ORGANOTIN(IV) COMPLEXES OF SCHIFF BASES: A REVIEW

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LIST OF ABBREVIATIONS

CHEMICALS, LIGANDS AND SOLVENTS

CD_3OD : Deuterated methanol
$CDCl_3$: Deuterated chloroform
CD_2Cl_2 : Deuterated dichloromethane
DMSO : Dimethyl sulfoxide
DMSO-d_6 : Deuterated dimethyl sulfoxide
DMF : N,N-dimethylformamide
DMA : Dimethylacetamide
H_2acen : N,N'-Ethylenebis(acetylacetoneimine)
H_2acpn : N,N'-Propylenebis(acetylacetoneimine)
H_2aceten : N,N'-Ethylenebis(2-hydroxyacetophenoneimine)
H_2acetdap : N,N'-Trimethylenebis(2-hydroxyacetophenoneimine)
H_2salen : N,N'-Ethylenebis(salicylaldimine)
H_2salpn : N,N'-Propylenebis(salicylaldimine)
H_2salaen : Bis(salicylic acid)ethylenediimine
H_2saldap-2-ol : N,N'-2-Hydroxytrimethylenebis(salicylaldimine)
H_2saladap-2-ol : Bis(salicylic acid)-2-hydroxytrimethylenediimine)
H_2salphen-*o* : N,N'-*o*-Phenylenebis(salicylaldimine)
H_2salap : N-2-Hydroxyphenylsalicylaldimine
H_2salatp : 2-(2-Hydroxyphenyl)benzothiazoline
Htdbm Pr^i : Thiodibenzoylmethane-i-propylimine
H_2 vanilen : Bis(vanillin)ethylenediimine
H_2salcen : N,N'-Ethylenebis(3-carboxysalicylaldimine)
HMPA : Hexamethylphosphoramide
THF : Tetrahydrofuran
TDPU : Trimethylsilyl-N-N'-diphenylurea

ABSTRACT

A comprehensive review on organotin(IV) complexes of Schiff bases is presented with special reference to their methods of synthesis, structural and thermal properties as well as their biological activity. The structures of these complexes are discussed on the basis of IR, electronic, multinuclear magnetic (^{1}H, ^{13}C and ^{119}Sn) NMR, X-ray and ^{119}Sn Mössbauer spectral studies. Mass fragmentation, thermal decomposition and antimicrobial activities of the complexes are also discussed.

1.1. INTRODUCTION

Schiff bases still occupy an important position as ligands in metal coordination chemistry even after almost a century since their discovery. Due to the ease of their preparation, diverse properties, medicinal, biochemical and industrial applications, the keen interest in the study of these compounds arose in the recent years. A number of metal coordination compounds of Schiff bases have been suggested as models to describe the energy transfer in biological systems (1). Formation of the complexes of organotin halides with β-ketoamines and Schiff bases have recently been of considerable interest amongst various group of chemists to study their structural properties and in view of their potential use as biocides. Sulphur, nitrogen, oxygen and fluorine have long been used to increase the biological activity of an organic moiety (2) and organotin compounds have also found applications in medicinal chemistry (3,4). The Schiff base complexes of organotin(IV) moieties have been widely investigated and the subject has also been reviewed (5). Interest in these compounds may be ascribed to their novel structural features, which are possibly caused by the multidenticity of Schiff base ligands. In view of the rapid progress including salient observations made in the relevant tin(IV) chemistry, an attempt is being made in this article to present a brief up to date review on the organotin(IV) complexes of Schiff bases with special reference to their synthetic methods, structural and thermal behaviour, and biological applications.

1.2. SYNTHESIS

1.2.1. Adducts

In view of the highly hydrolysable nature of organotin(IV) halides which are generally employed as starting materials, their complexes have been prepared by carrying out the reactions in anhydrous organic solvents such as n-hexane, benzene, acetone, methanol, ethanol or 1,4-dioxane.

Tanaka *et al* (6, 7) have synthesized 1:1 molecular adducts of dimethyltin(IV) and mono-n-butyltin(IV) chlorides with several N-substituted pyridine-2-carbaldimines:

$$R_nSnCl_{4-n} + C_5H_4NCH{=}NR' \longrightarrow R_nSnCl_{4-n}.(C_5H_4NCH{=}NR') \qquad (1)$$

[n = 2, R = Me, R' = Me, 4-MeC_6H_4 , 4-O$CH_3C_6H_4$ and 4-ClC_6H_4 (6); n = 1, R = Bu^n, R' = Me, Et, Bu^t, Ph, PhCH_2 , 4-MeC_6H_4 and 4-O$CH_3C_6H_4$ (7)].

Molecular adducts (1:2) of mono- and diorganotin(IV) chlorides with various N-alkyl(aryl)salicylaldimines (8-12), N-alkyl(aryl)-2-hydroxyacetophenoneimines (13) and N-alkyl(aryl)-2-hydroxy-1-naphthaldimines (14) have been synthesized by mixing the organotin(IV) chlorides with ligands in 1:2 molar ratio in anhydrous n-hexane or benzene. The complexes are immediately precipitated on mixing the reactants and only 1:2 adducts are formed even when the reactants are taken in 1:1 or 1:4 molar ratios (8, 13):

$$R_nSnCl_{4-n} + 2L \longrightarrow R_nSnCl_{4-n}.2L \qquad (2)$$

[when L = 2-HOC_6H_4CH=NR', R = R' = Et, Bu^n and Ph, n = 1 (9); R = R' = Me, Et, Bu^n and Ph, n = 2 (8-10); R = Ph, n = 1; R = Me and Ph, n = 2; R' = Ph, 4-ClC_6H_4 , 4-MeC_6H_4 , 4-O$CH_3C_6H_4$, 4-$NO_2C_6H_4$ and 3-$NO_2C_6H_4$ (11, 12); when L = 2-HOC_6H_4C(CH_3)=NR', R = Et, Bu^n and Ph, n = 1; R = Me, Et and Ph, n = 2; R' = Pr^n, Bu^n and Ph (13) and when L = 2-HO$C_{10}H_6$CH=NC_6H_4R', R = Ph, n = 1; R = Me and Ph, n = 2; R' = H, 4-Cl, 4-Me and 4-OCH_3 (14)].

Recently, the complexes of the type R_nSnCl_{4-n}.L where R = C_6H_5 , n = 2; R = CH_3 and C_6H_5 , n = 3 and the ligands (L) are neutral bidentate such as N-methyl-S-benzyl-β-N-(R)methylendithiocarbazates (where R = 2-furanyl, 2-methoxyphenyl, 4-methoxyphenyl and benzoylphenyl) have been reported from our laboratory (15).

Monofunctional terdentate Schiff bases obtained from the condensation of 2-aminopyridine with salicylaldehyde and 2-hydroxy-1-naphthaldehyde act only as neutral monodentate ligands yielding 1:2 adducts with mono- and diorganotin(IV) halides (16):

$$R_nSnX_{4-n} + 2L \longrightarrow R_nSnX_{4-n}.2L \qquad (3)$$

[R = Ph, X = Cl, n = 1; R = Ph, X = Cl and Br, n = 2; R = Me, X = Cl, n = 2; L = 2-HOC_6H_4CH=NC_5H_4N and 2-HO$C_{10}H_6$CH=NC_5H_4N (16)].

N-Hydroxyalkylsalicylaldimines and N-hydroxyalkylnaphthaldimines derived from the condensation of ethanolamine or substituted ethanolamines though potentially terdentate act similarly as monodentate forming 1:2 adducts with organotin(IV) halides (17, 18):

$$R_nSnX_{4-n} + 2(R'CH{=}NR''OH) \longrightarrow R_nSnX_{4-n}.2(R'CH{=}NR''OH) \qquad (4)$$

[R = Ph, n = 2, X = Cl; R = Ph, n = 1, X = Cl; R' = 2-HOC_6H_4 , R'' = $(CH_2)_2$ (17); R = Ph, n = 2, X = Cl and Br; R = Ph, n = 1, X = Cl; R' = 2-HO$C_{10}H_6$, R'' = $(CH_2)_2$ (17); R = Me, Et and Ph, n = 2, X = Cl; R' = 2-HOC_6H_4 , R'' = $(CH_2)_2$, CH(Me)CH_2 and CH(Et)CH_2 (18)].

Equimolar adducts of $RSnCl_3$, R_2SnX_2 and R_3SnCl with potentially bifunctional tetradentate ligands, N,N'-ethylenebis(acetylacetoneimines) [H_2acen] and N,N'-propylenebis(acetylacetoneimines) [H_2acpn] have been synthesized by Barbieri *et al* (19, 20) by mixing n-hexane, benzene, acetone or' 1,4-dioxane solutions of the reactants. The adducts are either precipitated immediately or crystallize from the solution on standing:

$$R_nSnX_{4-n} + H_2acen / H_2acpn \longrightarrow R_nSnX_{4-n}.(H_2acen / H_2acpn) \qquad (5)$$

[For H_2acen, R = Me, X = Cl, n = 1; R = Me, X = Cl and Br, n = 2; R = Bu^n and Ph, X = Cl, n = 2; R = Me, X = Cl, n = 3 (19, 20); for H_2acpn, R = Me and Ph, X = Cl, n = 2 (19)].

Reactions of mono- and diorganotin(IV) chlorides with equimolar amounts of N,N'-ethylenebis(salicylaldimines) [H_2salen] and N,N'-propylenebis(salicylaldimines) [H_2salpn] in anhydrous ethanol result in the formation of 1:1 molecular adducts (21-23):

$$R_nSnCl_{4-n} + H_2salen / H_2salpn \longrightarrow R_nSnCl_{4-n}.(H_2salen / H_2salpn) \qquad (6)$$

[For H_2salen, R = Me, Et, Pr^n, Bu^n and Ph, n = 2 (21-23); R = Me, Oct^n and Ph, n = 1 (22); for H_2salpn, R = Me, Et, Pr^n and Bu^n, n = 2 (23)].

Equimolar adducts of Ph_2SnX_2 (where X = Cl, ClO_4 , NO_3 and BF_4) with N,N'-bis(3-nitrobenzylidene)ethylenediamine have been synthesized by refluxing in dry methanol (24). Mehrotra and co-workers (25) have synthesized 1:1 molecular adducts of mono- and diorganotin(IV) chlorides with N,N'-ethylenebis(2-hydroxyacetophenoneimines) [H_2aceten] and N,N'-trimethylenebis(2-hydroxyacetophenoneimines) [H_2acetdap] by mixing their benzene solutions:

$$R_nSnCl_{4-n} + H_2aceten / H_2acetdap \longrightarrow R_nSnCl_{4-n}.(H_2aceten / H_2acetdap) \qquad (7)$$

[R = Et, Bu^n and Ph, n = 1; R = Me, Et, Bu^n and Ph, n = 2 (25)].

Khoo *et al* have reported 1:1 molar adducts by the reaction of triphenyltin chloride or triphenyltin isothiocynate with N-arylsalicylideneimines and N-aryl-2-hydroxynaphthylideneimines (26). They have also reported 1:1 molecular adducts of Me_2SnCl_2 with N-arylsalicylideneimines (27):

$$(C_6H_5)_3SnX / (CH_3)_2SnCl_2 + L \longrightarrow (C_6H_5)_3SnX.L / (CH_3)_2SnCl_2.L \qquad (8)$$

[X = Cl or NCS; L = 2-$HOC_6H_4CH{=}NC_6H_4R$, 2-$HOC_6H_3(OCH_3)CH{=}NC_6H_5$ and 2-$HOC_{10}H_6CH{=}NC_6H_4R$, where R = 4-CH_3 and 4-OCH_3 (26); for $(CH_3)_2SnCl_2$, L = 2-$HOC_6H_4CH{=}NC_6H_4R$, where, R = H or 4-OCH_3 (27)].

Molecular adducts (1:1) of di- and triorganotin chlorides with various Schiff bases obtained by the condensation of semicarbazide or thiosemicarbazide with salicylaldehyde, 2-hydroxynaphthaldehyde, 2-methoxybenzaldehyde, 4-methoxybenzaldehyde, furfuraldehyde, 2-hydroxyacetophenone, benzylmethyl ketone, benzil, acetophenone, 4-nitrobenzaldehyde, cyclohexanone, 5-chlorosalicylaldehyde and glyoxal have also been reported from our laboratory (28, 29):

$$R_nSnCl_{4-n} + R_1R_2C{=}NNHC(X)NH_2 \longrightarrow R_nSnCl_{4-n}.[R_1R_2C{=}NNHC(X)NH_2] \qquad (9)$$

[R = Ph, n = 3; R_1 = H, R_2 = 2-HOC_6H_4 , 4-$OCH_3C_6H_4$, 2-$OCH_3C_6H_4$, 2-$HOC_{10}H_6$, $\underbrace{C_4H_3O}$; R_1 = CH_3 , R_2 = 2-HOC_6H_4 , $C_6H_5CH_2$; R_1 = C_6H_5 , R_2 = C_6H_5CO; X = O or S (28); R_1 = H, R_2 = $H_2NC(S)NHN(C)H$, 4-$NO_2C_6H_4$; R_1 = CH_3 , R_2 = C_6H_5 ; $\underbrace{R_1R_2C}$ = $\underbrace{C_6H_{10}}$; X = S (29) ; R = Me, n = 3, R_1 = CH_3 , R_2 = C_6H_5 ; R_1 = H, R_2 = 4-$NO_2C_6H_4$, 5-Cl-2-HOC_6H_3 , $H_2NC(S)NHN(C)H$, X = S (29) ; R = Ph, n = 2, R_1 = H, R_2 = 2-HOC_6H_4, 4-$NO_2C_6H_4$, 5-Cl-2-HOC_6H_3 , $H_2NC(S)NHN(C)H$, 2-$OHC_{10}H_6$, 2-$OCH_3C_6H_4$, 4-$OCH_3C_6H_4$, $\underbrace{C_4H_3O}$; R_1 = CH_3,

$R_2 = C_6H_5$, $C_6H_5CH_2$, $\underline{R_1R_2C} = \underline{C_6H_{10}}$; X = S (29)].

Nickel(II) and copper(II) chelates of N,N'-ethylenebis(salicylaldimine) [Msalen] and N,N'-*o*-phenylenebis(salicylaldimine) [Msalphen-*o*] act as bidentate neutral donor ligands and yield 1:1 adducts with mono- and diorganotin(IV) chlorides (30-33):

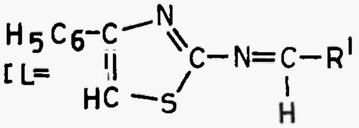
$$R_nSnCl_{4-n} + \text{Msalen / Msalphen-}o \longrightarrow R_nSnCl_{4-n}.(\text{Msalen / Msalphen-}o) \qquad (10)$$

[For Msalen, R = Me, Bu^n and Ph, n = 1, M = Ni(II) (30-32); R = Bu^n and Ph, n = 1, M = Cu(II) (32); R = Me and Ph, n = 2, M = Ni(II) (30, 31); for Msalphen-*o*, R = Bu^n and Ph, n = 1, M = Ni(II) and Cu(II) (33)].

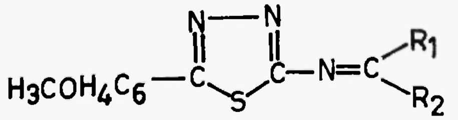
Recently, organotin(IV) derivatives of Schiff bases derived from the condensation of 2-hydroxy-1-naphthaldehyde or salicylaldehyde with substituted anilines in 1:1 or 1:2 molar ratios have been reported (34).

Recently, di- and triorganotin(IV) derivatives of Schiff bases derived from the condensation of heterocyclic amines, viz., 2-amino-4-phenylthiazole and 2-amino-5-(*o*-anisyl)-1,3,4-thiadiazole with different aldehydes or ketones have also been reported from our laboratory (35, 36).

$$R_nSnCl_{4-n} + L \longrightarrow R_nSnCl_{4-n}.L \qquad (11)$$



; R = Ph , n = 2 , R = Me and Ph, n = 3, $R^1 = C_6H_5$, 4-$\underline{C_4H_3O}$ (35) ; L=



; R = Ph , n = 2 , R = Me and Ph, n = 3, R^1 = H, R^2 = 2-HOC_6H_4 , 2-$HOC_{10}H_6$, $\underline{C_4H_3O}$; $R^1 = CH_3$, R^2 = 2-HOC_6H_4 , $C_6H_5CH_2$, CH_2COCH_3 (36)].

1.2.2. Substitution Derivatives

1.2.2.1. Deprotonation with triethylamine

Organotin(IV) chlorides react with dibasic tetradentate Schiff bases in the presence of triethylamine on refluxing in ethanol to yield the desired chelates, R_2SnL:

$$R_2SnCl_2 + H_2L \xrightarrow[\text{EtOH}]{2Et_3N} R_2SnL + 2Et_3N.HCl \qquad (12)$$

[R = Me and Ph; H_2L = Schiff bases derived from ethanolamine and biacetyl/benzil/9:10 phenanthrenequinone, and from ethylenediamine and *o*-vanillin (H_2vanilen) (37); R = Me, H_2L = Schiff bases derived from acetoin or benzoin and semicarbazide or thiosemicarbazide (38)].

1.2.2.2. Template synthesis

Reactions of isopropyl amine with diorganotin(IV) monothiodibenzoylmethanates on refluxing in benzene resulted in the formation of diorganotin(IV) chelates of thio-β-ketoamine (39):

$$R_2Sn[SC(Ph)=CHCOPh]_2 + 2pr^iNH_2 \longrightarrow R_2Sn[SC(Ph)=CHC(Ph)=NPr^i]_2 + 2H_2O \qquad (13)$$

[R = Me, Bu^n and Ph (39)].

1.2.2.3. By the sodium salt method

The sodium salt method has been found to be the most suitable method for the preparation of a wide variety of organotin(IV) chelates of monofunctional bidentate, bifunctional terdentate and tetradentate Schiff bases and β-ketoamines. Addition of a methanol solution of organotin(IV) halide to a solution of the sodium salt of the Schiff base prepared *in situ* by the reaction of Schiff base with sodium methoxide in anhydrous methanol under nitrogen results in the formation of the desired chelates:

$$R_2SnCl_2 + H_2L + 2NaOMe \longrightarrow R_2SnL + 2NaCl + 2MeOH \qquad (14)$$

[R = Me and Ph, H_2L = 2-$HOC_6H_4CH{=}NC_6H_4OH$-2, 2-$HOC_6H_4\underbrace{CHNHC_6H_4S}$, $PhCOCH{=}C(Me)NHC_6H_4OH$-2, $MeCOCH{=}C(Me)NHC_6H_4OH$-2 and $MeCOCH_2\underbrace{C(Me)NHC_6H_4S}$ (40-44); R = Ph and Bu, H_2L = 2-$HOC_6H_4CH{=}NCH_2CH_2OH$ (17); R = Me, H_2L = $HOC_6H_3XCH{=}NC_6H_3YOH$-2 where X = H, Y = H, 4-CH_3 , 4-Cl and 4-NO_2 ; X = 3-OCH_3 , Y = H, 4-CH_3 and 4-NO_2 ; X = 3-NO_2 , Y = H, 4-CH_3 and 4-NO_2 ; X = 5-NO_2 , Y = H, 4-CH_3 and 4-NO_2 ; X = 5-Cl, Y = H and 4-Cl (45); R = Me and Bu^n, H_2L = H_2salen (23); R = Me, Et and Ph, H_2L = H_2salen, H_2salaen, H_2saldap-2-ol and H_2saladap-2-ol (46, 47); R = Me and Ph, H_2L = H_2salen, H_2saldap, H_2salphen-*o* and H_2vanilen (48)].

Similarly, the chelates of the type Me_2SnL have been prepared by the reaction of the sodium salts of the Schiff bases derived from the condensation of salicylaldehyde with sulfathiazole, sulfaphenazole, sulfadiazine, sulfaguanidine, 2-(*p*-aminobenzene sulfonamide)-4,5-dimethyloxazole, sulfisoxazole and sulfapyridine with Me_2SnCl_2 (49). Reactions of the Na-salts of Schiff bases, $R^1C(OH){=}CHC(Me){=}NR^2$ (R^1 = Me, R^2 = 4-FC_6H_4 ; R^1 = Ph, R^2 = 4-FC_6H_4 and 2-ClC_6H_4) with Me_2SnCl_2 or Bu_2SnCl_2 in 1:1 or 1:2 molar ratios afford 5- and 6-coordinate tin complexes, $R_2Sn(Cl)L$ or R_2SnL_2 (R = Me, Bu; L = Schiff base anion) (50). Similarly, 5- or 6-coordinate di- and triorganotin(IV) chelates of semicarbazones and thiosemicarbazones in 1:1 or 1:2 molar ratio have been reported from our laboratory (51, 52). Tandon *et al* have also reported triorganotin(IV) chelates of Schiff bases by the reaction of Me_3SnCl with the sodium salts of the heterocyclic thiosemicarbazones (53):

$$Ph_2SnCl_2 + 2NaOMe + H_2L \longrightarrow Ph_2SnL + 2NaCl + 2MeOH \qquad (15)$$

$$R_3SnCl + NaOMe + HL \longrightarrow R_3SnL + NaCl + MeOH \qquad (16)$$

$$Ph_2SnCl_2 + 2NaOMe + 2HL' \longrightarrow Ph_2SnL'_2 + 2NaCl + 2MeOH \qquad (17)$$

[H_2L = $R_1R_2C{=}NNHC(X)NH_2$; X = O or S, R_1 = H, R_2 = 2-HOC_6H_4 , 2-$HOC_{10}H_6$; R_1 = CH_3 , R_2 = 2-HOC_6H_4 , (51) ; X = S, R_1 = H, R_2 = 5-Cl-2-HOC_6H_3 (52); HL = $R_1R_2C{=}NNHC(X)NH_2$; R = Ph, R_1 = H, R_2 = 4-$OCH_3C_6H_4$, 2-$OCH_3C_6H_4$, $\underbrace{C_4H_3O}$: R_1 = CH_3 , R_2 = $C_6H_5CH_2$; R_1 = C_6H_5 , R_2 = C_6H_5CO, X = O or S (51); R = Me, R_1 = CH_3 , R_2 = C_6H_5 ; R = Ph, R_1 = CH_3 , R_2 = C_6H_5 ; R_1 = H, R_2 = 4-$NO_2C_6H_4$; X = S (52) ; HL' = $R_1R_2C{=}NNH(S)NH_2$; R_1 = H, R_2 = 4-$NO_2C_6H_4$ (52)].

A large number of chelates of the types R_2SnL and R_3SnL, where L = anion of Schiff base such as S-alkyl-β-N-(substituted phenyl)methylendithiocarbazates, have also been reported by the reaction of the sodium salts of the Schiff bases with R_nSnCl_{4-n} (54-58):

$$R_nSnCl_{4-n} + Na_mL \longrightarrow R_nSnL + mNaCl \qquad (18)$$

[$H_mL = R^1R^2C{=}NN{=}C(SH)SR^3$; n = 3, m = 1, R = C_6H_5 , CH_3 and C_4H_9 , R^1 = H, R^2 = 2-pyridyl, R^3 = $CH_2C_6H_5$ and CH_3 ; R = C_6H_5 and C_4H_9 , $R^1 = R^3 = CH_3$, R^2 = CH_3 , C_2H_5 and C_6H_5 (54); n = 2, m = 2, R = CH_3 , C_2H_5 , C_4H_9 , C_8H_{17} and $C_6H_5CH_2$ and n = 3, m = 1, R = C_6H_5 , R^1 = H, R^2 = 2-HO-4-$OCH_3C_6H_3$, R^3 = $CH_2C_6H_5$ (55); n = 2, m = 2, R = C_6H_5 , R^1 = H, R^2 = 2-HOC_6H_4, 2-$HOC_{10}H_6$ and R^1 = CH_3 , R^2 = 2-HOC_6H_4 ; n = 3, m = 1, R = CH_3 and C_6H_5, R^1 = H, R^2 = 2-$OCH_3C_6H_4$, 4-$OCH_3C_6H_4$, $\underbrace{C_4H_3O}$ and R^1 = C_6H_5 , R^2 = COC_6H_5 , R^3 = $CH_2C_6H_5$ (56); n = 2, m = 2, R = $CH_2CH_2CO_2Me$, $CH_2CH_2CO_2Et$ and $CH_2CH_2CO_2Bu$, R^1 = H, R^2 = 2-HOC_6H_4 , 2-HO-4-$OCH_3C_6H_3$, 2-$HOC_{10}H_6$, R^3 = CH_3 and $C_6H_5CH_2$ (57, 58); $H_mL = R^1R^2C{=}NN(CH_3)C{=}S(SR^3)$, n = 3, m = 1, R = CH_3 and C_6H_5 , R^1 = CH_3 , R^2 = 2-HOC_6H_4 and R^1 = H, R^2 = 2-HOC_6H_4 , 2-$HOC_{10}H_6$, R^3 = $CH_2C_6H_5$ (15)].

The interaction of the sodium salts of the quadridentate Schiff bases with R_2SnCl_2 (R = Me and Ph) afforded many new organotin(IV) derivatives (59):

$$R_2SnCl_2 + H_2L + 2NaOMe \longrightarrow R_2SnL + 2NaCl + 2MeOH \qquad (19)$$

[$H_2L = R^1R^2C{=}N(R^3)N{=}CR^2R^1$; for R = CH_3, R^1 = H, R^2 = 2-HOC_6H_4, R^3 = $-CH_2-CH_2-$, $-CH_2CH(OH)CH_2-$, $-CH_2CH_2CH_2-$; R^1 = CH_3 , R^2 = 2-HOC_6H_4 , R^3 = $-CH_2CH_2-$; R^1 = H, R^2 = 2-HO-3-$COOHC_6H_3$, R^3 = $-CH_2-CH_2-$; for R = C_6H_5 , R^1 = H, R^2 = 2-HOC_6H_4, R^3 = $-CH_2CH_2-$; R^1 = H, R^2 = 2-HO-3-$COOHC_6H_3$, R^3 = $-CH_2CH(OH)CH_2-$ (59)].

Mehrotra and co-workers (60) have synthesized volatile trialkyltin(IV) complexes of N-substituted salicylaldimines by the reactions of trialkyltin(IV) chlorides with the sodium salts of the Schiff bases prepared *in situ* from sodium isopropoxide and the Schiff bases in isopropanol:

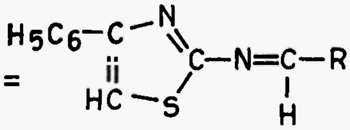
$$R_3SnCl + HOC_6H_4CH{=}NR^1 + NaOPr^i \longrightarrow R_3SnOC_6H_4CH{=}NR^1 + Pr^iOH + NaCl \qquad (20)$$

[R = Et, R^1 = Me, Et, Allyl, Pr^i, Bu^n and Ph; R = Pr^n, R^1 = Ph; R = Bu^n, R^1 = Bu^n and Ph (60)].

Recently, some new di- and triorganotin(IV) chelates of Schiff bases derived from the condensation of 2-amino-4-phenylthiazole and 2-amino-5-(*o*-anisyl)-1,3,4-thiadiazole with different aldehydes or ketones have been reported from our laboratory (35, 36).

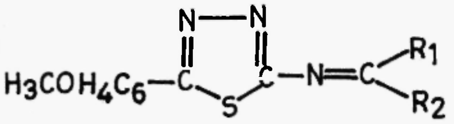
$$Ph_2SnCl_2\ /\ R_3SnCl + L'Na \xrightarrow{1:2\ /\ 1:1} Ph_2SnL'_2\ /\ R_3SnL' + 2NaCl\ /\ NaCl \qquad (21)$$

[L^1H =



; R = Ph or Me, R^1 = 2-HO C_6H_4 , 2-$HOC_{10}H_6$ (35);

L^1H =



; R = Ph or Me, R^1 = H, R^2 = 2-HOC_6H_4 , 2-$HOC_{10}H_6$; R^1 = CH_3 , R^2 = 2-HOC_6H_4 (36)].

1.2.2.4. By direct Sn–Cl bond cleavage reaction using silylated compounds

Recently, a new series of organotin(IV) compounds have been synthesized by the interaction of silylated dibasic quadridentate Schiff bases with R_2SnCl_2 (R = Me or Ph) and $MeSnCl_3$ (59, 61):

$$MeSnCl_3 + L(SiMe_3)_2 \longrightarrow MeSn(L)Cl + 2Me_3SiCl \qquad (22)$$

$$R_2SnCl_2 + L'(SiMe_3)_2 \longrightarrow R_2SnL' + 2Me_3SiCl \qquad (23)$$

[R = Me, H_2L and $H_2L' = R^1R^2C{=}N(R^3)N{=}CR^2R^1$, $R^1 = CH_3$, $R^2 = 2\text{-}HOC_6H_4$, $R^3 = -CH_2-CH_2-$ and C_6H_4 (61); R = Me or Ph, H_2L' = Schiff bases (59), as indicated in Eq. (19)]. When mononuclear complexes $[H_2salcen]SnR_2$, where [$H_2salcen$ = N,N'-ethylenebis(3-carboxy-salicylaldimine), R = Me or Ph] react with trimethylsilyl-N-N'-diphenylurea (TDPU) in THF resulting the silylated complexes $[(Me_3Si)_2salcenSnR_2]$. Desilylation of mononuclear complexes with R_2SnCl_2 (R = Me or Ph) yields di-tin (Sn−Sn) complexes $[R_2Sn(salcen)SnR_2]$. On the other hand, the silylated products of the mononuclear metal complexes $[M(H_2salcen)]$ (M = Ni or Pd) react with R_2SnCl_2 to yield hetero dinuclear complexes $[M(salcen)SnR_2]$ with Ni−Sn and Pd−Sn bonds.

$$\underset{\text{Mononuclear complex}}{[H_2salcen]SnR_2} \xrightarrow[1\,:\,2]{\text{TDPU in THF}} [(Me_3Si)_2salcenSnR_2] \xrightarrow{R_2SnCl_2} \underset{\text{dinuclear complex}}{[R_2Sn(salcen)SnR_2)]} \qquad (24)$$

$$\underset{\text{Mononuclear complex}}{[M(H_2salcen)]} \xrightarrow{\text{TDPU}} [M(salcen)(SiMe_3)_2] \xrightarrow[1\,:\,1]{R_2SnCl_2} \underset{\text{hetero dinuclear complex}}{[M(salcen)SnR_2]} \qquad (25)$$

(M = Ni or Pd)

The reactions of tetraorganosilicon compounds such as RCH_2SiMe_3 with $LSnCl_2$ where L = anion of dibasic quadridentate Schiff bases have been reported to yield new organotin(IV) compounds (62):

$$LSnCl_2 + 2C_6H_5CH_2SiMe_3 \longrightarrow C_6H_5CH_2(LSn)CH_2C_6H_5 + 2Me_3SiCl \qquad (26)$$

$$nLSnCl_2 + nMe_3SiCH_2C_6H_4CH_2SiMe_3 \longrightarrow$$

$$\underset{\text{polymer}}{[-Sn-CH_2C_6H_4CH_2(LSn)CH_2C_6H_4CH_2-Sn-]} + 2nMe_3SiCl \qquad (27)$$

1.2.2.5. By the potassium salt method

Recently, few di- and triorganotin(IV) derivatives of the Schiff base derived from *o*-hydroxyacetophenone and glycine have been synthesized by the reaction of the corresponding di- and triorganotin(IV) chlorides with the potassium salt of the Schiff base in 1:2 and 1:1 molar ratios, respectively, in refluxing benzene (63):

$$R_nSnCl_{4\,n} + m[HOC_6H_4C(Me){=}NCH_2COOK] \longrightarrow$$

$$[HOC_6H_4C(Me){=}NCH_2COO]_mSnR_n + mKCl \qquad (28)$$

[n = 3, m = 1; n = 2, m = 2; R = Me, Bu and Ph (63)].

However, a reaction between diorganotin(IV) dichloride and the potassium salt of the Schiff base in refluxing benzene in the presence of triethylamine yielded the corresponding 5-coordinate diorganotin(IV) derivatives (63):

$$R_2SnCl_2 + [HOC_6H_4C(Me){=}NCH_2COOK] \xrightarrow{Et_3N}$$

$$[OC_6H_4C(Me){=}NCH_2COO]SnR_2 + KCl + Et_3N.HCl \qquad (29)$$

[R = Me, Bu and Ph]

Recently, 5-coordinate organotin chelates have been prepared by treating $2\text{-}HOC_6H_4CH{=}NCH(R)CO_2K$ with R'_2SnCl_2 [R = H, Me, Me_2CHCH_2, $PhCH_2$ and $MeSCH_2CH_2$; R' = Bu and Ph (64, 65)].

1.2.2.6. By the thallium salt method

N,N'-Ethylenebis(salicylaldiminato)dimethyltin(IV), N,N'-ethylenebis(salicylaldiminato)-diphenyltin(IV) and (N-2-hydroxyphenylsalicylaldiminato)dimethyltin(IV) have been synthesized by the reaction of diorganotin(IV) chlorides with the thallium salts of the respective Schiff bases in anhydrous methanol or benzene (21):

$$R_2SnCl_2 + Tl_2salen \xrightarrow{MeOH} R_2Snsalen + 2TlCl\downarrow \qquad (30)$$

[R = Me and Ph]

$$Me_2SnCl_2 + Tl_2salap \xrightarrow{Benzene} Me_2Snsalap + 2TlCl\downarrow \qquad (31)$$

1.2.2.7. By ligand exchange

Monohalomonoorganotin(IV) chelates of bifunctional terdentate Schiff bases have been synthesized by the reactions of dimethyltin(IV) chelates of the Schiff bases with monoorganotin(IV) halides in n-hexane under dry nitrogen (66-68). The chelates either precipitate or crystallize out leaving dimethyltin(IV) dichloride in solution:

$$RSnCl_3 + Me_2SnL \longrightarrow RSnClL + Me_2SnCl_2 \qquad (32)$$

[R = Me, Oct^n and Ph; L is the dianion of $2\text{-}HOC_6H_4CH{=}NC_6H_4OH\text{-}2$, $PhC(OH){=}CHC(Me){=}NC_6H_4OH\text{-}2$, $2\text{-}HOC_6H_4\underbracket{CHNHC_6H_4S}$ or $MeCOCH_2\underbracket{C(Me)NHC_6H_4S}$ (66-68)].

1.2.2.8. By the reaction of organotin(IV) amides with Schiff bases

N,N'-Ethylenebis(acetylacetoneiminato)trimethyltin(IV) and -dimethyltin(IV) have been prepared by the reactions of Me_3SnNEt_2 and $Me_2Sn(NEt_2)_2$, respectively with H_2acen in refluxing benzene under dry nitrogen (69):

$$Me_3SnNEt_2 / Me_2Sn(NEt_2)_2 + H_2acen \longrightarrow Me_3SnHacen / Me_2Snacen + Et_2NH / 2Et_2NH \qquad (33)$$

1.2.2.9. By the reaction of trialkyltin(IV) alkoxides with Schiff bases

Trialkyltin(IV) derivatives of N-alkyl(aryl)salicylaldimines and 2,2-disubstituted benzothiazolines have been prepared by reacting the trialkyltin(IV) alkoxides with the Schiff bases in refluxing benzene (60, 70). The alcohol liberated during the course of the reaction is removed azeotropically with benzene for pushing the reactions to completion and the complexes are purified by distillation under reduced pressure. The same method (71) has also been used for the synthesis of dialkyltin(IV) derivatives of salicylaldimines:

$$R_3SnOR'' + HOC_6H_4CH{=}NR' \longrightarrow R_3SnOC_6H_4CH{=}NR' + R''OH \qquad (34)$$

[R = Pr^n, R' = Me, Et, Allyl, Pr^i and Bu^n, R'' = Et; R = Bu^n, R' = Me, Et, Allyl and Pr^i, R'' = Pr^i (60)].

$$R_3SnOEt + \underbracket{SC_6H_4NHC}R'R'' \longrightarrow R_3Sn\underbracket{SC_6H_4N{=}C}R'R'' + EtOH \qquad (35)$$

[R = Et, Pr^n and Bu^n ; R' = Me, R" = Me, Et, Bu^i and Ph; R' = Et, R" = Et and Bu^n (70)].

$$R_2Sn(OPr^i)_2 + HOC_6H_4C(R')=NR''OH \longrightarrow R_2\overline{SnOC_6H_4C(R')=NR''O} + 2Pr^iOH \qquad (36)$$

[R = Me, Et, Bu and Ph, R' = H and Me, R" = $-CH_2CH_2-$ and $-CH_2CH_2CH_2-$ (71)].

1.2.2.10. By the reactions of trialkyltin hydroxides and Schiff bases

Trimethyltin(IV) hydroxide reacts with 2,2-disubstituted benzothiazolines to yield trimethyltin(IV) chelates. Water formed during the course of the reaction is removed azeotropically with benzene and the chelates are purified by distillation under vacuum (70):

$$Me_3SnOH + \underline{SC_6H_4NHC}R'R'' \longrightarrow Me_3Sn\underline{SC_6H_4N=C}R'R'' + H_2O \qquad (37)$$

[R' = Me, R" = Me, Et, Bu^i and Ph; R' = Et, R" = Et and Bu^n (70)].

1.4.1.2.11. By the reaction of diorganotin(IV) oxides with Schiff bases

Reactions of diorganotin(IV) oxides with N-isopropylthiodibenzoylmethaneimine [$HtdbmPr^i$] in refluxing benzene result in the formation of diorganotin(IV) chelates and the liberation of water which is removed as an azeotrope with benzene (39):

$$R_2SnO + 2HtdbmPr^i \xrightarrow{C_6H_6} R_2Sn(tdbmPr^i)_2 + H_2O \qquad (38)$$

[R = Me, Bu^n and Ph (39)].

Similarly, di- and tributyltin(IV) chelates of semicarbazones and thiosemicarbazones have been prepared (38, 52, 72, 73):

$$Bu_2SnO + H_2L \ / \ 2HL \longrightarrow Bu_2SnL \ / \ Bu_2SnL_2 + H_2O \qquad (39)$$

[H_2L / HL = $R^1R^2C=NN=C(XH)NH_2$, R^1 = H, R^2 = 2-HOC_6H_4 , X = S (72) and X = O and S (73); R^1 = H, R^2 = 2-$HOC_{10}H_6$, X = S; R^1 = H, R^2 = C_6H_5 and R^1 = CH_3 , R^2 = 2-HOC_6H_4 , X = O and S (73); R^1 = CH_3 , R^2 = $HC(CH_3)OH$ and R^1 = C_6H_5 , R^2 = $HC(C_6H_5)OH$, X = O and S (38); R^1 = H, R^2 = 5-Cl-2-OHC_6H_3 ; R^1 = CH_3 , R^2 = C_6H_5 ; $\underline{R^1R^2C} = \underline{C_6H_{10}}$; X = S (52)].

$$(Bu_3Sn)_2O + 2HL \longrightarrow 2Bu_3SnL + H_2O \qquad (40)$$

[HL = $R^1R^2C=NN=C(XH)NH_2$, R^1 = H, R^2 = C_6H_5 and R^1 = CH_3, R^2 = 2-HOC_6H_4 ; X = O and S (73)].

The same method has also been adopted for the synthesis of a number of penta- and hexa-coordinate organotin(IV) chelates of the Schiff bases derived from S-alkyldithiocarbazate amines (72, 74-76):

$$R_nSnO \ / \ (R_mSn)_2O + H_2L \longrightarrow R_nSnL \ / \ (R_mSn)_2L + H_2O \qquad (41)$$

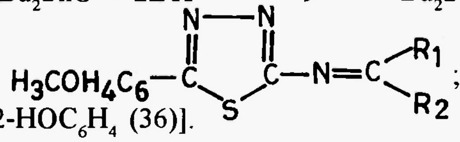
[H_2L = $R^1R^2C=NNC(SH)SR^3$; n = 2, R = Bu, R^1 = H and CH_3 , R^2 = 2-HOC_6H_4 , R^3 = CH_3 (74); n = 2, R = Bu, R^1 = H, R^2= 2-HOC_6H_4 , R^3 = $CH_2C_6H_5$ (72, 76); n = 2, R = Me, Bu and Ph, R^1 = CH_3 , R^2 = 2-HOC_6H_4 ; n = 2, R = Me, Bu and Oct and m = 3, R = Bu and Ph, R^1 = H, R^2 = 2-HO-4-ClC_6H_3 and 2-HO-4-BrC_6H_3 ; R^3 = $CH_2C_6H_5$ (75); n = 2, R = Me, Bu and Oct and m = 3, R = Bu, Oct and Ph, R^1 = H, R^2 = 2-HOC_6H_4, R^3 = $CH_2C_6H_5$ (76)].

Recently, some new dibutyltin(IV) chelates of the Schiff bases derived from the condensation of 2-amino-5-(*o*-anisyl)-1,3,4-thiadiazole with salicylaldehyde, 2-hydroxynaphthaldehyde and 2-

hydroxyactophenone have been prepared from our laboratory (36).

$$Bu_2SnO + 2L'H \xrightarrow{\text{Benzene-methanol}} Bu_2SnL'_2 + H_2O \qquad (42)$$

[L'H=



; R_1 = H, R_2 = 2-HOC_6H_4 , 2-$HOC_{10}H_6$; R_1 = CH_3, R_2 = 2-HOC_6H_4 (36)].

Sandhu *et al* have also synthesized new organotin(IV) chelates by the reaction of R_2SnO and the Schiff bases derived from the condensation of aromatic aldehydes with *o*-arsanilic acid (1:1) and from ethylenediamine with acetylacetone (1:2) (77):

$$R_2SnO + H_2L \longrightarrow R_2SnL + H_2O \qquad (43)$$

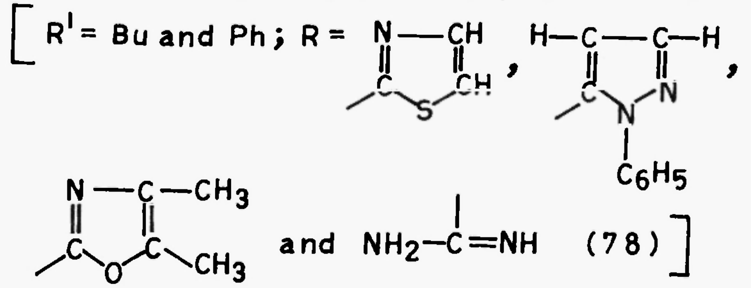
$$R_2SnO + H_2SB' \xrightarrow{1:1/1:2} R_2SnSB' \,/\, R_2Sn(HSB')_2 + H_2O \qquad (44)$$

[R = Me, Bu, Oct and Benz, H_2L = $R^1R^2C{=}NC_6H_4AsO_3H_2$, R^1 = H, R^2 = C_6H_5 , 2-$NO_2C_6H_4$, 2-ClC_6H_4, 3-$NO_2C_6H_4$; H_2SB' = $[-CH_2N{=}C(CH_3)CH{=}C(OH)CH_3]_2$ (77)].

Similarly, the reactions of diorganotin(IV) oxides and bis(tri-n-butyltin) oxide with the azomethines derived by the condensation of salicylaldehyde with various sulfadrugs, by the condensation of salicylaldehyde, *o*-hydroxyacetophenone or benzaldehyde with *o*-aminothiophenol, and by salicylaldehyde or *o*-hydroxynaphthaldehyde with *p*-flouroaniline yield 1:1 organotin(IV) chelates (78, 79):

$$R'_2SnO + HOC_6H_4CH{=}NC_6H_4SO_2NH{-}R \longrightarrow R'_2Sn(OC_6H_4CH{=}NC_6H_4SO_2N{-}R) + H_2O \qquad (45)$$

[R' = Bu and Ph; R =



and $NH_2-C{=}NH$ (78)]

$$Bu_2SnO + H_2L \,/\, 2HL' \longrightarrow Bu_2SnL \,/\, Bu_2SnL'_2 + H_2O \qquad (46)$$

$$(Bu_3Sn)_2O + 2HL' \longrightarrow 2Bu_3SnL' + H_2O \qquad (47)$$

[H_2L = 2-$HOC_6H_4C(CH_3){=}NC_6H_4SH$ and 2-$HOC_6H_4CH{=}NC_6H_4SH$; HL' = 2-$HOC_6H_4CH{=}NC_6H_4F$-4, 2-$HOC_{10}H_6CH{=}NC_6H_4F$-4 and $C_6H_5CH{=}NC_6H_4SH$ (79)].

Some new dibutyltin(IV) chelates of the dianionic tridentate Schiff bases derived from the condensation of salicylaldehyde or *o*-hydroxyacetophenone or pyruvic acid with different amino acids have recently been reported from our laboratory (80):

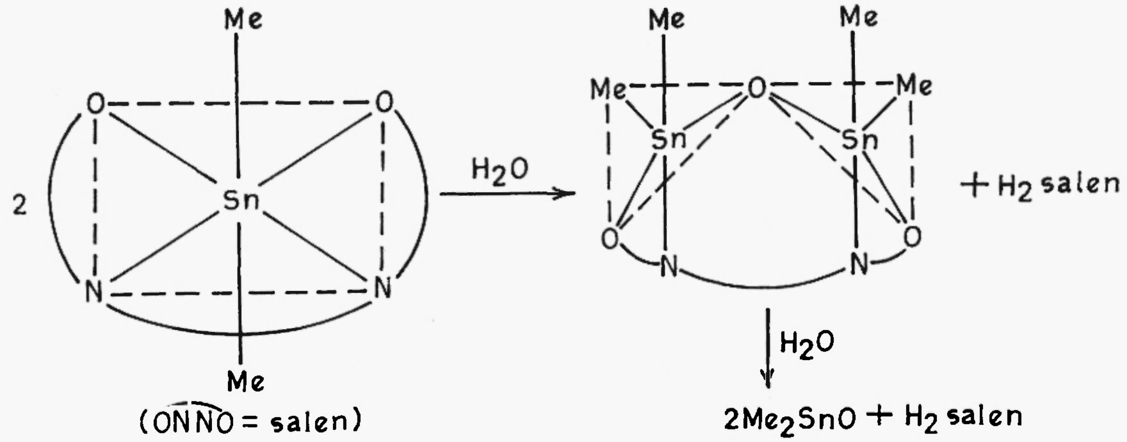
$$Bu_2SnO + H_2L \xrightarrow{\text{benzene}} Bu_2SnL + H_2O \qquad (48)$$

[H_2L = $R^1R^2C{=}N(R)COOH$, R^1 = H and CH_3 , R^2 = 2-HOC_6H_4 ; R^1 = CH_3 , R^2 = HOOC; R = $-CH_2-$, $-CH_2-CH_2-$, $>CH-CH_2-CH_3$, $-CH_2-CH_2-CH_2-$, $>CH-CH(CH_3)_2$, $>CH-CH_2-CH_2SCH_3$, $>CHC_6H_5$ (80)].

1.3. PROPERTIES

1.3.1. Hydrolytic Stability

Organotin(IV) adducts and chelates are highly susceptible to hydrolysis (38, 74). However, the chelates are more readily hydrolysed than the adducts and at least in one case the products of hydrolysis have been isolated and identified. Tanaka *et al* (48) have observed that when n-heptane is added to a solution of $Me_2Snsalen$ in reagent grade benzene and the mixture cooled, crystals of $(Me_2Sn)_2Osalen$ are deposited and H_2salen is recovered from the filtrate. When the solution of $(Me_2Sn)OSalen$ is exposed to air for longer periods, it finally changes into Me_2SnO:



(49)

1.3.2. Volatility and Thermal Stability

Most of the adducts and chelates of organotin(IV) moieties with the Schiff bases are non-volatile, crystalline solids which possess sharp melting points (26, 28, 29, 35-37, 51, 52, 76). Di- and tributyltin(IV) derivatives of Schiff bases derived from dithiocarbazate amines are highly viscous liquids (54, 74). However, the adducts of dimethyltin(IV) and diethyltin(IV) chlorides with N-alkyl(methyl, ethyl or n-butyl)salicylaldimines (8) are volatile and sublime unchanged in quantitative yields under reduced pressure. Trialkyltin(IV) derivatives of N-alkyl(aryl)salicylaldimines (60) and 2,2-disubstituted benzothiazolines (70) are also volatile yellow coloured liquids.

1.3.3. Molecular Association

Direct molecular weight measurements have been reported for a few adducts and chelates of organotin(IV) halides with the Schiff bases (35, 37, 38, 53, 57, 59, 74, 77). Osmometric measurements in methanol solution carried out by Barbieri *et al* (19, 81) on the adducts, $R_nSnCl_{4-n}\cdot H_2acen$, indicate that these dissociate and independent organotin halide, R_nSnCl_{4-n} and ligand, H_2acen, moieties are perhaps present in solution. Trialkyltin(IV) derivatives of N-alkyl(aryl)salicylaldimine (60) and 2,2-disubstituted benzothiazolines (70) as well as the chelates, R_2SnL (17, 40, 48, 76, 79) (where L is the dianion of a bifunctional terdentate or tetradentate ligand) and R_3SnL (where L is the anion of Schiff bases derived from the condensation of dithiocarbazate amines with a ketone or pyridine-2-carboxaldehyde) (54) are monomeric in solution.

Similarly, the adducts and chelates of tri- and diorganotin(IV) moieties with the Schiff bases derived from the condensation of 2-amino-4-phenylthiazole with different aldehydes have also been reported to be monomeric in nitrobenzene (35). Di- and tri-n-butyltin(IV) chelates of biionic and monoionic Schiff bases are monomeric (73). However, the adducts of organotin(IV) halides with potentially tetradentate neutral ligands have been assigned a polymeric structure in the solid state on the basis of infrared and Mössbauer spectral data (20, 22).

1.4. STRUCTURAL STUDIES

Structural aspects of the adducts as well as the chelates of organotin(IV) moieties with the Schiff bases have received much attention. Electronic and nuclear (^{1}H, ^{13}C and ^{119}Sn) magnetic resonance spectral studies along with molecular weight and conductance measurements have been carried out to throw light on the structures of the complexes in solution. On the other hand, infrared, Mössbauer and X-ray crystallographic studies of a few representative complexes have, of course, been made to elucidate the structures of these compounds in the solid state. Conclusions drawn on the basis of these studies are being summarised below:

1.4.1. Molar Conductance

Molar conductances of adducts of organotin(IV) chlorides with unidentate, monofunctional bidentate, bifunctional terdentate and bifunctional tetradentate ligands have been measured in nitrobenzene, N,N-dimethylformamide or methanol depending upon the solubility of the adducts and it has been found that the adducts behave as non-electrolytes (8-10, 13, 18, 25, 26, 28, 29, 35, 36). Molar conductance values of the organotin(IV) chlorides and their adducts with H_2acen (81) in methanol at about the same molar concentration have been found to be of the same order. It has been suggested that essentially the same conducting species are present in both systems. In comparison to the adducts, the chelates of organotin(IV) moieties of the Schiff bases show very low values of molar conductance indicating their non-electrolytic nature (15, 17, 35, 36, 38, 51, 52, 54, 59, 78, 80).

1.4.2. Electronic Spectra

Electronic spectra of the adducts $R_nSnCl_{4-n}.L$ (L = Schiff base ligands) usually correspond with those of the free ligands which strongly suggests that the ligands maintain their keto-amine hydrogen bonded configuration in the complexes also (28, 29, 35, 36, 81). On the other hand, the spectra of the chelates of organotin(IV) moieties with different Schiff bases were found to be quite different from those of the free Schiff bases suggesting the deprotonation of the Schiff bases in chelates (35, 36, 38, 43, 51, 52, 55-57, 74, 76, 80). It has been reported that a metal/metalloid is capable of forming dπ-pπ bonds with ligands containing nitrogen as the donor atom. The tin atom has its 5d orbitals completely vacant and hence L→M bonding can take place by the acceptance of a pair of electrons from the nitrogen atom of the ligand. In the electronic spectra of the adducts as well as of chelates, new additional charge transfer bands in the region 240-340 nm have also been reported (15, 35, 36, 51, 74).

1.4.3. Infrared Spectra

Infrared spectra of the adducts as well as of the chelates of organotin(IV) moieties provide valuable informations regarding the structures of the compounds in the solid state. Either an increase or decrease by a few wave numbers in the frequency of C=N stretching vibration which appears in the region 1585-1650 cm^{-1} in the spectra of the free Schiff bases has been generally observed and it has been inferred that the ligands coordinate to the tin atom through the azomethine nitrogen atom (5, 17, 24, 28, 29, 35-37, 51, 52, 54, 56, 73, 74). Phenolic νC−O appearing at ~ 1280 cm^{-1} in the IR spectra of the Schiff bases containing *o*-hydroxy group remains almost unaffected in the spectra of organotin(IV) adducts, indicating its non-participation in coordination (12, 17). However, in the spectra of organotin(IV) chelates phenolic ν(C−O) band is shifted to higher wave number indicating its participation in coordination (35, 36, 51, 55, 59, 60, 73, 80). In the spectra of the adducts of organotin(IV) halides with Cosalen, Nisalen and Cusalen, the frequency of phenolic νC−O increases from 1540 cm^{-1} in Msalen to 1550-1560 cm^{-1} in adducts suggesting coordination of metal chelate to organotin(IV) halide through phenolic oxygen atoms which attain 3-coordination (30-33).

The frequencies of the Sn−C stretching vibrations are not affected to any appreciable extent by a change in coordination number of tin, but those of the Sn−X stretching modes are very much diminished by an increase in coordination number of tin from 4 to 6. However, the number of the νSn−C and the νSn−Cl bands appearing in the spectra of the adducts gives an indication of the geometry of the R_nSnX_{4-n} moiety. In the octahedral adducts of R_2SnCl_2 with N-alkyl(aryl)salicylaldimines (8, 12), N-alkyl(aryl)-2-hydroxyacetophenoneimines (13), N-alkyl(aryl)-2-hydroxy-1-naphthaldimines (14) and N,N'-ethylenebis(acetylacetoneimine) (20); and adducts of R_2SnX_2 with N,N'-bis(3-nitrobenzylidene)ethylenediamine (X = Cl, ClO_4, NO_3, BF_4) (24), only single bands pertaining to ν_{as}Sn−C and ν_{as}Sn−Cl or ν_{as} Sn−X have been observed which indicate a *trans*-R_2 and *trans*-Cl_2 or *trans*-X_2 geometry for the R_2SnCl_2 or R_2SnX_2 moiety. However, in the spectra of 1:1 adducts of Me_2SnCl_2 with Nisalen (31) and Ph_2SnCl_2 with Schiff bases of S-alkyldithiocarbazate amines (15), only a single band for ν_{as}Sn−C at 575 cm^{-1} and ~ 270 cm^{-1}, respectively, and two bands for ν_{as}Sn−Cl and ν_sSn−Cl in the range 292-270 and 256-230 cm^{-1}, respectively, have been observed which indicate a *trans*-R_2 and *cis*-Cl_2 geometry for the adducts.

The infrared spectra of organotin(IV) chelates of the types R_2SnL / R_2SnL_2 (where L = anions of bidentate or tetradentate Schiff bases such as salen, R = alkyl or aryl) exhibit only one band in the range 570-550 cm^{-1} for alkyl and 270-229 cm^{-1} for phenyl which could be assigned to ν_{as}Sn−C in a *trans*-octahedral R_2Sn(IV) moiety (15, 35, 51, 82, 83). On the other hand, the spectra of some octahedral Bu_2SnL_2 chelates (L = Schiff base anion) show two bands at 600 and 510 cm^{-1} for the ν_{as}Sn−C and ν_sSn−C, respectively, suggesting a *cis*-Bu_2Sn(IV) moiety in octahedral geometry (52, 73).

Two bands due to the ν_{as}Sn−C and ν_sSn−C have been reported for penta-coordinate triorganotin(IV) chelates, R_3SnL (L = bidentate Schiff base anion) suggesting that all the three organic groups are not equivalent and do not occupy the equatorial positions (51, 56). The spectra of some penta-coordinate diorganotin(IV) chelates, R_2SnL (L = tridentate Schiff base anion) exhibit two bands due to the $\nu_{as}Sn{-}C$ and $\nu_{s}Sn{-}C$ suggesting a bent R_2Sn moiety (*cis*-organic groups) in trigonal bipyramidal geometry (41, 43, 55, 56).

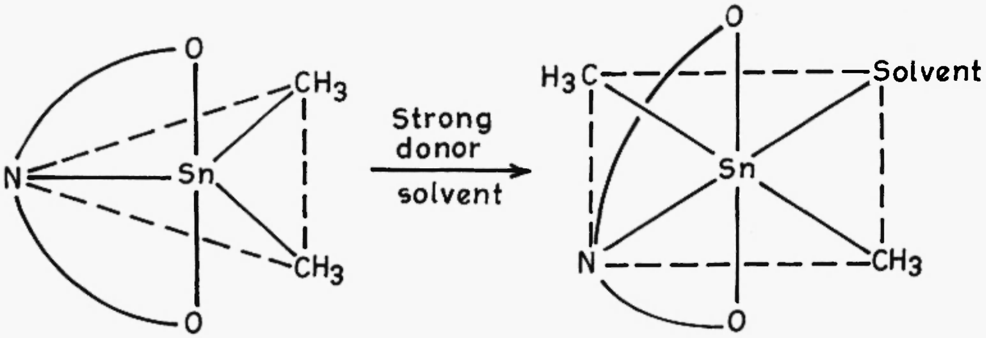
1.4.4. Nuclear (^{1}H, ^{13}C and ^{119}Sn) magnetic resonance spectral studies

Proton magnetic resonance (PMR) spectra of the adducts of mono-, di- and triorganotin(IV) halides with H_2acen have been studied by Barbieri *et al* (82) and by Smith and Dodd (84). It has been observed that in CD_3OD, $CDCl_3$ and CD_2Cl_2 solution, the ligand resonances from the adduct are in each case the same as those of the free ligand (84). Similarly, complete dissociation is indicated for $Me_3SnCl.H_2$acen and $Me_2SnCl_2.H_2$acen by the coincidence of the tin−methyl proton resonance signals and $^{117}Sn{-}CH_3$ and $^{119}Sn{-}CH_3$ coupling constants measured for the organotin(IV) chlorides and their H_2acen adducts (81). Their osmometric measurements have also indicated the complete dissociation (19, 81)

Recently, Khoo *et al* have reported (26) that in the PMR spectra of $Ph_3SnX.L$ (where X = Cl or NCS, L = N-arylsalicylideneimines and N-aryl-2-hydroxynaphthylideneimines) the sharp singlet due to the azomethine proton of the ligands (δ 8.50-9.20 ppm) remains unchanged on coordination, indicating that the N-atom is not coordinated to the metal. On the other hand, the peak due to the phenolic proton of the ligands (δ 13.00-15.00 ppm) becomes significantly broadened on complex formation. Coordination through oxygen is expected to result in a weakening of the O−H bond, and a strengthening of the C=N----H hydrogen bond, which in turn leads to the observed broadening of the peak due to phenolic proton. Similar observations have also been reported for the complexes of dimethyltin dichloride with N-arylsalicylideneimines (27). The coordination through oxygen has also been confirmed by the comparison of the ^{13}C NMR spectral data of the ligands such as N-salicylideneaniline and N-salicylidene-*p*-methoxyaniline, and their Me_2SnCl_2 complexes (27). The azomethine carbon signal remains unchanged whereas the signal due to the carbon attached to the phenolic oxygen moves downfield (δ 0.4-0.6 ppm) indicating coordination through oxygen. The coupling constants $^{2}J(^{119}Sn{-}CH_3)$ determined for dimethyltin dichloride N-salicylideneaniline and dimethyltin dichloride N-salicylidene-*p*-methoxyaniline are 70.8 and 71.2 Hz, respectively (27).

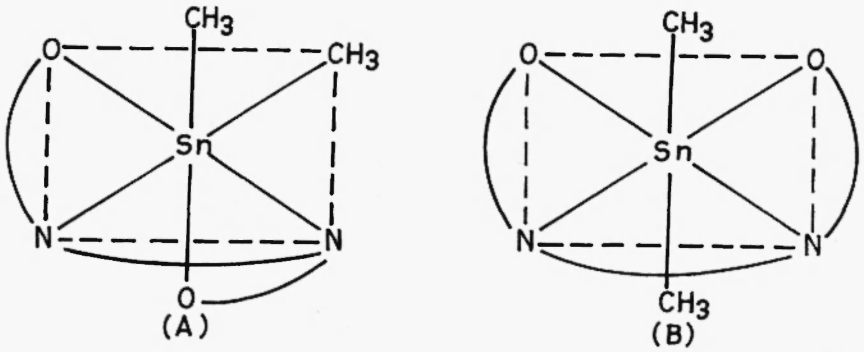
PMR spectra of dimethyltin(IV) chelates of bifunctional terdentate ligands having ONO and SNO donor atom systems have been studied by Barbieri *et al* (43) and on the basis of position of $Me_2Sn(IV)$ signals and the value of $J(^{117}Sn{-}CH_3$ and $^{119}Sn{-}CH_3)$, a trigonal bipyramidal structure with a bent $Me_2Sn(IV)$ moiety has been proposed for these complexes. A series of dimethyltin(IV) chelates of bifunctional terdentate ligands prepared by the condensation of substituted salicylaldehydes with substituted 2-aminophenol has been studied by PMR spectroscopy in a number of weak and strong donor solvents by Tanaka *et al* (45). The coupling constants between tin-119 and the methyl protons attached directly to the tin atom ($J\ ^{119}Sn{-}CH_3$), and the average value of those between tin-117 and tin-119 nuclei and the azomethine proton ($J\ ^{117/119}Sn{\leftarrow}N{=}\overset{|}{C}{-}H$) through three bonds including the $N{\rightarrow}Sn$ bond have been measured in $CDCl_3$

and DMSO-d_6. Distinct values of $J(^{117/119}Sn \leftarrow N{=}C{-}H)$ of the order of 45.9-50.0 Hz and 30.5-47.9 Hz in $CDCl_3$ and DMSO-d_6, respectively suggest that the complexes do not dissociate and maintain five- coordination around tin(IV) even in strong donor solvents. Low $J(^{119}Sn{-}CH_3)$ values (78.0-85.0 Hz) in weak donor solvents like $CDCl_3$, CH_3NO_2 and $(CH_3)_2CO$ correspond to a bent $Me_2Sn(IV)$ moiety in a trigonal bipyramidal arrangement whereas $J(^{119}Sn{-}CH_3)$ values as high as 93.0-109.8 Hz obtained in strong donor solvents (DMSO-d_6 and HMPA) correspond to almost a linear $Me_2Sn(IV)$ species in an octahedral arrangement. It has been reported that an initially bent C−Sn−C moiety in a 5-coordinate environment present in poor donor solvents changes to an almost linear C−Sn−C geometry due to the coordination of a molecule of the strong donor solvent, thereby, raising the coordination number of tin from 5 to 6 (Eq.50).



(50)

The PMR spectrum of N,N'-ethylenebis(salicylaldiminato)dimethyltin(IV), Me_2Snsalen, was studied by Murray *et al* (21) and Tanaka *et al* (23) in $CDCl_3$ solution. Murray *et al* (21) observed two distinct sharp lines at δ 0.68, 0.92; 3.70, 3.89 and 7.98, 8.32 ppm for each group of $Me_2Sn(IV)$, $-CH_2CH_2-$ and $-N{=}CH-$ protons. However, Tanaka *et al* (23) reported two lines only for the $Me_2Sn(IV)$ protons at δ 0.72 and 0.75 ppm whereas the $-CH_2CH_2-$ and $-CH{=}N-$ protons appeared as singlets at δ 4.07 and 8.07 ppm, respectively. Although Tanaka and co-workers suggested the existence of two isomers (*cis/trans*) for the complex at least in solution, Murray and co-workers proposed a *cis*-structure having a non-planar salen^{-2} moiety. Later on, Tanaka *et al* (48) succeeded in isolating the two isomers in the solid state and studied the *cis/trans* isomerization in a number of solvents. The value of equilibrium constant K for the *cis/*

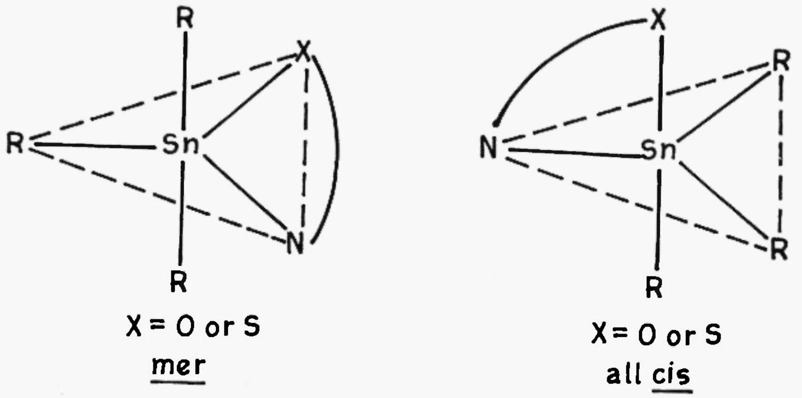


(A) (B)

Fig. 1: Structures of *cis-* (A) and *trans-* (B) isomers of Me_2Snsalen.

trans isomerisation reaction and the variable temperature PMR spectra indicated the *cis*-isomer [Fig. 1(A)] to be favoured in non-coordinating solvents (CH_2Cl_2 and $C_6H_5NO_2$) and at room temperature whereas the *trans*-isomer (Fig 1(B)] predominated in strong donor solvents (DMA and HMPA) and at higher temperatures.

In the PMR spectra of organotin(IV) chelates of various Schiff bases (28, 35-38, 51-53, 55, 56, 71, 73, 74, 77-79) slight downward chemical shift in the value of δ −CH=N− protons may arise due to the participation of the azomethine nitrogen in chelation. Disappearance of −OH, −NH or −SH signals of mono- or bifunctional Schiff bases in the PMR spectra of their organotin(IV) chelates indicates the chelation of the ligand moiety through deprotonated oxygen, nitrogen or sulphur atom (15, 35, 36, 38, 51-53, 56-58, 73, 74, 78). On the basis of the PMR spectral data, the complexes of trialkyltin(IV) species with monofunctional bidentate Schiff bases such as N-alkyl(aryl)salicylaldimines (60) and 2,2-disubstituted benzothiazolines (70) have been assigned five-coordinated structures with trigonal bipyramidal geometries (Fig. 2).



X = O or S
mer

X = O or S
all cis

Fig. 2: Structures of $R_3Sn(\overset{\frown}{XN})$, [where $\overset{\frown}{XN}$ = N-alkyl(aryl)salicylaldimines or 2,2-disubstituted benzothiazolines].

^{13}C and ^{119}Sn NMR spectra of dibutyltin(IV), tributyltin(IV) or trimethyltin(IV) chelates of monofunctional bidentate and bifunctional terdentate Schiff bases having NO or NS and ONO or SNO donor systems, respectively, have been studied by Tandon *et al* (53, 73, 74, 79). The ^{13}C chemical shifts for carbons attached to O, S and N indicate the involvement of O, S and N in coordination. The values of $^1J(^{119}Sn-^{13}C)$ in these complexes in the range 607.7-555.0 Hz and $^1J(^{117}Sn-^{13}C)$ at 570.2 Hz only for Bu_2SnL (L = anion of semicarbazone of benzaldehyde) indicate the five-coordination around tin. Further, these complexes give sharp signals between -100 and -190 ppm in ^{119}Sn NMR, which also support the five-coordination around tin in a trigonal bipyramidal geometry. The value of $^1J(^{119}Sn-^{13}C)$ has also been used to calculate C−Sn−C angles which are 140-143° in the octahedral complexes, R_2SnL [where L = dianion of S-methyl-β-N-(substituted phenyl)methylendithiocarbazate; R = $CH_2CH_2CO_2Me$, $CH_2CH_2CO_2Et$, $CH_2CH_2CO_2Bu$] (57).

1.4.5. ^{119}Sn Mössbauer and X-ray crystallographic studies

^{119}Sn Mössbauer spectroscopy has been frequently employed to throw light on the structures of Schiff base and β-ketoamine complexes of organotin(IV) species and the data have been reviewed in two articles (85, 86).

Barbieri *et al* (20, 22) have studied Mössbauer spectra of the adducts of organotin(IV) halides with potentially tetradentate N,N'-ethylenebis(acetylacetoneimine) and N,N'-ethylenebis-(salicylaldimine). Large values of quadrupole splitting (Q.S.) (3.62-4.49 mm s^{-1}) and isomeric shift (I.S.) (1.26-1.62 mm s^{-1}) along with the temperature dependence of the Mössbauer parameters indicate a polymeric *all trans*-octahedral structure for the adducts of diorganotin(IV) halides in the solid state in which the planar R_2SnX_2 moieties are bridged by the *trans*-isomer of the bis-monodentate ligand. The *all trans*-octahedral polymeric structure of $Me_2SnCl_2.H_2$salen has been further confirmed by Randaccio (87) with the help of X-ray crystallography.

Point charge model calculations have also been done to deduce the configuration of the adducts, $RSnCl_3.H_2$salen (R = Me, Oct^n and Ph) (22) and $Me_3SnCl.H_2$acen (88). It has been reported that these adducts are octahedral and possess polymeric structure in which Me_3SnCl and $RSnCl_3$ moieties with T shaped Me_3Sn and $SnCl_3$ geometry are bridged by two separate ligand moieties.

Mössbauer spectra of the adducts of R_2SnCl_2 and $RSnCl_3$ with Msalen (M = Ni and Cu) have also been studied (30-33). It has been suggested that the chelates, Msalen, act as a bidentate oxygen donor ligand and the unimolecular adducts possess an octahedral structure having *trans*-R_2 , *cis*-Cl_2 geometry in R_2SnCl_2 adducts and T shaped $SnCl_3$ moiety in the adducts of $RSnCl_3$. The structure of Me_2SnCl_2.Nisalen (Fig. 3) has been further confirmed by X-ray crystallography (89).

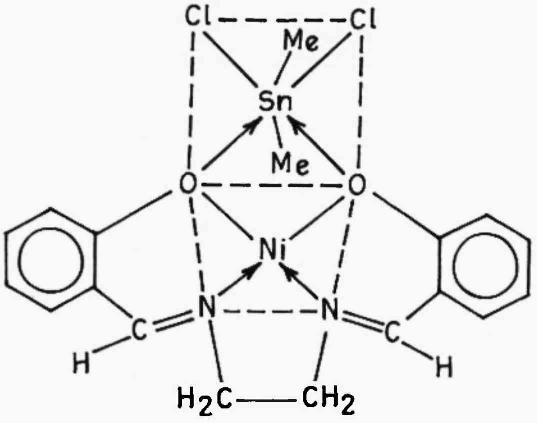


Fig. 3: Structure of Me_2SnCl_2.Nisalen.

It has been reported (26) that the adducts of triphenyltin(IV) chloride or isothiocyanate with the Schiff bases such as N-arylsalicylideneimines and N-aryl-2-hydroxynaphthylideneimines have the Q.S. 3.14-3.38 mm s^{-1} which support the trigonal bipyramidal geometry with three phenyl groups in the equatorial plane. This conclusion has been further confirmed (26) by the X-ray structural determination of isothiocyanatotriphenyl(1-[(4'-methylphenylimino)-methyl]-2-naphthol)tin(IV). This complex has a trigonal bipyramidal structure, with the three phenyl groups occupying the equatorial positions around the tin atom, while the O atom of the ligand and the N of the NCS group occupy the axial positions (Fig. 4). The Sn atom is slightly distorted from equatorial plane defined by the three bonding C atoms of the phenyl groups (0.050(4) A°). The average Sn—C(Ph) distance is 2.115(6) A° and the O—Sn—N angle is 177.94(14)°. The NCS group is almost linear, the NCS angle being 178.1(5)° and the Sn—N, N—C and C—S distances are 2.230(5), 1.144(6) and 1.605(6) A°, respectively. A striking feature of the structure is that the phenolic proton of the ligand has moved to the imine nitrogen and the Schiff base is thus

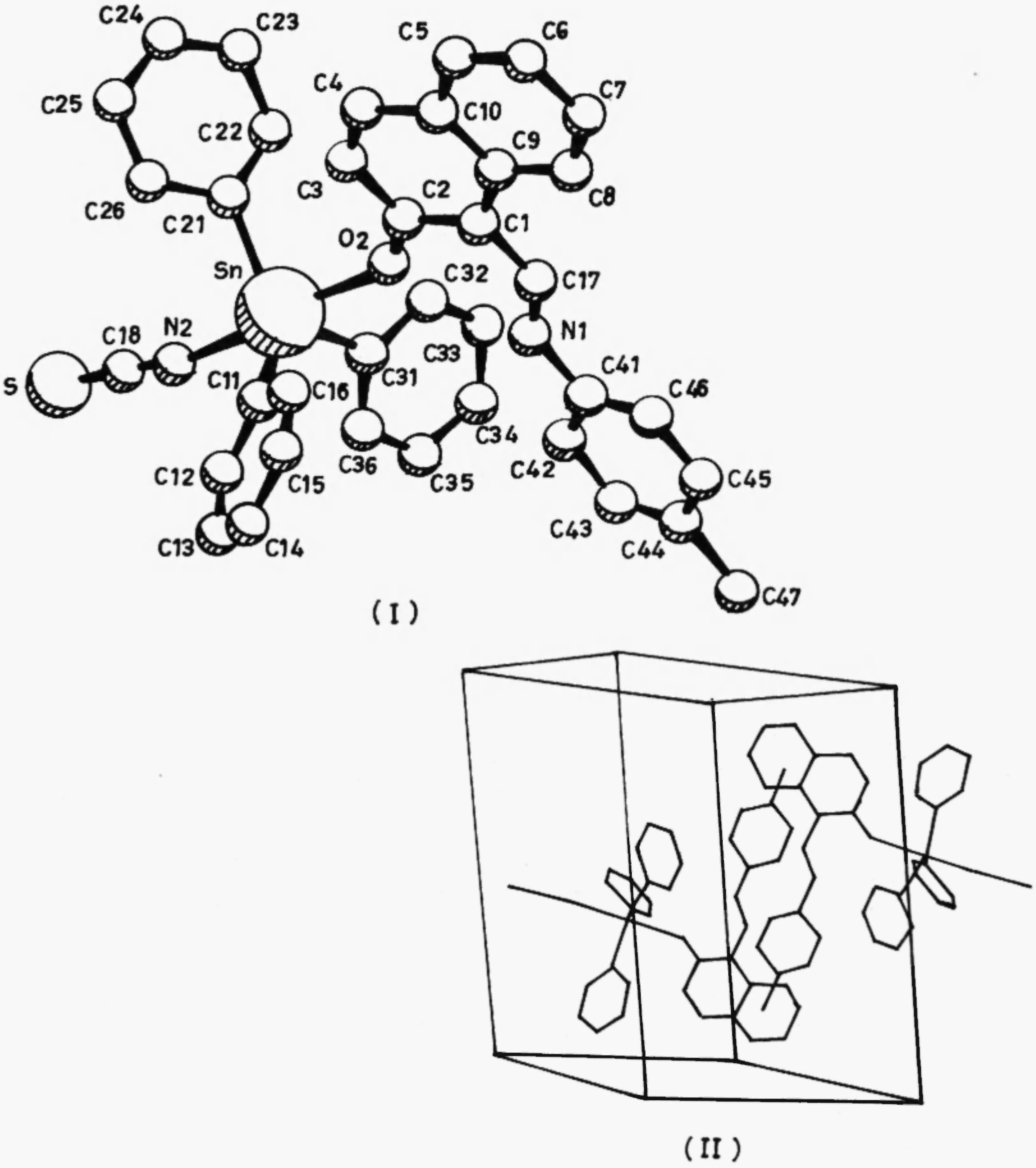


Fig. 4: **Molecular configuration (I) and stereoview of packing arrangement(II) of isothiocyanatotriphenyl- (1-[(4'-methylphenylimino)-methyl]-2-naphthol)tin(IV).**

coordinated in the form of a zwitter ion. It has been reported (26) that the complexes pack together in the crystal in pairs of centrosymmetrically - related dimers, with the Schiff bases lying flat, one above the other, and head-to-tail relative to each other, as shown in Fig. 4(II). The coordination of the Schiff bases through oxygen, not through the azomethine nitrogen has also been confirmed by the X-ray structural analysis of the complex of dimethyltin dichloride with 2-(*p*-methoxyphenyliminomethyl)phenol (90).

Barbieri *et al* have also studied the Mössbauer spectra of chelates R_2SnL (91) derived from bifunctional terdentate Schiff bases and the complexes depict trigonal bipyramidal geometry. X-ray crystallographic data have further shown that the three R_2SnL complexes, $Me_2Snsalap$ (92, 93), $Ph_2Snsalap$ (94), and $Ph_2Snsalatp$ (95) [where salap and salatp are the dianions of N-2-hydroxyphenylsalicylaldimine and 2-(2-hydroxyphenyl)benzothiazoline, respectively] possess distorted trigonal bipyramidal structure with the azomethine nitrogen atom and both carbon atoms (attached to tin) occupying equatorial sites; the axial sites being occupied by the other two ligand atoms (O, O or O, S).

The Mössbauer data of triphenyltin(IV) chelates of monofunctional bidentate semicarbazones or thiosemicarbazones suggest trigonal bipyramidal geometry with phenyl groups occupying two equatorial and one axial sites (51).

On the basis of Mössbauer data of the chelates RSnClL (where L is the dianion of bifunctional terdentate Schiff bases having ONO or ONS donor atom system) (68), it has been suggested that the chelates possibly have polymeric trigonal bipyramidal structure although the monomeric trigonal bipyramidal and oxygen or sulphur bridged dimeric octahedral geometries can not be ruled out completely.

Mössbauer spectra of $Me_2Snsalen$ and other homologous compounds $R_2Snsalen$ have been studied (47, 83). Slightly lower Q.S. (3.46 mm s^{-1}) and I.S. (1.13 mm s^{-1}) values indicate a distorted *trans*-R_2 structure with C−Sn−C angle less than 180°C (Fig. 5). The crystal and molecular structure of the compound, $Me_2Snsalen$, has also been determined by Randaccio and co-workers (96) and C−Sn−C angle in $Me_2Snsalen$ has actually been found to be 160°.

The Mössbauer data of diorganotin(IV) chelates, Bu_2SnL (L = dianions of thiosemicarbazones) suggested octahedral geometry with *cis*-R groups (36, 52, 73, 79). X-ray structural studies on the compound, $Bu_2Sn[OC_6H_4CH{=}NNC(S)NH_2]$, revealed monoclinic lattice with a = 16.90 A°, b = 9.71 A°, c = 8.60 A°, and β = 103°.45' (73).

Ruddick and Sams (47, 97, 98) have studied the magnetically perturbed Mössbauer spectra of N-2-hydroxyphenylsalicylaldiminatotriphenyltin(IV), $Ph_3SnHsalap$. On the basis of positive sign of quadrupole coupling constant and the value of asymmetric parameter of the electric field gradient which is close to unity, an uncommon *mer*-octahedral structure (Fig. 6) has been assigned to the complex.

Mehrotra *et al* have also applied the Mössbauer technique to elucidate the structures of the adducts of dimethyltin(IV), dibutyltin(IV), ethyltin(IV) and butyltin(IV) chlorides with N-

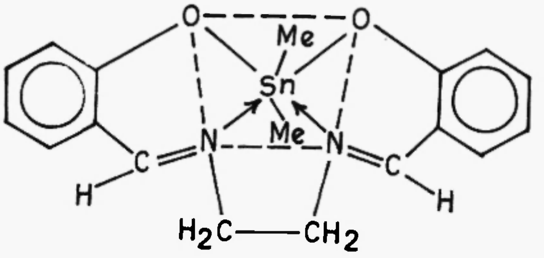


Fig. 5: Structure of Me_2Snsalen.

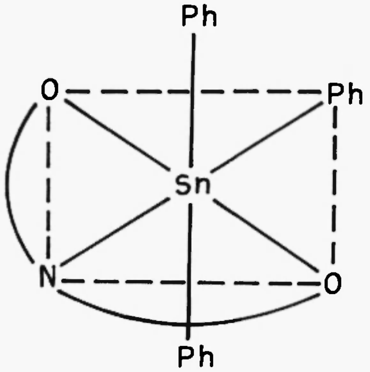


Fig. 6: Structure of Ph_3SnHsalap.

alkyl(aryl)salicylaldimines(8), N-alkyl(aryl)-2-hydroxyacetophenoneimines (13), N-hydroxyalkylsalicylaldimines (18) and N,N'-alkylenebis(2-hydroxyacetophenoneimines) (25). From the observed large quadrupole splittings (3.95-4.44 mm s^{-1}) and isomeric shifts (1.25-1.61 mm s^{-1}) of all the adducts of diorganotin(IV) chlorides, the existence of *trans*-R_2Sn(IV) moieties in octahedral arrangement around tin atom has been suggested for the above complexes. Comparatively, smaller values of Q.S. (1.76-2.11 mm s^{-1}) and I.S. (0.78-0.89 mm s^{-1}) in the adducts of $EtSnCl_3$ appear to indicate, on the other hand, a T-shaped $SnCl_3$ moiety in octahedral geometry.

1.5. MASS SPECTRAL STUDIES

The mass spectral fragmentation schemes of the $Bu_2Sn[OC_6H_4C(CH_3)=NNC(S)NH_2]$, $Bu_2Sn[OC_6H_4CH=NNC(S)NH_2]$, $Bu_2Sn[OC_6H_4C(CH_3)=NNC=S(SCH_3)]$, $Bu_2Sn[OC_6H_4CH=NNC=S(SCH_2C_6H_5)]$ and $Bu_3Sn(OC_6H_4CH=NC_6H_4F)$ have been reported by Tandon *et al* (72-74, 79). The fragmentation starts with the simple cleavage of a Sn—Bu bond eliminating Bu of 57 a.m.u. leading to the formation of a three-coordinate Sn fragment ion. The Sn—S bond is more readily cleaved than the Sn—O bond showing, thereby, the strong nature of the latter. Some low abundance ions containing Sn—S at m/e 151 are also obtained by the processes which do not involve cleavage of bonds to metal. The last step in the fragmentation is the removal of a HCN molecule, which is characteristic of the Schiff base complexes.

1.6. THERMAL STUDIES

A survey of the existing literature revealed that very little work has been done on the thermal decomposition of organotin(IV) compounds. The interpretation of pyrolysis reactions involved in the decomposition of various organotin(IV) derivatives has been shown to be difficult because of the lack of informations on the thermal decomposition of simple organotin(IV) compounds. Thermogravimetric analysis of diorganotin(IV) complexes of Schiff bases obtained by the condensation of aromatic aldehyde with *o*-arsanilic acid and 1,2-ethylenediamine with acetylacetone have been carried out (77). No proper conclusion has been made from the weight loss except the loss of water upto 180°C. Recently, thermal decomposition scheme of triphenyltin chloride benzilsemicarbazone has been reported from our laboratory in the temperature range 27-715°C using TG, DTG and DTA techniques (99). The decomposition of the complex takes place in four steps in the temperature range 127-550°C, giving SnO_2 as end product. The thermal decomposition of Ph_3SnCl(Benz.SCZ) is shown in Fig.7.

Recently, thermal decomposition of Ph_3SnCl(L-I), Ph_2SnCl_2(L-2) and Me_3Sn(L-3) (35), where (L-1), (L-2) and (HL-3) are Schiff bases derived from the condensation of 2-amino-4-phenylthiazole with 4-methoxybenzaldehyde, furfuraldehyde and salicylaldehyde, respectively, and Ph_2SnCl_2(L-1), Ph_3SnCl(L-2), Ph_2Sn(L-3) and Ph_3Sn(L-4) (29, 52), where (L-1), (L-2), (L-3) and (HL-4) are the Schiff bases derived from the condensation of thiosemicarbazide with acetophenone, glyoxal, 5-chlorosalicylaldeyde and 4-nitrobenzaldehyde, respectively, and Ph_3SnCl(HL-1), $Ph_2Sn(L\text{-}1)_2$, Me_3SnCl(L-2), Ph_3SnCl(L-3) and Ph_3Sn(L-4) (36), where (HL-1), (L-2), (L-3) and (HL-4) are the Schiff bases derived from the condensation of 2-amino-5-(*o*-anisyl)-1,3,4-thiadiazole with 2-hydroxynaphthaldehyde, benzylmethyl ketone, acetylacetone and salicylaldehyde, respectively, have been reported from our laboratory and in each case the end product is either SnO_2 or SnS which has been confirmed by IR spectra and X-ray determination.

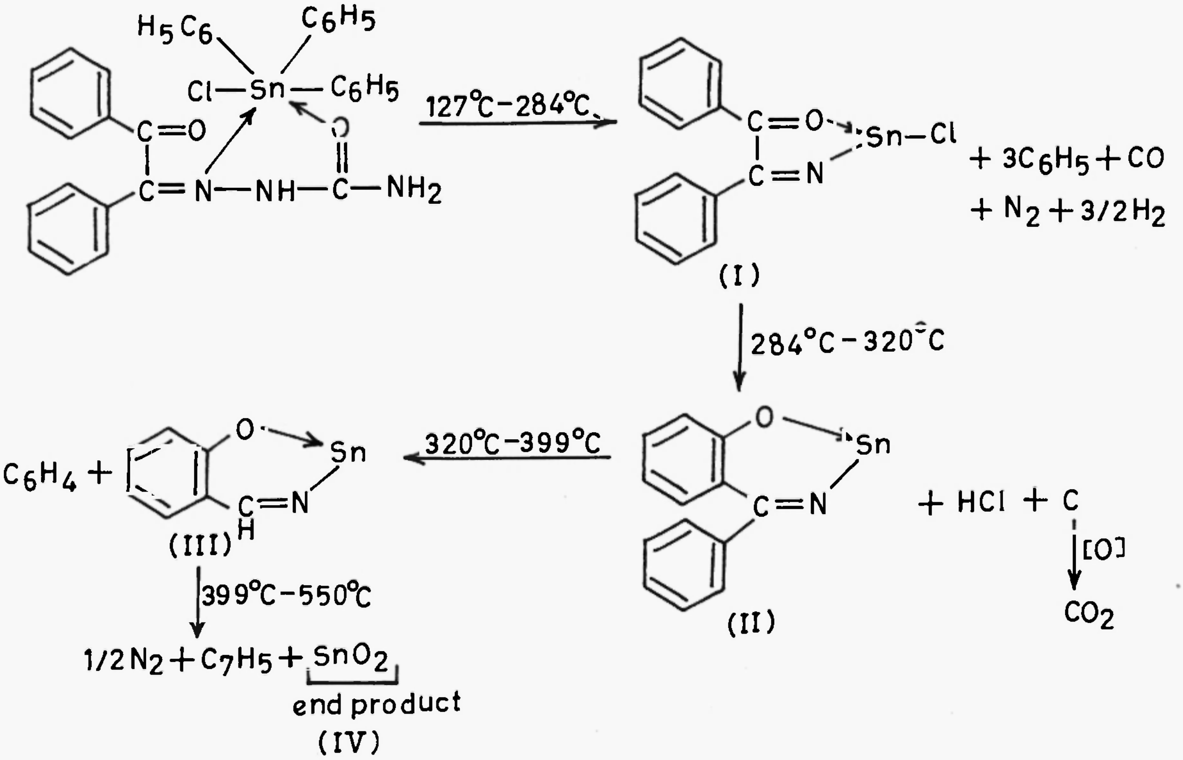


Fig. 7: Proposed scheme for decomposition of Ph_3SnCl(Benz.SCZ).

Thermal decompositions of chloro(2-furanyl)semicarbazonotriphenyltin(IV), (2-hydroxyphenyl)methylsemicarbazonodiphenyltin(IV), (4-methoxyphenyl)thiosemicarbazono-triphenyltin(IV) (100), S-benzyl-β-N-(2-hydroxyphenyl)methylendithiocarbazatodiphenyltin(IV), S-benzyl-β-N-(benzoylphenyl)methylendithiocarbazatotriphenyltin(IV) and N-methyl-S-benzyl-β-N-(2-hydroxyphenylethylidene)dithiocarbazatotriphenyltin(IV) have also been reported from our laboratory and in each case the end product is either SnO_2 or mixture of SnO + S or SnS_2 which has been confirmed by X-ray determination (101).

1.7. ANTIMICROBIAL ACTIVITY

Only scanty references are available on the antimicrobial activity of organotin(IV) Schiff base complexes. Organotin(IV) complexes of Schiff bases containing S and F are potentially active at low doses on axenically grown *Entamoeba histolytica trophozoities* (strain NIH-20). Tri-n-butyltin(2-fluorobenzaldehyde)-S-benzyldithiocarbazate shows remarkable activity at an extremely low dose even after 48 hr (102).

The antifungal activities of trimethyltin(IV) complexes of heterocyclic thiosemicarbazones have been evaluated against different pathogenic fungi (53). Di- and Tri-n-butyltin(IV) chelates of monofunctional bidentate or bifunctional tridentate Schiff bases derived from salicylaldehyde/ 2-hydroxy-l-naphthaldehyde with fluoroaniline and benzaldehyde/2-hydroxyacetophenone with *o*-aminothiophenol are highly active towards pathogenic bacteria (79). None of the chelates or Schiff bases is active against gram-negative bacterium such as *Escherichia coli* whereas all the chelates show marked activity against gram-positive bacteria (*Bacillus subtilis* and *Staphylococcus aureus*) as compared to the corresponding Schiff bases, which suggest that the complex formation increasing the activity (79). The complexes of the type n-Bu_2SnL (where L = dianion of S-methyl-β-N-(2-hydroxyphenyl)methylendithiocarbazate) are found to be active against P388 lymphocytic leukemia (74).

Antimicrobial activity of di- and triorganotin(IV) complexes of thio Schiff bases derived from the condensation of 2-amino-4-phenylthiazole (35), thiosemicarbazide (29,52) and 2-amino-5-(*o*-anisyl)-1,3,4-thiadiazole (36) with different aldehydes or ketones have been carried out against *E. coli, B. subtilis, S. typhi, A. terrus, C. falcatum Went* (35) and *Streptococcus faecalis, Klebisiella pneumoniae, Escherichia coli, Pseudomonas aeruginosa, Staphylococcus aureus* Penicillin resistance (2500 units), *Candida albicans, Cryptococcus neoformans, Sporotrichum schenkii, Trichophyton mentagrophytes and Aspergillus fumigatus* (29, 36, 52). All these complexes have remarkable antifungal and antibacterial activities which are higher than those of the Schiff bases.

Some di- and triorganotin(IV) complexes of thio Schiff bases derived from the condensation of 2-amino-4-phenylthiazole, thiosemicarbazide and 2-amino-5-(*o*-anisyl)-1,3,4-thiadiazole with different aldehydes and ketones have also been tested for herbicidal, insecticidal and fungicidal activities, and against animal freeliving nematode. The results (36) indicated that only a few complexes were found to be active against various important herbicide and fungicide species. None of the complexes were found to be active against insects and freeliving nematode.

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