<sub>2</sub>, (LH)Sn(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> and (L)SnCl(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>). In the complexes of the type LSnR<sub>2</sub>, R represents the organic groups, CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub> and the ester -CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub> attached to tin and LH or L represents mono or doubly deprotonated Schiff base ligands.

The Schiff base ligands used were obtained by the condensation of salicylaldehyde, 5-chloro and 5-bromo salicylaldehyde, 2-hydroxy-3-methoxybenzaldehyde, or 2-hydroxy-1-naphthaldehyde with the propanol amine, 2-amino-2-methyl-1-propanol. The Schiff bases and their complexes are characterized on the basis of their elemental analyses, IR, <sup>1</sup>H, <sup>13</sup>C and <sup>119</sup>Sn NMR spectral studies and X-ray crystal studies.

A single X-ray crystal diffraction study of the complex,



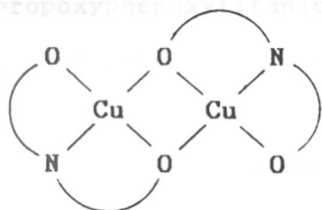
$[\text{OC}_6\text{H}_4\text{CH}=\text{N}-\text{C}(\text{CH}_3)_2-(\text{CH}_2\text{O})\text{Sn}(\text{CH}_3)_2]_2$ , confirms the structure to be dimeric. The crystals are monoclinic, space group  $\text{P2}_1/\text{c}$  with  $a = 7.498(2)$ ,  $b = 15.135(2)$ ,  $c = 12.472(2)\text{\AA}$ ,  $\beta = 95.99(2)^\circ$ , volume =  $1407.6(5)\text{\AA}^3$ ,  $Z = 2$ ,  $D_c = 1.604 \text{ g/cm}^3$ . The final discrepancy factors are  $R = 0.022$  and  $R_w = 0.028$  for 1770 observed reflections. Half of the molecule is linked to the other half by centre of symmetry via alkoxy oxygen atom. Each alkoxy groups of the two Schiff bases coordinate to two tin atoms to form a dimeric structure. Thus each tin atom has a distorted octahedral structure coordinating through the phenolic O, azomethine N, two bridging alkoxy oxygens, two methyl groups.

However the estertin Schiff base complexes,  $(\text{L})\text{SnCl}(\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3)$  and  $(\text{L})\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3)_2$  are suggested to have a mononuclear hexacoordinated structure in which one of the ester groupings coordinates to tin. In these mononuclear complexes the Schiff base possibly acts as a dianionic tridentate moiety by coordinating through alkoxy  $-\text{CH}_2-\text{O}$ , azomethine nitrogen and phenoxide ion to tin. These estertin complexes are suggested to have an octahedral geometry.

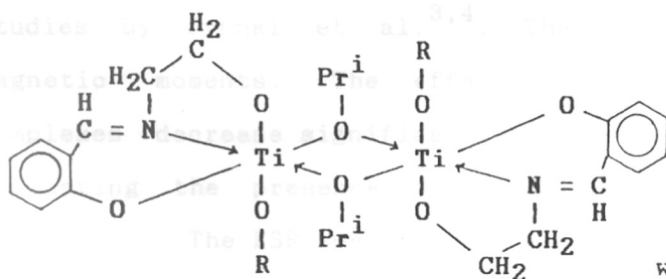
Sulphur dioxide molecule inserts into the tin-methyl/phenyl bond in the above Schiff base complexes to give mono insertion products. The complexes are found to be tin-O-sulphinates of the formula:  $(\text{L})\text{RSn}(\text{SO}_2\text{R})$  and  $(\text{LH})(\text{C}_6\text{H}_5)_2\text{Sn}(\text{SO}_2\text{C}_6\text{H}_5)$  [where  $\text{R} = \text{CH}_3$  or  $\text{C}_6\text{H}_5$ ] on the basis of IR spectral studies.

## I N T R O D U C T I O N

Yamada et al<sup>1</sup> have synthesized and characterized Cu(II) complexes containing alkanol amine Schiff bases [(OH)XC<sub>6</sub>H<sub>3</sub>CH=N-R-OH; where X = H or 3-CH<sub>3</sub>O and R = (CH<sub>2</sub>)<sub>3</sub>]. The magnetic moments found for the complexes were subnormal, which was assigned due to exchange interaction between Cu(II) metal ions. Molecular weight determination of the complexes were in agreement with binuclear structure as shown below:

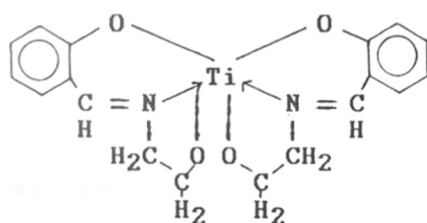


Prashar et al<sup>2</sup> have reacted Ti(OPr<sup>i</sup>)<sub>4</sub> with same type of Schiff base, HOC<sub>6</sub>H<sub>5</sub>CH=N-(CH<sub>2</sub>)<sub>2</sub>-OH [SBH<sub>2</sub>] derived from salicylaldehyde and 2-hydroxyethylamine in different molar ratios and isolated complexes of the type Ti(OPr<sup>i</sup>)<sub>2</sub>(SB) [I] and Ti(SB)<sub>2</sub> [II]. The complex, Ti(OPr<sup>i</sup>)<sub>2</sub>(SB), has been found to interchange



[I]

where R = Pr<sup>i</sup> or OC<sub>6</sub>H<sub>5</sub>

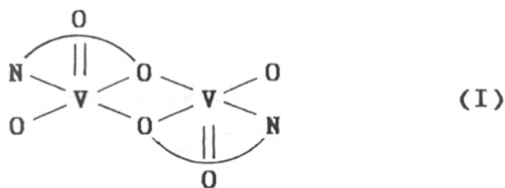


[II]

its isopropoxy groups with higher alcohols, glycols and phenols. The molecular weights of the products have been determined ebullioscopically and the possible structure reported. The compounds diisopropoxytitanium(IV)salicylidene-2-oxyethylamine and isopropoxyphenoxytitanium(IV)salicylidene-2-oxyethylamine are dimeric, but titanium-bis-salicylidene-2-oxyethylamine, di-*tert*-butoxy and di-phenoxytitanium salicylidene-2-oxyethylamine products are found to be monomeric.

Many oxovanadium(IV) complexes of Schiff bases derived from salicylaldehyde, 5-chlorosalicylaldehyde, 3,5-dichlorosalicylaldehyde, 5-bromosalicylaldehyde, 3-methoxysalicylaldehyde or 2-hydroxy naphthaldehyde, and isopropanolamine or ethanolamine have been prepared and characterized by elemental analysis, IR, electronic and ESR spectral data and magnetic susceptibility studies by Syamal et al.<sup>3,4</sup>. The complexes show subnormal magnetic moments. The effective magnetic moments of the complexes decrease significantly as the temperature is lowered indicating the presence of antiferromagnetic exchange in the complexes. The ESR spectra of the complexes exhibit the half-

field spectra suggesting the presence of triplet state ( $S = 1$ ) in these complexes. On the basis of magnetic susceptibility and ESR data a dimeric structure (I) with singlet ground state ( $S = 0$ ) has been proposed for these complexes.

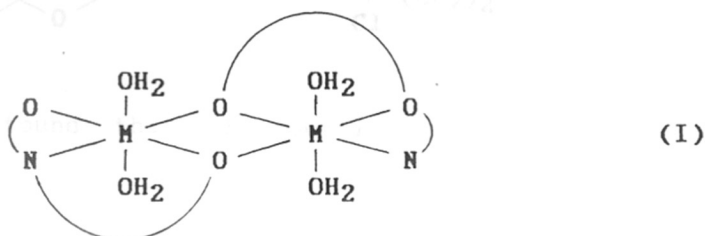


Similarly Kuge et al<sup>5</sup> have isolated oxovanadium(IV) Schiff base complexes of the type,  $[VO(X-sal.Y-O)]$ , with the Schiff base such as (N-hydroxyalkylsalicylideneimine),  $[HOC_6H_3XCH=N-Y-OH]$ ; where  $X = H$  or  $OCH_3$  and  $Y = (CH_2)_2$  or  $(CH_2)_3$ . The magnetic moments observed for the complexes are found to be subnormal. The subnormal magnetic moment was considered to be due to an exchange interaction between vanadium(IV) ions and a binuclear structure has been assigned for these complexes.

Oxovanadium(IV) complexes, derived from salicylaldehyde derivatives and alkanolamines, were synthesized and fully characterized by elemental analysis, IR and electronic spectra, magnetic susceptibility measurements, molecular weight determination and thermal analysis by Kuge et al<sup>6</sup>. Multinuclear structures were proposed for these complexes, in solid state, but the solution in 1,2-dichloroethane exhibit presence of binuclear complex. In pyridine solution the multinuclear structure is

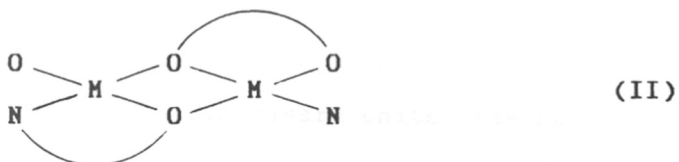
broken down into mononuclear pyridine adducts.

Several binuclear complexes of the composition  $M_2L_2 \cdot 4H_2O$ ,  $M_2L'_2 \cdot 4H_2O$  [ $M = Co(II), Ni(II)$ ],  $M_2L_2$ ,  $M_2L'_2$  [ $M = Cu(II), Zn, Cd$  and  $Hg(II)$ ] have been synthesized by Mahapatra et al<sup>7</sup>. The  $LH_2$  and  $L'H_2$  are tridentate Schiff bases derived from benzoin with 2-amino-2-methyl-1-propanol or 1-amino-2-propanol. The complexes of the first two categories  $M_2L_2 \cdot 4H_2O$  and  $M_2L'_2 \cdot 4H_2O$  (I) are



where  $M = Co(II), Ni(II)$

bimetallic octahedral whereas binuclear square planar structures have been assigned to the later categories (II) on the basis of their elemental analysis, conductance, magnetic susceptibility,

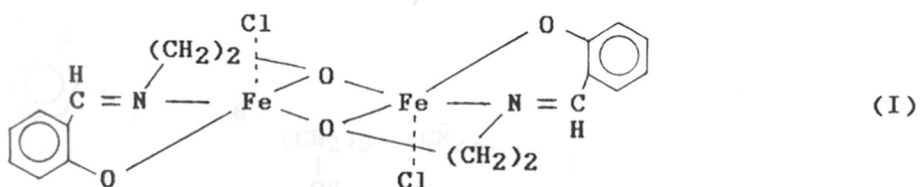


where  $M = Cu(II), Zn, Cd$  and  $Hg(II)$

IR and electronic spectral data.

A binuclear iron(III) complex (I),  $[Fe(SALPA)Cl]_2$ , containing a four membered iron-oxygen ring was prepared by

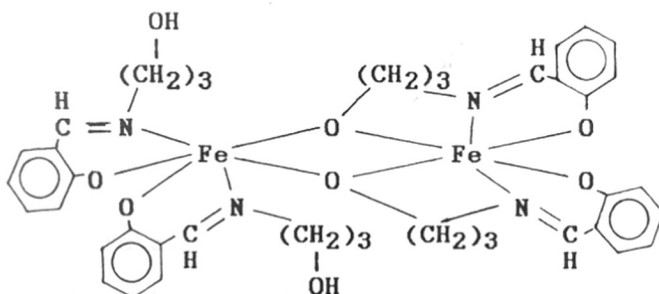
Berfrand et al<sup>8</sup> by mixing iron(III)chloride and the Schiff base [HOC<sub>6</sub>H<sub>4</sub>CH=N-(CH<sub>2</sub>)<sub>3</sub>-OH], [SALPAH<sub>2</sub>], in methanol. The compound was recrystallised from tetrahydrofuran. From the X-ray study it has



been found that the coordination of the iron can be square pyramidal with the three oxygens and the nitrogen atoms forming the planar base and the iron is 0.55 Å above this base.

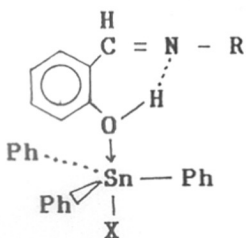
The five-coordinated binuclear complex, [Fe(SALPA)Cl]<sub>2</sub> reacts readily with sodium peroxide to give a red crystalline product<sup>9</sup>, [Fe(SALPA)<sub>2</sub>(SALPAH)<sub>2</sub>], which exhibits antiferromagnetic behaviour. The three-dimensional X-ray crystal structure analysis of the toluene solvate of the complex revealed the presence of six-coordinate iron atoms linked closely by bridging propoxide groups into dinuclear units having a planar, four membered  $\text{Fe}-\text{O}-\text{Fe}$  ring. Hydrogen binding between the uncoordinated alcohol groups and the phenolic oxygens connects the dimeric units into infinite, doubly linked chains. The iron atoms have virtually identical geometries having distorted octahedron with trans nitrogens, two bridging cis  $M_2$  oxygens, two terminal oxygens. However the iron atoms are found to be

nonequivalent



since the two bridging propoxide groups are chelated to the same iron atom. The preparation of  $\text{Fe}_2(\text{SALPA})_2(\text{SALPAH})_2$  is discussed and the structure is correlated with the magnetic and spectral properties of several mononuclear and dinuclear iron(III) complexes.

Khoo et al<sup>10</sup> have prepared several addition complexes of the type  $\text{Ph}_3\text{SnX}:\text{o-HOC}_6\text{H}_4\text{CH}=\text{NR}$  ( $\text{X} = \text{Cl}, \text{NCS}$ ;  $\text{R} = \text{HOCH}_2\text{CH}_2$ ) by the reaction of triphenyltin-chloride or -isothiocyanate with the *N*-alkylsalicylideneimines. The complexes are non-electrolytes in nitrobenzene. The IR, PMR and Mössbauer spectroscopic studies of the complexes indicate that the ligands are behaving as monodentates bonding via the phenolic oxygen atom, and have trigonal bipyramidal geometry with the phenyl groups occupying the equatorial positions as shown in (I).



(I)

Srivastava et al<sup>11</sup> have synthesized 1:2 molecular addition complexes of  $\text{Ph}_2\text{SnCl}_2$  with Schiff bases,  $\text{H}_2\text{SB}$ , derived from ethanol amine and salicylaldehyde in which the Schiff base coordinated to tin through azomethine nitrogen atom. Similar reaction in presence of a base in 1:1 molar proportion yield chlorine substitution products of the formula  $\text{Ph}_2\text{Sn}(\text{SB})$ . The structure of the complex is assigned as trigonal bipyramidal on the basis of IR spectral data.

The present study deals with the preparation and characterization of several novel organotin(IV) Schiff base complexes by the reactions of organotin chlorides and propanol amine. These complexes have been well characterized by their elemental analysis, IR,  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{119}\text{Sn}$  NMR studies. The X-ray crystal study of  $[\text{OC}_6\text{H}_4\text{CH-N-C}(\text{CH}_3)_2\text{-CH}_2\text{-O})\text{Sn}(\text{CH}_3)_2]_2$  is also discussed.



## E X P E R I M E N T A L

The starting chemicals used were of reagent or analytical grade and were used without further purification. The solvents were dried and distilled before use. Infrared spectra were recorded as KBr pellets,  $\text{CH}_2\text{Cl}_2$  solution or as nujol mulls, on a Perkin-Elmer FT-IR spectrophotometer model 1620. The proton NMR spectra were recorded using a Varian FT-80A spectrometer or Bruker WH-90 spectrometer in  $\text{CDCl}_3$  solution. The  $^{13}\text{C}$  and  $^{119}\text{Sn}$  NMR spectra were measured with a Bruker MSL 300 spectrometer at 75.47 and 111.89 MHz respectively. The spectra were recorded in  $\text{CDCl}_3$  solution at ambient temperature. The  $^{13}\text{C}$  chemical shifts are related to  $\text{CDCl}_3$  signal ( $^{13}\text{C}$   $\text{CDCl}_3 = 76.9$  ppm) and  $\delta(^{119}\text{Sn})$  values are related to external neat tetramethylstannane.

Dimethyl/diphenyl-tin dichloride and triphenyltin hydroxide used were of Alfa Inorganics, U.S.A. The ester-tin compounds  $\text{Cl}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3)_2$  and  $\text{Cl}_3\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3)$  were prepared according to method reported in literature<sup>12</sup>.

### Preparation of 2-N-salicylideneimino-2-methyl-1-propanol and its complexes:

#### Preparation of 2-N-salicylideneimino-2-methyl-1-propanol

[SAPAH<sub>2</sub>] [31]

Salicylaldehyde (4.05 g; 33 mmol) and 2-amino-2-methyl-1-propanol,  $\text{NH}_2\text{-C}(\text{CH}_3)_2\text{-CH}_2\text{-OH}$ , (2.94 g; 33 mmol) were mixed in ethanol (50 ml)

and the solution heated to reflux on a water bath for ~ 4 h. The resulting yellow solution was concentrated to a small volume to yield a syrupy liquid which was poured on crushed ice (made out of distilled water) and stirred vigorously for 30 minutes. The pale yellow solid separated was filtered and washed with small portions of ice-cold water and air-dried. Yield 4.14 g (65%); m.p. 68°. The Schiff base was freely soluble in benzene, CCl<sub>4</sub>, CHCl<sub>3</sub> and insoluble in hexane. It was also soluble in water to some extent at room temperature but less soluble in ice-cold water.

Preparation of the complexes was carried out in a round bottom flask of 100 ml capacity fitted with reflux condenser or partial take of condenser. Stirring of the solution was done using a magnetic stirrer. A good vacuum pump fitted with a dry trap was used to remove solvent.

#### Preparation of (SAPA)Sn(CH<sub>3</sub>)<sub>2</sub> [32]

The Schiff base [LH<sub>2</sub>] (0.19 g; 1 mmol) was dissolved in benzene (50 ml) and to this was added Me<sub>2</sub>SnO (0.17 g; 1 mmol). The reaction mixture was heated to reflux and the water formed was removed azeotropically. The benzene solution after filtration and concentration gave a yellow microcrystalline solid which was washed with hexane and dried in vacuo. The product was recrystallized from CH<sub>2</sub>Cl<sub>2</sub> - hexane mixture. Yield 0.24 g (71%); m.p. 175°.

**Preparation of (SAPA)Sn(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> [33]**

A solution of 2-N-salicylideneimino-2-methyl-1-propanol in chloroform (20 ml) was added slowly with vigorous stirring to a solution of Ph<sub>2</sub>SnCl<sub>2</sub> (0.34 g; 1 mmol) in CHCl<sub>3</sub> (20 ml) taken in 100 ml round bottom flask fitted to partial take off condenser. After the addition was complete, the reaction mixture was refluxed for ten minutes and cooled. Ammonia solution was added dropwise to neutralize the liberated acid and the ammonium chloride formed was removed by filtration. The filtrate was further refluxed for about 2 h., and removal of solvent in vacuo gave a yellow solid. The solid was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 ml) and solution cooled at -24°C. Precipitation of the product from CH<sub>2</sub>Cl<sub>2</sub> solution was effected by layering n-hexane over the cooled solution. The yellow crystalline solid separated was filtered, washed with n-hexane and dried in vacuo. Yield 0.29 g (62%); m.p. 170°.

**Preparation of (SAPAH)Sn(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> [34]**

A mixture of Ph<sub>3</sub>SnCl (0.22 g; 1 mmol) and the Schiff base 2-N-salicylideneimino-2-methyl-1-propanol in chloroform (50 ml) was refluxed on a water bath for 10 min. A few drops of ammonia solution were added to neutralize the liberated acid and the ammonium chloride formed was removed by filtration. The filtrate was further refluxed for about two hours, evaporated to dryness under reduced pressure and the resulting solid was dissolved in methylene chloride (5 ml), n-hexane was then added. Any solid

which separated was filtered off and the filtrate was concentrated in vacuo to yield the complex. Yield 0.34 g (63%); m.p. 46°.

#### Preparation of (SAPA)SnCl(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>) [35]

A solution of the Schiff base (SAPAH<sub>2</sub>) (0.19 g; 1 mmol) and the estertin compound, Cl<sub>3</sub>Sn(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>), (0.31 g; 1 mmol) were reacted in CHCl<sub>3</sub> (20 ml). The reaction mixture was refluxed for ten minutes and cooled. Dilute ammonia solution was added dropwise to neutralize the liberated acid and the ammonium chloride formed was removed by filtration. The filtrate was further refluxed for about 2 h, and the removal of solvent, gave a yellow solid. The solid was dissolved in 10 ml CH<sub>2</sub>Cl<sub>2</sub>, cooled in ice-salt mixture bath and precipitation of the product was effected by layering n-hexane over the well cooled solution. The yellow crystalline solid separated was filtered, washed with n-hexane and dried in vacuo. Yield 0.30 g (69%); m.p. 105°.

#### Preparation of (SAPA)Sn(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>)<sub>2</sub> [36]

A solution of Schiff base [SAPAH<sub>2</sub>] (0.19 g; 1 mmol) in chloroform (20 ml) was added dropwise to a stirred solution of Cl<sub>2</sub>Sn(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>)<sub>2</sub> (0.36 g; 1 mmol) in CHCl<sub>3</sub> (20 ml). After the addition was completed, the reaction mixture was refluxed for ten minutes and then cooled. Dilute ammonia solution was added dropwise to neutralize the liberated acid and the solid ammonium chloride formed was removed by filtration. The filtrate was

further refluxed for about 2 h, and the removal of solvent in vacuo gave a yellow solid. The complex was recrystallized from  $\text{CH}_2\text{Cl}_2$ -pet.ether mixture using the precipitation technique as described above. The yellow crystalline solid separated was filtered, washed with n-hexane and dried in vacuo. Yield 0.36 g (69%); m.p.  $123^\circ$ .

### $\text{SO}_2$ INSERTION REACTION:

#### Preparation of $(\text{CH}_3\text{SO}_2)\text{SnCH}_3(\text{SAPA})$

The complex  $(\text{SAPA})\text{Sn}(\text{CH}_3)_2$  (0.5 g) was finely ground and kept in a well cooled Schlenk tube fitted with a gas inlet tube reaching the bottom. Dry sulphur dioxide gas was condensed into the flask till the volume reached 3 ml. The tube was shaken occasionally and kept for 2 h. in the refrigerant, after which it was taken out and the liquid sulphur dioxide was allowed to evaporate. The yellow crystalline solid substance obtained was kept in vacuum at room temperature for 1 h., m.p.  $175^\circ$ . Yield 90% (0.54 g). The complexes were insoluble in organic solvents.

Similarly other complexes  $(\text{C}_6\text{H}_5\text{SO}_2)\text{SnC}_6\text{H}_5(\text{L})$  and  $\text{C}_6\text{H}_5\text{SO}_2\text{Sn}(\text{C}_6\text{H}_5)_3$  were prepared.

**Preparation of 2-N-chorosalicylideneimino-2-methyl-1-propanol and its complexes**

**Preparation of 2-N-chorosalicylideneimino-2-methyl-1-propanol [ClSAPAH<sub>2</sub>] [37]**

An ethanolic solution of 2-amino-2-methyl-1-propanol (1.70 g; 2 mol) was gradually added to an ethanolic solution of chorosalicylaldehyde (3.14 g; 2 mol) with vigorous shaking. The resulting solution was then refluxed over a water bath for 3-4 h. and concentrated to small volume and allowed to stand overnight. On adding pet.ether a yellow solid mass formed which was collected, washed and recrystallised from benzene. Yield 2.94 g (83%); m.p. 110°.

**Preparation of (ClSAPA)Sn(CH<sub>3</sub>)<sub>2</sub> [38]**

The mixture of Me<sub>2</sub>SnO (0.17 g; 1 mmol) and the Schiff base, 2-N-chorosalicylideneimino-2-methyl-1-propanol (0.23 g; 1 mmol) in benzene (50 ml) was refluxed for 8 h. The liberated water was collected by using partial take off condenser. After the completion of the reaction, the excess benzene was removed under reduced pressure to yield yellow solid which was recrystallised from n-hexane/benzene (1:1). Yield 0.24 g (63%); m.p. 230°.

**Preparation of (ClSAPA)Sn(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> [39]**

To the chloroform solution of Ph<sub>2</sub>SnCl<sub>2</sub> (0.34 g; 1 mmol) a chloroform solution (10 ml) of Schiff base ClSAPAH<sub>2</sub> (0.23 g; 1 mmol) was added. The clear solution obtained was refluxed for 10

min. and cooled. The pH of the reaction mixture was raised to 7 by adding aq. ammonia (1:1) drop by drop with constant stirring. About 4-5 drops of ammonia solution was required to attain the desired pH measured with the help of a pH paper. The ammonium chloride formed was filtered off. Filtrate was further refluxed for 2 h. and then concentrated to ~ 5 ml, when yellow crystals separated which were filtered and washed with pet. ether and dried in vacuum. Yield 0.29 g (58%); m.p. 162°.

#### Preparation of (ClSAPAH)Sn(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> [40]

The complex was prepared in a similar manner as in [32] using Ph<sub>3</sub>SnOH (0.37g; 1 mmol) and 2-N-chlorosalicylideneimino-2-methyl-2-amino-1-propanol (0.23 g; 1 mmol). Yield 0.32 g (56%).

#### Preparation of (ClSAPA)SnCl(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>) [41]

To a solution of ClSAPAH<sub>2</sub> (0.23 g; 1 mmol) in CHCl<sub>3</sub> (10 ml), a equimolar amount of the ester, Cl<sub>3</sub>Sn(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>)(0.31 g; 1 mmol) in 20 ml chloroform was added with stirring. The mixture was refluxed for 15 min. and the pH was adjusted by addition of ammonia solution. The precipitated ammonium chloride was filtered off and the filtrate was refluxed for 3 h; concentration of the solution under vacuum yielded 0.25 g (62%) of the yellow compound; m.p. 139°.

#### Preparation of (ClSAPA)Sn(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>)<sub>2</sub> [42]

The complex was prepared by refluxing a CHCl<sub>3</sub> solution of the Schiff base 2-N-chlorosalicylideneimino-2-methyl-1-propanol (0.23g; 1 mmol) and the ester, Cl<sub>2</sub>Sn(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>)<sub>2</sub> (0.36 g; 1

mmol) in 1:1 molar ratio and processed as described above.

Yield 0.32 g (62%); m.p. 118<sup>o</sup>.

**Preparation of 2-N-bromosalicylideneimino-2-methyl-1-propanol and its complexes.**

**Preparation of 2-N-5-bromosalicylideneimino-2-methyl-1-propanol [BrSAPAH<sub>2</sub>] [43]**

2-Amino-2-methyl-1-propanol (1.78 g; 2 mol) and 5-bromosalicylaldehyde (4.02 g; 2 mol) were mixed in ethanol (50 ml) and the solution was refluxed on a water bath for ~ 4 h. The resulting yellow solution was concentrated to a small volume to yield a syrupy liquid which was cooled in ice-salt mixture and on vigorous stirring gave yellow solid. The product was filtered, washed with pet. ether and air dried. Yield 3.81 g (70%); m.p. 110<sup>o</sup>. The Schiff base was soluble in benzene, CCl<sub>4</sub>, CHCl<sub>3</sub> and insoluble in hexane.

**Preparation of (BrSAPA)Sn(CH<sub>3</sub>)<sub>2</sub> [44]**

The benzene solution of Schiff base [BrSAPAH<sub>2</sub>] (0.27 g; 1 mmol) was added Me<sub>2</sub>SnO (0.17 g; 1 mmol). The reaction mixture was heated to reflux and the water formed during the reaction was removed azeotropically. The benzene solution after filtration and upon concentration gave a yellow crystalline solid which was filtered, washed with n-hexane and dried in vacuo. Yield 0.26 g (61%); m.p. 215<sup>o</sup>.



#### Preparation of (BrSAPA)Sn(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> [45]

A solution of 2-N-5-bromosalicylideneimino-2-methyl-1-propanol in chloroform (20 ml) was added slowly with vigorous stirring to a solution of Ph<sub>2</sub>SnCl<sub>2</sub> (0.34 g; 1 mmol) in CHCl<sub>3</sub> (20 ml). After the addition was complete, the contents were refluxed for ten minutes and cooled. Ammonia solution was added dropwise to neutralize the liberated acid and the ammonium chloride formed was removed by filtration. The filtrate was further refluxed for about 2 h, and the solvent was removed in vacuo to get a yellow solid. The solid was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 ml) and solution cooled at -24°C. Precipitation of the product was effected by layering n-hexane over the cooled solution. The yellow crystalline solid separated was filtered, washed with n-hexane and dried in vacuo. Yield 0.35 g (65%); m.p. 170°.

#### Preparation of (BrSAPAH)Sn(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> [46]

Ph<sub>3</sub>SnOH (0.37 g; 1 mmol) was mixed with the Schiff base 2-N-5-bromosalicylideneimino-2-methyl-1-propanol in benzene (50 ml) (0.27 g; 1 mmol) and refluxed for 8 h. The water formed during the reaction was collected azeotropically using a partial take-off condenser fitted to the flask. After the reaction, the benzene solution was concentrated to a small volume. The yellow crystals separated from the solution were washed with pet. ether and dried in vacuo. Yield 0.37 g (59%); m.p. 152°.

**Preparation of (BrSAPA)SnCl(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>) [47]**

A solution of Schiff base (BrSAPAH<sub>2</sub>) (0.27 g; 1 mmol) and Cl<sub>3</sub>Sn(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>) (0.31 g; 1 mmol) were mixed in CHCl<sub>3</sub> (20 ml) in a round bottom flask. The reaction mixture was refluxed for ten minutes and then cooled. To neutralize the hydrochloric acid formed during the reaction, dilute ammonia solution was added dropwise and the ammonium chloride precipitated was removed by filtration. The filtrate was further refluxed for about 2 h, and the removal of solvent gave a yellow solid. The solid was dissolved in 10 ml CH<sub>2</sub>Cl<sub>2</sub> and the solution cooled in ice-salt mixture bath and the compound was isolated as above. The yellow crystalline solid separated was filtered, washed with n-hexane and dried *in vacuo*. Yield 0.32 g (63%); m.p. 61°.

**Preparation of (BrSAPA)Sn(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>)<sub>2</sub> [48]**

A solution of Schiff base [BrSAPAH<sub>2</sub>] (0.27 g; 1 mmol) in chloroform (20 ml) was added dropwise to a stirred solution of Cl<sub>2</sub>Sn(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>)<sub>2</sub> (0.36 g; 1 mmol) in CHCl<sub>3</sub> (20 ml) taken in a flask and the reaction mixture was refluxed for ten minutes and then cooled. Dilute ammonia solution was added dropwise to neutralize the liberated acid and the ammonium chloride formed was removed by filtration. The filtrate was further refluxed for about 2 h, and the removal of solvent *in vacuo* gave a yellow solid. The complex was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>-pet. ether mixture using the precipitation technique as described above. The yellow crystalline solid separated was filtered, washed with n-

hexane and dried in vacuo. Yield 0.35 g (62%); m.p. 102°.

preparation of 2-N-(2-hydroxy-3-methoxybenzylidene)imino-2-methyl-1-propanol and its complexes

Preparation of 2-N-(2-hydroxy-3-methoxybenzylidene)imino-2-methyl-1propanol (OVPAH<sub>2</sub>) [49]

2-Amino-2-methyl-1-propanol (1.70 g; 2 mol) was mixed with absolute ethyl alcohol (15 ml) taken in a flask and to it added an alcoholic solution of 2-hydroxy-3-methoxy benzaldehyde (2.04 g; 2 mol). The reaction mixture was refluxed on a water bath for 2 h. to yield reddish brown solution. After complete removal of the solvent the brown slurry obtained was cooled and the product precipitated by adding dry pet. ether, filtered, washed with pet. ether and dried under vacuum. Yield 3.62 g (81%); m.p. 110°.

Preparation of (OVPA)Sn(CH<sub>3</sub>)<sub>2</sub> [50]

Freshly prepared and dried dimethyltin oxide (0.17 g; 1 mmol) was mixed with the Schiff base, OVPAH<sub>2</sub> (0.22 g; 1 mmol) in benzene (50 ml) and refluxed for 8 h. The water formed in the reaction was collected azeotropically using a partial take off condenser fitted to the flask. After the reaction, the benzene solution was concentrated to small volume. The dark yellow crystals separated were filtered and washed with pet. ether and dried in vacuum. Yield 0.24 g (66%); m.p. 220°.

Preparation of (OVPA)Sn(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> [51]

A solution of Ph<sub>2</sub>SnCl<sub>2</sub> in CHCl<sub>3</sub> (0.34 g; 1 mmol) was added

to a  $\text{CHCl}_3$  solution of the Schiff base,  $\text{OVPAH}_2$  (0.22 g; 1 mmol) with shaking. The mixture was heated on water bath for 10 min. and cooled. A few drops of ammonia soln. was added to neutralize the liberated acid, the precipitated  $\text{NH}_4\text{Cl}$  was filtered off and the filtrate was refluxed for 2 h. The solution was concentrated to about 5 ml and 10 ml of pet. ether was added. On standing for several hours bright yellow crystals separated, which were washed with pet. ether and vacuum dried. Yield 0.29 g (59%); m.p.  $141^\circ$ .

#### Preparation of $(\text{OVPAH})\text{Sn}(\text{C}_6\text{H}_5)_3$ [52]

The Schiff base 2-N-(2-hydroxy-3-methoxybenzylidene)imino-2-methyl-1-propanol (0.22 g; 1 mmol) and  $\text{Ph}_3\text{SnOH}$  (0.37 g; 1 mmol) were reacted in benzene (50 ml) as in 4.1 to yield the complex as a yellow solid product. Yield 0.33 g (58%); m.p.  $96^\circ$ .

#### Preparation of $(\text{OVPA})\text{SnCl}(\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3)$ [53]

A mixture of  $\text{Cl}_3\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3)$  (0.31 g; 1 mmol) and the Schiff base,  $\text{OVPAH}_2$  (0.22 g; 1 mmol) in  $\text{CHCl}_3$  (50 ml) was heated on water bath for 10 min. A few drops of ammonia solution were added and the resulting ammonium chloride was filtered off. The filtrate was refluxed for 2 h, concentrated, cooled and petroleum ether added. The yellow solid separated was recrystallised from benzene. Yield 0.28 g (61%); m.p.  $114^\circ$ .

#### Preparation of $(\text{OVPA})\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3)_2$ [54]

A solution of  $\text{OVPAH}_2$  (0.22 g; 1 mmol) in  $\text{CHCl}_3$  was added to a stirred solution of  $\text{Cl}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3)_2$  (0.36 g; 1 mmol) in

$\text{CHCl}_3$ . The resulting solution was heated on a water bath, a few drops of ammonia solution were added and the solid  $\text{NH}_4\text{Cl}$  filtered. The filtrate was refluxed for 1 h, concentrated, and cooled. The yellow crystalline product obtained was recrystallised from chloroform-pet. ether mixed solvent. Yield 0.32 g (63%); m.p.  $118^\circ$ .

**Preparation of 2-N-(2-hydroxy-1-naphthaldehyde)imine-2-methyl-1-propanol (NaphPAH<sub>2</sub>) [55]**

The ligand was prepared by refluxing equimolar amounts of 2-hydroxy-1-naphthaldehyde (3.48 g; 2 mol) and 2-amino-2-methyl-1-propanol (1.78 g; 2 mol) in ethanol (50 ml) for about 3 h. on water bath. The Schiff base was isolated as described in [49]. Yield 4.14 g (85%); m.p.  $121^\circ$ .

**Preparation of (NaphPA)Sn(CH<sub>3</sub>)<sub>2</sub> [56]**

The Schiff base 2-N-(2-hydroxy-1-naphthaldehyde)imine-2-methyl-1-propanol (0.24 g; 1 mmol) was taken in benzene (50 ml) and solid  $\text{Me}_2\text{SnO}$  (0.17 g; 1 mmol) was added to it and refluxed. The water formed in the reaction was collected azeotropically. The benzene solution upon concentration gave a crystalline orange-yellow solid. Yield 0.25 g (65%); m.p.  $235^\circ$ .

**Preparation of (NaphPA)Sn(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> [57]**

$\text{Ph}_2\text{SnCl}_2$  (0.34 g; 1 mmol) and the Schiff base, NaphPAH<sub>2</sub> (0.24 g; 1 mmol) were dissolved separately in minimum volume of chloroform and then mixed with shaking. The mixed solution was heated on water bath for ten minutes and ammonia solution was

added until the liberated acid was neutralized. The  $\text{NH}_4\text{Cl}$  formed was filtered off and the filtrate refluxed for 2 h, concentrated to a small volume say 2-3 ml and an equal volume of ethanol was added. On refrigerating the solution overnight, bright yellow crystals of the complex were separated which were purified from chloroform-ethanol mixture. Yield 0.32 g (63%); m.p.  $174^\circ$ .

#### Preparation of $(\text{NaphPAH})\text{Sn}(\text{C}_6\text{H}_5)_3$ [58]

$\text{Ph}_3\text{SnOH}$  (0.37 g; 1 mmol) and the Schiff base,  $\text{NaphPAH}_2$  (0.24 g; 1 mmol) were refluxed in benzene (50 ml). After azeotropic removal of water formed during the reaction, the clear solution was processed to obtain yellow crystalline solid. Yield 0.38 g (64%); m.p.  $103^\circ$ .

#### Preparation of $(\text{NaphPA})\text{SnCl}(\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3)$ [59]

A mixture of  $\text{Cl}_3\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3)$  (0.31 g; 1 mmol) and  $\text{NaphPAH}_2$  (0.24 g; 1 mmol) were dissolved in chloroform. The reaction mixture was refluxed for 10 minutes, ammonia added to neutralize the acid, the  $\text{NH}_4\text{Cl}$  formed was filtered off and the solution was further refluxed for an hour and then the compound was isolated as described in 57. Yield 0.29 g (60%); m.p.  $99^\circ$ .

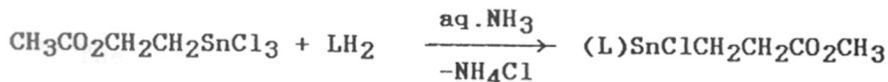
#### Preparation of $(\text{NaphPA})\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3)_2$ [60]

A chloroform solution (15 ml) of the  $\text{NaphPAH}_2$  (0.24 g; 1 mmol) was added to a solution of  $\text{Cl}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3)_2$  in  $\text{CHCl}_3$  (0.36 g; 1 mmol) with occasional shaking. The mixture was heated for 10 minutes and cooled. A few drops of ammonia solution were

added to neutralize the liberated acid. Then the solution was filtered and refluxed for 3 h and processed as in [59] to get yellow crystalline compound. Yield 0.29 g (55%); m.p. 85°.

## RESULTS AND DISCUSSION

The complexes described in this chapter have been synthesized by refluxing  $R_2SnCl_2$  [where  $R=CH_3$ ,  $C_6H_5$  or  $CH_2CH_2CO_2CH_3$ ],  $(C_6H_5)_3SnCl$  and  $(CH_3CO_2CH_2CH_2)SnCl_3$ , with stoichiometric amounts of dibasic Schiff base,  $(H_2L)$  in chloroform medium using aq. ammonia as HCl acceptor.



The complexes,  $(L)Sn(CH_3)_2$  and  $(LH)Sn(C_6H_5)_3$  have been prepared by an alternative procedure in which  $Me_2SnO/Ph_3SnOH$  reacts with stoichiometric quantity of Schiff base in refluxing benzene followed by azeotropic removal of eliminated water.

These complexes are yellow crystalline solids soluble in benzene, chloroform and methylene chloride and insoluble in hexane. The complexes isolated are presented in Tables (4.1, 4.6, 4.9,

4.12, 4.15) together with their analytical data.

**IR spectral studies of 2-N-salicylideneimino-2-methyl-1-propanol and its complexes (Table 4.2)**

The IR spectrum of the Schiff base in nujol, shows two medium intensity bands at 3255 and 3167  $\text{cm}^{-1}$  attributed to the  $\nu$  (OH) of alcoholic and hydrogen bonded phenolic hydroxyl groups respectively. In the region below 1700  $\text{cm}^{-1}$ , the strong bands at 1631 and 1611  $\text{cm}^{-1}$  are due to  $\nu$ (C=N) and  $\nu$ (C=C) respectively<sup>(13)</sup>. The strong band at 1582  $\text{cm}^{-1}$  is assigned to coupled vibration of  $\nu$ (C=N + C=C) group<sup>(14)</sup>. The characteristic band at 1280  $\text{cm}^{-1}$  is due to coupled vibration of phenolic ( $\nu$ CO +  $\delta$ OH)<sup>(15)</sup>. The region below 1200  $\text{cm}^{-1}$  shows a large number of bands mostly due to CH deformations and ring breathing. The bands at 795 and 764  $\text{cm}^{-1}$  are due to o-substituted benzene rings.

The IR spectra of the complexes 32, 33, 35 and 36 do not show any band attributable to  $\nu$ (OH), indicating deprotonation of alcoholic and phenolic protons by tin. The band due to  $\nu$ (C=N) at 1631  $\text{cm}^{-1}$ , in the Schiff base has been shifted to lower frequency region and seen at  $\sim$  1620  $\text{cm}^{-1}$  and in above complexes indicating azomethine nitrogen lone pair coordination to tin. The phenolic  $\nu$ (C-O) has been shifted to  $\sim$  1320  $\text{cm}^{-1}$ , suggesting increased C-O bond order as a result of complex formation<sup>(15)</sup>.

The far IR spectra of the complex 32, shows medium intensity bands at 523  $\text{cm}^{-1}$  which is attributable to  $\nu$ (Sn-C)<sup>(16)</sup>. The band



at  $452\text{ cm}^{-1}$  is assigned for  $\nu(\text{Sn-O})$ .

The starting estertin chlorides,  $\text{Cl}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3)_2$  and  $\text{Cl}_3\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3)$ , show the characteristic bands due to ester  $\nu(\text{C=O})$ , which were observed at  $1672$  and  $1654\text{ cm}^{-1}$  in di and tri chloro estertin suggesting the ester CO bonded to tin. The appearance of a single band due to  $\nu(\text{CO})$  indicate both the groups are equivalent and trans to each other whereas in the case of complex 36 two bands are observed due to  $\nu(\text{C=O})$  at  $1732$  and  $1682\text{ cm}^{-1}$  which suggest the presence of free and coordinated ester groupings (Table 4.2).

The IR spectrum of complex 34 shows medium band at  $3356\text{ cm}^{-1}$  due to  $\nu(\text{OH})$ , suggesting free nature of alcoholic (OH). In this complex the Schiff base functions as monobasic bidentate ligand, coordinating through phenoxy oxygen and azomethine nitrogen to tin. All other features are nearly similar to that of above complexes.

**$^1\text{H}$  NMR spectral studies of 2-salicylideneimino-2-methyl-1-propanol and its complexes (Table 4.3)**

$^1\text{H}$  NMR spectrum of the Schiff base in  $\text{CDCl}_3$  shows signals at 1.28, 3.58 and 8.31 ppm due to  $\text{CH}_3$ -,  $\text{CH}_2\text{-O}$ -and azomethine protons respectively. A broad signal extending from 12.26 to 15.01 ppm centered at 13.60 ppm is due to hydrogen bonded phenolic and alcoholic OH protons. No separate signal was observed for alcoholic OH proton in the expected region ca. 4-7 ppm when recorded in  $\text{CDCl}_3$  as solvent. The integrated peak height for the

broad hydrogen bonded OH signal and azomethine proton is in the ratio of 12:7, which again indicates that broad signal is due to two hydroxyl protons. Further D<sub>2</sub>O exchange studies show complete disappearance of this broad signal which confirms the above assignment.

In order to study the nature of hydrogen bonding of alcoholic OH proton, the ligand spectrum was recorded in DMSO-d<sub>6</sub>. The spectrum showed a signal at 4.95 ppm attributable to alcoholic OH and another broad signal at 14.40 ppm due to hydrogen bonded phenolic OH and both disappeared on D<sub>2</sub>O exchange. These studies show that in a non-coordinating solvent such as CDCl<sub>3</sub> the alcoholic and phenolic OH protons are intramolecularly hydrogen bonded and appear in the downfield region, whereas in a hydrogen bond weakening solvent such as DMSO- the alcoholic OH proton appear separately, indicating that the alcoholic OH proton being weakly hydrogen bonded, intermolecularly, with azomethine group which breaks up in a coordinating solvent such as DMSO.

The <sup>1</sup>H NMR spectrum of the complexes 32, 33, 35 and 36 do not show any signal due to hydroxyl protons suggesting proton replacement by tin. No significant shift has been observed for azomethine (CH) proton after nitrogen coordination to tin. The methylene protons in the complexes 32, 33, 35 and 36 are deshielded as a result of deprotonation and bonding of alkoxy group to tin. In the spectrum of the complex 34, the resonance

signal found at 7.2 ppm is due to free alcoholic proton which is confirmed by D<sub>2</sub>O exchange studies. The methylene protons show a marginal shift of 0.09 ppm in the higher magnetic field which again supports free nature of alcoholic OH. In this complex the ligand acts as monobasic bidentate moiety by the coordination of phenoxide ion and azomethine nitrogen. The C(CH<sub>3</sub>)<sub>2</sub> protons in all complexes show marginal downfield shift as expected and the aromatic protons resonate in the expected region of 6.44 - 8.02 ppm (Table 4.3).

In the complex 32, the resonance due to (Sn-CH<sub>3</sub>) proton is observed as a sharp singlet at 0.63 ppm having two satellite signals on either side of this signal as doublets due to coupling of methyl protons with <sup>117</sup>Sn and <sup>119</sup>Sn nuclei. The coupling constants observed were  $^2J(^{117}\text{Sn}, ^1\text{H}) = 72 \text{ Hz}$  and  $^2J(^{119}\text{Sn}, ^1\text{H}) = 76 \text{ Hz}$ . This increase in coupling constants compared to those in Me<sub>2</sub>SnCl<sub>2</sub> [ $^2J(^{117}\text{Sn}, ^1\text{H}) = 66 \text{ Hz}$ ;  $^2J(^{119}\text{Sn}, ^1\text{H}) = 70 \text{ Hz}$ ] is suggested to be due to increase in the coordination number of tin as a result of complex formation<sup>17</sup>. Further, satellite signals are also observed for azomethine and methylene protons with coupling constants of  $^3J(^{119}\text{Sn}, ^1\text{H}) = 46 \text{ Hz}$  and  $^3J(^{119}\text{Sn}, ^1\text{H}) = 34 \text{ Hz}$  respectively which again confirms the mode of bonding to tin.

The spectrum of complex 36 shows two triplets centered at 1.89 and 2.21 ppm and a singlet at 3.68 ppm due to α-CH<sub>2</sub>, β-CH<sub>2</sub> and OCH<sub>3</sub> protons of the ester residue respectively. The shift to

higher magnetic field compared to those of the complex  $\text{Cl}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3)$  is attributed to replacement of electronegative chlorine atoms by the donor atoms  $\text{O}-\overset{\text{N}}{\text{O}}$  of chelating Schiff base <sup>(18)</sup>. Similar upfield shift is observed in complex 35 for  $\alpha\text{-CH}_2$ ,  $\beta\text{-CH}_2$  and  $\text{OCH}_3$  as compared to  $\text{Cl}_3\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3)$ .

**<sup>13</sup>C NMR spectral studies of 2-N-salicylideneimino-2-methyl-1-propanol and its complexes**

The <sup>13</sup>C NMR spectral data of tin(IV) complexes and the ligand are presented in Table 4.4. The spectrum of the Schiff base in  $\text{CDCl}_3$  shows signals at 23.74, 60.86, 70.90 and 162.25 ppm  $\text{CH}_3$  due to  $(\text{CH}_3)_2$ , C (quaternary C),  $\text{CH}_2\text{-O}$  and azomethine (CH) carbons respectively. The resonance due to phenolic carbon is seen at 163.07 ppm, whereas other aromatic carbons resonate between 118-132 ppm. In the complexes 32 and 33, a large deshielding (6-7 ppm) has been observed for both the phenolic and azomethine carbons. The alkoxy,  $\text{CH}_2\text{-O-}$ , carbon also shows a similar downfield shift by 3-4 ppm. These data indicate the participation of these groups in bond formation. In complex 34 the phenolic and azomethine carbons show the expected downfield shift; whereas the alkoxy methylene carbon does not show any change in its resonance which supports the bonding of phenolic and azomethine groups to the metal and non bonding nature of the alkoxy group. The complex 35 shows a marginal downfield shift of

0.75 ppm for azomethine carbon, whereas the phenolic CO and alkoxy CH<sub>2</sub>-O have been shifted downfield by 3.8 and 0.6 ppm respectively. Large downfield shifts have been observed for these carbons in the complex 36 as in the case of diorganotin(IV) complexes 32 and 33. The spectra of the Cl<sub>3</sub>SnCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub> and Cl<sub>2</sub>Sn[CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>] show sharp signals due to α-CH<sub>2</sub>, β-CH<sub>2</sub> and -C=O (ester) at  $\sim 2.0$ ,  $\sim 2.9$  and  $\sim 3.8$  ppm respectively. An upfield shift has been observed for β-CH<sub>2</sub> and alkoxy carbon atom in complex 35 and 36 which indicates weakening of intramolecular ester coordination to tin. The ester carbonyl carbon in the complexes 35 and 36 resonates at higher magnetic field as compared to the starting ester tin chlorides<sup>(19)</sup> as a singlet at 167.87 and 170.9 ppm respectively. Further the appearance of a single signal may suggest fast exchange of metal-bonded and non bonded carbonyl groups leading to magnetic equivalence of ester grouping<sup>(20)</sup>. Further, for the determination of the structure of the complexes, their tin-carbon coupling constants  $^1J(\text{Sn}, ^{13}\text{C})$  and  $^{119}\text{Sn}$  NMR have been studied.

The tin-carbon coupling constants  $^1J(^{119}\text{Sn}, ^{13}\text{C})$  for the dimethyltin complex 32, is 638.15 Hz. The C-Sn-C bond angle  $\theta$ , calculated from the above coupling constants using the expression<sup>(21)</sup>  $|^1J(^{119}\text{Sn}, ^{13}\text{C})| = 11.4 \theta - 875$  is  $132^\circ$ . This value is consistent with an octahedral geometry with *trans* disposition of methyl groups in the complex 32 as shown in fig. 4.1. The above data suggest the structure of diorganotin(IV) Schiff base

complexes to be dimeric (except estertin Schiff base complexes) (fig. 4.1)

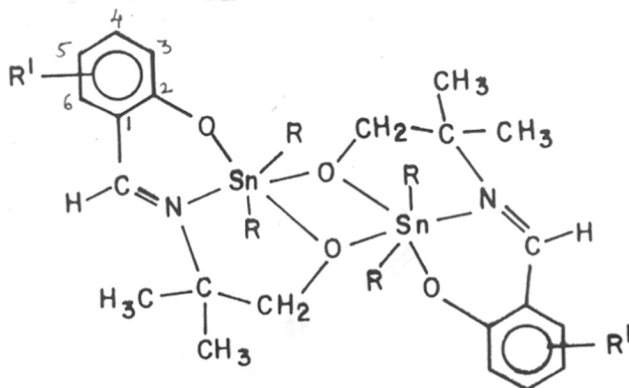


FIG. 4.1

$^{119}\text{Sn}$  NMR spectral studies of 2-N-salicylideneimino-2-methyl-1-propanol Schiff base complexes (Table 4.4)

The ( $^{119}\text{Sn}$ ) chemical shift value observed for the complex 32 is at 150.1 ppm which is consistent with the value reported for the well characterized pentacoordinated complex  $\text{Me}_2\text{Sn}(\text{SAB})^{20}$ . The structure of these complexes might be pentacoordinated in solution. In the diphenyltin(IV) complex, 33,  $\delta(^{119}\text{Sn})$  value is at -322.72 ppm. Similar upfield shift of  $\delta(^{119}\text{Sn})$  by 150-170 ppm is reported when methyl groups in  $\text{Me}_2\text{Sn}(\text{chelate})$  are replaced by phenyl groups<sup>(22)</sup>. The tin atoms in the ester tin complexes 35 and 36 resonate at -200.00 ppm and -224.30 ppm respectively compared to  $\delta(^{119}\text{Sn})$  in the dimethyltin complex 32. The

increased shielding is attributed to the coordination of ester carbonyl to tin thereby increasing the electron density at tin.

The complexes 35 and 36 are assigned to have a distorted octahedral geometry as shown in fig. 4.2.

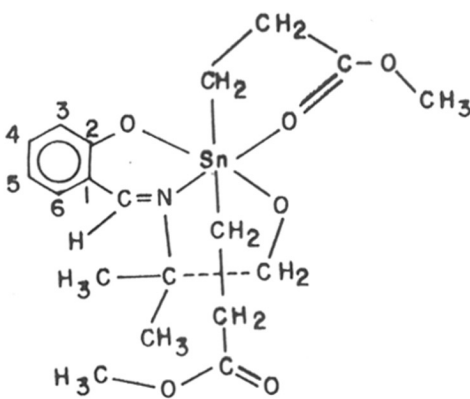


FIG. 4.2

#### REACTIVITY OF ORGANOTIN COMPLEXES TOWARDS $\text{SO}_2$

The complexes 32, 33 and 34 insert one molecule of sulphur dioxide into Sn-C bond giving complexes of the type  $(\text{SAPA})\text{CH}_3\text{Sn}(\text{SO}_2\text{CH}_3)$ ,  $(\text{SAPA})\text{C}_6\text{H}_5\text{Sn}(\text{SO}_2\text{C}_6\text{H}_5)$  and  $(\text{SAPAH})(\text{C}_6\text{H}_5)_2\text{Sn}(\text{SO}_2\text{C}_6\text{H}_5)$  respectively (Table 4.5). These complexes are stable at room temperature. On treatment with dil. HCl,  $\text{SO}_2$  is evolved and this has been utilized for the estimation

of  $\text{SO}_2$  in these complexes.

The IR spectra of the insertion products show characteristic bands at  $\sim 1040 \text{ cm}^{-1}$  and  $\sim 885 \text{ cm}^{-1}$  due to  $\nu_{\text{as}}(\text{S-O})$  and  $\nu_{\text{s}}(\text{S-O})$  respectively which is consistent with O-sulphinate structure for the complex <sup>(23)</sup>.



Table 4.1. Analytical data for 2-N-Salicylideneimino-2-methyl  
propanol tin(IV) Schiff base complexes.

No. Compound	m.p. (°C)	Elemental analysis [found(cal)](%)			
		Sn	C	H	N
31 SAPAH <sub>2</sub>	68	-	68.45	7.97	7.03
C <sub>11</sub> H <sub>15</sub> NO <sub>2</sub>		-	(68.37)	(7.82)	(7.25)
32 (SAPA)Sn(CH <sub>3</sub> ) <sub>2</sub>	175	34.82	45.66	5.67	4.01
C <sub>13</sub> H <sub>19</sub> NO <sub>2</sub> Sn		(34.91)	(45.92)	(5.64)	(4.12)
33 (SAPA)Sn(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	170	25.38	59.61	4.75	2.91
C <sub>23</sub> H <sub>23</sub> NO <sub>2</sub> Sn		(25.57)	(59.52)	(5.00)	(3.02)
34 (SAPAH)Sn(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	46	21.91	64.01	5.25	2.36
C <sub>29</sub> H <sub>29</sub> NO <sub>2</sub> Sn		(21.89)	(64.23)	(5.39)	(2.58)
35 (SAPA)SnCl(CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> CH <sub>3</sub> )	105	27.33	41.70	4.51	3.15
C <sub>15</sub> H <sub>20</sub> ClNO <sub>4</sub> Sn		(27.45)	(41.66)	(4.66)	(3.24)
36 (SAPA)Sn(CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	123	24.33	46.95	5.46	2.77
C <sub>19</sub> H <sub>27</sub> NO <sub>6</sub> Sn		(24.52)	(47.14)	(5.62)	(2.89)

Table 4.2. IR data for 2-N-Salicylideneimino 2-methyl propanol tin(IV) Schiff base complexes. ( $\nu$ ,  $\text{cm}^{-1}$ )

No.	(OH)	(C=N)+(C=C)	(C-O)(L)	(C=O)(est)	(C-O)(est)
31	3255,3167	1631,1582	1280	-	-
I	- -	- -	-	1654	1231
II	- -	- -	-	1672	1225
32	- -	1617,1536	1323	-	-
33	- -	1619,1543	1317	-	-
34	3356 -	1617,1540	1318	-	-
35	- -	1622,1544	1303	1666	1260,1210
36	- -	1625,1533	1334	1732,1682	1265,1216

I.  $\text{Cl}_3\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3)$

II.  $\text{Cl}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3)_2$

Table 4.3.  $^1\text{H}$  NMR data for 2-N-salicylideneimino-2-methyl-1-propanoltin(IV) Schiff base complexes. ( $\delta$ , ppm)

No.	CH <sub>3</sub>	CH <sub>2</sub> -O	CH	OH	$\alpha$ -CH <sub>2</sub>	$\beta$ -CH <sub>2</sub>	OCH <sub>3</sub> (est)	Sn(CH <sub>3</sub> ) <sub>2</sub>	Aromatic protons				
									H <sub>3</sub>	H <sub>4</sub>	H <sub>5</sub>	H <sub>6</sub>	
31	1.28	3.55	8.31	13.66	-	-	-	-	6.75	7.23	6.88	7.30	
I	-25.85	-	-	-	2.2	2.93	3.97	-	-	-	-	-	
II	-23.45	-	-	-	1.89	2.90	3.76	-	-	-	-	-	
32	1.36	3.76	8.27	-	-	-	-	0.63	6.60	7.15	6.69	7.33	
33	1.33	3.90	8.30	-	-	-	-	-	-----	6.55	--	8.02	-----
34	1.35	3.46	8.29	7.20	-	-	-	-	-----	6.48	--	7.74	-----
35	1.32	3.75	8.33	-	1.60	2.84	3.75	-	6.65	7.22	6.75	7.35	
36	1.30	3.74	8.28	-	1.50	2.66	3.68	-	6.50	7.12	6.61	7.20	

Complex 36. Ester

Complex 32.  $^2J(^{117}\text{Sn}-^1\text{H}) = 72 \text{ Hz}$ ;  $^2J(^{119}\text{Sn}-^1\text{H}) = 76 \text{ Hz}$

Chemical shift:  $^3J(^{117}\text{Sn}-^1\text{H})(\text{CH}_2) = 34 \text{ Hz}$ ;  $^3J(^{119}\text{Sn}-^1\text{H})(\text{CH}) = 46 \text{ Hz}$

Table 4.4.  $^{13}\text{C}$  and  $^{119}\text{Sn}$  NMR data for 2-N-salicylideneimino-2-methyl-1-propanol tin(IV) complexes. (ppm)

No.	$(\text{CH}_3)_2$	$>\text{C}<$	$\text{CH}_2\text{-O}$	$\text{CH}$	$\alpha\text{-CH}_2$	$\beta\text{-CH}_2$	$\text{C=O(est)}$	$^{119}\text{Sn}(\delta, \text{ppm})$
31	23.74	60.86	70.90	162.25	-	-	-	-
I	-	-	-	-	25.02	29.23	177.00	
II	-	-	-	-	24.15	28.39	181.13	
32	25.66	62.21	73.85	168.86	-	-	-	-150.10
33	25.85	62.69	73.75	169.45	-	-	-	-322.72
34	23.43	60.95	69.98	162.82	-	-	-	-323.44
35	23.90	61.33	71.50	163.00	18.33	29.16	168.35	-200.00
36	25.86	63.12	74.02	163.83	17.50	28.87	176.88	-224.30

Complex 32.  $\text{Sn}(\text{CH}_3)_2 = 0.11$  ppm;  $^1\text{J}(^{119}\text{Sn}, ^{13}\text{C}) = 638.15$  Hz

Complex 35. Ester  $\text{OCH}_3 = 53.98$  ppm;  $^1\text{J}(^{119}\text{Sn}, ^{13}\text{C})(\alpha\text{-CH}_2) = 769.04$  Hz ;  
 $^2\text{J}(^{119}\text{Sn}, ^{13}\text{C})(\beta\text{-CH}_2) = 49.90$  Hz

Complex 36. Ester  $\text{OCH}_3 = 52.10$  ppm;  $^1\text{J}(^{119}\text{Sn}, ^{13}\text{C})(\alpha\text{-CH}_2) = 768.36$  Hz ;  
 $^2\text{J}(^{119}\text{Sn}, ^{13}\text{C})(\beta\text{-CH}_2) = 53.25$  Hz

Chemical shift of aromatic carbons. (ppm)

No.	$\text{C}_1$	$\text{C}_2$	$\text{C}_3$	$\text{C}_4$	$\text{C}_5$	$\text{C}_6$
31	118.73	163.07	117.81	131.87	118.11	132.70
32	117.59	169.34	116.67	135.07	122.72	136.28
33	117.72	170.11	116.63	129.56	122.99	135.36
34	119.12	171.07	116.59	132.35	122.37	132.54
35	118.04	167.87	117.26	135.19	122.85	135.82
36	118.31	170.90	116.10	132.89	123.30	136.70

Complex 33.  $\text{Sn}(\text{C}_6\text{H}_5)_2 = 127.92\text{-}130.06$  ppm and  $136.79\text{-}137.49$  ppm

Complex 34.  $\text{Sn}(\text{C}_6\text{H}_5)_3 = 128.13\text{-}129.01$  ppm,  $129.63\text{-}130.04$  ppm  
and  $136.80\text{-}137.25$  ppm.

Table 4.5 Sulphur dioxide insertion compounds of organotin (IV) chelates

Compound	Color	m.p. (°C)	IR frequencies (cm <sup>-1</sup> )	
			$\nu_{as}(S-O)$	$\nu_s(S-O)$
(SAPA)CH <sub>3</sub> Sn(SO <sub>2</sub> CH <sub>3</sub> )	Yellow	175	1047	897
(SAPA)C <sub>6</sub> H <sub>5</sub> Sn(SO <sub>2</sub> C <sub>6</sub> H <sub>5</sub> )	Yellow	130	1070	873
(SAPAH)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> Sn(SO <sub>2</sub> C <sub>6</sub> H <sub>5</sub> )	Yellow	70	1034	890

IR spectral studies of 2-N-chlorosalicylideneimino-2-methyl-1-propanol [ClSAPAH<sub>2</sub>] and its organotin(IV) complexes (Table 4.7)

A high frequency shift has been observed for phenolic and alcoholic hydroxyl stretching vibrations in the Schiff base [ClSAPAH<sub>2</sub>] which may be attributed to the presence of electronegative chlorine atom in the aromatic ring. The  $\nu(\text{C}=\text{N})$  and  $\nu(\text{C}=\text{C})+(\text{C}=\text{N})$  frequencies are observed at 1633 and 1573  $\text{cm}^{-1}$  respectively. The phenolic  $[\nu(\text{C}-\text{O}) + \delta(\text{OH})]$  is discernible at 1280  $\text{cm}^{-1}$ .

The IR spectra of the complexes except the complex 40 show complete absence of phenolic and alcoholic hydroxyl stretching bands indicating proton replacement followed by complex formation. The complex 40 shows alcoholic  $\nu(\text{OH})$  at 3216  $\text{cm}^{-1}$ , which suggests bidentate nature of Schiff base in this complex. In all the complexes  $\nu(\text{C}=\text{N})$  is observed at lower frequency region as compared to the Schiff base suggesting the coordination of the nitrogen lone pair to tin. The phenolic  $\nu(\text{C}-\text{O})$  of the Schiff base observed at 1280  $\text{cm}^{-1}$ , has been shifted to higher wave numbers at  $\sim 1315 \text{ cm}^{-1}$  in complexes due to increased  $\nu(\text{C}-\text{O})$  bond order as a result of C-O bonding to tin. Only one medium intensity band is seen at 523  $\text{cm}^{-1}$  due to  $\nu(\text{Sn}-\text{C})$  in the complex 38. An additional band at 453  $\text{cm}^{-1}$  is assigned to  $\nu(\text{Sn}-\text{O})$ .

The spectra of complex 41 shows a strong band at 1652  $\text{cm}^{-1}$ , as in the starting  $\text{Cl}_3\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3)$  which suggests the presence of coordinated ester grouping whereas in the complex 42,

two strong bands are observed due to  $\nu(\text{C}=\text{O})$  at 1730 and 1685  $\text{cm}^{-1}$ , which indicates the presence of the free and coordinated ester groupings respectively.

**$^1\text{H}$  NMR spectral studies of 2-chlorosalicylideneimino-2-methyl-1-propanol and its organotin(IV) complexes (Table 4.8)**

The Schiff base shows, signals at 1.35, 3.60 and 8.25 ppm assignable to  $\text{CH}_3$ -,  $\text{CH}_2$ -O and azomethine protons respectively. Both phenolic and alcoholic OH protons resonate as a very broad band at 14.25 ppm. The broad nature of the signal indicates the presence of hydrogen bonded phenolic and alcoholic hydroxyls which disappeared on  $\text{D}_2\text{O}$  exchange. In the complexes 38, 39, 41 and 42 this signal is completely absent suggesting replacement of protons by tin. In the phenyltin complex, 40, a signal is observed at 7.17 ppm due to alcoholic OH proton, indicating participation of phenolic OH group in the bond formation with tin. Marginal shielding is observed for azomethine (CH) proton in all the complexes studied. Due to deprotonation of alcoholic proton and its participation in bond formation with tin, the methylene protons get deshielded. The  $\text{CH}_3$  protons of the ligand are also slightly deshielded.

The dimethyltin complex 38 shows a singlet at 0.66 ppm at slightly lower magnetic field compared to the complex  $(\text{SAPA})\text{Sn}(\text{CH}_3)_2$  with satellite signals on either side due to  $(^{117}\text{Sn}, ^1\text{H})$  and  $(^{119}\text{Sn}, ^1\text{H})$  couplings.

$^{13}\text{C}$  and  $^{119}\text{Sn}$  NMR spectral studies of complex  $(\text{ClSAPA})\text{Sn}(\text{CH}_3)_2$ 

High-resolution  $^{13}\text{C}$  NMR spectrum of this complex (Table 4.18) is compared with the Schiff base  $\text{ClSAPAH}_2$ . A large downfield shift ( $\sim 6$  ppm) has been observed for both azomethine (CH) and phenolic (C-O) carbons as compared with the free Schiff base. The methylene  $\text{CH}_2\text{-O}$  carbon also moved to lower magnetic field due to complex formation. The chemical shift difference observed for  $\text{Me}_2\text{Sn-}$  group in the chloro Schiff base complex is 0.55 ppm to down field compared to that in the complex 38. This deshielding may possibly be attributed to increased bond order of tin-carbon bonds in this complex.

It has been noticed that tin chemical shift,  $\delta(^{119}\text{Sn})$  values reflect the nature of donor atoms to which tin is bonded. The complex,  $(\text{ClSAPA})\text{Sn}(\text{CH}_3)_2$  shows  $(^{119}\text{Sn})$  chemical shift at -147.23 ppm, which suggests its pentacoordinated geometry atleast in solution.



Table 4.6. Analytical data for 2-N-5-chlorosalicylideneimino-2-methyl propanol and its organotin(IV) complexes.

No. Compound	m.p. (°C)	Elemental analysis [found(cal)](%)			
		Sn	C	H	N
37 C1SAPAH <sub>2</sub>	110	-	48.45	5.07	5.03
C <sub>11</sub> H <sub>14</sub> ClNO <sub>2</sub>		-	(48.55)	(5.19)	(5.15)
38 (C1SAPA)Sn(CH <sub>3</sub> ) <sub>2</sub>	230	31.82	41.36	4.77	3.81
C <sub>13</sub> H <sub>18</sub> ClNO <sub>2</sub> Sn		(31.70)	(41.70)	(4.85)	(3.74)
39 (C1SAPA)Sn(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	270	23.58	55.60	4.19	2.86
C <sub>23</sub> H <sub>22</sub> ClNO <sub>2</sub> Sn		(23.81)	(55.41)	(4.45)	(2.81)
40 (C1SAPAH)Sn(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	low melting	20.69	60.27	4.64	2.20
C <sub>29</sub> H <sub>28</sub> ClNO <sub>2</sub> Sn		(20.58)	(60.40)	(4.89)	(2.43)
41 (C1SAPA)SnCl(CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> CH <sub>3</sub> )	65	27.53	41.22	4.55	3.35
C <sub>15</sub> H <sub>19</sub> Cl <sub>2</sub> NO <sub>4</sub> Sn		(27.29)	(41.42)	(4.40)	(3.22)
42 (C1SAPA)Sn(CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	>250	22.83	44.25	5.16	2.57
C <sub>19</sub> H <sub>26</sub> ClNO <sub>6</sub> Sn		(22.89)	(44.01)	(5.05)	(2.70)

Table 4.7. IR data for 2-N-5-chlorosalicylideneimino 2-methyl propanol and its organotin(IV) complexes. ( $\nu$ ,  $\text{cm}^{-1}$ )

No.	$\nu(\text{OH})$	$\nu(\text{C=N})+(\text{C=C})$	$\nu(\text{C-O})(\text{L})$	$\nu(\text{C=O})(\text{est})$	$\nu(\text{C-O})(\text{est})$
37	3271, 3189	1633, 1573	1280	-	-
38	- -	1614, 1518	1326	-	-
39	- -	1620, 1531	1315	-	-
40	3216 -	1620, 1530	1307	-	-
41	- -	1624, 1534	1302	1652	1266, 1229
42	- -	1621, 1524	1317	1730, 1685	1260, 1225

Table 4.8.  $^1\text{H}$  NMR data for 2-N-5-chlorosalicylideneimino-2-methyl propanol and its organotin(IV) complexes. ( $\delta$ , ppm)

No.	CH <sub>3</sub>	CH <sub>2</sub> -O	CH	OH	$\alpha$ -CH <sub>2</sub>	$\beta$ -CH <sub>2</sub>	OCH <sub>3</sub> (est)	Sn(CH <sub>3</sub> ) <sub>2</sub>	Arom.protons
37	1.35	3.60	8.27	14.25	-	-	-	-	6.80 - 7.33
38	1.36	3.77	8.28	-	-	-	-	0.68	6.65 - 7.39
39	1.34	3.85	8.28	-	-	-	-	-	6.94 - 8.21
40	1.37	3.91	8.30	7.17	-	-	-	-	6.88 - 8.11
41	1.30	3.98	8.31	-	1.75	2.97	3.85	-	6.80 - 7.58
42	1.29	3.95	8.25	-	1.61	2.72	3.69	-	6.65 - 7.41

Complex 38.  $^2\text{J}(^{117}\text{Sn}-^1\text{H}) = 76 \text{ Hz}$ ;  $^2\text{J}(^{119}\text{Sn}-^1\text{H}) = 78 \text{ Hz}$

$^3\text{J}(^{117}\text{Sn}-^1\text{H})(\text{CH}_2) = 33 \text{ Hz}$ ;  $^3\text{J}(^{119}\text{Sn}-^1\text{H})(\text{CH}) = 43 \text{ Hz}$

IR spectral studies of 2-N-bromosalicylideneimino-2-methyl-1-propanol [BrSAPAH<sub>2</sub>] and its organotin(IV) complexes (Table 4.10)

The IR spectrum of the Schiff base, BrSAPAH<sub>2</sub>, in nujol exhibits two medium intensity bands at 3294 and 3113 cm<sup>-1</sup> due to the  $\nu(\text{OH})$  of alcoholic and hydrogen bonded phenolic hydroxyl groups respectively. This high frequency shift in both OH groups as compared with SAPAH<sub>2</sub> may be due to presence of halogen Br atom in aromatic ring. The strong band at 1568 cm<sup>-1</sup> is assigned to coupled vibration of  $\nu(\text{C}=\text{N} + \text{C}=\text{C})$  group. The characteristic band at 1282 cm<sup>-1</sup> is due to coupled vibration of phenolic  $\nu(\text{C}=\text{O}) + \delta(\text{OH})$ .

The IR spectra of the complexes, 44, 45, 47 and 48, is flat in  $\nu(\text{OH})$  region, indicating replacement of alcoholic and phenolic OH protons by tin. The triphenyltin(IV) complex, 46, shows alcoholic  $\nu(\text{OH})$  at 3226 cm<sup>-1</sup> indicating its non-participation in bond formation. The  $\nu(\text{C}=\text{N})$  in the ligand has been shifted from 1633 cm<sup>-1</sup> to ~ 1620 cm<sup>-1</sup> in the complexes suggests coordination of nitrogen lone pair to tin. The phenolic  $\nu(\text{C}=\text{O})$  has been shifted to ~ 1310 cm<sup>-1</sup>, indicating the tin complex formation via deprotonation. The dimethyltin(IV) complex, 44, shows one medium intensity band due to  $\nu(\text{Sn}-\text{C})$  in the far IR as in the case of (SAPA)Sn(CH<sub>3</sub>)<sub>2</sub>. The  $\nu(\text{Sn}-\text{O})$  is seen at 464 cm<sup>-1</sup>. The estertin complexes 47 and 48 show similar shift in ester  $\nu(\text{C}=\text{O})$  as that of (SAPA)SnCl(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>) and (SAPA)Sn(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>)<sub>2</sub> suggesting ester carbonyl coordination to tin.

<sup>1</sup>H NMR spectral studies of 2-N-bromosalicylideneimino-2-methyl-1-propanol and its organotin(IV) complexes (Table 4.11)

The Schiff base furnishes resonances due to CH<sub>3</sub>, CH<sub>2</sub>-O- and azomethine protons at 1.31, 3.57, and 8.22 ppm respectively. A broad signal is observed at 14.22 ppm similar to the Schiff bases SAPAH<sub>2</sub> and ClSAPAH<sub>2</sub> due to hydrogen bonded phenolic and alcoholic OH protons.

The Schiff base complexes 44, 45, 47 and 48 do not show this broad signal due to hydroxyl protons suggesting proton replacement by tin. No significant shift has been observed for azomethine (CH) proton after nitrogen coordination to tin. The methylene protons in the complexes 44, 45, 47 and 48 are deshielded as a result of deprotonation of alcoholic OH and bond formation to tin. The alcoholic OH resonate at 7.15 ppm in the triphenyltin complex, 46, suggesting bidentate nature of the Schiff base. The methylene protons show a marginal shift of ~ 0.1 ppm in the higher magnetic field which again supports the free nature of alcoholic OH. The CH<sub>3</sub> protons of alkoxy residue of the Schiff base in all the complexes show marginal downfield shift as expected and the aromatic protons resonate in the expected region of 6.40-8.20 ppm.

The sharp signal due to Sn-CH<sub>3</sub> is observed at 0.7 ppm as a singlet in complex 44. As in above dimethyltin Schiff base complexes, satellite peaks are also observed [Table 4.11].

The similar higher magnetic field shift is also observed for  $\alpha$ -CH<sub>2</sub>,  $\beta$ -CH<sub>2</sub> and OCH<sub>3</sub> in complex 47 and 48 as compared to those of the complex Cl<sub>2</sub>Sn(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>) and Cl<sub>3</sub>Sn(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>) respectively.

### <sup>13</sup>C and <sup>119</sup>Sn NMR spectral studies of (BrSAPA)Sn(CH<sub>3</sub>)<sub>2</sub>

The <sup>13</sup>C NMR spectral data of complex 44 and the Schiff base are presented in Table 4.18. For both the phenolic and azomethine carbons large deshielding (6 ppm) has been observed. The alkoxy (CH<sub>2</sub>-O-) carbon also show a similar downfield shift by 2.2 ppm. These data indicate the participation of these groups in bond formation. The (<sup>119</sup>Sn) chemical shift value observed for (BrSAPA)Sn(CH<sub>3</sub>)<sub>2</sub> is at -147.07 ppm.

Table 4.9. Analytical data for 2-N-5-bromosalicylideneimino-2-methyl propanol and its organotin(IV) complexes.

No. Compound	m.p. (°C)	Elemental analysis [found(cal)](%)			
		Sn	C	H	N
43 BrSAPAH <sub>2</sub>	110	-	48.45	5.07	5.03
C <sub>11</sub> H <sub>14</sub> BrNO <sub>2</sub>		-	(48.55)	(5.19)	(5.15)
44 (BrSAPA)Sn(CH <sub>3</sub> ) <sub>2</sub>	215	28.22	37.16	4.17	3.21
C <sub>13</sub> H <sub>18</sub> BrNO <sub>2</sub> Sn		(28.34)	(37.27)	(4.33)	(3.34)
45 (BrSAPA)Sn(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	170	21.58	50.61	4.15	2.31
C <sub>23</sub> H <sub>22</sub> BrNO <sub>2</sub> Sn		(21.86)	(50.87)	(4.08)	(2.58)
46 (BrSAPAH)Sn(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	152	19.19	56.27	4.64	2.20
C <sub>29</sub> H <sub>28</sub> BrNO <sub>2</sub> Sn		(19.11)	(56.07)	(4.54)	(2.26)
47(BrSAPA)SnCl(CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> CH <sub>3</sub> )	61	23.33	35.02	3.55	2.55
C <sub>15</sub> H <sub>19</sub> BrClNO <sub>4</sub> Sn		(23.21)	(35.23)	(3.75)	(2.74)
48(BrSAPA)Sn(CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	102	20.83	40.75	4.46	2.67
C <sub>19</sub> H <sub>26</sub> BrNO <sub>6</sub> Sn		(21.08)	(40.53)	(4.66)	(2.49)

Table 4.10. IR data for 2-N-5-bromosalicylideneimino 2-methyl propanol and its organotin(IV) complexes ( $\nu$ ,  $\text{cm}^{-1}$ ).

No.	OH	(C=N)+(C=C)	(C-O)(L)	(C=O)(est)	(C-O)(est)
43	3294, 3213	1633, 1568	1282	-	-
44	- -	1617, 1517	1327	-	-
45	- -	1620, 1526	1308	-	-
46	3226 -	1622, 1526	1280	-	-
47	- -	1622, 1528	1303	1686	1260, 1210
48	- -	1620, 1524	1316	1731, 1690	1265, 1207



Table 4.11.  $^1\text{H}$  NMR data for 2-N-5-bromosalicylideneimino-2-methylpropanol and its organotin(IV) complexes ( $\delta$ , ppm).

No.	CH <sub>3</sub>	CH <sub>2</sub> -O	CH	OH	$\alpha$ -CH <sub>2</sub>	$\beta$ -CH <sub>2</sub>	OCH <sub>3</sub> (est)	Sn(CH <sub>3</sub> ) <sub>2</sub>	Arom.protons
43	1.31	3.57	8.22	14.22	-	-	-	-	6.70 - 7.35
44	1.40	3.82	8.35	-	-	-	-	0.69	6.40 - 7.42
45	1.40	4.00	8.31	-	-	-	-	-	6.95 - 8.20
46	1.40	3.51	8.40	7.15	-	-	-	-	6.89 - 8.00
47	1.39	3.95	8.33	-	1.62	2.85	3.78	-	6.58 - 7.53
48	1.38	3.65	8.21	-	1.59	2.76	3.70	-	6.55 - 7.40

Complex 44.  $^2\text{J}(^{117}\text{Sn}-^1\text{H}) = 74$  Hz;  $^2\text{J}(^{119}\text{Sn}-^1\text{H}) = 78$  Hz

$^3\text{J}(^{117}\text{Sn}-^1\text{H})(\text{CH}_2) = 36$  Hz;  $^3\text{J}(^{119}\text{Sn}-^1\text{H})(\text{CH}) = 45$  Hz

**IR spectral studies of 2-N-2-hydroxy-3-methoxybenzylideneimino-2-methyl-1-propanol [OVPAH<sub>2</sub>] and its organotin(IV) complexes (Table 4.13)**

As compared with the Schiff base, SAPAH<sub>2</sub>, there is low frequency shift for alcoholic  $\nu(\text{OH})$  and a high frequency shift for phenolic  $\nu(\text{OH})$  in the Schiff base OVPAH<sub>2</sub>. The strong bands at 1633 and 1613  $\text{cm}^{-1}$  are due to  $\nu(\text{C}=\text{N})$  and  $\nu(\text{C}=\text{C})$  respectively. The band at 1235  $\text{cm}^{-1}$  is assigned for the coupled vibration of  $\nu(\text{CO} + \delta \text{OH})$ .

The organotin(IV) complexes 50, 51, 53 and 54 do not show bands due to hydroxyl groups indicating deprotonation of alcoholic and phenolic protons by tin. The complex 52 shows alcoholic  $\nu(\text{OH})$  at 3232  $\text{cm}^{-1}$  suggesting non-involvement of alcoholic  $\nu(\text{OH})$  in complex formation. The 1633  $\text{cm}^{-1}$  band due to  $\nu(\text{C}=\text{N})$  in the Schiff base has been shifted to lower frequency region in the complexes indicating coordination of the azomethine nitrogen lone pair to tin. The phenolic  $\nu(\text{C}-\text{O})$  has also been shifted to  $\sim 1250 \text{ cm}^{-1}$ , in the complexes as a result of chelate ring formation through phenoxy oxygen and azomethine nitrogen coordination to tin. The  $\nu(\text{Sn}-\text{C})$  is observed at 539  $\text{cm}^{-1}$  in complex 50. The band at 471  $\text{cm}^{-1}$  can be assigned for  $\nu(\text{Sn}-\text{O})$ . The mono estertin(IV) complex 53 shows  $\nu(\text{C}=\text{O})$  at 1659  $\text{cm}^{-1}$  which confirms coordination of ester group to tin whereas in the case of complex 54 two strong bands are observed due to  $\nu(\text{C}=\text{O})$  at 1731 and 1700  $\text{cm}^{-1}$  which suggests free and coordinated ester groupings.

**<sup>1</sup>H NMR spectral studies of 2-N-2-hydroxy-3-methoxybezeliideneimino-2-methyl-1-propanol and its organotin(IV) complexes (Table 4.14)**

<sup>1</sup>H NMR spectrum of the Schiff base in CDCl<sub>3</sub> shows signals at 1.32, 3.58, 3.86 and 8.23 due to CH<sub>3</sub>-, CH<sub>2</sub>-O, OCH<sub>3</sub> and azomethine protons respectively. Both phenolic and alcoholic OH protons resonate to give a broad signal centered at 13.83 ppm. The very broad nature of this signal clearly indicates strong hydrogen bonding. This signal disappears completely after deuteration confirming the assignment.

The broad signal due to hydroxyl protons in the Schiff base is absent in complexes 50, 51, 53 and 54 suggesting proton replacement by tin. The azomethine (CH) proton in the complexes resonates almost in same position as that of Schiff base. The methylene protons are deshielded as a result of deprotonation of alcoholic OH. The CH<sub>3</sub> protons show marginal downfield shift and the aromatic protons resonate in the expected region of 6.65-8.21 ppm. The ring OCH<sub>3</sub> in the complexes is almost at the same position as that of the Schiff base.

The complex 52 shows sharp signal at 7.18 ppm due to alcoholic OH which suggests monobasic bidentate bonding of the Schiff base through phenoxy and azomethine nitrogen to tin. An upfield shift has been observed for methylene and methyl protons.

The resonances due to (Sn-CH<sub>3</sub>) in the complex 50 are observed as a sharp singlet at 0.72 ppm having two satellite

signals on either side as doublets due to coupling of methyl protons with  $^{117}\text{Sn}$  and  $^{119}\text{Sn}$  nuclei. Further, satellite signals are also observed for azomethine and methylene protons as in the case of other organotin(IV) complexes which again confirms the mode of bonding to tin.

### $^{13}\text{C}$ and $^{119}\text{Sn}$ NMR spectral studies of $(\text{OVPA})\text{Sn}(\text{CH}_3)$

As compared with the  $^{13}\text{C}$  NMR spectra of the Schiff base,  $\text{OVPAH}_2$ , the complex 50 (Table 4.18) show large deshielding for azomethine (CH) and phenolic (C-O) carbons. The resonance due to alkoxy  $\text{CH}_2\text{-O}$  carbon shifts by 3 ppm to lower magnetic field in the complex as a result of proton replacement by tin. The  $\text{CH}_3$  group attached to tin resonates at higher magnetic field and appears at 0.81 ppm. The ( $^{119}\text{Sn}$ ) chemical shift value observed for complex 50 is at -148.34 ppm which is consistent with the  $\delta(^{119}\text{Sn})$  value reported for penta-coordinated complex in solution.

Table 4.12. Analytical data for 2-N-2-hydroxy-3-methoxybenziledene imino-2-methyl propanol and its organotin(IV) complexes.

No. Compound	m.p. (°C)	Elemental analysis [found(cal)](%)			
		Sn	C	H	N
49 OVPAH <sub>2</sub>	110	-	64.45	7.37	6.03
C <sub>12</sub> H <sub>17</sub> NO <sub>3</sub>		-	(64.55)	(7.68)	(6.27)
50 (OVPA)Sn(CH <sub>3</sub> ) <sub>2</sub>	220	32.22	45.36	5.77	3.81
C <sub>14</sub> H <sub>21</sub> NO <sub>3</sub> Sn		(32.08)	(45.44)	(5.72)	(3.79)
51 (OVPA)Sn(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	162	23.89	58.61	4.72	2.64
C <sub>24</sub> H <sub>25</sub> NO <sub>3</sub> Sn		(24.02)	(58.33)	(5.10)	(2.83)
52 (OVPAH)Sn(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	low melting	20.61	62.67	4.64	2.20
C <sub>30</sub> H <sub>31</sub> NO <sub>3</sub> Sn		(20.74)	(62.96)	(5.46)	(2.45)
53 (OVPA)SnCl(CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> CH <sub>3</sub> )	139	25.59	41.32	4.45	3.45
C <sub>16</sub> H <sub>22</sub> ClNO <sub>5</sub> Sn		(25.66)	(41.55)	(4.79)	(3.03)
54 (OVPA)Sn(CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	118	23.03	46.85	5.36	2.87
C <sub>20</sub> H <sub>29</sub> NO <sub>7</sub> Sn		(23.09)	(46.72)	(5.69)	(2.72)

Table 4.13. IR data for 2-N-2-hydroxy-3-methoxybezeliideneimino-2-methyl propanol and its organotin(IV) complexes. ( $\nu$ ,  $\text{cm}^{-1}$ )

No.	OH	(C=N)+(C=C)	(C-O)(L)	(C=O)(est)	(C-O)(est)
49	3238,3226	1633,1613	1235	-	-
50	3232 - 3.58	1616,1542	1272	-	-
51	3232 - 3.80	1615,1551	1246	-	-
52	3232 - 3.88	1617,1541	1251	-	-
53	3232 - 3.92	1626,1555	1250	1659	1266,1229
54	3232 - 4.00	1618,1551	1246	1731	1263,1210

Table 4.14.  $^1\text{H}$  NMR data for 2-N-2-hydroxy-3-methoxybeziledeneimino-2-methylpropanol and its organotin(IV) complexes. ( $\delta$ , ppm)

No.	CH <sub>3</sub>	CH <sub>2</sub> -O	OCH <sub>3</sub>	CH	OH	$\alpha$ -CH <sub>2</sub>	$\beta$ -CH <sub>2</sub>	OCH <sub>3</sub> (est)	Sn(CH <sub>3</sub> ) <sub>2</sub>	Aromatic protons
49	1.32	3.58	3.86	8.23	13.83	-	-	-	-	6.58 - 7.24
50	1.38	3.80	3.85	8.35	-	-	-	-	0.72	6.41 - 7.42
51	1.36	3.88	3.84	8.30	-	-	-	-	-	6.93 - 8.21
52	1.37	3.92	3.87	8.35	7.18	-	-	-	-	6.85 - 8.18
53	1.33	4.00	3.85	8.36	-	1.74	2.95	3.84	-	6.70 - 7.58
54	1.34	3.97	3.84	8.31	-	1.60	2.70	3.70	-	6.66 - 7.42

Complex 50.  $^2\text{J}(^{117}\text{Sn}-^1\text{H}) = 76$  Hz;  $^2\text{J}(^{119}\text{Sn}-^1\text{H}) = 77$  Hz

$^3\text{J}(^{117}\text{Sn}-^1\text{H})(\text{CH}_2) = 35$  Hz;  $^3\text{J}(^{119}\text{Sn}-^1\text{H})(\text{CH}) = 48$  Hz

**IR spectral studies of 2-N-2-hydroxy-1-naphthylideneimino-2-methyl-1-propanol [NaphPAH<sub>2</sub>] and its organotin(IV) complexes (Table 4.16)**

In the Schiff base, NaphPAH<sub>2</sub>, both alcoholic and phenolic hydroxyls are shifted to lower wavenumbers as compared to the Schiff base, SAPAH<sub>2</sub>. The  $\nu(\text{C}=\text{N})$  and  $\nu(\text{C}=\text{C})$  frequencies are observed at 1632 and 1550  $\text{cm}^{-1}$  respectively and the phenolic  $\nu(\text{C}-\text{O})$  is at 1286  $\text{cm}^{-1}$ .

The IR spectra of complex 58 shows alcoholic  $\nu(\text{OH})$  at 3165  $\text{cm}^{-1}$  similar to other triphenyltin(IV) homologues. All other complexes show complete absence of phenolic and alcoholic OH stretching vibrations indicating replacement of protons by tin. A low frequency shift is observed for  $\nu(\text{C}=\text{N})$  in the complexes, suggesting the coordination of the nitrogen lone pair to tin. The phenolic  $\nu(\text{C}-\text{O})$  has been shifted to higher wave numbers ~ 1325  $\text{cm}^{-1}$  due to increased C-O bond order as a result of CO bonding to tin. The far IR spectra of the Schiff base complex 56 display one band at 536  $\text{cm}^{-1}$  which may be assigned to trans methyl groups. The  $\nu(\text{Sn}-\text{O})$  is seen at 464  $\text{cm}^{-1}$ .

The mono and diestertin(IV) complexes 59 and 60 show coordination of ester C=O as that of other estertin Schiff base complexes.

**<sup>1</sup>H NMR spectral studies of 2-N-2-hydroxy-1-naphthylideneimino-2-methyl-1-propanol and its organotin(IV) complexes (Table 4.17)**

<sup>1</sup>H NMR spectrum of the Schiff base, exhibits signals at



1.50, 3.69 and 8.68 ppm assignable to  $\text{CH}_3$ -,  $\text{CH}_2$ -O and azomethine protons respectively. Signals due to both naphthalenic OH and alcoholic OH protons are seen as a broad band at 14.26 ppm as in other Schiff bases. In complex 58 a signal due to alcoholic OH proton is observed at 7.13 ppm indicating participation of only the phenolic OH in the bond formation with tin. The complexes 56, 57, 59 and 60 do not show any signal due to hydroxyl protons suggesting replacement of both phenolic and alcoholic proton and by tin. Marginal shielding has been observed for azomethine (CH) proton in the complexes studied. As a result of deprotonation of alcoholic proton, the methylene protons are deshielded. The  $\text{CH}_3$  protons are also slightly deshielded.

In the complex 56 a sharp singlet is observed at 0.68 ppm due to  $\text{CH}_3$ -Sn protons. Two satellite peaks are seen on either side of the singlet because of ( $^{117}\text{Sn}, ^1\text{H}$ ) and ( $^{119}\text{Sn}, ^1\text{H}$ ) couplings. Satellite signals are also observed for azomethine and methylene protons. All these data confirm the mode of bonding to tin.

### $^{13}\text{C}$ and $^{119}\text{Sn}$ NMR spectral studies of $(\text{NaphPA})\text{Sn}(\text{CH}_3)_2$ (Table 4.18)

In complex 56 a large lowfield shift (8.25 ppm) has been observed for azomethine (CH) and phenolic (C-O) has shifted to highfield by 7.62 ppm compared with the ligand. The  $\text{CH}_2$ -O carbon suffers low-field shift. In the complex 56 the  $\text{Sn}(\text{CH}_3)_2$  group is observed at very high field at -0.08 ppm. The ( $^{119}\text{Sn}$ ) chemical

shift is observed at -148.34 ppm, which confirms its pentacoordinated geometry<sup>21</sup> in solution.

Table 4.15. Analytical data for 2-N-2-hydroxy-1-naphthalenedeneimino-  
-2-methyl propanol and its organotin(IV) complexes.

No. Compound	m.p. °C	Elemental analysis [found(cal)](%)			
		Sn	C	H	N
55 NaphPAH <sub>2</sub>	110	-	64.45	7.37	8.03
C <sub>15</sub> H <sub>17</sub> NO <sub>2</sub>		-	(64.55)	(7.68)	(6.27)
56 (NaphPA)Sn(CH <sub>3</sub> ) <sub>2</sub>	235	30.21	52.36	5.77	3.81
C <sub>17</sub> H <sub>21</sub> NO <sub>2</sub> Sn		(30.43)	(52.35)	(5.43)	(3.59)
57 (NaphPA)Sn(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	174	23.19	63.21	4.71	2.67
C <sub>27</sub> H <sub>25</sub> NO <sub>2</sub> Sn		(23.08)	(63.07)	(4.90)	(2.72)
58 (NaphPAH)Sn(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	103	20.11	66.67	4.94	2.20
C <sub>33</sub> H <sub>31</sub> NO <sub>2</sub> Sn		(20.04)	(66.92)	(5.28)	(2.36)
59 (NaphPA)SnCl(CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> CH <sub>3</sub> )	99	24.59	47.32	4.45	2.65
C <sub>19</sub> H <sub>22</sub> ClNO <sub>4</sub> Sn		(24.60)	(47.29)	(4.60)	(2.90)
60 (NaphPA)Sn(CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	85	22.03	51.85	5.36	2.87
C <sub>23</sub> H <sub>29</sub> NO <sub>6</sub> Sn		(22.22)	(51.71)	(5.47)	(2.62)

**Table 4.16.** IR data for 2-N-2-hydroxy-1-naphthalideneimino 2-methyl propanol and its organotin(IV) complexes ( $\nu$ ,  $\text{cm}^{-1}$ ).

No.	OH	(C=N)+(C=C)	(C-O)(L)	(C=O)(est)	(C-O)(est)
55	3173,3053	1632,1550	1286	-	-
56	- -	1616,1536	1310	-	-
57	- -	1618,1541	1304	-	-
58	3165 -	1617,1542	1315	-	-
59	- -	1620,1547	1349	1660	1262,1210
60	- -	1621,1545	1259	1731, 1711	1260,1207

Table 4.17.  $^1\text{H}$  NMR data for 2-N-2-hydroxy-1-naphthaledeneimino-2-methylpropanol and its organotin(IV) complexes ( $\delta$ , ppm).

No.	CH <sub>3</sub>	CH <sub>2</sub> -O	CH	OH	$\alpha$ -CH <sub>2</sub>	$\beta$ -CH <sub>2</sub>	OCH <sub>3</sub> (est)	Sn(CH <sub>3</sub> ) <sub>2</sub>	Aromatic protons
55	1.50	3.69	8.68	14.26	-	-	-	-	6.55 - 7.75
56	1.46	3.85	9.24	-	-	-	-	0.68	6.78 - 7.94
57	1.49	3.95	8.28	-	-	-	-	-	6.94 - 8.21
58	1.48	4.01	8.30	7.13	-	-	-	-	6.89 - 8.11
59	1.50	4.12	8.31	-	1.75	2.97	3.85	-	6.80 - 7.59
60	1.29	3.95	8.25	-	1.61	2.72	3.69	-	6.65 - 7.41

Complex 56.  $^2\text{J}(^{117}\text{Sn}-^1\text{H}) = 76$  Hz;  $^2\text{J}(^{119}\text{Sn}-^1\text{H}) = 78$  Hz

$^3\text{J}(^{117}\text{Sn}-^1\text{H})(\text{CH}_2) = 32$  Hz;  $^3\text{J}(^{119}\text{Sn}-^1\text{H})(\text{CH}) = 54$  Hz

Table 4.18.  $^{13}\text{C}$  and  $^{119}\text{Sn}$  NMR data for the Schiff bases  
and its dimethyl tin complexes (ppm).

No.	$(\text{CH}_3)_2$	$>\text{C}<$	$\text{CH}_2\text{-O}$	$\text{CH}$	$\text{C-O}$	$\text{Sn}(\text{CH}_3)_2$	$\overset{\text{Y}}{\text{C-O}}(\text{OCH}_3)$ (phenolic)	$\text{OCH}_3$	$^{119}\text{Sn}$ ( $\delta$ , ppm)
37	23.36	60.99	70.60	161.24	161.24	-	-	-	-
38	25.26	62.35	73.33	167.35	167.55	0.66	-	-	-147.23
43	23.83	61.47	71.14	161.40	161.67	-	-	-	-
44	25.29	62.38	73.34	167.44	167.86	0.10	-	-	-147.07
49	23.73	60.62	70.89	162.25	149.58	-	156.42	56.17	-
50	25.67	62.43	73.88	169.03	151.96	0.81	160.30	56.43	-148.34
55	23.97	58.75	70.33	154.50	179.24	-	-	-	-
56	26.00	62.60	74.36	162.75	171.62	-0.08	-	-	-150.71

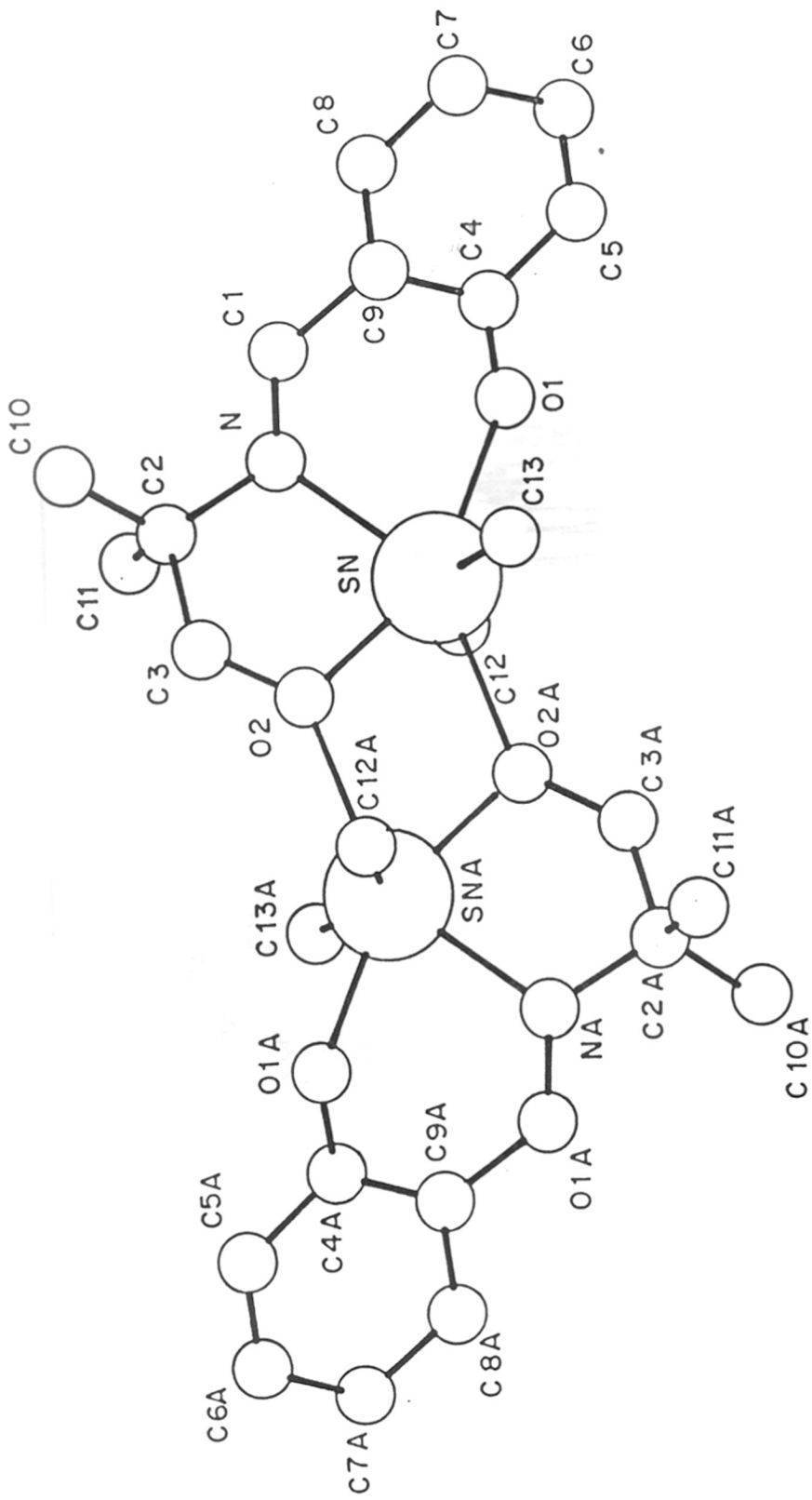


FIG. 4.3 : X RAY CRYSTAL STRUCTURE OF  $[(OC_6H_4CH=N-C(CH_3)_2CH_2O)_2Sn(CH_3)_2]_2$





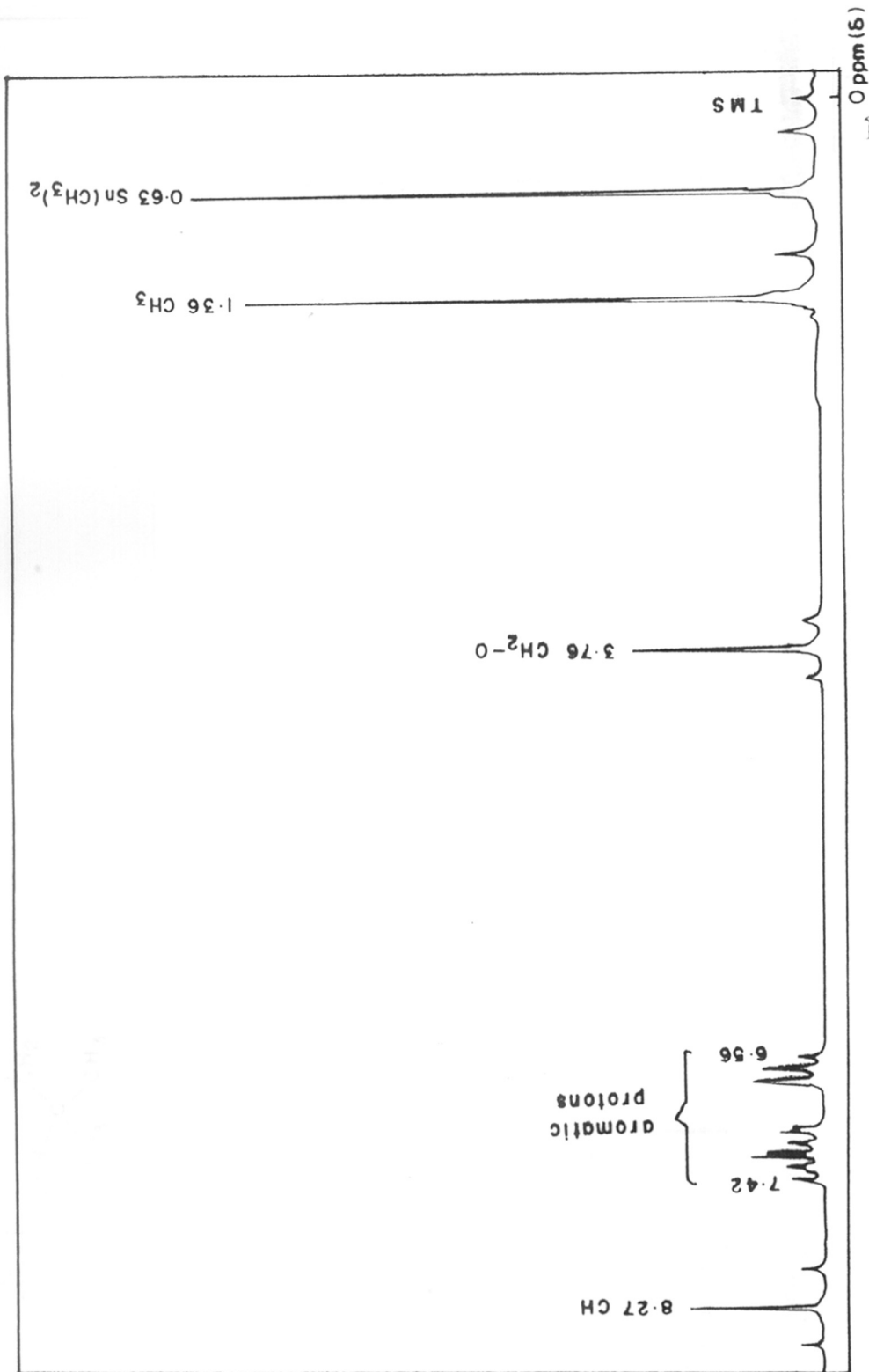


FIG. 4.5: <sup>1</sup>H NMR SPECTRUM OF (SAPA) Sn(CH<sub>3</sub>)<sub>2</sub> IN CDCl<sub>3</sub>.

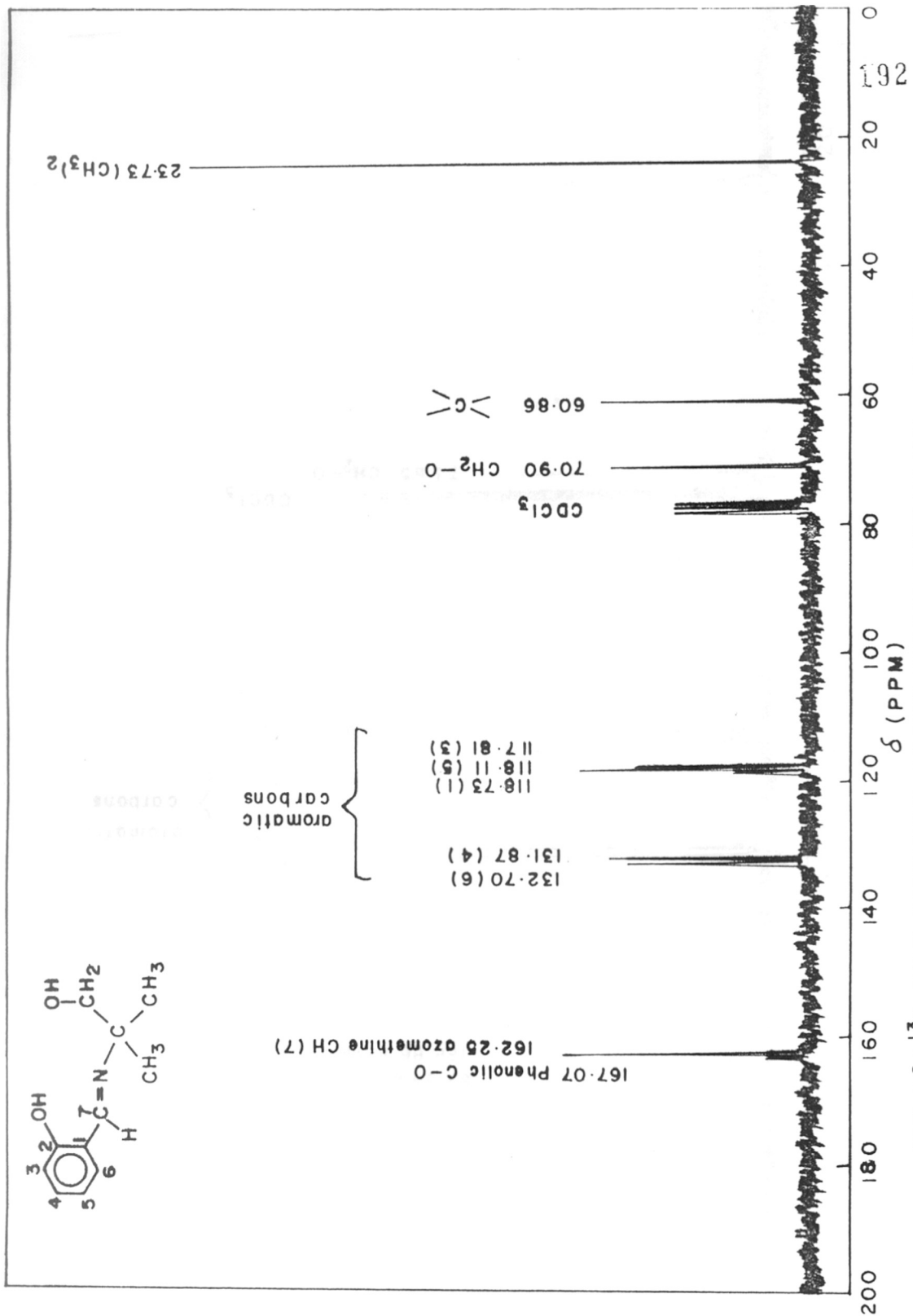


FIG. 4-6: <sup>13</sup>C NMR SPECTRUM OF THE SCHIFF BASE SAPAH<sub>2</sub> IN CDCl<sub>3</sub>

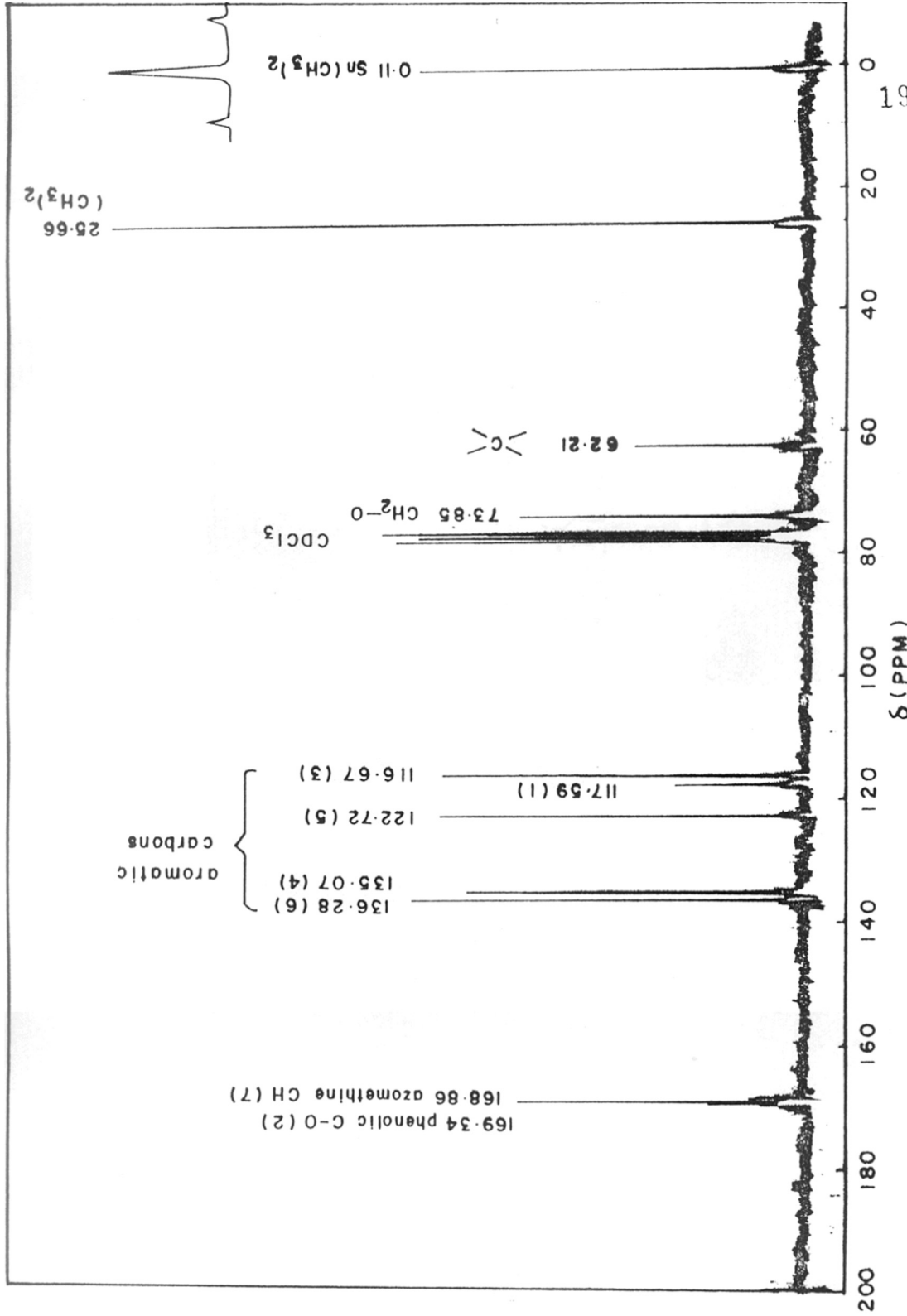


FIG. 4.7: <sup>13</sup>C NMR SPECTRUM OF (SAPA) Sn(CH<sub>3</sub>)<sub>2</sub> IN CDCl<sub>3</sub>

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**CHAPTER 5**

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SYNTHESIS AND SPECTROSCOPIC INVESTIGATIONS OF SOME BINUCLEAR ORGANOTIN(IV) COMPLEXES OF (BIS)SALICYLALDEHYDE MALONOYLDIHYDRAZONE AND CRYSTAL STRUCTURE STUDY OF  $[(\text{CH}_3\text{CH}_2)_2\text{Sn}]_2[\text{OC}_6\text{H}_4\text{CH}=\text{N}-\text{N}=\text{C}(\text{O})]_2\text{CH}_2$ .

S U M M A R Y

The Schiff base,  $[\text{HOC}_6\text{H}_4\text{CHN}-\text{NHCO}]_2\text{CH}_2$  [ $\text{H}_4\text{L}$ ], derived from the condensation of salicylaldehyde and malonyldihydrazine, reacted with organotin chlorides to yield binuclear complexes of the type  $\text{R}_2\text{Sn}[\text{L}]\text{SnR}_2$  [where  $\text{R} = \text{CH}_3-$ ,  $\text{C}_2\text{H}_5-$ ,  $\text{C}_4\text{H}_9-$ ,  $\text{C}_6\text{H}_5-$ ,  $\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_2-$ ,  $\text{C}_6\text{H}_5\text{CH}_2-$ ]. The complexes were characterized and the structures have been assigned on the basis of their elemental analysis, IR,  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{119}\text{Sn}$  NMR spectral data, and X-ray crystallographic data. In these complexes, the ligand functions as a flexibly bridging tetrabasic hexadentate moiety binding two tin atoms through ONO donor atoms and both tins are in trigonal bipyramidal environment.

A single X-ray crystal diffraction study of the complex,  $[(\text{CH}_3\text{CH}_2)_2\text{Sn}]_2[\text{OC}_6\text{H}_4\text{CH}=\text{N}-\text{N}=\text{C}(\text{O})]_2\text{CH}_2$  confirms the structure to be binuclear. The crystals are monoclinic, space group  $\text{I}2/a$  with  $a = 12.312(2)$ ,  $b = 11.526(2)$ ,  $c = 18.858(2)\text{\AA}$ ,  $\beta = 94.69(2)^\circ$ , volume =  $2667.1(7)\text{\AA}^3$ ,  $Z = 4$ ,  $D_c = 1.718 \text{ g/cm}^3$ . The final discrepancy factors are  $R = 0.042$  and  $R_w = 0.055$  for 1698 observed reflections. Half of the molecule is bridged to the other half by two fold symmetry via C(13) atom. The tin atom has

distorted trigonal bipyramidal co-ordination with two oxygens occupying axial positions while two ethyl groups and azomethine nitrogen occupy the equatorial positions. The two ethyl groups co-ordinated to Sn are *cis* to each other.

## I N T R O D U C T I O N

Hydrazones have found wide application<sup>1</sup> in synthetic chemistry for the preparation of compounds of most diverse structure and in analytical chemistry for identification and isolation of carbonyl compounds, and for the detection of a large number of plasticisers and stabilizers for polymers, polymerisation initiators, antioxidants, etc. However, the most valuable property of hydrazones is, perhaps, their great physiological activity. Among them are found herbicides, insecticides, nematocides, rodenticides, and plant growth regulators. The value of hydrazones in fighting tuberculosis is well known. Substituted hydrazones have been found to exhibit spasmolytic activity, hypotensive action, and activity against leukemia, sarcomas, and other malignant neoplasms. The possibility is being investigated by using substituted hydrazones for the treatment of schizophrenia, leprosy and other illnesses<sup>1-3</sup>.

Buutto et al<sup>4</sup> have prepared several mono hydrazides such as salicylhydrazide, 5-chloro- and 5-bromo-salicylhydrazide and 2-



hydroxy-3-naphth-hydrazide etc. and their condensation products with various aldehydes and ketones to get hydrazone derivatives. These condensation products were investigated for biological applications in view of the possibility of their less toxicity than the parent hydrazides, as a result of the blocking of the free  $\text{NH}_2$  group. They found that the tuberculostatic activity was highly dependent on the molecular structure of these compounds.

Ma et al<sup>5</sup> have studied antitubercular activity of salicylic acid hydrazide and its hydrazone derivatives and found that hydrazones derived from phenolic aldehydes are more active against *M. tuberculosis*.

Bhatt et al<sup>6</sup> have synthesized and carried out antimicrobial studies of some indole-3-carboxaldehyde malonic acid hydrazones. These compounds were found to be active against *S. aureus* and *E. coli*. The compounds with 3-chloro, 4-chloro, 4-nitro, 3-methoxy, 4-ethoxy, 2-methyl, 4-methyl and 3,4-dimethyl substitution in the phenyl ring were active against *S. aureus*. Compounds with 3-nitro, 4-methoxy, 3-methyl, 4-methyl and without substitution in the phenyl ring were more active against *S. aureus* than *E. coli*. The compounds were tested for their antituberculosis activity and it was observed that 4-chloro, 4-nitro, 4-methoxy, 4-methyl and 3,4-dimethylphenyl derivatives were found to be mono active.

The dihydrazones derived from the condensation of *o*-hydroxyaromatic aldehydes or ketones and di-acyl- or diaroyl

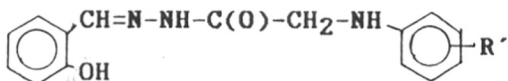
dihydrazides are similar to mono acyl- or aroyl hydrazones in all respects except that they possess two hydrazone groupings which are separated from each other by intervening methylene chains of varying lengths or by phenyl or pyridyl groups.

Tin(IV) complexes of salicylaldehyde isonicotinoylhydrazone (SINH) and salicylaldehyde nicotinoylhydrazone (SNH), were reported by Agarwal et al<sup>7</sup>. These isomeric hydrazones act as bidentate ligands in the addition complexes and as a tridentate ligands in the deprotonated complexes. An octahedral geometry around tin(IV) is proposed.

Ni(II), Cu(II), and Zn(II) complexes of polymeric Schiff bases, derived from glyoxal and organic acid monohydrazides and dihydrazides, have been reported by Narang et al<sup>8</sup>. The stereochemistry of Ni(II) complex reported to be octahedral, the Cu(II) complex planar and the Zn(II) to be tetrahedral. The hydrazide grouping, (-C(O)-NH-N<), in the ligands acts as a coordinating unit through the azomethine nitrogen.

Aminbhavi et al<sup>9</sup> have prepared the phenylglycyl hydrazones, 2-HOC<sub>6</sub>H<sub>4</sub>CH:NNHCOCH<sub>2</sub>NHC<sub>6</sub>H<sub>4</sub>R (I)(LH<sub>2</sub>)(R = H, 2-Cl, 4-Cl, 2-Me, 4-Me, 2-MeO, 4-MeO) by condensation of the appropriate phenylglycyl hydrazide with salicylaldehyde in ethanol. Complexation of (I) with Me<sub>2</sub>SiCl<sub>2</sub> or Ph<sub>2</sub>SnCl<sub>2</sub> gave hexacoordinated silicon, tin complexes of the type R<sub>2</sub>MCl<sub>2</sub>.L (where R = Me or Ph and M = Si or Sn) with ligand chelation via the azomethine N and the ketonic O

atoms. Ligands (I) and the complexes derived were tested for antibacterial activity. It was observed that ring substituted phenylglycyl analogues



where  $R' = \text{H, o-Cl, p-Cl, o-CH}_3, \text{p-CH}_3, \text{o-CH}_3, \text{p-OCH}_3$

had a greater zone of inhibition compared to phenylglycyl hydrazone. The para substituted compounds had better activity than the ortho isomers and the chlorosubstituted compounds were good bacteriostats (bacterio static property).

A number of new complexes of the compositions  $\text{VO}(\text{H}_2\text{aafh})\text{SO}_4$ , and  $\text{M}(\text{H}_2\text{aafh})\text{Cl}_2$  and  $\text{M}(\text{aafh})(\text{H}_2\text{O})_2$  [ $\text{M} = \text{Mn}(\text{II}), \text{Co}(\text{II}), \text{Ni}(\text{II}), \text{Cu}(\text{II})$  or  $\text{Zn}(\text{II})$  and  $\text{H}_2\text{aafh} = \text{acetylacetonabis-(2-furoylhydrazone)}$ ] have been synthesized and characterized by Singh et al<sup>10</sup>. Molar conductance values of these complexes indicated the 1:1 electrolytic nature of the vanadyl complex, the 1:2 ionic behaviour of the  $\text{Cu}(\text{H}_2\text{aafh})\text{Cl}_2$  complex and the non-electrolytic nature of the remaining complexes in DMF solution. Magnetic susceptibility and spectral studies such as infra red, electronic and electron spin resonance were used to elucidate the structure of the complexes and the mode of bonding of the ligand. The infrared spectral studies indicate that  $\text{H}_2\text{aafh}$  behaves as a tetradentate ligand forming adducts bonding through the two carbonyl oxygens and the two azomethine nitrogens and complexes bonding through the two enolic oxygens and the two azomethine

nitrogens. IR and molar conductance studies establish penta coordination of vanadyl and six coordination of other divalent metals. The electronic spectral data in conjunction with the magnetic susceptibility suggest an octahedral geometry for the six-coordinate complexes and a square pyramidal for the five-coordinate vanadyl complex. The dimeric nature of the copper(II) adduct has been inferred from the ESR studies.

Rao et al<sup>11</sup> have reacted acetone(N-benzoyl)glycyl hydrazone (BzAGH) with trivalent lanthanide metal ions to obtain complexes of the type  $[\text{Ln}(\text{BzAGH})\text{Cl}(\text{H}_2\text{O})_3]\text{Cl}_2$  where Ln = La(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III) and Dy(III). The complexes have been characterized by elemental analyses, molar conductance, magnetic, electronic, IR,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectral techniques. Molar conductance studies in 0.001 M MeOH solutions indicate a 2:1 electrolytic behaviour of all the complexes. The nephelauxetic ratio, the bonding parameter, the Sinha's parameter and the covalency angular overlap parameter have been calculated from the electronic spectra of the Pr(III), Nd(III) and Sm(III) complexes. The IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral studies support non-involvement of the benzamide carbonyl group and the participation of azomethine nitrogen and the carbonyl oxygen of the hydrazide moiety in coordination with metal ion. Based on the above physico-chemical studies, the empirical formula  $[\text{M}(\text{BzAGH})\text{Cl}(\text{H}_2\text{O})_3]\text{Cl}_2$  has been proposed for the present

complexes involving a neutral bidentate functional ligand and a six-coordinate metal ion.

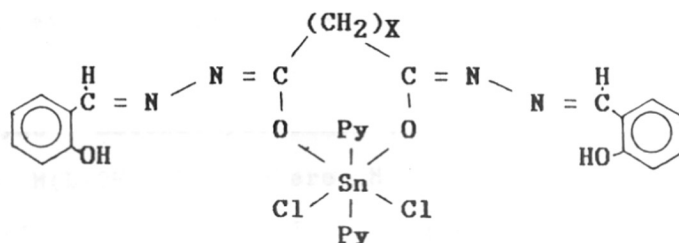
New complexes of acylmonohydrazones with Co(II), Ni(II) and Cu(II) have been synthesized and characterized on the basis of analytical, conductivity, magnetic moment, TGA, DTA, Infrared, electronic and ESR spectral data<sup>12</sup>. Metal to ligand ratio, in these complexes, has been found to be 1:1. Infra red spectral data show that the ligand behaves as a dibasic tetradentate moiety in all these complexes except in the case of Cu(II) complexes, where they act as dibasic tridentate ligands with O:N:O donor sequence. Co(II) and Ni(II) complexes have octahedral geometry while Cu(II) complexes have square-planar structures.

Singh et al<sup>13</sup> have prepared stable tin complexes of 2-furan thiocarboxyhydrazide (Hfth), 4-hydroxyphenylthiocarboxyhydrazide (Hoth), and salicylaldehyde-2-furanthiocarboxyhydrazide (H<sub>2</sub>L) and assigned the compositions as Ph<sub>2</sub>SnCl<sub>2</sub>.Hfth, R<sub>2</sub>Sn(LH)<sub>2</sub> (R = Ph, Bu; L = Hfth, Hoth), Ph<sub>2</sub>SnCl<sub>2</sub>.H<sub>2</sub>L, Ph<sub>2</sub>Sn(HL)Cl and Bu<sub>2</sub>SnL. All the complexes were octahedral except for Bu<sub>2</sub>SnL which was five-coordinate with a distorted trigonal bipyramidal geometry around the tin atom.

Binuclear dioxomolybdenum(IV) complexes with dihydrazones of the type (LH<sub>4</sub>) {where LH<sub>4</sub> = [HOC<sub>6</sub>H<sub>3</sub>RCHN-N(H)-CO]<sub>2</sub>(CH<sub>2</sub>)<sub>n</sub> and n = 0, 1, 2, 4, 8; R = H or OCH<sub>3</sub>} are reported by Mahale et al<sup>14</sup>. The complexes studied are of the type (MoO<sub>2</sub>)<sub>2</sub>[(OC<sub>6</sub>H<sub>3</sub>RCHN-N(H)-

$\text{CO})_2(\text{CH}_2)_n](\text{Py})_2$  in which the ligand coordinates in the enol form, forming octahedral structures containing *cis*-dioxomolybdenum groups.

Mahale et al<sup>15</sup> have reacted titanil perchlorate and tin tetrachloride with dihydrazones ( $\text{H}_4\text{L}$ ) derived from dihydrazide of dicarboxylic acids and salicylaldehyde or 3-methoxy salicylaldehyde, in alcoholic medium and in presence of pyridine, to form the complexes  $(\text{TiO})_2(\text{L})(\text{Py})_2$  and  $\text{SnCl}_2(\text{LH}_2)(\text{Py})_2$ , respectively. The IR spectral studies show that the ligands react in the enol form. Thermal stabilities of complexes are also discussed. Conductivity measurements show that the complexes are non-electrolytes. A hexacoordinated polymeric structure is assigned to titanium(IV) complexes, whereas tin(IV) complexes are found to be mononuclear coordinating through two enolic oxygens, two nitrogens of pyridine and two chlorine atoms as shown in fig.



(where  $X = 0, 1, 2, 4, 8$ )

Reactions of disalicylaldehyde adipoyldihydrazone with uranyl acetate dehydrate and uranyl nitrate hexahydrate in aqueous and ethanolic media, under different experimental conditions, were

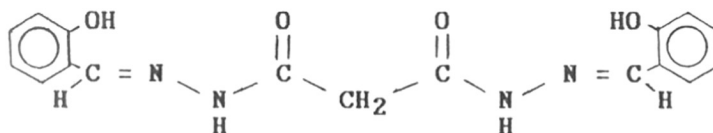
studied<sup>16</sup> and the resulting complexes  $[\text{UO}_2(\text{H}_2\text{L}_2)(\text{H}_2\text{O})]_n$ ,  $[\text{UO}_2(\text{H}_2\text{L}_2)]_3n\text{H}_2\text{O}$ , and their the oxalato and pyridine adducts such as  $[\text{UO}_2(\text{H}_2\text{L}_2)(\text{C}_2\text{O}_4)]_n 2n\text{H}_2\text{O}$  and  $[(\text{UO}_2)_2(\text{L}_2)(\text{Py})_2(\text{H}_2\text{O})_4]$  were characterized on the basis of their elemental analysis and thermoanalytical data. The structural assignment of the complexes was carried out by using molar conductance, magnetic moment and ESR, IR, electronic and  $^1\text{H}$  NMR spectroscopic studies. In these complexes, the ligand functions as a bridging monobasic tetradentate, dibasic hexadentate and tetradentate moiety and oxalate groups act as chelating bidentate and bridging tetradentate ligands. The nine and ten coordinated uranium atoms with ligand atoms arranged in the equatorial plane around the linear uranyl group and in the heterobimetallic complex as in  $[\text{UO}_2\text{Zn}(\text{L}_2)(\text{H}_2\text{O})_2]_2 2n\text{H}_2\text{O}$  have been reported. The zinc atom is considered to have tetrahedral stereochemistry.

Narang et al<sup>17</sup> have prepared polymeric complexes, of 2-hydroxy-1-naphthaldehyde oxaldihydrazone (HNODH), 2-hydroxy-1-naphthaldehyde malondihydrazone (HNMDH) with the empirical composition  $\text{M}(\text{L}-2\text{H}) \cdot n\text{H}_2\text{O}$  where  $\text{M} = \text{Fe}(\text{II}), \text{Mn}(\text{II}), \text{Co}(\text{II}), \text{Ni}(\text{II}), \text{Cu}(\text{II}), \text{Zn}(\text{II}), \text{Cd}(\text{II})$  and  $\text{Hg}(\text{II})$ ;  $\text{L} = \text{HNODH}$  and  $\text{HNMDH}$  and  $n = 0, 1, 2$ . The complexes, obtained were intensely coloured, insoluble in common organic solvents, and characterized by their elemental analysis, magnetic susceptibility, electronic and IR spectral data. The absence of anions indicated that the ligand binds the metal ions through deprotonated hydroxyl and the imino

groups. All the complexes are assigned to have octahedral, polymeric structures.

In the present chapter a detailed synthesis of organotin complexes of the (bis)salicylaldehyde malonoyldihydrazone [H<sub>4</sub>L] and their characterization by IR, NMR spectral studies is reported. X-ray structure analysis of the compound,  $[(\text{CH}_3\text{CH}_2)_2\text{Sn}]_2[\text{OC}_6\text{H}_4\text{CH}=\text{N}-\text{N}=\text{C}(\text{O})]_2\text{CH}_2$  is also given. The complexes are new and reported for the first time.

The structure of the ligand is given below:



## EXPERIMENTAL

The starting chemicals were of reagent or analytical grade. The solvents were dried and distilled before use. Infrared spectra were recorded in nujol mull, KBr pellets or as  $\text{CH}_2\text{Cl}_2$  solution on a Perkin-Elmer Model 1620 FT-IR spectrophotometer. The proton NMR spectra were recorded, using a Varian FT-80 A spectrometer and WH-90 spectrometer, in  $\text{CDCl}_3$  solution. The  $^{119}\text{Sn}$  NMR spectra were recorded on a Bruker MSL 300 spectrometer at 111.89 MHz. The  $^{119}\text{Sn}$  NMR spectra with complete proton noise decoupling were recorded in  $\text{CH}_2\text{Cl}_2$  solution at ambient



temperature. The chemical shifts were determined relative to tetramethyltin (negative signs indicate upfield shifts from  $\text{Me}_4\text{Sn}$  ( $\delta = 0$  ppm)). The ligand, (bis)salicylaldehyde malonoylhydrazone,  $[\text{HOC}_6\text{H}_4\text{CHN-NCO}]_2\text{CH}_2[\text{H}_4\text{L}]^{17}$  and the estertin,  $\text{Cl}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3)_2$ , were prepared according to methods reported in the literature<sup>18</sup>.

### X - R A Y D I F F R A C T I O N   A N A L Y S I S :

Crystals of the complex,  $[(\text{CH}_3\text{CH}_2)_2\text{Sn}]_2[\text{OC}_6\text{H}_4\text{CH=N-N=C(O)}]_2\text{CH}_2$ , were grown from benzene and a needle shaped yellow crystal of size  $0.08 \times 0.12 \times 0.80$  mm was used for intensity data collection on Enraf Nonius CAD-4F/11M single crystal X-ray diffractometer using MoK radiation ( $\lambda = 0.7107 \text{ \AA}$ ). Cell parameters were determined by least-squares refinement of 24 machine centered reflections within the range of  $28^\circ \leq 2\theta \leq 36^\circ$ . Reflections were measured with an index range of  $h$  0 to 13,  $k$  0 to 12 and  $l \pm 21$  using  $w/2\theta$  scan mode and with an average speed of  $1^\circ \text{ min}^{-1}$  at  $T = 293 \text{ K}$ . Out of 1975 unique reflections collected within a range of 0 to  $23.5^\circ$ , 1698 were treated as observed with  $I \geq 3\sigma(I)$  where  $\sigma(I)$  is the esd based on counting statistics and were used for structure determination and refinement of structural parameters. Corrections for  $L_p$  and absorption were made using NRCVAX programs<sup>19</sup>. Crystals belong to monoclinic space group

I2/a with  $a = 12.312(2)$ ,  $b = 11.526(2)$ ,  $c = 18.858(2)$  Å,  $\beta = 94.69(2)^\circ$ ,  $V = 2667.1(7)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.718$  g/cm<sup>3</sup>. The structure was solved by direct methods using MULTAN<sup>19</sup>. The two Sn atoms were located from an E-map. Remaining non-hydrogen atoms were obtained by subsequent difference fourier synthesis (H atoms obtained geometrically fixed and confirmed by a difference fourier were held during refinement). A full matrix refinement<sup>19</sup> of scale factor, positional and anisotropic thermal parameters for non hydrogen atoms converged to  $R = 0.042$  and  $R_w = 0.055$ . Weights based on counting statistics were used.

#### Preparation of H<sub>4</sub>L

The Schiff base was prepared by boiling a mixture of salicylaldehyde (2.44 g; 20 mmol) and malonoyl hydrazide (1.32 g; 10 mmol) dissolved in ethanol (50 ml) and refluxed for 4 h. The resulting yellow product was filtered, washed with ethanol and air dried. Yield 2.89 g (85%); m.p. 240<sup>o</sup>.

#### Preparation of [(CH<sub>3</sub>)<sub>2</sub>Sn]<sub>2</sub>(L) [61]

The Schiff base, (0.34 g; 1 mmol) was suspended in benzene (50 ml) and to it was added freshly prepared (CH<sub>3</sub>)<sub>2</sub>SnO (0.34 g; 2 mmol). The reaction mixture was heated to reflux and the water formed was removed azeotropically. The benzene solution upon concentration yielded a yellow crystalline solid which was washed with n-hexane and dried *in vacuo*. Yield 0.44 g (89%); m.p. 168<sup>o</sup>.

#### Preparation of [(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Sn]<sub>2</sub>(L) [62]

A solution of the ligand, H<sub>4</sub>L (0.34 g; 1 mmol), in benzene

(20ml) and  $(C_2H_5)_2SnCl_2$  (0.50 g; 2 mmol) were mixed together in presence of  $(C_2H_5)_3N$ , an HCl acceptor, (0.4 g; 4 mmol) and refluxed for 5 h. The precipitate,  $(C_2H_5)_3N.HCl$ , formed during the reaction was removed by filtration. The filtrate was concentrated to a small volume and cooled in ice-salt mixture. The precipitation of the product was effected by layering n-hexane over the cooled solution. The yellow crystalline solid separated was filtered, washed with n-hexane and dried in vacuo. Yield 0.50 g (72%); m.p.  $165^\circ$ .

#### Preparation of $[(C_4H_9)_2Sn]_2(L)$ [63]

A solution of  $(C_4H_9)_2SnO$  (0.5 g; 2 mmol) in benzene (10 ml) was mixed with benzene solution of the ligand, (bis)salicylaldehyde malonoylhydrazone, (25 ml) (0.34 g; 1 mmol) and refluxed for 8 h. The water formed during the reaction was collected azeotropically using a partial take-off condenser fitted to the flask. After the completion of the reaction, the benzene solution was concentrated to a small volume. The yellow crystals separated from the solution were washed with n-hexane and dried in vacuo; Yield 0.55 g (69%); m.p.  $98^\circ$ .

#### Preparation of $[(C_6H_5)_2Sn]_2(L)$ [64]

A 20 ml THF solution of  $(C_6H_5)_2SnCl_2$  (0.68 g; 2 mmol) was added with stirring to a benzene solution containing 1 mmol of the ligand. The reaction mixture was centrifuged, the precipitate was separated and filtrate was concentrated to a

small a volume and refrigerated for 24 hrs (temp.  $-8^{\circ}\text{C}$ ). The yellow crystals separated were washed with THF/n-hexane and dried *in vacuo*. Yield 0.62 g (70%); m.p.  $160^{\circ}$ .

#### Preparation of $[(\text{C}_6\text{H}_5\text{CH}_2)_2\text{Sn}]_2(\text{L})$ [65]

A mixture of  $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{SnCl}_2$  (0.74 g; 2 mmol), triethylamine (0.4 g; 4 mmol) and the ligand (0.34 g; 1 mmol) in 30 ml benzene and stirred vigorously for 1 h, the resulting turbid solution was centrifuged and the compound was isolated in a similar manner as described in 64. Yield 0.68 g (72%); m.p.  $150^{\circ}$ .

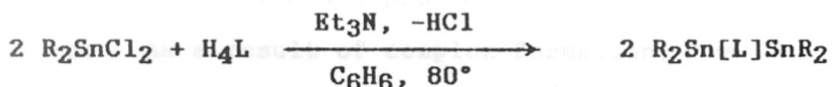
#### Preparation of $[(\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3)_2\text{Sn}]_2(\text{L})$ [66]

The estertin dichloride,  $\text{Cl}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3)_2$  (0.72 g; 2 mmol), triethylamine (0.4 g; 4 mmol) and the ligand, (bis)salicylaldehyde malonoyldihydrazone (0.34 g; 1 mmol) were mixed in benzene and refluxed for 4 h. The precipitated triethylamine hydrochloride was filtered off and the filtrate upon concentration *in vacuo*, gave yellow crystals. Yield 0.67 g (71%); m.p.  $102^{\circ}$ .

## RESULTS AND DISCUSSION

The Schiff base, (bis)salicylaldehyde malonoyldihydrazone ( $\text{H}_4\text{L}$ ), is an hexadentate ligand which functions as dibasic in the keto form and tetrabasic moiety in the enol form under suitable experimental conditions. The ligand forms binuclear diorganotin complexes by utilizing all the four hydroxyl groups during

complex formation. In the present study, the reaction of organotin chlorides with  $H_4L$  in 2:1 molar ratio in benzene medium using triethylamine as HCl acceptor, resulted in the formation of binuclear complexes of the type  $R_2Sn[L]SnR_2$  [where  $R=CH_3, C_2H_5, C_4H_9, C_6H_5, C_6H_5CH_2$  or  $CH_3COOCH_2CH_2$ ], with the replacement of all the four protons from the ligand.



The colour, melting point and elemental analyses are summarized in Table 5.1. The complexes are yellow solids and soluble in benzene and chloroform but insoluble in hexane. The results of the elemental analyses are consistent with the suggested formulae for the complexes.

#### IR spectral data of (bis)salicylaldehyde malonoylhydrazone and its organotin(IV) complexes:

The IR spectral data of Schiff base and the complexes are given in Table 5.2. The Schiff base,  $H_4L$ , does not show any band attributable to free phenolic  $\nu(OH)$  as it is strongly hydrogen bonded and might be overlapped with  $\nu(CH)$  vibrations and hence could not be assigned unequivocally. The medium bands due to  $\nu(NH)$  are seen at  $3279\text{ cm}^{-1}$  and  $\nu(C=N)$  at  $1608\text{ cm}^{-1}$ . The band at  $1673\text{ cm}^{-1}$  is assigned for  $\nu(C=O)$  (amide I). Amide II band is observed at  $1569\text{ cm}^{-1}$ . The phenolic  $\nu(C-O)$  is seen at  $1263\text{ cm}^{-1}$ .

The bands at 959 and 971  $\text{cm}^{-1}$  are attributed to N-N stretching vibrations.

The IR spectra of the complexes (61-66) do not show any band attributable to  $\nu(\text{OH})$  or  $\nu(\text{NH})$  indicating replacement of NH and OH protons by the metal. The amide I band at 1673  $\text{cm}^{-1}$  in the spectrum of the ligand, is absent in the spectra of complexes, suggesting enolization and proton replacement during the complex formation. As a result of complex formation, the IR spectra show two bands due to two non-identical  $\nu(\text{C}=\text{N})$  groups linked through N-N bond at  $\sim 1610$  and  $\sim 1540$   $\text{cm}^{-1}$  respectively, as compared to a single band at 1608  $\text{cm}^{-1}$  in the free Schiff base. The high frequency band is assigned to non-coordinated  $\nu(\text{C}=\text{N})$ , whereas the low frequency band to coordinated azomethine  $\nu(\text{C}=\text{N})$ . The shift of the azomethine  $\nu(\text{C}=\text{N})$ , to lower wavenumber is attributed to the partial double bond character of the  $\text{C}=\text{N}$  bond due to chelate formation. The phenolic  $\nu(\text{C}-\text{O})$  is observed at 1263  $\text{cm}^{-1}$  in the free ligand which is shifted to  $\sim 1300$   $\text{cm}^{-1}$  in complexes indicating Sn-O-C bond formation via deprotonation of the phenolic  $\nu(\text{OH})$ . The  $\nu(\text{N}-\text{N})$  modes are shifted to higher wavenumbers and appear at  $\sim 975$  and 990  $\text{cm}^{-1}$  due to increased N-N bond order in the chelated structure<sup>20</sup>. The far IR spectrum of the complex  $[(\text{CH}_3)_2\text{Sn}]_2(\text{L})$  display bands at 544 and 477  $\text{cm}^{-1}$  which may be assigned to *cis* (Sn-CH<sub>3</sub>)<sub>2</sub> methyl groups. The  $\nu(\text{Sn}-\text{O})$  is seen at 451  $\text{cm}^{-1}$ . The IR spectra of  $\text{Cl}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3)_2$  exhibits intramolecular coordinated carbonyl band at 1672  $\text{cm}^{-1}$ .

Complex 66 shows two strong bands at 1731 and 1714  $\text{cm}^{-1}$  due to  $\nu(\text{C}=\text{O})$ , which suggests coordinated and free ester groupings. The  $\nu(\text{C}-\text{OR})$  frequency found at  $\sim 1220 \text{ cm}^{-1}$  in estertin<sup>21</sup> is observed as a split band at 1260 and 1213  $\text{cm}^{-1}$ . The low-frequency shift could be due to the non-involvement of one of the ester groups in coordination to tin to give a  $-\text{C}=\text{O} \rightarrow \text{Sn}$  band.

**<sup>1</sup>H NMR spectral data of (bis)salicylaldehyde malonoylhydrazone and its organotin(IV) complexes:**

The <sup>1</sup>H NMR spectral data of the Schiff base and complexes are given in Table 5.3. Due to poor solubility of the ligand in  $\text{CDCl}_3$ , its NMR spectrum was recorded in  $\text{DMSO}-d_6$ . The signal at 3.23 ppm was assigned to  $\text{CH}_2$  protons. The aromatic protons resonate between 6.53 and 7.58 ppm as a cluster of signals. The two sharp signals observed at 8.19 and 8.33 ppm are due to azomethine protons suggesting magnetic non-equivalence of both  $\text{HC}=\text{N}$  groups. The four signals at 9.9, 10.95 and 11.33, 11.70 ppm are due to NH and OH protons respectively, which disappear on  $\text{D}_2\text{O}$  exchange. Hence the doublets due to  $\text{CH}(\text{azomethine})$ , NH and OH may suggest the non-equivalence of the two halves of the Schiff base.

The <sup>1</sup>H NMR spectra of the complexes in  $\text{CDCl}_3$  do not show signals due to OH and NH protons, suggesting deprotonation followed by complex formation. The azomethine proton suffers deshielding and appears as a singlet at  $\sim 8.5$  ppm. This suggests

coordination of azomethine nitrogen to tin. The resonance due to  $\text{CH}_2$  protons is observed at  $\sim 3.3$  ppm. In  $[(\text{CH}_3)_2\text{Sn}]_2(\text{L})$  complex the methyl group bonded to tin appears as a sharp singlet at 0.78 ppm. The two satellite signals observed on either side of this methyl signal are due to the coupling of  $^{117}\text{Sn}$  and  $^{119}\text{Sn}$  nuclei with the methyl protons, the coupling constants being  $^2J(^{117}\text{Sn}, ^1\text{H})$  72 Hz and  $^2J(^{119}\text{Sn}, ^1\text{H})$  76 Hz. This increase in coupling constants compared to those in  $\text{Me}_2\text{SnCl}_2$  [ $^2J(^{117}\text{Sn}, ^1\text{H}) = 66$  Hz;  $^2J(^{119}\text{Sn}, ^1\text{H}) = 70$  Hz] is suggested to be due to increase in the coordination number of tin as a result of complex formation<sup>22</sup>. Further, satellite signals are also observed for azomethine CH proton with coupling constants of  $^3J(^{119}\text{Sn}, ^1\text{H}) = 46$  Hz which confirms the proposed mode of bonding to tin. In the case of diethyltin chelate a multiplet due to ethyl group is observed between 0.92 and 2.03 ppm, and the dibutyltin chelate shows a multiplet between 0.87 and 1.61 ppm due to butyl group.

$^1\text{H}$  NMR spectra of  $\text{Cl}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3)_2$  shows two triplets centered at 1.9 and 2.9 ppm due to  $\alpha\text{-CH}_2$  and  $\beta\text{-CH}_2$  respectively. These resonances are shifted to higher magnetic field and are seen at 1.69 and 2.77 ppm in complex 66. The shielding may be attributed to the replacement of electronegative chlorine atom by the donor atoms oxygen and nitrogen.

$^{119}\text{Sn}$  NMR spectral data of (bis)salicylaldehyde malonoylhydrazone organotin(IV) complexes:

The tin chemical shift, ( $^{119}\text{Sn}$ ), values of the complexes



$[(\text{CH}_3)_2\text{Sn}]_2(\text{L})$ ,  $[(\text{C}_2\text{H}_5)_2\text{Sn}]_2(\text{L})$ ,  $[(\text{C}_4\text{H}_9)_2\text{Sn}]_2(\text{L})$ , and  $[(\text{C}_6\text{H}_5\text{CH}_2)_2\text{Sn}]_2(\text{L})$ , observed are at -152.40, -160.51, -189.44, and -336.30 ppm respectively. These  $\delta(^{119}\text{Sn})$  values fall in the range of five-coordinate tin(IV) compounds<sup>23</sup>. As the carbon number of the alkyl group attached to tin increases an upfield shift of  $^{119}\text{Sn}$  resonances has been noticed. Otera<sup>23</sup> has observed similar upfield shift for tin resonances for pentacoordinated and hexacoordinated organotin(IV) complexes containing different alkyl groups. The  $\delta(^{119}\text{Sn})$  value observed for  $[(\text{CH}_3)_2\text{Sn}]_2(\text{L})$  at -152.40 ppm is consistent with the reported  $\delta(^{119}\text{Sn})$  value for the well characterized pentacoordinated complex  $\text{Me}_2\text{Sn}(\text{SAB})$ <sup>23</sup>.

The above data suggest the structure of the binuclear diorganotin(IV) complexes as shown below in fig. 5.1.

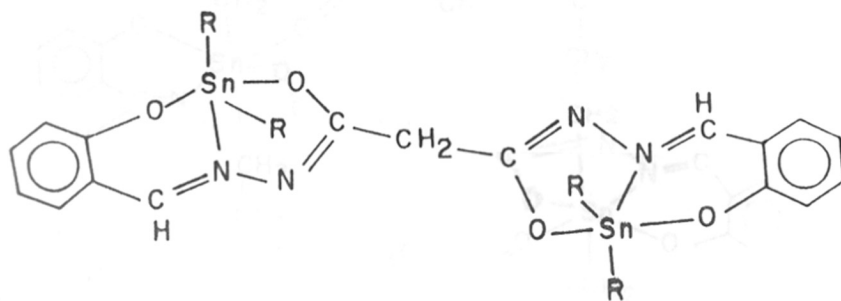


FIG. 5.1

The ( $^{119}\text{Sn}$ ) resonance for the complex,  $[(\text{C}_6\text{H}_5)_2\text{Sn}]_2(\text{L})$ , is at  $-324.72$  ppm. Replacement of methyl groups by phenyl groups, in general, results in an upfield shift of  $\delta(^{119}\text{Sn})$  which is comparable with the shift observed between  $\text{Me}_2\text{SnCl}_2$  and  $\text{Ph}_2\text{SnCl}_2$ <sup>24</sup>.

The estertin complex,  $[(\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3)_2\text{Sn}]_2(\text{L})$ , shows the  $^{119}\text{Sn}$  chemical shift value at  $-246.30$  ppm. The observed large shielding has been attributed to the increased coordination number of tin as a result of ester carbonyl coordination.

All these spectral data are consistent with a distorted octahedral geometry for complex 66 with *trans* ester groupings. The structure of complex 66 is shown below in fig. 5.2.

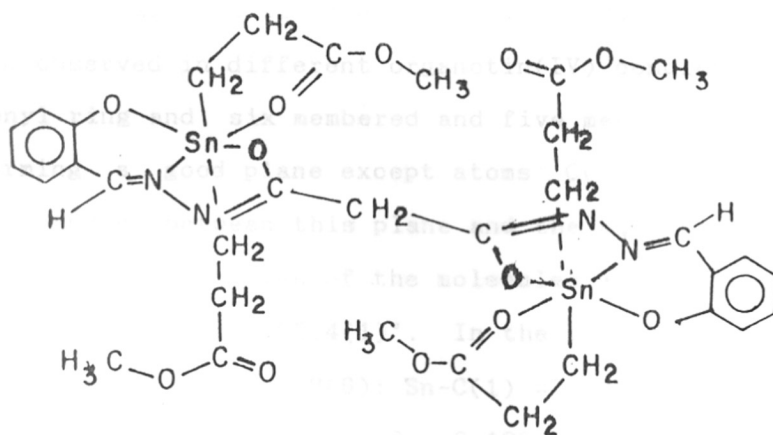


FIG. 5.2

**X-ray crystal data of the complex  $[\text{CH}_3\text{CH}_2)_2\text{Sn}]_2[\text{OC}_6\text{H}_5\text{CH}=\text{N}-\text{N}=\text{C}(\text{O})]_2\text{CH}_2$ :**

Fig. 5.3 gives the perspective view of the molecule along with the crystallographic numbering of atoms. The atomic parameters along with their esd's and equivalent isotropic thermal parameters for non hydrogen atoms are given in Table 5.4. Table 5.5 gives the bond lengths and angles.

Half of the molecule is bridged to the other half by twofold symmetry via C(13) atom which lies on the two fold axis. The tin atom has distorted trigonal bipyramidal coordination with two oxygen atoms occupying axial positions. The tin atom is displaced by  $0.053(5)\text{\AA}$  from the equatorial plane defined by two carbon atoms of ethyl groups and azomethine nitrogen while O(1) [2.041(7)] and O(2) [2.121(8)] are displaced on either side of the plane. Similar distorted trigonal bipyramidal coordination has been observed in different organotin(IV) complexes<sup>19, 25-30</sup>. The phenyl ring and six membered and five membered chelate rings are forming a good plane except atoms C(12) and O(2). The dihedral angle between this plane and the equatorial plane is  $86.7(2)^\circ$ . The two halves of the molecules are inclined to each other at an angle of  $105.4(1)^\circ$ . In the present study Sn-N = 2.206(6); Sn-O(1) = 2.098(6); Sn-C(1) = 2.102(8) and Sn-C(3) = 2.119(8) $\text{\AA}$  are short while Sn-O = 2.193(6) $\text{\AA}$  fall in the middle range<sup>19,25-30</sup>.

There are no intermolecular contacts less than  $3.4\text{\AA}$  showing that the molecules are packed by Van der Waals interactions in the crystal.

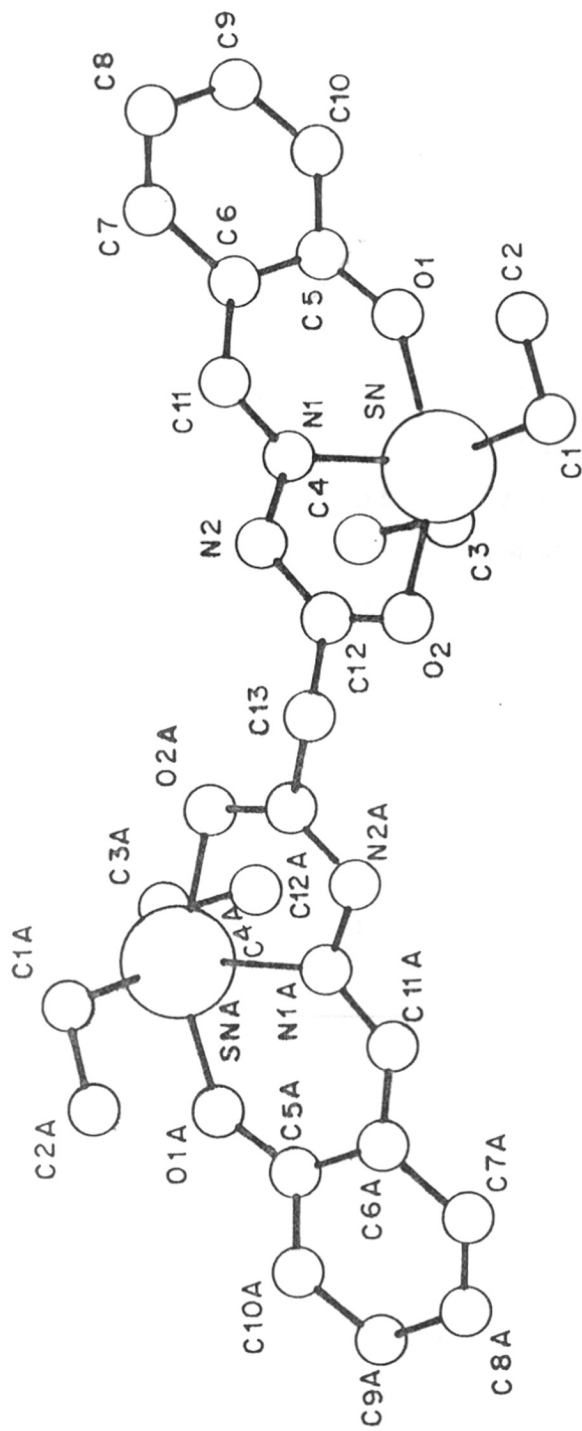


FIG. 5.3 : X-RAY CRYSTAL STRUCTURE OF  $[(CH_3CH_2)_2Sn]_2[OC_6H_4CH=N-N=C(O)]_2CH_2$ .

Table 5.1. Analytical data for organotin(IV) complexes of  
(bis)salicylaldehyde malonoylhydrazone.

no	Compound	Colour	m.p.	Elemental analysis (%) Found (Calcd.)			
				Sn	C	H	N
61	$[(CH_3)_2Sn]_2(L)$ $Sn_2C_{21}H_{24}N_4O_4$	Yellow	168	37.29 (37.45)	39.81 (39.79)	3.68 (3.82)	8.90 (8.84)
62	$[(C_2H_5)_2Sn]_2(L)$ $Sn_2C_{25}H_{32}N_4O_4$	"	165	34.25 (34.41)	43.41 (43.52)	4.70 (4.68)	8.01 (8.12)
63	$[(C_4H_9)_2Sn]_2(L)$ $Sn_2C_{33}H_{48}N_4O_4$	"	98	29.45 (29.59)	49.33 (49.41)	5.87 (6.03)	7.00 (6.98)
64	$[(C_6H_5)_2Sn]_2(L)$ $Sn_2C_{41}H_{32}N_4O_4$	"	160	26.75 (26.91)	55.66 (55.82)	3.71 (3.66)	6.21 (6.35)
65	$[(C_6H_5CH_2)_2Sn]_2(L)$ $Sn_2C_{45}H_{40}N_4O_4$	"	150	25.25 (25.30)	57.44 (57.61)	3.41 (4.30)	5.89 (5.97)
66	$[(CH_2CH_2CO_2CH_3)_2Sn]_2(L)$ $Sn_2C_{33}H_{40}N_4O_{12}$	"	102	25.66 (25.74)	42.85 (42.98)	4.27 (4.37)	5.89 (6.08)

Table 5.2. IR spectral bands of (bis)salicylaldehyde malonoylhydrazone and its organotin(IV) complexes. ( $\nu$ ,  $\text{cm}^{-1}$ )

No.	NH	(C=O) (amide-I)	(C=N)	Amide II + (C-O)(L)	(C-O)(L)	(N-N)
H <sub>4</sub> L	3279s, 3189w	1673	1608	1569	1263	959,971
61	-	-	1613,1542	1532	1308	980,998
62	-	-	1611,1538	1526	1312	975,997
63	-	-	1607,1541	1524	1297	963,984,1001
64	-	-	1608,1543	1530	1298	970,996
65	-	-	1609,1542	1523	1297	970,1000
66	-	-	1608,1538	1526	1300	970,1006

Ester C=O of complex 66 = 1731,1714

Ester C-O of complex 66 = 1260,1213

Table 5.3.  $^1\text{H}$  and  $^{119}\text{Sn}$  NMR spectral data for (bis)salicylaldehyde malonoylhydrazone and its organotin(IV) complexes. ( $\delta$ , ppm)

ligand/ Complex	Aliphatic	CH	CH <sub>2</sub>	NH	OH	Aromatic protons	$\delta(^{119}\text{Sn})$
H <sub>4</sub> L	-	8.19, 8.33	3.23	10.95	11.70	6.53-7.58	-
61	0.78	8.57	3.30	-	-	6.60-7.37	-152.40
62	0.92-2.03	8.52	3.28	-	-	6.52-7.32	-160.51
63	0.87-1.61	8.56	3.31	-	-	6.57-7.36	-189.44
64	-	8.45	3.30	-	-	6.66-8.02	-324.72
65	-	8.51	3.38	-	-	6.73-7.62	-336.30
66	-	8.53	3.35	-	-	6.65-7.40	-246.30

Complex 61;  $^2\text{J}(^{117}\text{Sn}, ^1\text{H}) [\text{Sn}(\text{CH}_3)_2] = 72 \text{ Hz}$

$^2\text{J}(^{119}\text{Sn}, ^1\text{H}) [\text{Sn}(\text{CH}_3)_2] = 76 \text{ Hz}$

$^3\text{J}(^{119}\text{Sn}, ^1\text{H}) [\text{CH}] = 46 \text{ Hz}$

Complex 66.  $\alpha\text{-CH}_2 = 1.69 \text{ ppm}$

$\beta\text{-CH}_2 = 2.77 \text{ ppm}$

$\text{OCH}_3$  (ester) = 3.68 ppm

Table 5.4 Atomic Parameters x,y,z and Biso  
for non-H atoms.  
E.S.Ds. refer to the last digit printed.

Atom	x	y	z	Biso( $\text{\AA}^2$ )
SN	.51054( 4)	.02213( 5)	.37602( 3)	3.83( 3)
O 1	.4790( 5)	.0772( 5)	.2703( 3)	5.5( 3)
O 2	.6141( 4)	-.0529( 5)	.4645( 3)	4.1( 2)
N 1	.6464( 5)	-.0703( 5)	.3315( 3)	3.6( 3)
N 2	.7128( 4)	-.1380( 5)	.3789( 3)	3.6( 3)
C 1	.3869( 6)	-.1059( 7)	.3746( 4)	3.9( 4)
C 2	.3626( 7)	-.1595( 8)	.3022( 5)	5.7( 5)
C 3	.5283( 7)	.1933( 8)	.4136( 5)	5.3( 4)
C 4	.6177(10)	.2590(10)	.4011( 7)	10.8( 9)
C 5	.5216( 7)	.0556( 7)	.2118( 4)	4.2( 4)
C 6	.6145( 7)	-.0146( 7)	.2066( 4)	4.1( 4)
C 7	.6591( 7)	-.0294( 9)	.1402( 4)	5.6( 5)
C 8	.6139( 9)	.0225(10)	.0804( 5)	6.3( 5)
C 9	.5216( 9)	.0901( 9)	.0844( 5)	6.1( 5)
C10	.4763( 7)	.1068( 8)	.1483( 5)	5.0( 4)
C11	.6705( 6)	-.0742( 7)	.2666( 4)	4.2( 4)
C12	.6883( 5)	-.1223( 7)	.4438( 4)	3.4( 3)
C13	.7500( 0)	-.1954( 9)	.5000( 0)	3.4( 5)



TABLE 5. BOND DISTANCES (Å) AND BOND ANGLES (°) WITH  
 E.S.D.'S IN PARENTHESES

SN --O 1	2.098( 6)		
SN --O 2	2.193( 6)		
SN --N 1	2.206( 6)		
SN --C 1	2.119( 8)		
SN --C 3	2.102( 9)		
		O 1 --SN --O 2	153.3( 2)
		O 1 --SN --N 1	82.6( 2)
		O 1 --SN --C 1	97.0( 3)
		O 1 --SN --C 3	92.4( 3)
		O 2 --SN --N 1	71.8( 2)
		O 2 --SN --C 1	96.2( 3)
		O 2 --SN --C 3	94.3( 3)
		N 1 --SN --C 1	103.0( 3)
		N 1 --SN --C 3	121.4( 3)
		C 1 --SN --C 3	135.5( 3)
O 1 --C 5	1.284(10)		
O 2 --C12	1.298( 9)	SN --O 1 --C 5	134.5( 5)
N 1 --N 2	1.399( 8)	SN --O 2 --C12	113.2( 5)
N 1 --C11	1.283( 9)		
		SN --N 1 --N 2	116.6( 4)
		SN --N 1 --C11	128.4( 5)
		N 2 --N 1 --C11	114.9( 6)
N 2 --C12	1.297( 9)		
C 1 --C 2	1.506(12)	N 1 --N 2 --C12	110.9( 6)
C 3 --C 4	1.372(15)	SN --C 1 --C 2	112.7( 5)
C 5 --C 6	1.411(12)		
C 5 --C10	1.409(12)	SN --C 3 --C 4	121.5( 8)
		O 1 --C 5 --C 6	124.1( 7)
		O 1 --C 5 --C10	119.2( 7)
		C 6 --C 5 --C10	116.6( 7)
C 6 --C 7	1.418(11)		
C 6 --C11	1.449(11)	C 5 --C 6 --C 7	120.3( 7)
		C 5 --C 6 --C11	123.7( 7)
		C 7 --C 6 --C11	116.0( 7)
C 7 --C 8	1.355(13)		
C 8 --C 9	1.385(16)	C 6 --C 7 --C 8	121.3( 9)
C 9 --C10	1.382(13)		
		C 7 --C 8 --C 9	119.1(10)
		C 8 --C 9 --C10	121.1( 9)
		C 5 --C10 --C 9	121.5( 8)
		N 1 --C11 --C 6	126.6( 7)
C12 --C13	1.509( 9)		
		O 2 --C12 --N 2	126.4( 7)
		O 2 --C12 --C13	117.3( 6)
		N 2 --C12 --C13	116.2( 6)

Table for deposition  
Atomic Parameters x,y,z and Biso.  
for hydrogen atoms.

	x	y	z	Biso
H 1A	.317	-.070	.391	4.7
H 1B	.409	-.170	.410	4.7
H 2C	.303	-.220	.302	6.2
H 2A	.337	-.098	.266	6.2
H 2B	.429	-.198	.285	6.2
H 3A	.520	.193	.468	5.8
H 3B	.463	.241	.392	5.8
H 4C	.620	.337	.424	10.1
H 4A	.688	.215	.426	10.1
H 4B	.631	.264	.351	10.1
H 7	.727	-.080	.137	6.4
H 8	.647	.012	.032	6.7
H 9	.486	.127	.039	6.6
H10	.407	.157	.150	5.8
H11	.736	-.125	.255	5.0
H13	.697	-.249	.523	3.3

Table for deposition  
Anisotropic thermal parameters for non-H atoms of C25H32N4O4Sn2

Atom	u11	u22	u33	u12	u13	u23
SN	4.33( 4)	5.15( 4)	4.78( 3)	-.06( 3)	-1.31( 2)	-.09( 3)
O 1	7.6( 4)	8.4( 5)	4.8( 4)	2.1( 4)	-.7( 3)	1.3( 3)
O 2	3.7( 3)	7.4( 4)	4.2( 3)	1.0( 3)	-1.2( 2)	.1( 3)
N 1	3.8( 4)	5.9( 4)	3.9( 4)	-.9( 3)	-.7( 3)	-.3( 3)
N 2	3.2( 3)	6.4( 5)	3.8( 4)	.0( 3)	-1.1( 3)	.7( 3)
C 1	3.4( 4)	4.8( 5)	6.4( 5)	.0( 4)	-.8( 4)	-1.1( 4)
C 2	5.6( 6)	7.4( 6)	8.0( 7)	.1( 5)	-2.8( 5)	-1.4( 5)
C 3	5.7( 6)	7.2( 7)	7.2( 6)	-1.4( 5)	.9( 5)	-.8( 5)
C 4	13.6(11)	9.7(10)	18.6(14)	-3.9( 9)	7.8(11)	-5.3( 9)
C 5	5.4( 5)	5.6( 6)	4.7( 5)	-1.2( 4)	-1.3( 4)	.8( 4)
C 6	5.2( 5)	6.4( 6)	3.9( 4)	-1.5( 4)	-1.2( 4)	.3( 4)
C 7	5.8( 6)	10.7( 8)	4.8( 5)	-.9( 6)	-.5( 4)	.6( 5)
C 8	8.0( 7)	11.4( 9)	4.3( 5)	-2.2( 7)	-.1( 5)	1.3( 6)
C 9	9.7( 8)	7.6( 7)	5.3( 6)	-2.5( 6)	-3.2( 6)	1.8( 5)
C10	6.2( 6)	6.7( 6)	5.6( 6)	-1.0( 5)	-1.5( 5)	1.7( 5)
C11	4.3( 5)	6.7( 6)	4.7( 5)	-.8( 4)	-.7( 4)	-.6( 4)
C12	2.6( 4)	5.4( 5)	4.7( 5)	-1.0( 4)	-1.3( 4)	.0( 4)
C13	2.8( 6)	6.1( 8)	3.7( 6)	.0( 0)	-.5( 5)	.0( 0)

Temp=-2(Pi)\*\*2(u11\*h\*h\*astar\*astar+---+2\*u12\*h\*k\*astar\*bstar+---)

The uij values have been multiplied by 100.

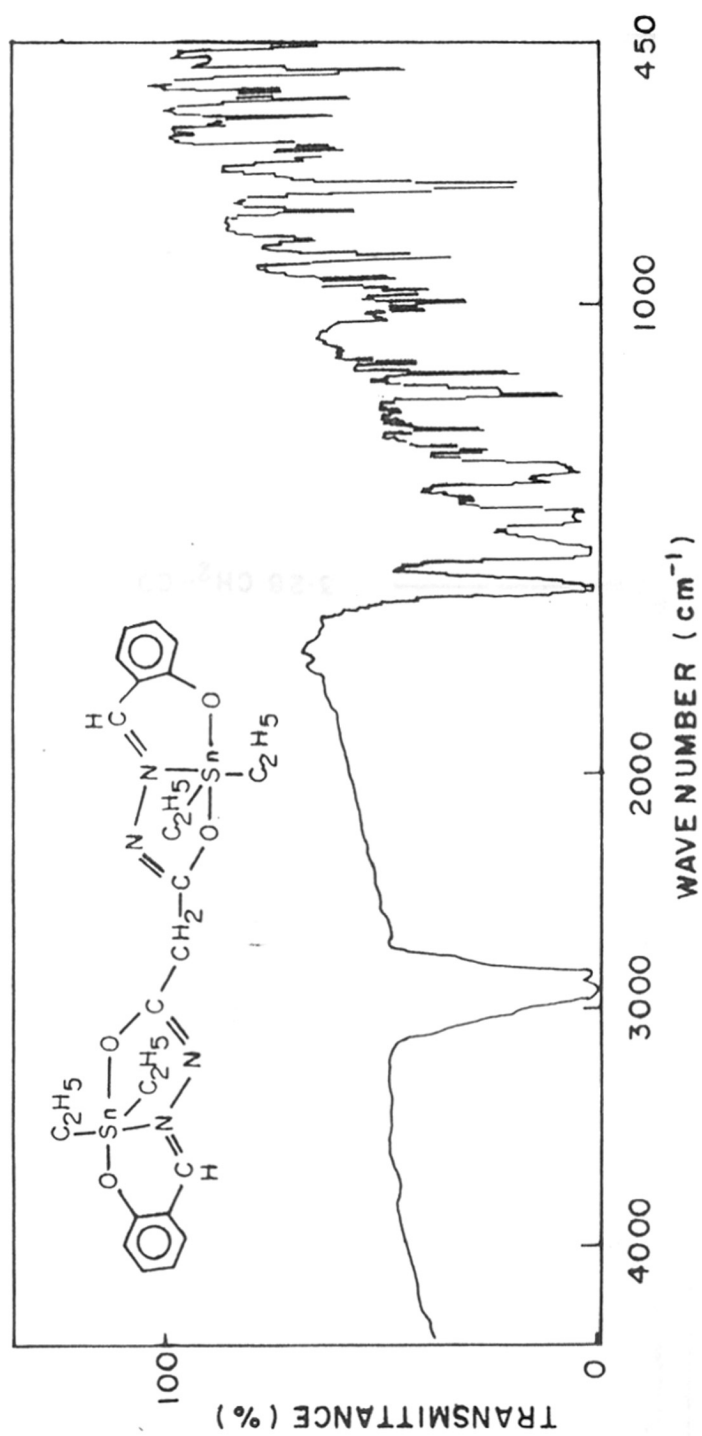


FIG. 5.4 : IR SPECTRUM OF  $[(C_2H_5)_2Sn]_2(L)$  IN NUJOL.



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## CHAPTER 6

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**MASS SPECTRAL STUDIES OF SCHIFF BASES AND THEIR ORGANOTIN(IV)  
COMPLEXES.**

A number of metal coordination compounds of Schiff bases have been suggested as models to describe the energy transfer in biological systems<sup>1</sup>. Some papers<sup>2,3</sup> have appeared revealing the influence of Schiff base donor atoms on the ionization potential and mass spectral fragmentation. However, the fragmentation patterns of Schiff base metal complexes are still very scanty<sup>4-7</sup>.

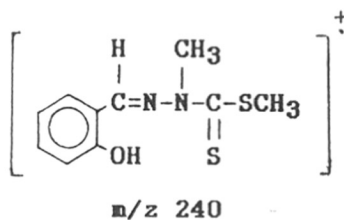
Saxena et al<sup>8</sup> have carried out electron impact induced fragmentation studies on some diorganotin complexes of the type  $Bu_2SnL$  (where L is the anion having donor system  $O \overset{\curvearrowright}{N} \overset{\curvearrowright}{S}$  such as salicylaldehyde-thiosemicarbazone or salicylaldehyde-S-benzylthiocarbamate). Tandon et al<sup>9</sup> have studied mass spectral fragmentation pattern of pentacoordinated dibutyltin(IV) dithiocarbamate complexes of the type  $n-Bu_2SnL$  (where L = dianion of S-methyl- $\beta$ -N-(2-hydroxyphenyl)methylene and methyl dithiocarbamate). Further, they have reported mass spectral features of dibutyltin(IV) complexes of semi- and thiosemicarbazones<sup>10</sup>. Marcel et al<sup>11</sup> have prepared dibutyl/diphenyl tin(IV) derivatives of 2,6-pyridinecarboxylic acid and their mass spectral studies have been reported. Dimethyltin(IV) complexes with N-salicylidene derivatives of aroyhydrazines, 5-methylhydrazinecarbodithioate and 4-substituted thiosemicarbazides have been prepared and their mass spectra have reported by Iskander et al<sup>12</sup>. The mass spectral studies on

chelated diphenyltin(IV) complexes of the type  $\text{Ph}_2\text{SnL}$ , where L is  $\text{RC}_6\text{H}_4\text{C}(\text{CO})\text{N}_2\text{CHC}_6\text{H}_4\text{O}$  with R = H, p- $\text{NO}_2$ , p-Cl, p-Br, p- $\text{CH}_3$ , o- $\text{OCH}_3$ , o- $\text{NH}_2$ , m- $\text{NO}_2$ , m- $\text{OCH}_3$  and 3,5-dinitro, have been reported by Jitao et al<sup>13</sup>.

In this chapter, we report for the first time the mass spectral fragmentation of some of the Schiff bases prepared by us and their organotin(IV) complexes.

1. **S-Methyl-N-methyl- $\beta$ -N-(2-hydroxyphenyl)methylendithiocarbazate (HSMNMSaD)**

The mass spectrum of the Schiff base shows strong molecular ion peak at m/z 240 (95%). Loss of  $\text{SCH}_3$  from the molecular ion produces a small but significant peak at m/z 193 (3%). Simple cleavage of N-N bond of the molecular ion gives rise the base peak at m/z 120 (100%), which could be a doublet due to two different structures A and B as shown in fig. 1. The fragment B with elimination of  $\text{NCH}_3$ , gives the peak at m/z 91.



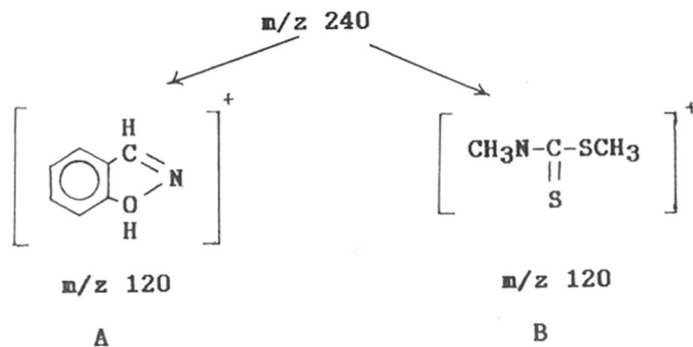
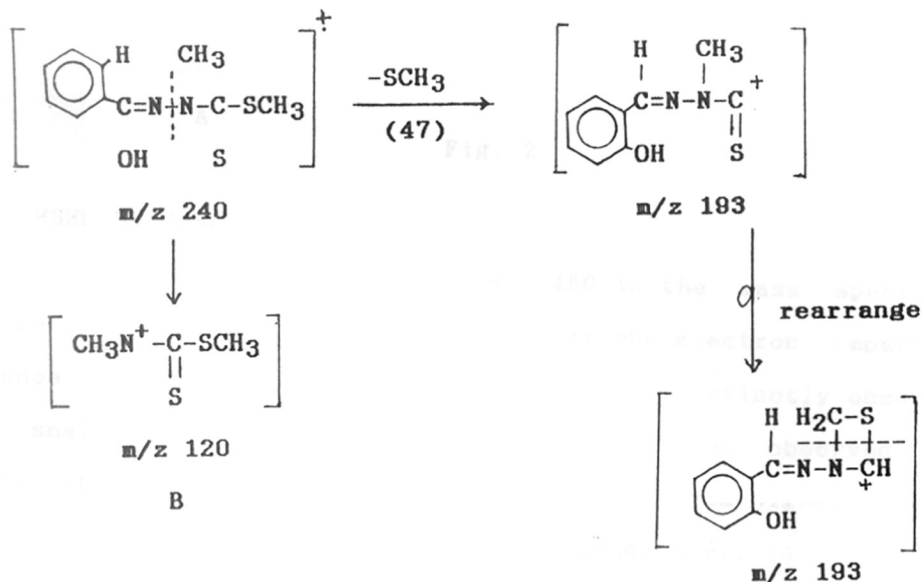


Fig. 1

The another path of fragmentation mode is as shown in fig. 2, in which the fragment at m/z 193 rearranges before it loses the neutral molecule  $\text{H}_2\text{C}=\text{S}$  giving the peak at m/z 147, which in its turn loses another neutral molecule  $\text{HCN}$ , giving the peak at m/z 120. The fragmentation pattern is as given below:



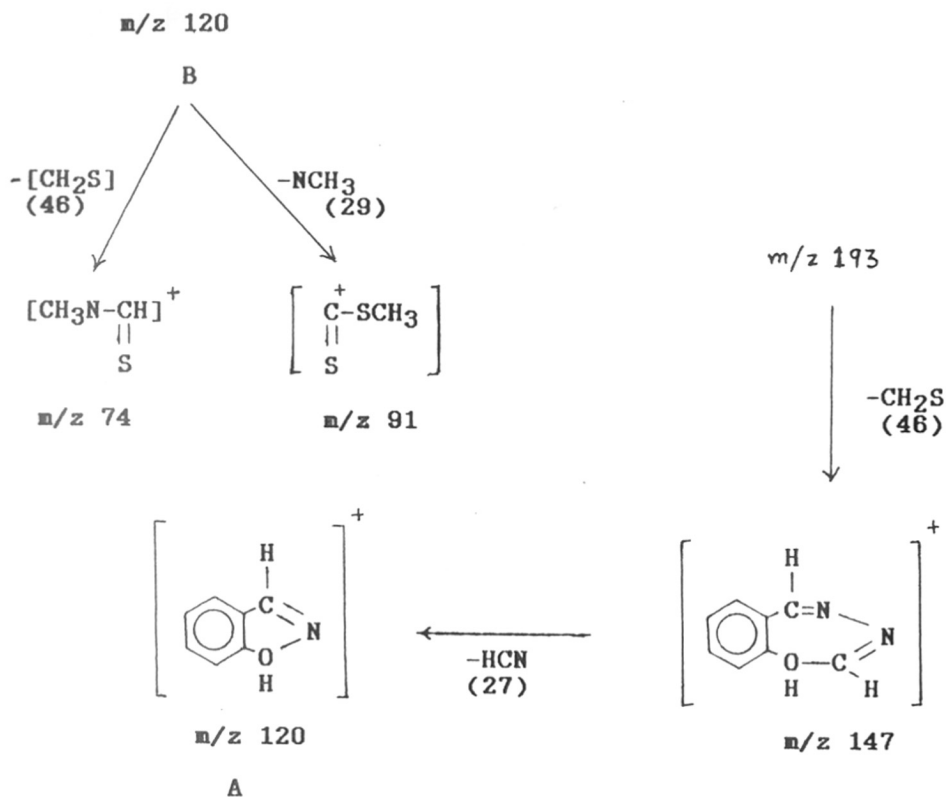


Fig. 2

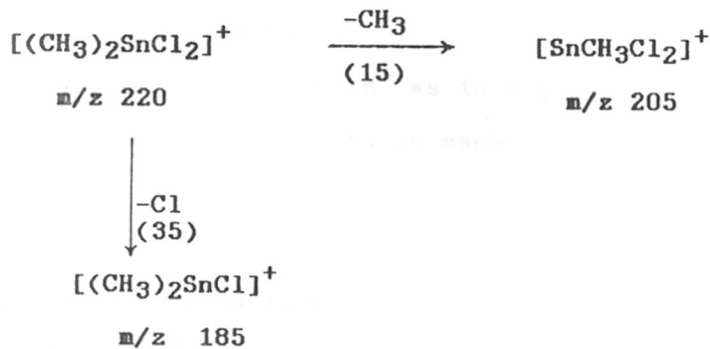
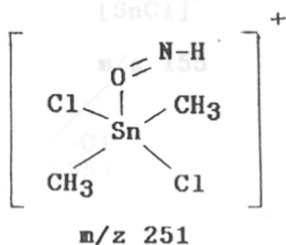
## 2. HSMNMSa.Me<sub>2</sub>SnCl<sub>2</sub>

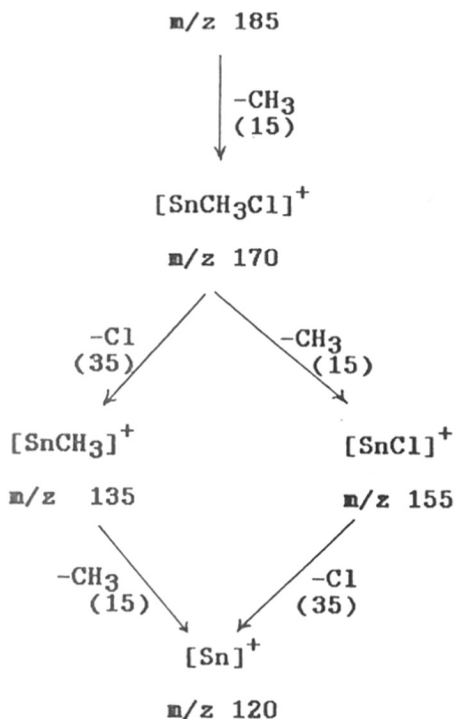
The molecular ion  $M^+$  at  $m/z$  460 in the mass spectrum is absent due to its less stability under the electron impact and hence only the mass spectrum of  $\text{Me}_2\text{SnCl}_2$  is distinctly observable. A small peak at  $m/z$  251 (about 2.5%) is also observed which indicates that this fragment ion is formed from higher fragment or from  $M^+$  ion of tin complex with ligand. i.e.,  $[460 M^+]$ . The formation of the complex is also well supported by IR and NMR

data.

The mass spectrum of  $\text{Me}_2\text{SnCl}_2$  fragment which is obtained from the  $\text{M}^+$  ion, indicates all the characteristics of Sn-atom isotopes peaks and as well as the chlorine pattern wherever Cl-atom/atoms involved. The degradation of  $[\text{Me}_2\text{SnCl}_2]^+$  is as shown below.

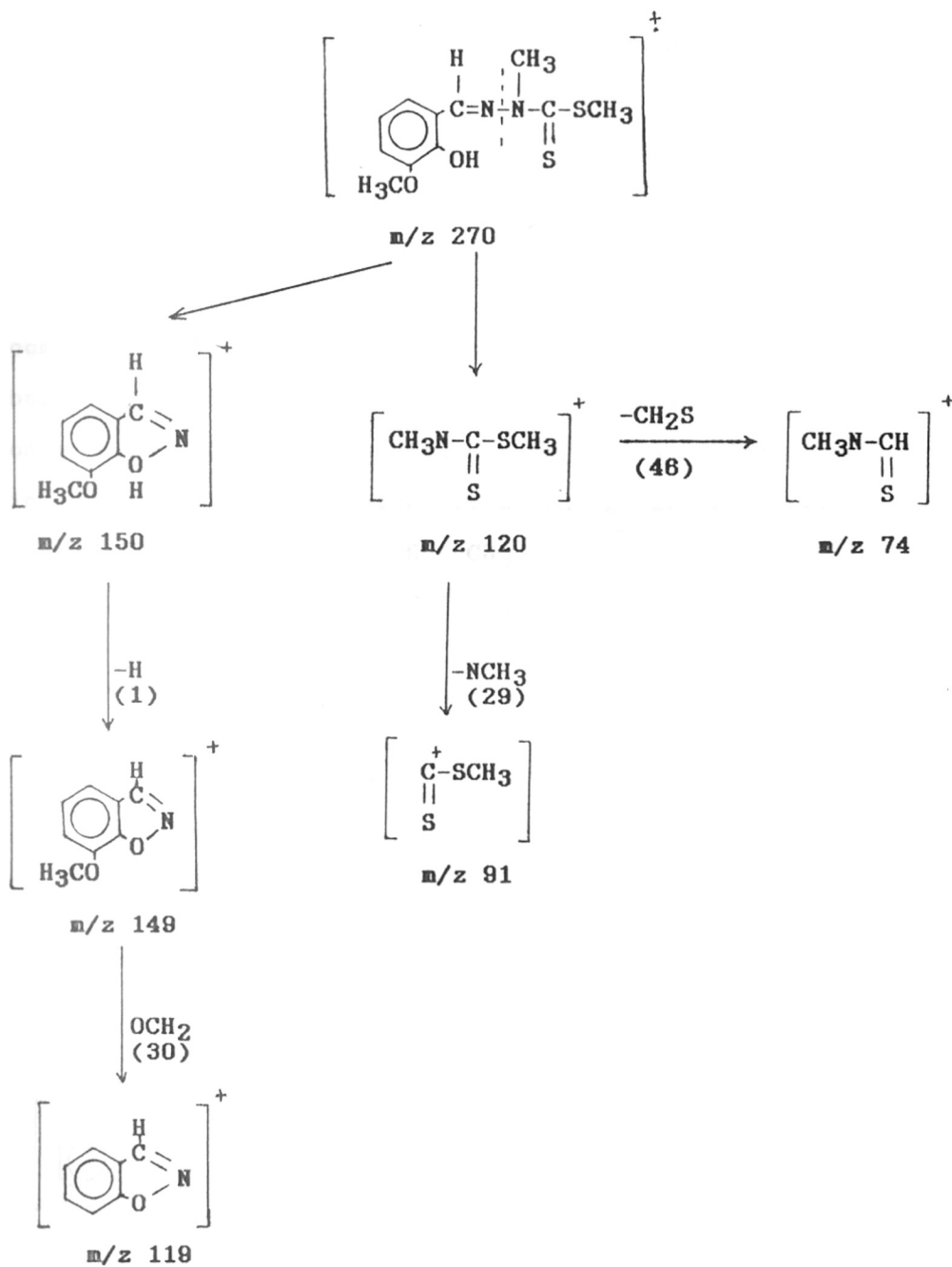
The probable structure for the peak at  $m/z$  251 may be shown as following fig below.





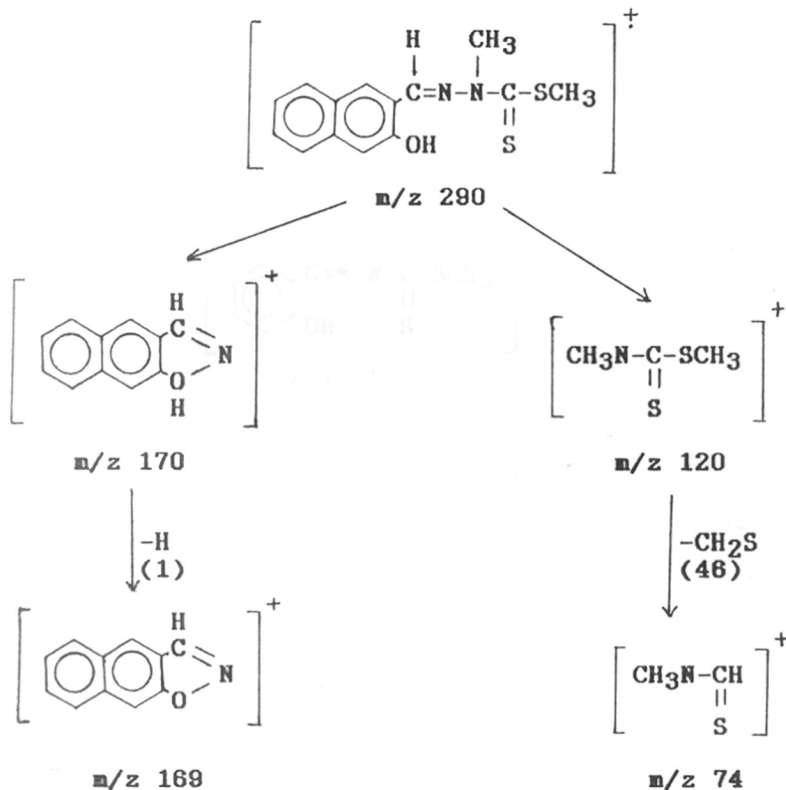
3. S-methyl-N-methyl-β-N-(2-hydroxy-3-methoxyphenyl)methylenedithiocarbamate (HSMNMVD)

Similar fragmentation pattern as in compound 1, is observed with an increase of 30 mass units in each fragment due to OCH<sub>3</sub> substituent. The striking difference is the loss of a proton from the fragment ion at m/z 150 giving the peak at m/z 149 while the fragment at m/z 120 of unsubstituted compound (No. 1) which corresponds to m/z 150, does show loss of proton but of much smaller intensity.



4. S-methyl-N-methyl-β-N-(2-hydroxy-1-naphthaldehyde)methylen  
dithiocarbamate (HSMNMND)

The expected α-cleavage to C=N operating between N-N bond gives two fragments with m/z 120 and m/z 170. Further fragmentation of the latter is quite interesting as it loses a proton, a behaviour similar to the fragment ion at m/z 150 of the complex in which OCH<sub>3</sub> is substituted on phenyl ring of Schiff base in ortho position to OH group. It means the substitutions on phenyl ring in two complexes have the same electron movements in removing the proton from OH group of Schiff base.



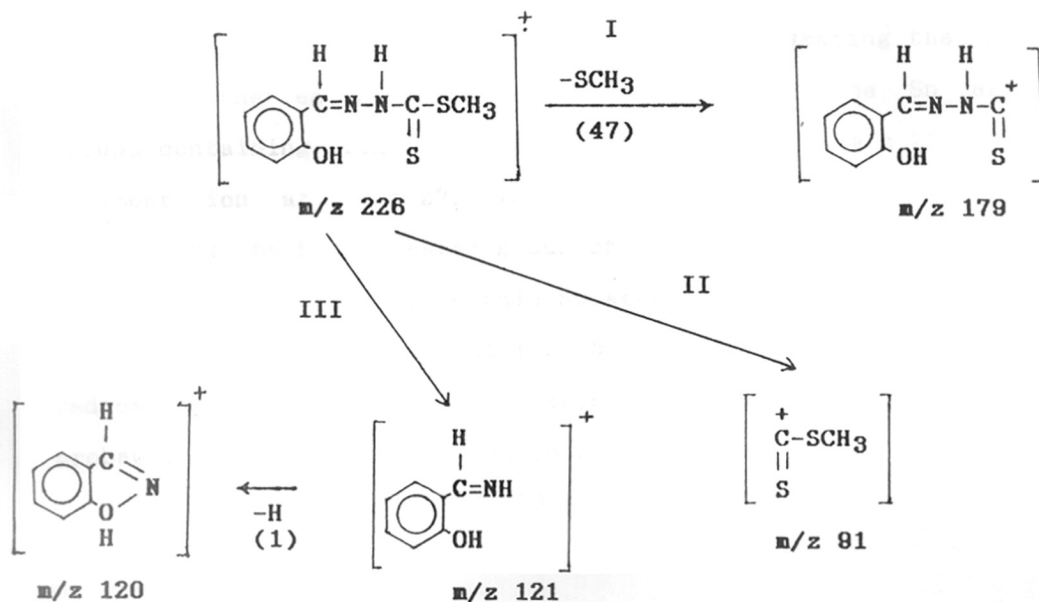


### 5. S-Methyl- $\beta$ -N-(2-hydroxyphenyl)methylendithiocarbazate

[H<sub>2</sub>SMSaD]:

In routes I and II  $\alpha$ -cleavage is possible on both sides of C-atom attached to sulphur by double bond, giving two fragments m/z 179 and m/z 91.

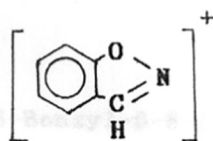
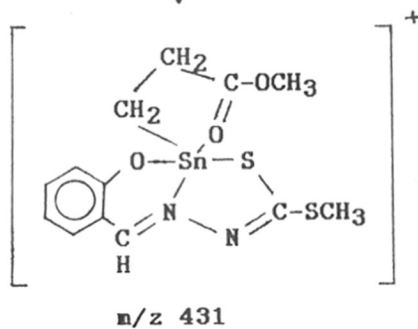
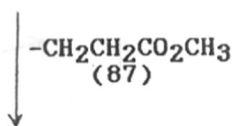
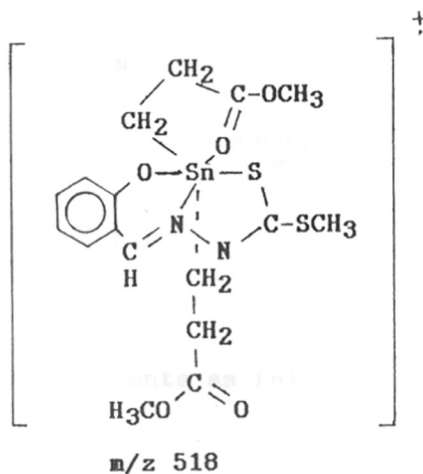
In route III, it is an  $\alpha$ -cleavage between two N-atoms fragmenting to m/z 120. It is seen from mass spectrum that the peak at m/z 121 is also equally intense as the peak at m/z 120; this is probably due to migration of H-atom from NH. The fragment peak at m/z 120 also indicates that it loses H-atom giving rise the fragment peak at m/z 119. The fragmentation is as below:



### 6. $(\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3)_2\text{Sn}(\text{SMSaD})$

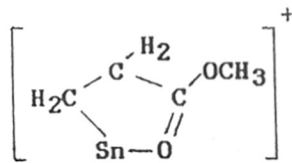
The molecular ion  $m/z$  518, could not be seen because it was unstable under electron impact. It easily loses one ester group with 87 a.m.u.  $[\text{CH}_2\text{CH}_2\text{COOCH}_3]$  giving some-what stable fragment at  $m/z$  431, leaving the positive charge on Sn atom.

The fragment ion at  $m/z$  431 on further fragmentation gives different fragment ions  $m/z$  119,  $m/z$  105 and  $m/z$  207. The Sn-atom is reduced to lower valence state while still bonded to ester group [ $m/z$  207] which indicates the characteristic Sn-isotopes pattern. This fragment at  $m/z$  207 finally eliminates ester-group and thereby the formation of atomic Sn with its characteristic isotopic pattern observed in the mass spectrum. Instead of eliminating the whole side chain  $[\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3]$  from  $\text{M}^+$  ion, it eliminates first  $\text{CH}_2=\text{CH}_2$  and  $\text{C}=\text{O}$  groups while migrating the  $\text{OCH}_3$  group at the end of the side chain to Sn atom. The Sn ester groups containing fragments bonded are observed at  $m/z$  238. The fragment ion at  $m/z$  238, in its turn fragments to  $m/z$  151 eliminating the bonded ester group of 87 a.m.u. The fragments at  $m/z$  238 and at  $m/z$  151 contain Sn atom evidently from their isotope peaks. The fragment  $m/z$  151 due to  $\text{Sn}-\text{OCH}_3$  is found to reduce itself to metallic Sn atom in the mass spectra. The probable fragmentation pattern is given below:



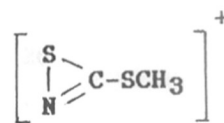
$m/z$  119

does not contain Sn



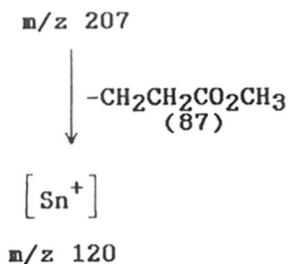
$m/z$  207

shows Sn-pattern

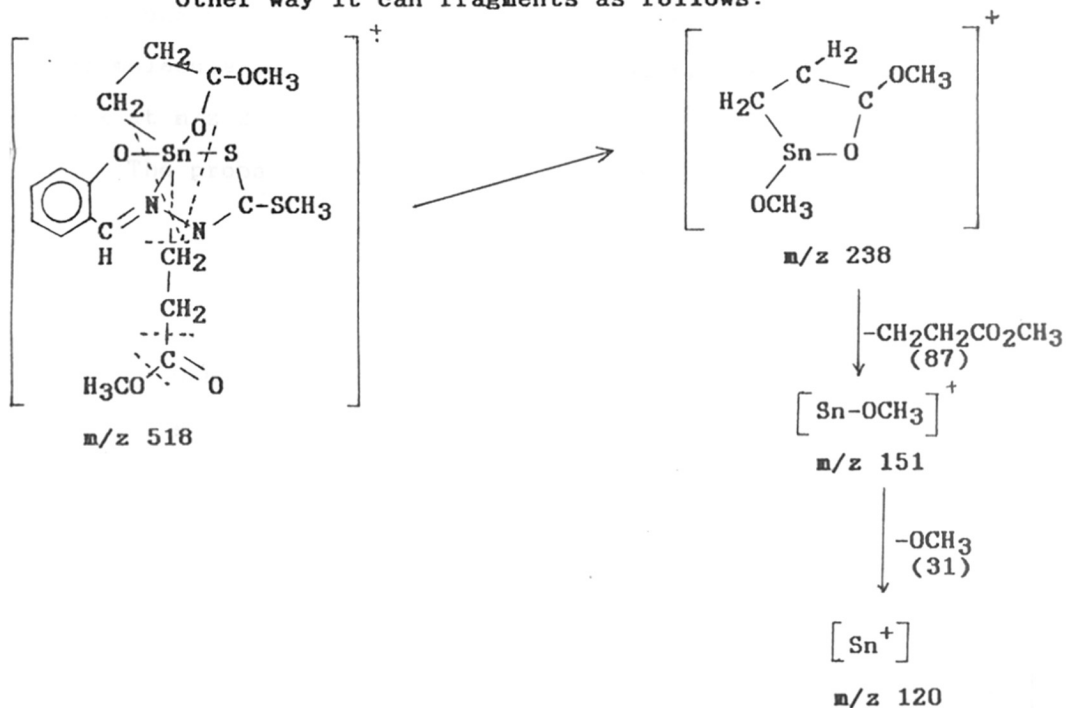


$m/z$  105

does not contain Sn



Other way it can fragments as follows:



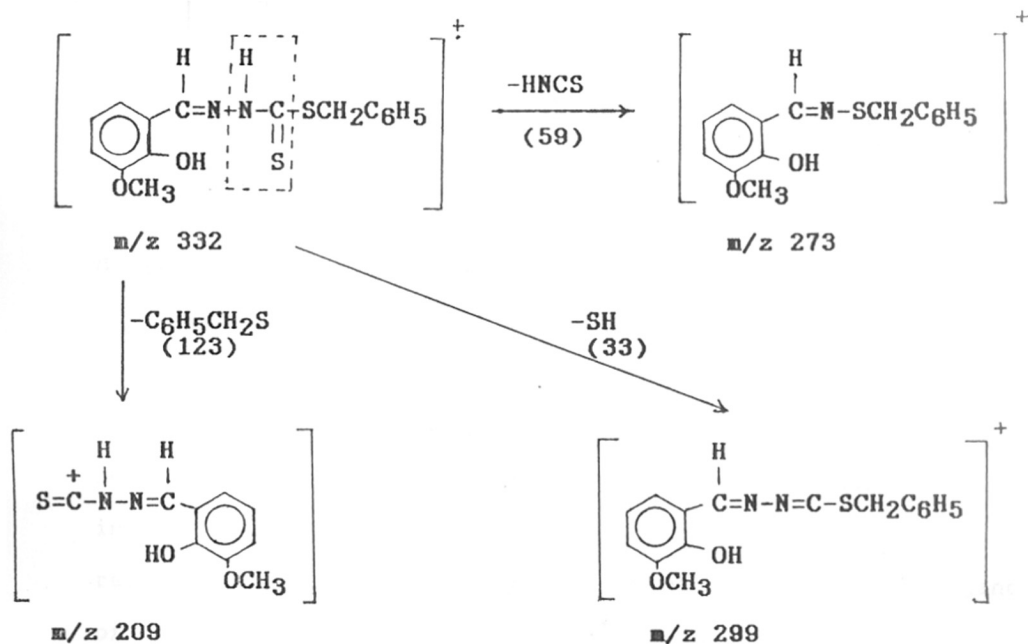
7. S-Benzyl- $\beta$ -N-(2-hydroxy-3-methoxyphenyl)methylendithio carbazate [ $\text{H}_2\text{SBVD}$ ]:

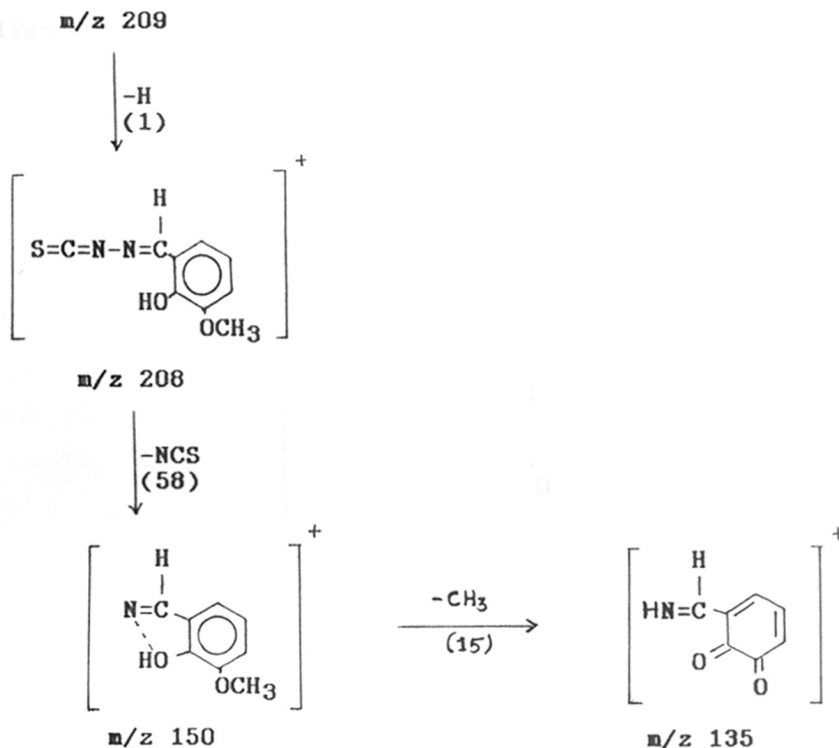
Mass spectrum of this Schiff base shows a molecular ion peak at  $m/z \ 332$ . The base peak at  $m/z \ 91$  could be due to tropylium

ion. The molecular ion eliminates SH and the fragment appears at  $m/z$  299. The molecular ion eliminates  $C_6H_5CH_2S + H$  stepwise to give rise to the fragment  $m/z$  209 and  $m/z$  208. The sharp peak at  $m/z$  135 may be due to cleavage of  $CH_3$  and  $NCS$  from the fragment at  $m/z$  208.

The effect of substituted phenyl ring at the end of the long side chain is reflected in the mass spectrum of this complex. The molecule ion eliminates the neutral species  $H\ NCS$  showing the peak at  $m/z$  273.

The probable fragmentation pattern is as shown below:



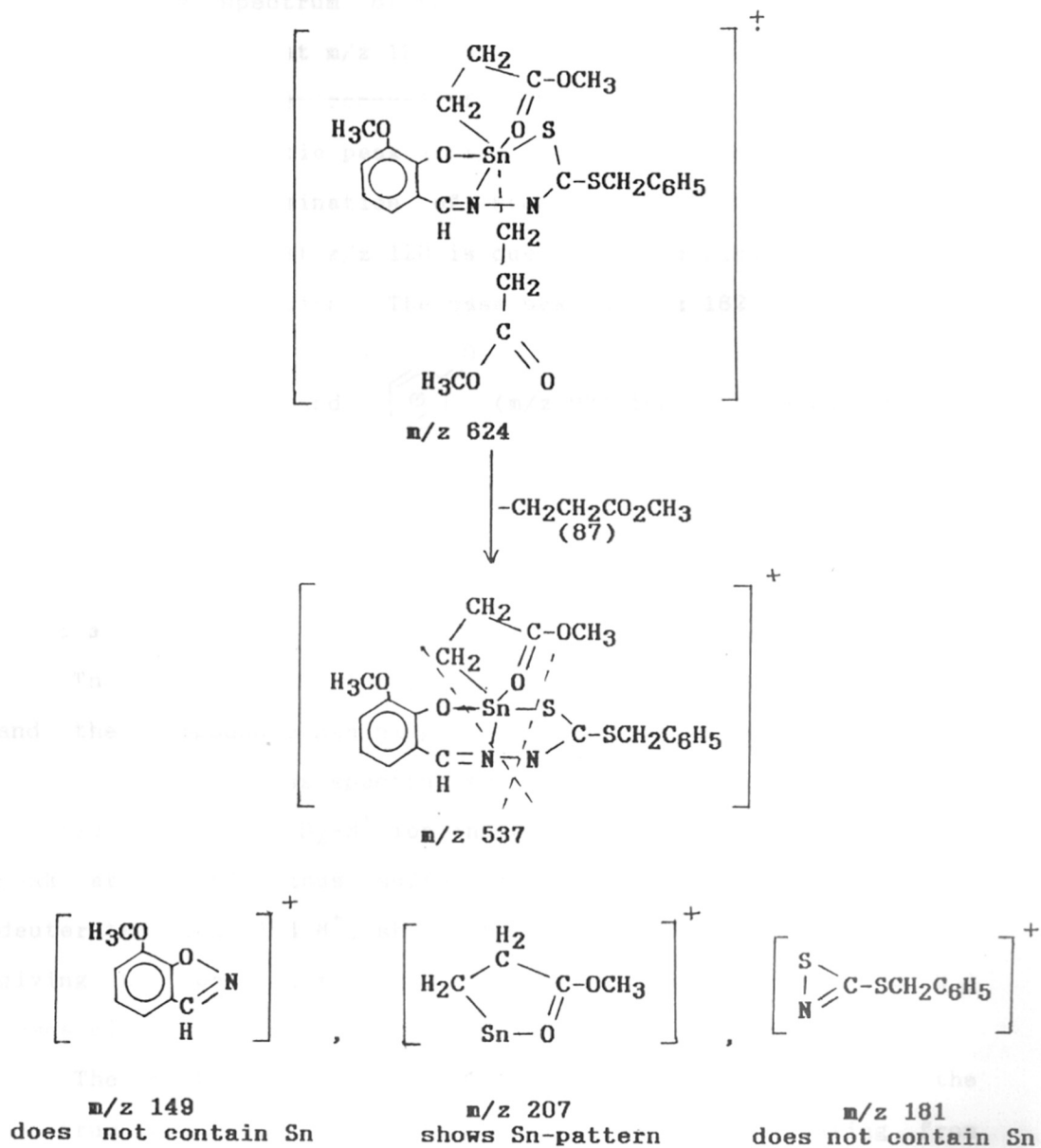


### 8. $(\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3)_2\text{Sn}(\text{SBVD})$

The molecular ion at  $m/z$  624 easily eliminates  $\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$  giving the fragment ion at  $m/z$  537. This resulting ion [537] breaks into three fragments at  $m/z$  149,  $m/z$  181 which do not contain Sn atom, and  $m/z$  207 which does contain Sn atom as indicated by the characteristic isotope Sn pattern. The Sn atom remains intact with the cyclic structure of another ligand unit of mass 87. It is seen that Sn-C bond is more stable in cyclic structure than the long chain ones. The cyclic structure of one

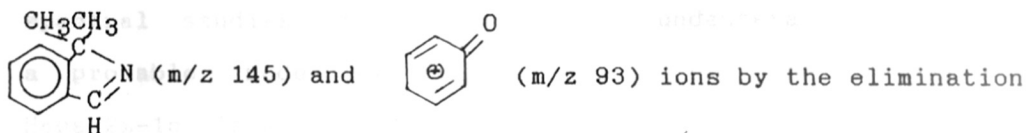
ligand is confirmed by NMR also.

The fragmentation pattern is given below:



### 9. 2-N-salicylideneimino-2-methyl-1-propanol [H<sub>2</sub>sa-2m-1p]

The mass spectrum of the Schiff base, H<sub>2</sub>sa-2m-1p, shows molecular ion peak at m/z 193 (65%). The base peak at m/z 162 is resulting from the removal of CH<sub>2</sub>OH from the molecular ion. Another characteristic peak at m/z 121 is due to salicyledene ion formation and elimination of H(CH<sub>3</sub>)<sub>2</sub>C-OH [1,1 methyl 2-ol-ethane]. The peak at m/z 120 is due to simple cleavage of C-N bond before H-migration. The base peak at m/z 162 gives rise to



of OH and  $\left[ \text{HCN} + \text{CH}_3\text{-C}^+ \begin{array}{l} \text{CH}_3 \\ \text{CH}_3 \end{array} \right]$  respectively.

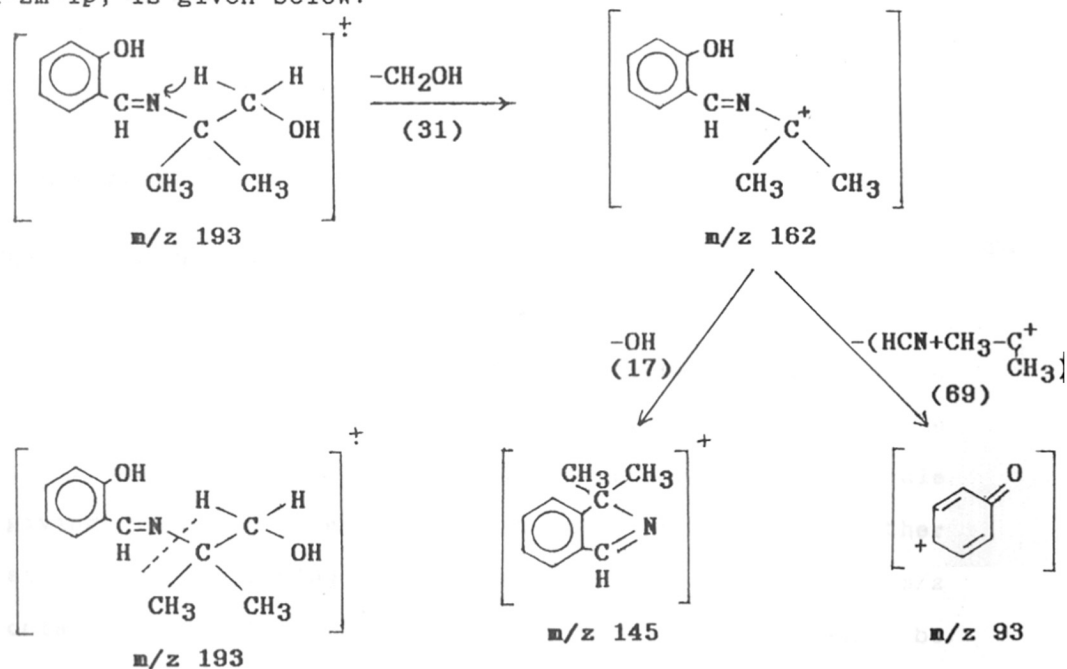
#### Deuteration studies:

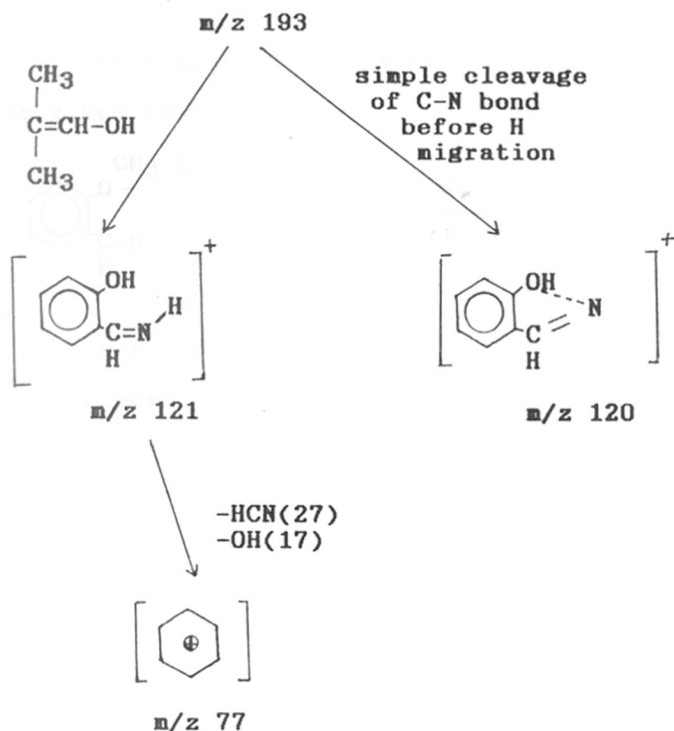
The above Schiff base, H<sub>2</sub>sa-2m-1p, was deuterated with D<sub>2</sub>O and the compound containing phenolic OD and alcoholic OD was obtained. The mass spectrum shows molecular ion at m/z 195, shifted by 2 a.m.u. D<sub>2</sub>-M<sup>+</sup> ion indicating the loss of 32 giving the peak at m/z 163, thus suffering a loss of CH<sub>2</sub>OD. The singly deuterated ion (194 M<sup>+</sup>) shows the loss of 70 due to phenolic OD giving the peak at m/z 145. Thus the molecular ion (193 M<sup>+</sup>) loses alcoholic OH group and gives a peak at m/z 145.

The peak at m/z 121 is due to a rearranged fragment in the spectrum of precursor ion. One of the H atom migrating from



$C(CH_3)_2CH_2OH$  to N atom before elimination of alcoholic  $-CH_2OH$  from molecular ion. There are two possibilities for migration of H from alcoholic OH group or from  $CH_2$  group to which OH group is attached. In the fully deuterated compound,  $(D_2-M^+)$ , this peak is seen at  $m/z$  122 due to phenolic OD. In partially deuterated molecule,  $(D_1-M^+)$ , in which phenolic OH is not deuterated, the rearranged peak appears at  $m/z$  121 due to loss of  $[C(CH_3)_2CHOH]$  from molecular ion. On the basis of mass spectral studies of deuterated and undeuterated compounds, a probable mode of fragmentation of the Schiff base,  $H_2sa-2m-1p$ , is given below:

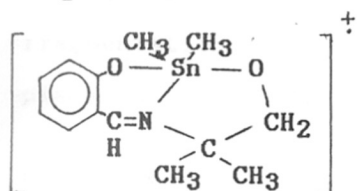




#### 10. $(\text{CH}_3)_2\text{Sn}[\text{sa}-2\text{m}-1\text{p}]$

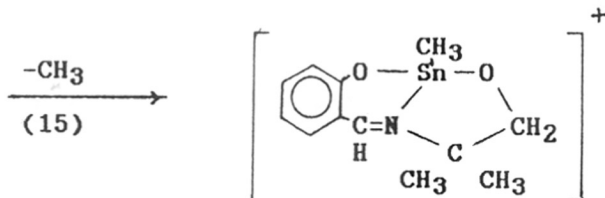
In the mass spectrum of the complex the base peak is observed at  $m/z$  311 which is produced by successive elimination of the two  $\text{CH}_3$ - groups bonded to the Sn atom and not from the ligand. The base peak at  $m/z$  311 eliminates a neutral molecule  $\text{CH}_2\text{O}$  giving rise to the fragment at  $m/z$  281 which further eliminates  $\text{CH}_3\text{-C-CH}_3$  giving the peak at  $m/z$  239. The peak at  $m/z$  225 containing Sn atom [as shown in spectrum] can only be explained to be formed by elimination of a small closed ring from the base peak  $m/z$  311 as shown in scheme II.

The fragmentation pattern for the tin complex of the ligand is given below:



m/z 341

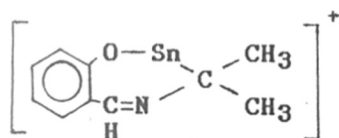
Scheme I



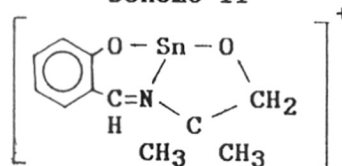
m/z 326

-CH<sub>3</sub>  
(15)

Scheme II

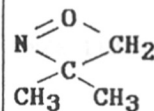


m/z 281

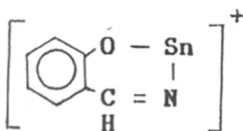


m/z 311 (base peak)

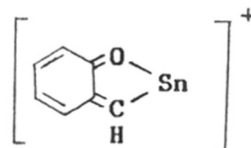
elimination  
of



(86)



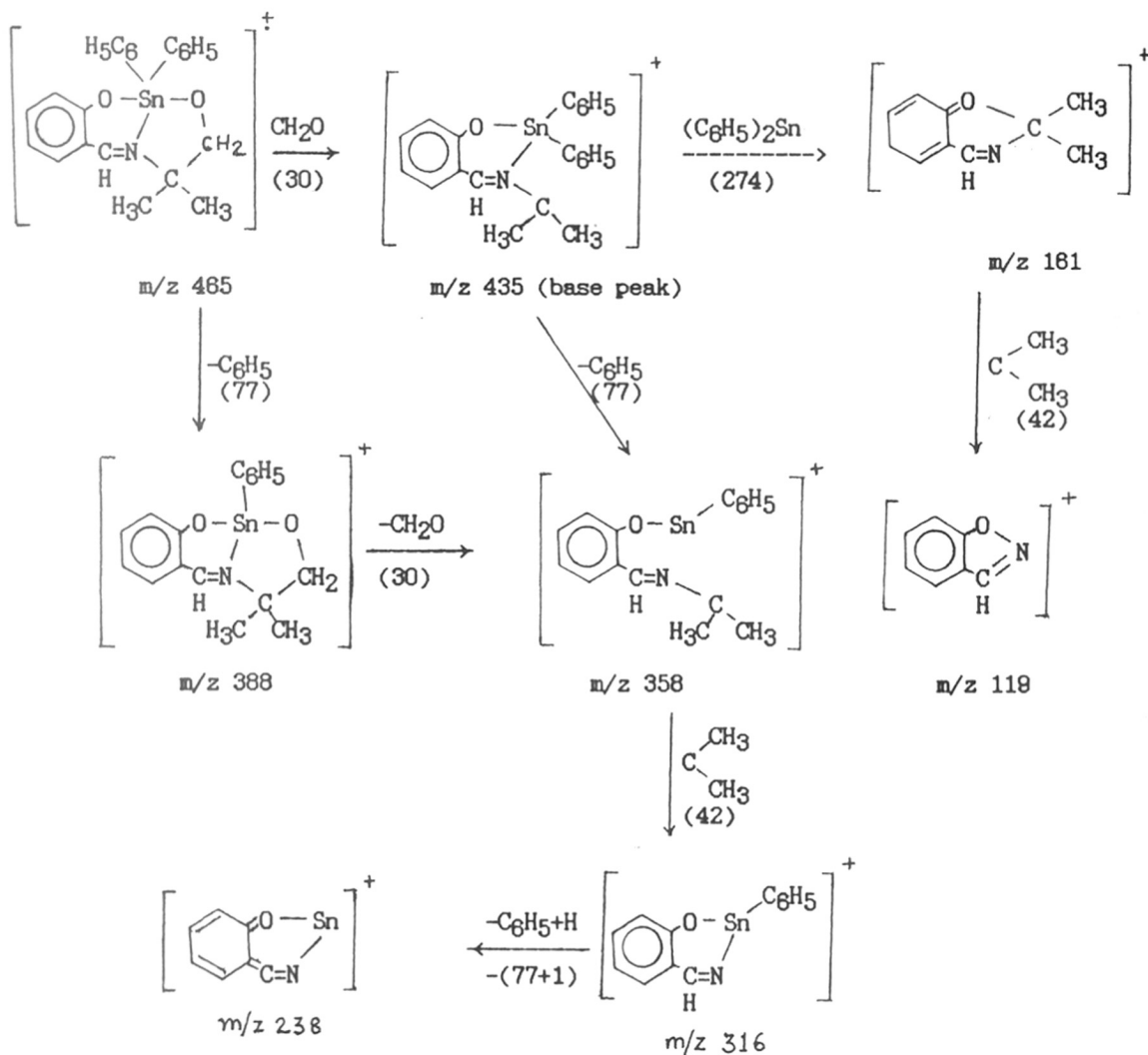
m/z 239

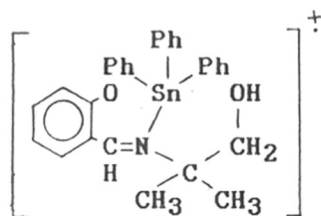


m/z 225

11.  $(C_6H_5)_2Sn[sa-2m-1p]$ 

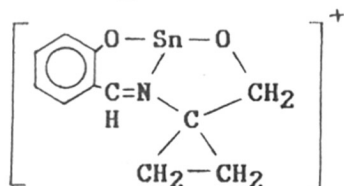
The fragmentation pattern is similar to complex No. 10 except some difference occurring in the sequence of fragmentation modes due to the presence of two phenyl rings in place of two methyl groups attached to the metal.



12.  $(C_6H_5)_3Sn[Hsa-2m-1p]$ 

m/z 543

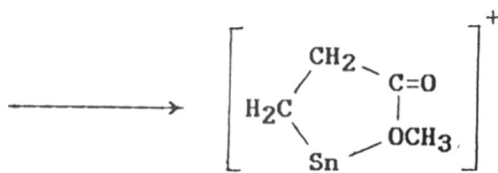
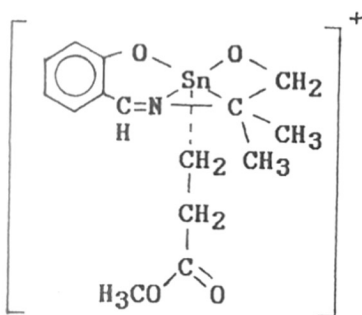
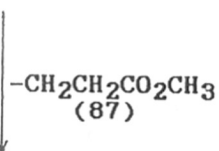
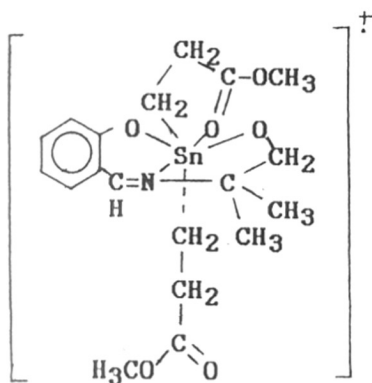
In mass spectrum of the complex the peak due to  $M^+$  at 543 is absent, but a characteristic fragment was found at m/z 309, due to loss of 3 phenyl groups and 3 hydrogen atoms i.e., loss of  $3 \times 78 = 234$ , and the probable structure is shown below. This is the only one fragment containing Sn in this spectrum. All other peaks are insignificant.



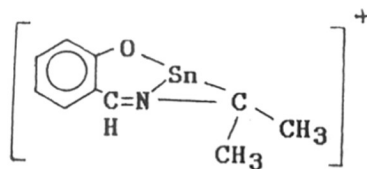
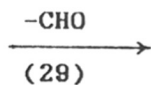
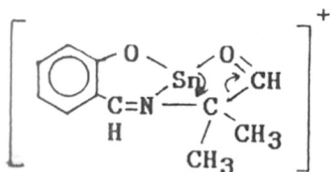
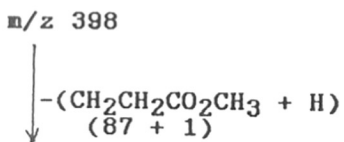
m/z 309

13.  $(CH_2CH_2CO_2CH_3)_2Sn[sa-2m-1p]$ 

The mass spectral studies of estertin Schiff base complexes follow a similar pattern of fragmentation modes found in compound Nos. 8, 13 and 14. The fragmentations are as follows.

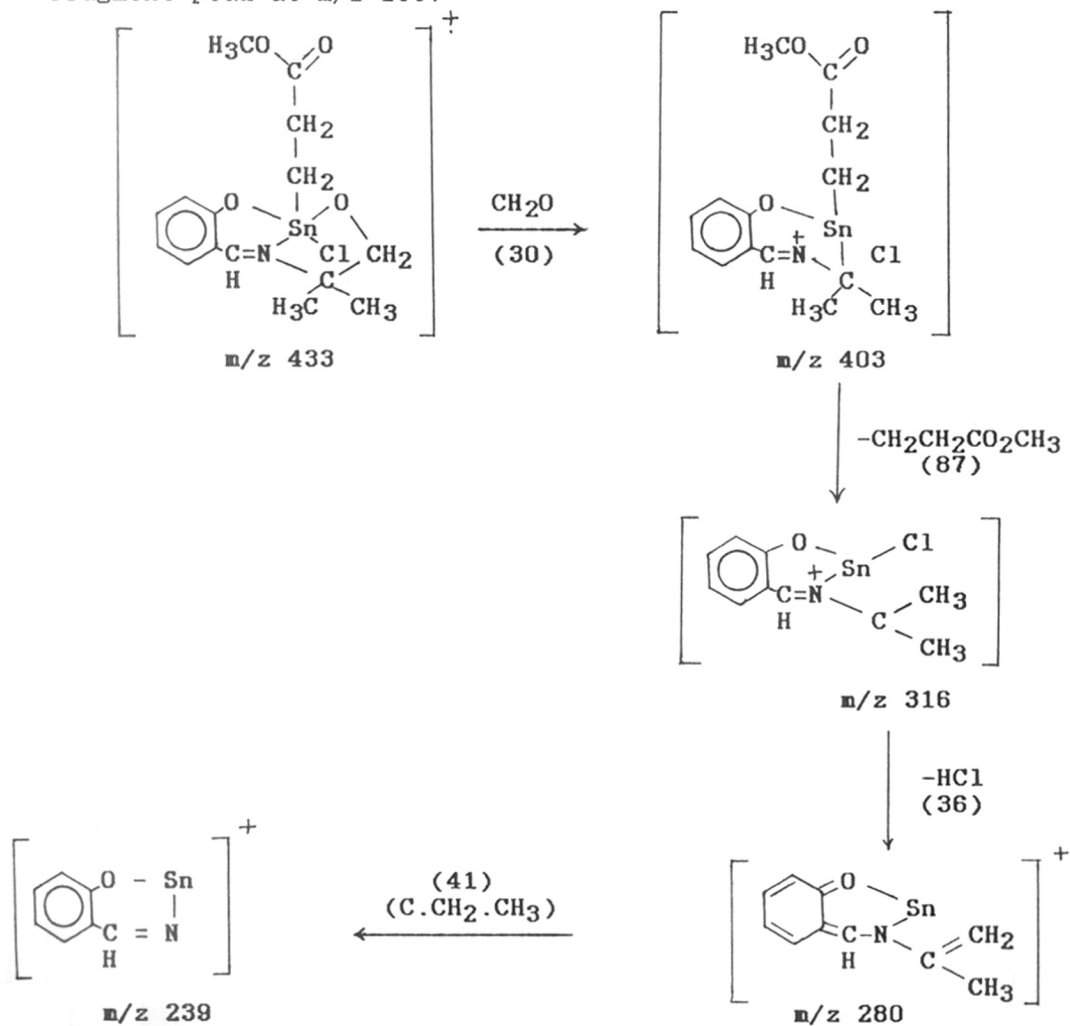


cyclic ester containing  
Sn only and rest part is  
diminishing.



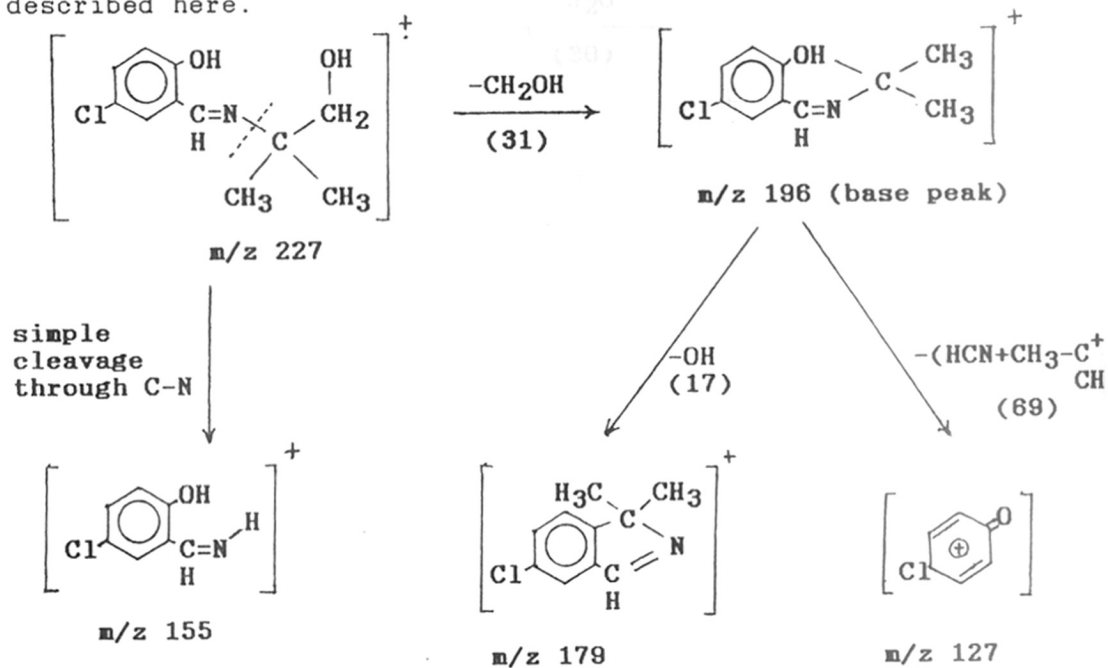
14.  $(\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3)\text{SnCl}[\text{sa-2m-1p}]$ 

This complex is similar to compound No. 13 except that a bonded ester group is replaced by Cl atom. The fragmentation mode is given below. The fragment at  $m/z$  280 eliminates 41 a.m.u. giving fragment peak at  $m/z$  239.

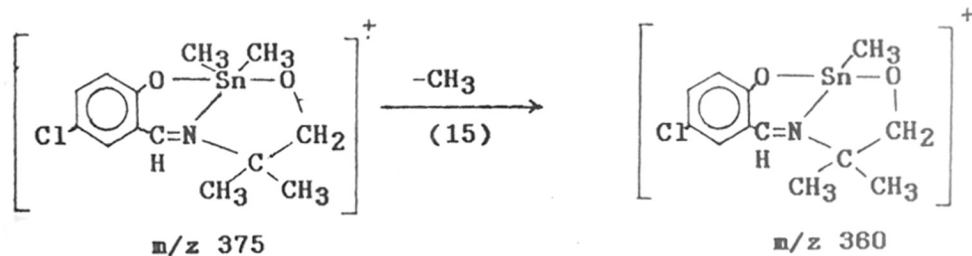


15. 2-N-chlorosalicylideneimino-2-methyl-1-propanol [ $\text{H}_2\text{Cl.sa-2m-1p}$ ]

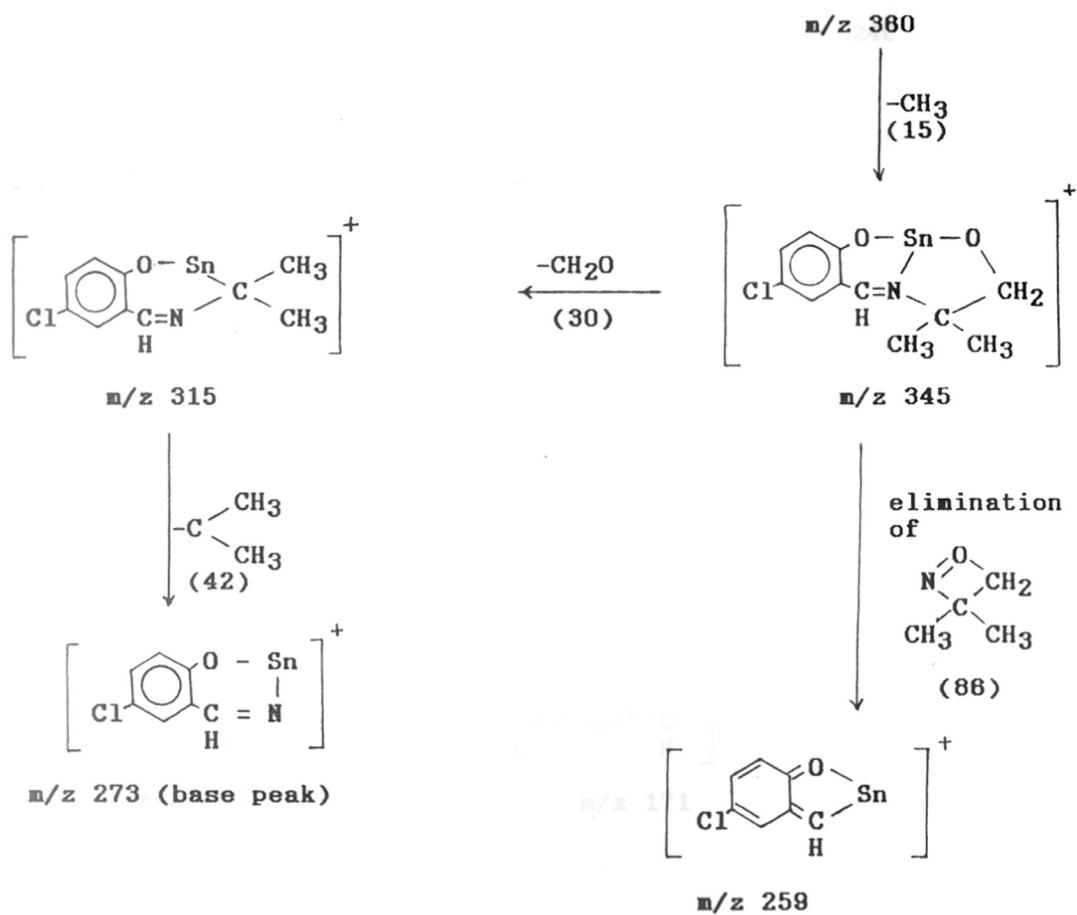
The mass spectral studies of chloro/bromo/2-hydroxy-3-methoxyphenyl/2-hydroxy-1-naphthalenedene 2-methyl-1-propanol and their organotin Schiff base complexes have been carried out and the most probable fragmentation pattern of these complexes is described here.



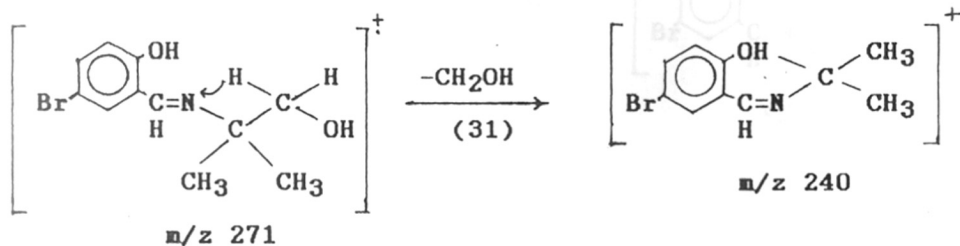
16.  $(\text{CH}_3)_2\text{Sn}[\text{Cl.sa-2m-1p}]$

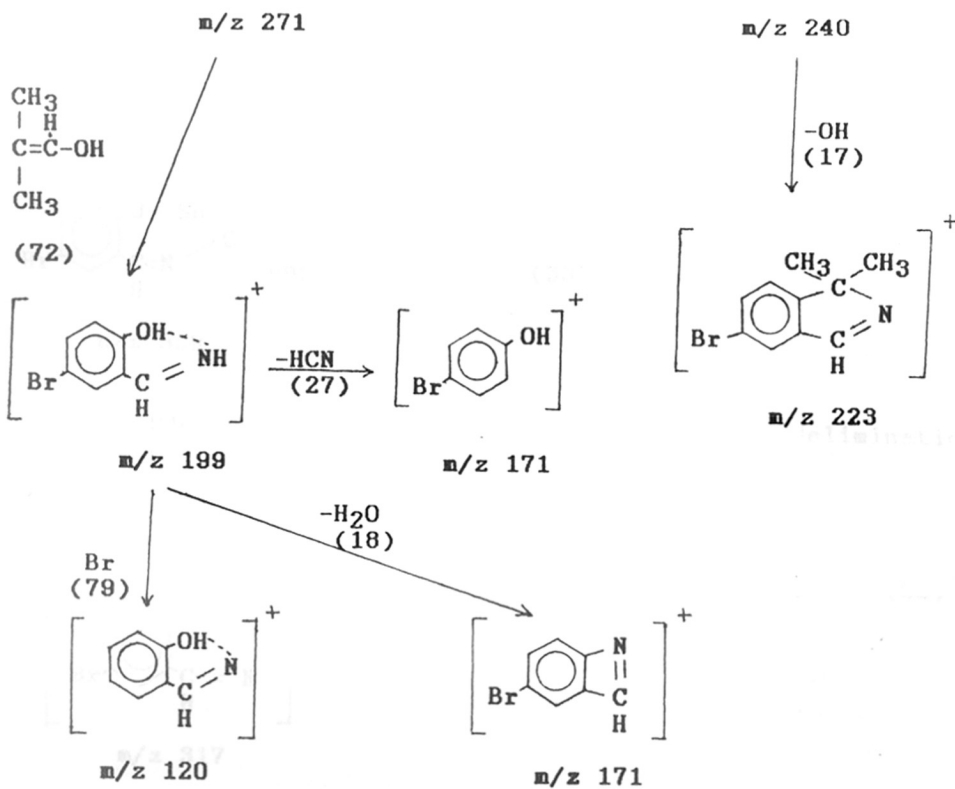
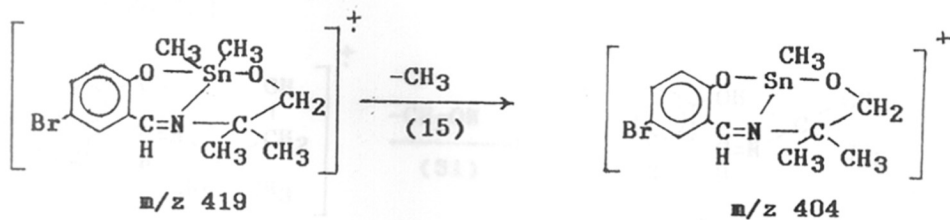


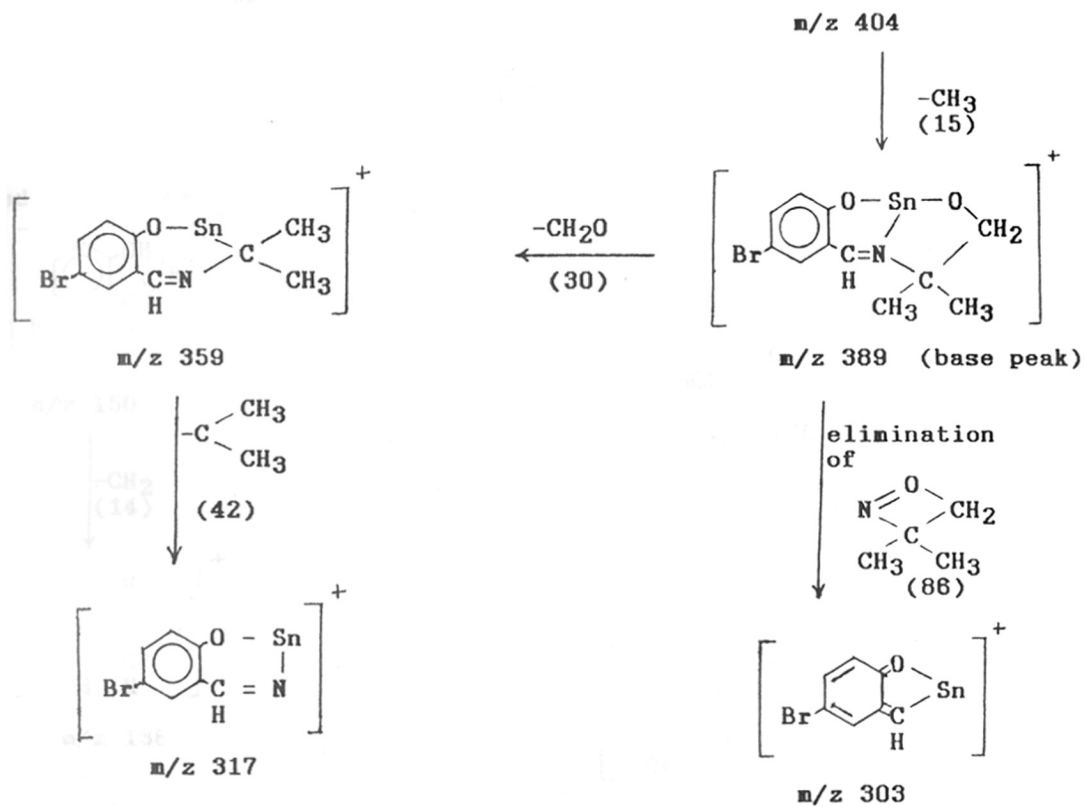




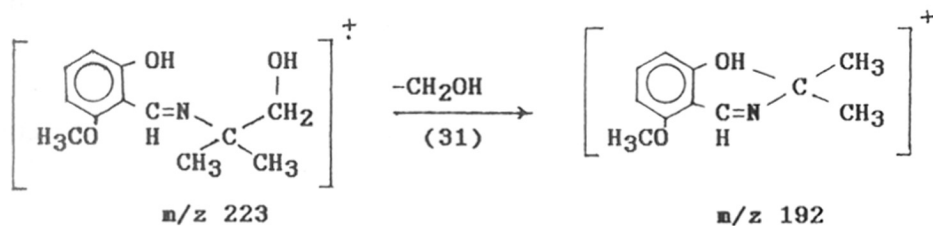
17. 2-N-bromosalicylideneimino-2-methyl-1-propanol [H<sub>2</sub>Br.sa-2m-1p]

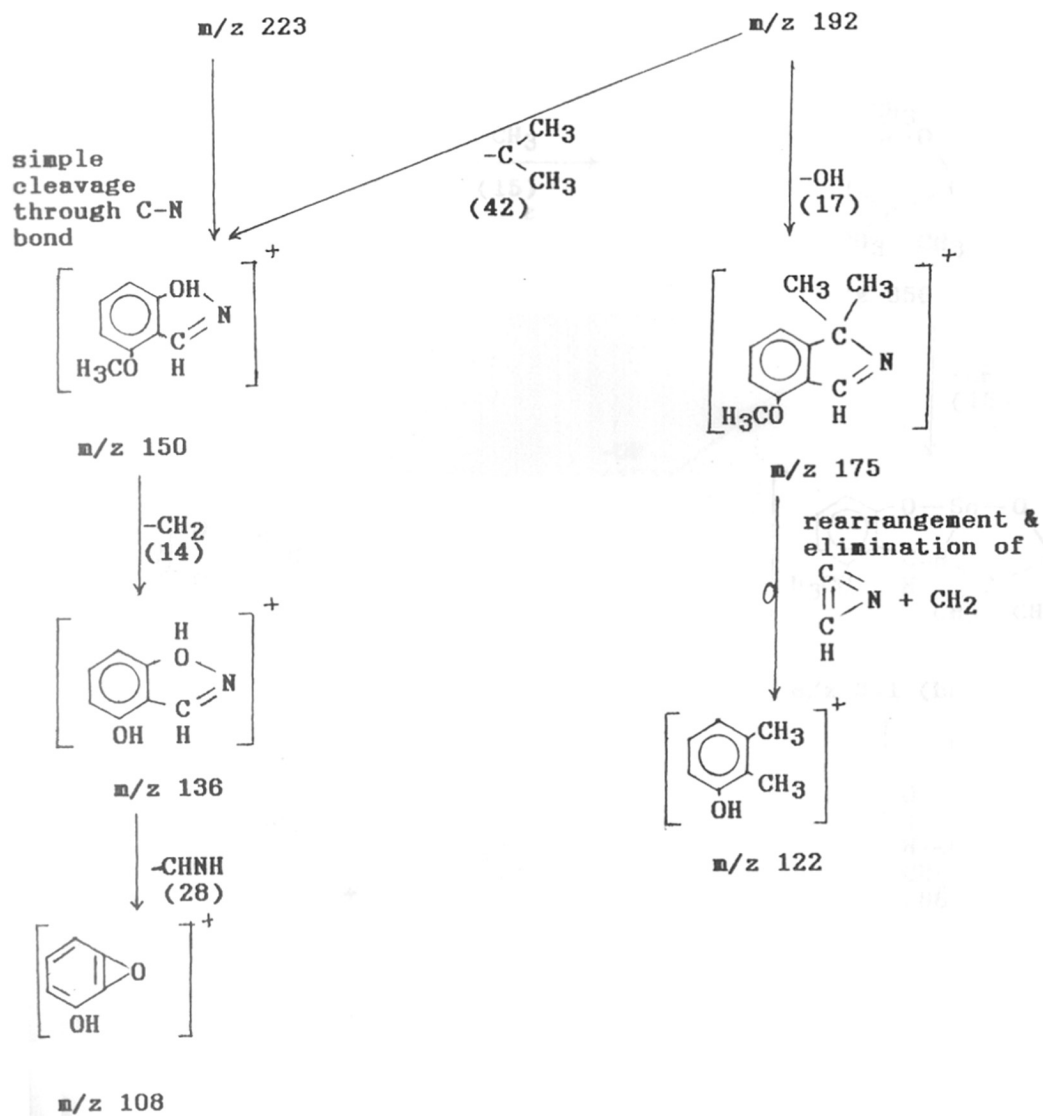


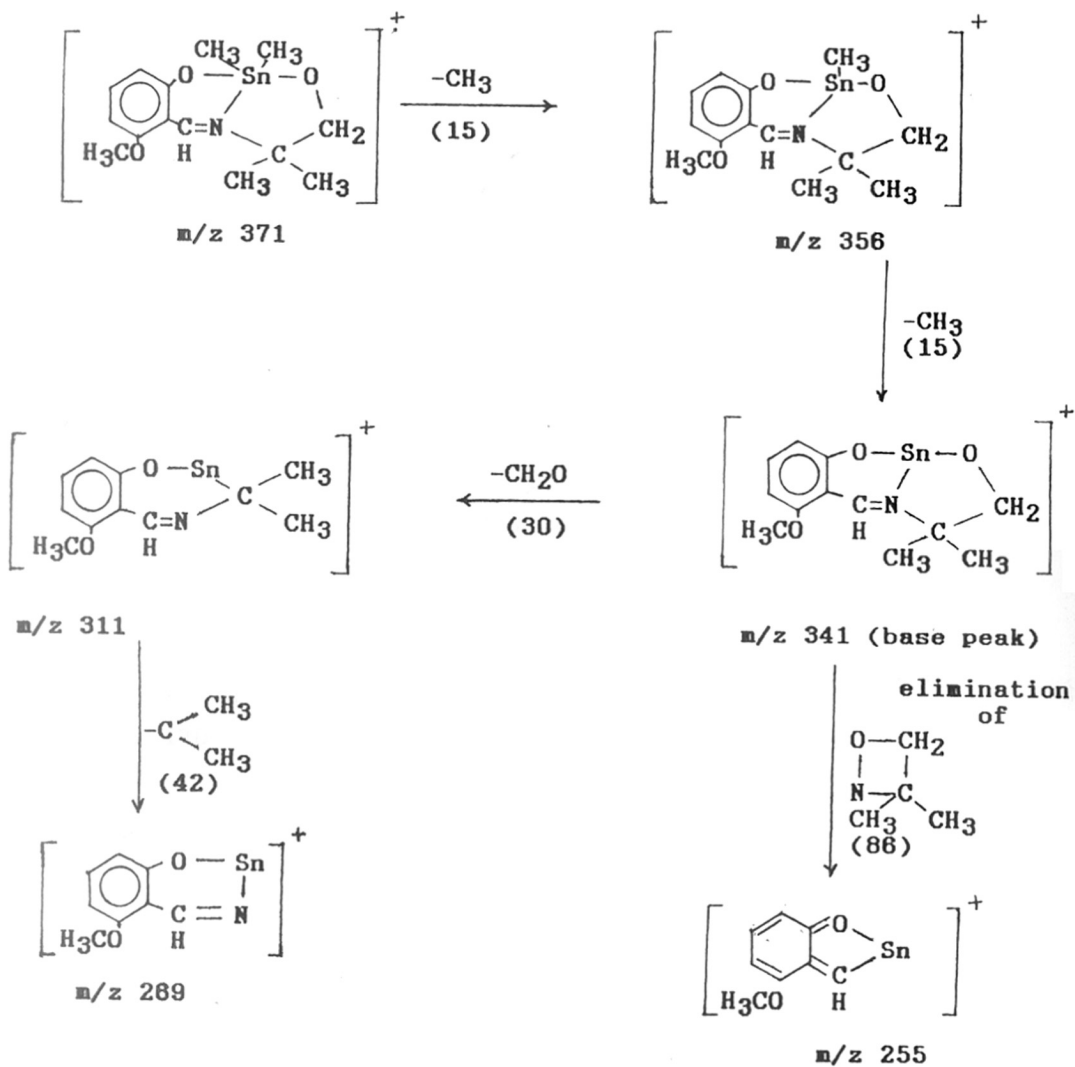
18.  $(\text{CH}_3)_2\text{Sn}[\text{Br.sa-2m-1p}]$ 



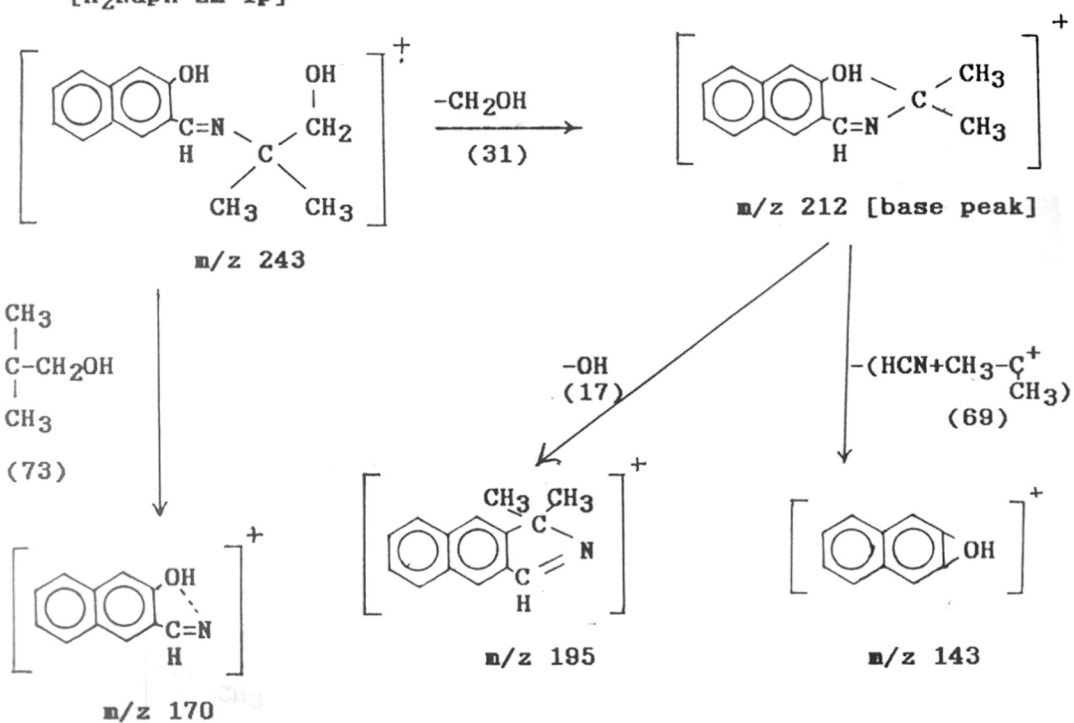
19. 2-N-(2-hydroxy-3-methoxyphenylene)imino-2-methyl-1-propanol  
[H<sub>2</sub>ov-2m-1p]

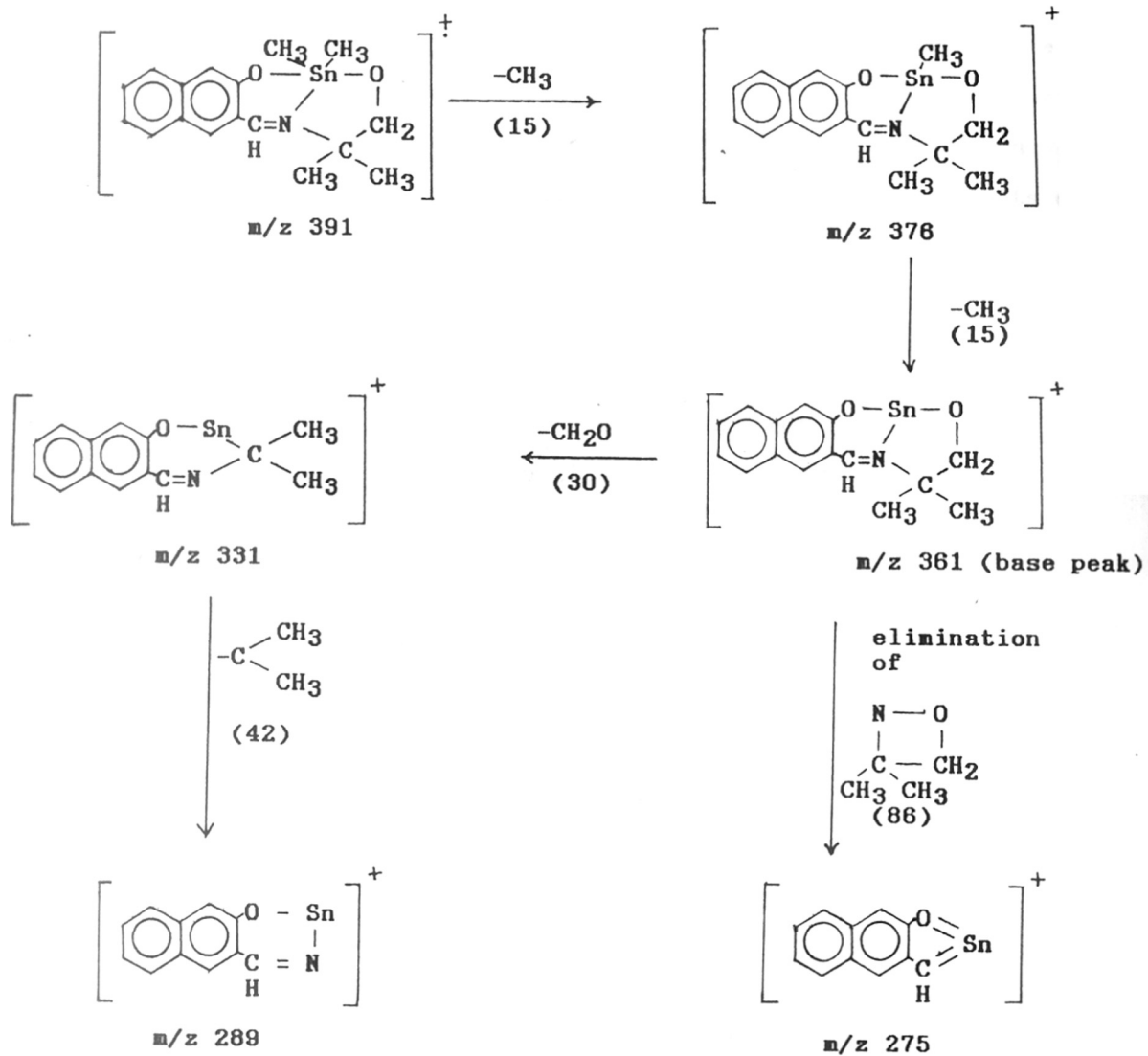




20.  $(\text{CH}_3)_2\text{Sn}[\text{ov-2m-1p}]$ 

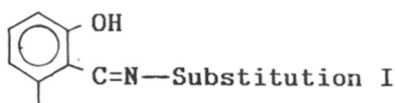
## 21. 2-N-(2-hydroxy-1-naphthaledene)imino-2-methyl-1-propanol

[H<sub>2</sub>Naph-2m-1p]

22.  $(\text{CH}_3)_2\text{Sn}[\text{Naph-2m-1p}]$ 

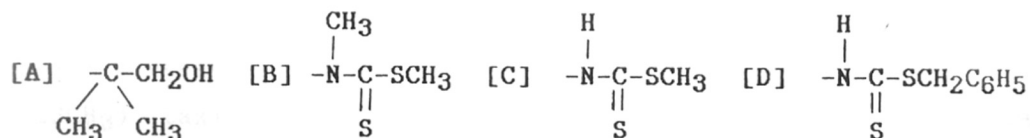
## C O N C L U S I O N

In summary, the mass spectra of the Schiff base tin complexes are recorded and compared. All complexes were purified before scanning mass spectra and were recorded on Mass spectrometer Finnigan Mat 1020 B. The various substituents on N-atom and phenyl ring of the Schiff bases are as follows:



Substitution II

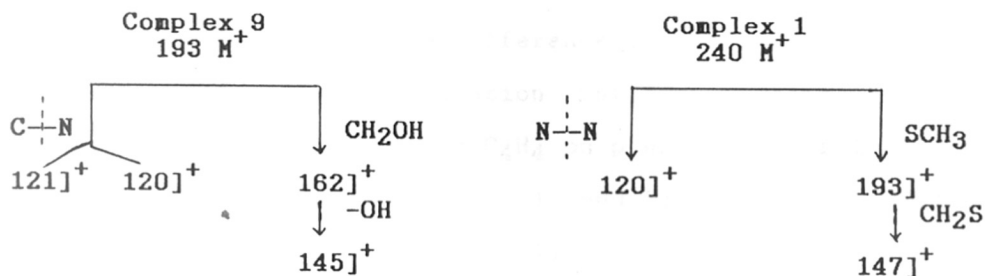
Substitution I



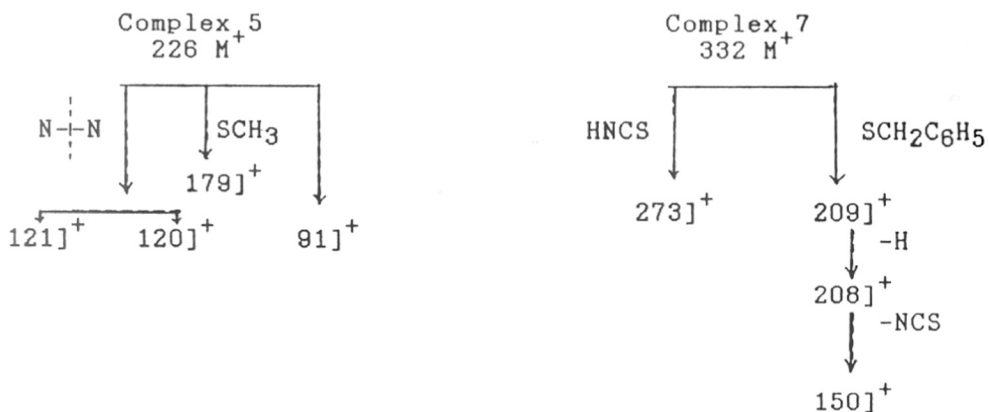
Substitution II

[A] H [B] OCH<sub>3</sub> [C] C<sub>4</sub>H<sub>4</sub>

Degradation →







Complexes [9, 15, 17, 19, 21] indicate loss of CH<sub>2</sub>OH or corresponding group of atoms. Each complex has its characteristic fragment peak. The complex [9] only shows loss of phenolic OH. The complexes [1, 3 & 4] shows loss of CH<sub>2</sub>S through the rearrangement of the previous fragment. The complex [5] has a highly characteristic fragment due to end group of the molecule (SCSCH<sub>3</sub>) taking positive charge and eliminating the rest of the molecule. The particular fragment of complex [7] has been observed due to elimination of HNCS. All these complexes are similar in fragmentation at N-C or N-N bond arising two peaks with H-atom migration except complex 1, in which the peak at m/z 120 may be a doublet due to difference in their structure.

The mode of fragmentation pattern remains intact by substituting Cl, Br, OCH<sub>3</sub> and C<sub>4</sub>H<sub>4</sub> on phenyl ring of the complex 9, that is complex nos. 15, 17, 19 and 21. The only difference in case of halogen substituents is the migration of H-atom from

end group of the molecule [i.e., from substituent I] to the phenyl ring side while C-N or N-N bond breaks.

The complexes of halogen substitution indicate loss of 72 a.m.u. from molecular ion while in complexes of OCH<sub>3</sub> and C<sub>4</sub>H<sub>4</sub> substitution show loss of 73 a.m.u. from molecular ion.

The complex nos. 6 and 8 show almost similar fragmentation pattern by losing first one ester group, i.e. loss of 87 a.m.u. Similarly complex no. 13 and 14 show loss of 87 a.m.u. due to ester group.

The tin complexes with Schiff bases are studied for their mass spectral fragmentations. Since tin has its own characteristic isotopic cluster, it is easy to point out the fragments having Sn-atom in their structure. The various substituted Sn-atom e.g., (CH<sub>3</sub>)<sub>2</sub>, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>, (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> chain ether (CH<sub>2</sub>)<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub> and ring/chain ether are able to form complexes with Schiff base [complex nos. 10, 11, 12, 13, 14]. The mass spectral fragmentation modes are quite interesting. the complex of having Sn(CH<sub>3</sub>)<sub>2</sub> [complex nos. 10, 16, 18, 20 & 22] losses both methyl groups one after another and then expected reactions like loss of CH<sub>2</sub>OH, C(CH<sub>3</sub>)<sub>2</sub> etc. taking place. In case of complex having phenyl group attached to Sn-atom, viz. Sn(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> [complex no. 11] the mass spectral reactions (i) loss of C<sub>6</sub>H<sub>5</sub> of Sn-atom and (ii) the usual losses of CH<sub>2</sub>O, C(CH<sub>3</sub>)<sub>2</sub> are quite competent as they are proceeding simultaneously. This indicates that Sn atom

has more affection of carbon atom in phenyl ring than that of in methyl group. But surprisingly, when Sn atom attached by three phenyl rings, the complex no. [12] is observed to fragment all the three phenyl rings along with 3 protons giving only one very stable fragment which is not fragmenting further and having all isotopic cluster of Sn-atom.

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## LIST OF PUBLICATIONS

## A. Published/communicated:

1. "Synthesis and characterization of bis(carboalkoxyethyl)tin(IV) Schiff base complexes".  
Mrs. M.P. Degaonkar, Mrs. S. Gopinathan and C. Gopinathan.  
Syn. React. Inorg. Met-Org. Chem., 22(10) (1992) 1591
2. "New chelated complexes of bis- $\beta$ -carboalkoxyethyltin (IV) dichloride with S-benzylthiocarbamate Schiff bases".  
S.Gopinathan, M.P.Degaonkar and C.Gopinathan.  
Applied Org.met. Chem., 6, (1992) 69
3. "Study on molecular addition complexes of organo-tin(IV) with N-methyl-S-methylthiocarbamate Schiff bases".  
Mrs.S. Gopinathan, Mrs. M.P.Degaonkar, A.M. Hundekar and C. Gopinathan.  
Indian J.Chem., 32A (1993) 262
4. "Study on organotin(IV) complexes of dibasic tridentate Schiff bases containing ONO donor atoms".  
Mrs. S. Gopinathan, Mrs. M.P. Degaonkar, A. M. Hundekar.  
Applied Org.met.Chem., 7, (1993) 63
5. "Synthesis and spectroscopic investigations of some binuclear organotin(IV) complexes of (bis)salicylaldehyde malonoyl dihydrazone and crystal structure study of  $[(C_2H_5)_2Sn]_2[OC_6H_4CHN-NCO]_2CH_2$ ".

Mrs. M.P. Degaonkar, Mrs. V.G. Puranik, S.S. Tavale, Mrs S. Gopinathan and C. Gopinathan.

Bull Chem. Soc. Japan (1993) (communicated)

6. "Binuclear tin(IV) complexes of N-(hydroxypropyl) substituted salicylideneimines and X-ray crystal study of the complex  $[(OC_6H_4CH=N-C(CH_3)_2-(CH_2O)Sn(CH_3)_2]_2$ .

Mrs. M.P. Degaonkar, Mrs. V.G. Puranik, S.S. Tavale, Mrs S. Gopinathan and C. Gopinathan.

J. Organomet. Chem. (1993) (Communicated)

B. Presented in symposium:

1. "Synthesis and investigations in some binuclear organotin(IV) complexes of (bis)salicylaldehyde malonoyldihydrazone".

Mrs. M.P. Degaonkar, Mrs. Sarada Gopinathan and C. Gopinathan, Presented at the symposium in Organometallic Chemistry at Indian Institute of Technology, New Delhi (6-8 December 1993)

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