A BRIEF DISCUSSION OF ORGANOTIN CO-ORDINATION COMPOUNDS.

Introduction

Vigorous research activities in recent years are being noticed throughout the world in the field of Organotin Compounds, as a result of an unique combination of their physical, chemical, structural and biocidal properties. By the definition of Gilman et al.(1) Organotin Compounds must contain at least one tin-carbon bond. As there is no known naturally occurring Organotin Compound , the first Organotin Compound was reported by Frankland (2,3) in 1849 though he could not characterise it properly until 1853. Lowig (4) in 1852 isolated an Organotin Compound by the reaction of sodium-tin alloy upon ethyl iodide. These works marked the beginning of chemistry of organotin compounds. After them, a number of significant contributions followed during the next few decades.

Quite a few reviews in this area have been published. The first major review work covering the literature upto about 1935 was that of Krause and Von Grosse (5). Ingham, Rosenberg and Gilman (1) extended the literature through 1959. An exhaustive list of Organotin Compounds was compiled by Weiss (6) covering the literature from 1937 to 1964. From 1964, the literature of Organotin Chemistry is being published in annual surveys (7-16). The tin annual survey covering the year 1974 has been published (17). Another review of organo derivatives of tin and lead with

464 references has been published by Harrison (18). Apart from these review articles several books have recently been published (19-22).

In the recent years Organotin Chemistry appears to be on the threshold of large-scale commercial development. Organotin Compounds have been successfully utilised in the stabilisation of polyvinyl chloride plastics, as rubber antioxidants, Ziegler type catalysts in the polymerisation of olefins, agricultural fungicides and as active ingredients in certain veterinary medicine etc. (23).

Bonding in Organotin Compounds:

Before going to describe the Organotin Compounds in detail, it would be pertinent to discuss briefly the nature of bonding in these compounds.

Tin, the element of atomic number 50, is a member of group IVA of the periodic table. The electronic configuration (24) of tin ($[Kr]4d^{10}\ 5s^2 5p^2$) in the ground state is a 3p state with two unpaired electrons in the p-sub-shell available for bonding resulting in a two-covalent tin. The common four-covalent state of tin is derived from the sp^3 hybridisation by promoting one of the paired s electrons to the next higher p level. Covalences of two and four would then be expected for this element in neutral molecules. However four-covalent state occurs far more

frequently than the two covalent state and the great majority of Organotin Compounds possess a four-covalent tin atom. The marked increase in stabilities of R_4Sn compounds over R_2Sn types demonstrates the effect of increased hybridisation. Metal-carbon bond strengths have been reviewed by Skinner (25). The values of mean bond dissociation energies of group IV metals and carbon are C-C : 87, C-Si : 70, C-Ge: 60, C-Sn: 50, C-Pb: 31 K.Cal/mole. Thus the mean bond dissociation energies decrease in descending the group. Furthermore the values of the mean bond dissociation energies are of course dependent on the nature of organic group.

The covalent radius of tin atom is 1.40$\AA^{o}$ and is often independent of the nature of the ligand. Only when there is an accumulation of strongly negative ligands around the tin atom there is some decrease in bond lengths. Thus the bonding of tin appears to be almost entirely covalent in these compounds at least in crystalline solids, in non-polar media and in the vapour state. However the electronegativity of tin is less than that of the most common ligands, e.g., Carbon, nitrogen, oxygen, halogen and even hydrogen and hence the bonds are expected to be sufficiently polar. Closely connected with this is the inductive effect which tin atoms or stannyl groups exert on their surroundings. The bond polarisation $C^{-\delta} - Sn^{+\delta}$ are dependent upon the substitution at carbon as well as at tin. N.M.R. data on organotin compounds (26-27) also emphasise this. According to Eaborn et al (28) polarisation is increased by electron donar substituents in the para

position of a phenyl group bonded to tin and as expected, electron attracting group decreases the polarisation.

There are many controversies (29-39) about the existence of the π-character of the bond formed between tin and other elements. According to West (29) and Drago et al.(30) there may be some π-character in a bond between tin and an element possessing p-electrons. Thus in a Sn-X bond where X is C(sp^2), N, O, S or halogens, it is possible that, opposing the inductive electron drift, there may be some overlap between a filled p-orbital on X and an empty 5d orbital on tin causing a transfer of electron density in the opposite direction. NMR (31-32), infrared (33), ultraviolet (34) and dipole moment data (34) of phenyl tin compounds and the acid strength of substituted benzoic acid, p-$Me_3MC_6H_4COOH$ (M = C, Si, Ge, Sn), give some evidence of interaction between the electrons of the phenyl group and the 5d orbitals of tin in these compounds. Anderson et al.(35) have shown that there is no $d\pi - p\pi$ bonding in the tin-pyridine linkage. Evidence of $d\pi - p\pi$ interaction between tin and certain transition metals are also available (36-37). That $d\pi - p\pi$ bonding is operative is evident from the higher values of Sn-Cl stretching frequencies in certain tin compounds (38) and tin-oxygen frequency in $(Ph_3Sn)_2O$ (39).

It is expected that the presence of the lone pair ($5p^2$) in the low oxidation state [Sn(II)] would result in lower

co-ordination number compared to the higher oxidation state of the element [Sn(IV)]. But there is no definite correlation between valency state and the maximum co-ordination number. Tin (IV) can show co-ordination number greater than four and Okawara et al.(40-41) have reviewed the structures of organotin compounds that display a co-ordination number greater than four. In the present discussions, only the Organic Compounds of tetravalent tin would be considered.

Since the present investigation is on the preparation and other studies of organotin dithiocnates and related compounds, we believe that it would be most appropriate to have a prior discussion of the methods of the preparations, properties and structural aspects of organotin co-ordination compounds before presenting our findings.

The organotin co-ordination compounds range from some unstable adducts to stable complex compounds with the nature of the ligands.

Organotin adducts:

Organotin Compounds can act as : Lewis acids reacting with certain electron pair donors i.e., Lewis bases to form addition compounds. In many cases unstable and ill defined organotin compounds have been characterised through the formation of their stable crystalline adducts. All the three types of organo (mono-,

di- and tri-) tin compounds can form adducts with mono-, di- and polydentate ligands. The acceptor strength of Organotin compounds is determined by the nature of ligand, nature of organic group and the substituents bonded to tin. And as expected, the ability of organotin halides to form adducts increases in the series $R_3SnX < R_2SnX_2 < RSnX_3$ (42-43). The acceptor strength of a series of Me_3SnX compounds is found to be proportional to the electronegativity of the substituent bonded on tin (44). The stronger the electron attracting power of the substituent, the less the electron density around tin and the acceptor strength increases accordingly. Thus the order of acceptor strength of the Me_3SnX moiety is

$$F^- > Cl^- > Br^- > I^-$$

These simple rules are, however, complicated by the fact that apparent acceptor strength depends also on the nature of the donor (43). For instance the stability of the donor-acceptor complexes with nitranilines yield the sequence:

$$Me-\Phi-SnCl_3 > \Phi-SnCl_3 > Cl-\Phi-SnCl_3 > Ph-\Phi-SnCl_3$$

whereas the sequence with nitrophenylenediamines is:

$$Cl-\Phi-SnCl_3 > \Phi-SnCl_3 > Me-\Phi-SnCl_3 > Ph-\Phi-SnCl_3$$

1:1 Complexes of hexamethyl phosphoric triamide (HMPA) with Ph_3SnX (X = Cl, Br, I, N_3, CN) have been prepared (45-46), the general reaction being

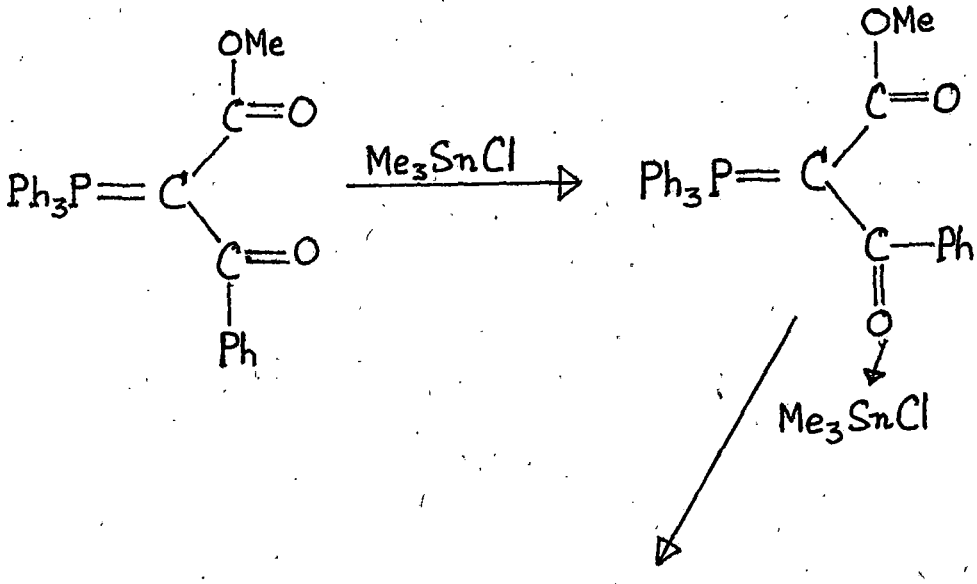
$$Ph_3SnX + HMPA \xrightarrow[\text{or pet-ether}]{\text{in chloroform}} Ph_3SnX \cdot HMPA.$$

Kumar Das (47) has prepared complexes of the type $R_3SnX.L$ (where R = Me, Ph; X = Cl, NO_3 and L = HMPA, DMSO, Phen. etc). However, he was not able to prepare the 1:2 adduct of Ph_3SnNO_3 with DMSO as reported earlier (48). Reaction of $Ph_3SnCl.$ HMPA complex with I^- and N_3^- gives the corresponding $Ph_3SnX.HMPA$ (X = I, N_3) complexes (45). The $Ph_3SnNO_3.L$ (L = HMPA, DMSO and Phen.) complexes appear to be relatively good electrolytes in absolute alcohol, suggesting the nitrate moiety to be only weakly co-ordinated to tin. Evidence for co-ordinated nitrato groups in these complexes comes from I.R. data and these three complexes have been suggested to be penta co-ordinated from the Mossbauer spectra (47).

A large number of 1:1 adducts of triphenyl tin chloride with substituted pyridine-N-oxides are known (49) and the stability constants of complexes $Me_3SnCl.L$ (L = substituted pyridine-N-oxide) have been measured (50). Pyridine gives stable adducts with Me_3SnCl. These compounds are prepared by mixing solutions

containing equimolecular amounts of the two reactants in pet-ether, when the complexes precipitate (51).

Examples of co-ordination compounds containing the triphenyl phosphine oxide and triphenylarsine oxide ligands are $R_3SnX.L$, where R = Me, Ph; X = Cl, Br, I and L = Ph_3PO and Ph_3AsO (52-53). The complex $Me_3SnCl.OPPh_3$ was also reported to be formed during an attempted complex formation between the disubstituted ylide(A) and Me_3SnCl (54)



$Me_3SnCl.OPPh_3 + PhC{\equiv}C.CO_2Me$

The complexation of trimethyl tin halides in donor solvents eg., acetone, dioxan, dimethylether, pyridine, DMF, DMSO,

HMPT and tetramethyl ethylene diamine have been studied by means of ^1H N.M.R. spectroscopy and equilibrium constants evaluated for the $Me_3SnX.L_n$ complexes (55).

While early workers favoured pyridine complexes for the characterisation of triorganotin halides, to-day the most stable adducts derived from the bidentate ligands 2,2'-bipyridyl or 1,10-phenanthroline are preferred. These derivatives are readily made by mixing solutions containing equimolar amounts of the two reactants in an inert solvent, such as benzene, when the complexes precipitate (56,57,58).

Smith and Liengme (59) reported the formation of 1:1 complexes of triorganotin chlorides and thiocyanates with tridentate chelating agents 3-[2-(1,10-phenanthrolyl)]-5,6-diphenyl-1,2,4-triazine (I) and 3-[2-(1,10-phenanthrolyl)]-5,6-dimethyl-1,2, 4-triazine (II). The complexes isolated were : $(CH_3)_3SnCl.L$; $(C_6H_5)_3SnCl.L$ (L = I and II) and $(C_6H_5)_3Sn(NCS).L$ (L = I). These complexes are stable cryotalline solids which behave as non-electrolytes in nitrobenzene.

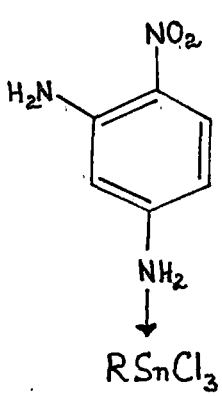
With diorganotin dihalides, pyridine, bipyridyl, phenanthroline and terpyridyl form adducts which vary in composition. Thus the isolated complexes have the compositions: $Me_2SnCl_2 . 2Py$; $Me_2SnCl_2.Phen$ (51,60); $Me_2SnX_2.bipy$ (51,58) (X = Cl, Br, I); $2R_2SnX_2.Terpy$ (58) (R = Me, Ph; X = Cl, Br, I). Although with diorganotin dihalide and diisothiocyanates, 1:1 adducts are formed

but by treating diphenyltin diisocyanate with 2-2'-bipyridyl the 2:1 adduct $[Ph_2Sn(NCO)_2]_2$.bipy was obtained (61). These complexes were precipitated quantitatively from pet-ether or benzene by mixing the required reactants. Pyrazine (62) and tripyridylamine (63) apparently function as bidentate ligands giving stable 1:1 adducts with organotin dihalides. $R_2SnCl_2.2(P\text{-tolyl})_2SO$ (where R = Me or Ph) and $R_2SnX_2.L$ ($L = BipyO_2$, $diphosO_2$ etc.; R = Me, Ph) complexes have also been reported (47). With dimethyl formamide (DMF), Ar_2SnX_2 formed complexes of the type Ar_2SnX_2. 2DMF (Ar = Ph, O-, P-tolyl, benzyl and X = Cl, Br, I). These were prepared by mixing the reactant in any molar ratio (64). The interaction of the $Ar_2SnCl_2.2DMF$ with other Lewis bases stronger than DMF such as 1, 10-phenanthroline, 2,2'-bipyridine, DMSO and N, N-dimethyl acetamide resulted in complete substitution of the ligand verifying the weak donor ability of the DMF compared to the ligand examined (64). Mention may also be made of the adducts: $Me_2SnCl_2.(Ph_3PO)_2$ (53) and $Bu_2SnX_2.Phen.$ (65).

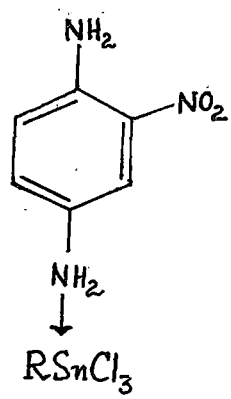
Jaura et al.(66) have prepared compounds of the type $RPhSnCl_2.L$ (where R = Me, Et, n-Bu, benzyl and L = bipyridyl and phenanthroline) by precipitating bipyridyl adducts in pet-ether and phenanthroline adducts in carbon disulfide. These adducts were non-electrolytes in nitrobenzene. An octahedral arrangement with cis-chlorine atoms around tin has been suggested. By the direct interaction of diaryltin dichlorides in acetonitrile with mono-, di- and tri-ethanolamines adducts of the general

formula $Ar_2SnCl_2.nL$ (where Ar = Ph, O-, m-, p-tolyl; n = 1 for MEA and DEA, and n = 2 for TEA) have been isolated by Srivastava et al.(67). All these complexes are white crystalline solids with thermal stability and inert to atmosphere. A cis-aryl-trans-halogen arrangement about octahedral tin has been suggested. Both MEA and DEA function as bidentate ligands, bonding through both oxygen and nitrogen atoms while TEA acts as a unidentate ligand via the oxygen atom.

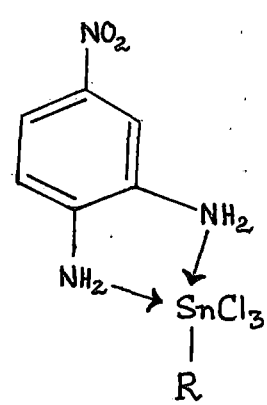
Complexes of $RSnCl_3$ (R = Me, n-Bu, Ph) with aromatic bases such as 1,3-diamino-4 nitrobenzene and 1,4-diamino-3-nitrobenzene were investigated by U.V. absorption spectroscopy(43). The compounds have absorption bands at 398 nm and 396 nm respectively which suggest that only the amino group in para and meta positions are participating in the co-ordinative bond to tin (structure A and B).



(A)



(B)



(C)

These 1:1 complexes thus form examples of five co-ordination around tin. In 1,2-diamino-4-nitrobenzene, however both ortho-amino groups co-ordinate with tin forming a chelate compound with hexa co-ordinate tin (structure C).

1:1 complexes are also reported between some nitroanilines and nitrophenylene diamines and 4-chlorophenyl tin; 4-tolyltin- and 4-biphenyl tin-trichlorides (43). $PhSnCl_3$ also forms addition compounds with diphenyl-ethylene (68) and perinapthenone (69).

A number of butyl tin trichloride adducts with different lewis bases have been prepared by Davies et al.(70). These complexes were $BuSnCl_3.2L$ (L = Ph_3PO, Py, DMSO, etc.). The 1:1 complexes of $BuSnCl_3$ with bipyridyl (56) and phenanthroline (71) are also reported. 1:1 adducts have also been reported (58) to be formed from $MeSnX_3$ (X = Br or I) and bipyridyl. But terpyridyl complexes reported (58) are of variable compositions e.g., $3BuSnCl_3.2$ Terpy, $MeSnBr_3$.Terpy, $MeSnI_3$.Terpy. Clark et al.(72) have reported some 1:1 adducts of $RSnX_3$ (R = Me, Et, Bu and X = Br, I) with phenanthroline and bipyridyl. These were prepared by mixing approximately equimolecular benzene solution of the reactants where as $MeSnCl_3.2Py$, $MeSnCl_3$.bipy and $MeSnCl_3$.phen have been precipitated by mixing the reactants in CCl_4 (for py and bipy) and CS_2 (for phen) (51). In some cases these compounds have been suggested to be octa-co-ordinated.

Apart from these organotin adducts, some of which are quite stable, we would like to discuss now on some more stable

organotin co-ordination complexes. which comprise of give a large number of stable complexes. Organotin moities form different types of compounds with suitable ligands like acetylacetone and other β-diketones, oximes and hydroxamic acid, oxines, tropolone, Kojic acid, Dithiocarbamic acid, Xanthate (Aryl azo) benzoic acids and Schiff bases.

Organotin acetylacetonates and other β-diketonates:

One of the most important class of bidentate oxygen donors are the β-diketones. The ability of organotin moieties to react with β-diketones to form stable organotin complexes of high co-ordination is well established.

The organotin acetylacetonates are principally of the types $R_3Sn(acac)$, $R_2Sn(acac)_2$, $RSn(acac)_3$, $RSnX(acac)_2$, $RSnX(OR')(acac)$ and $RSn(acac)_n(OR')_{3-n}$. Other β-diketonates can be classified similarly.

Triorganotin acetylacetonates, $R_3Sn(acac)$ (acac = $CH_3COCHCOCH_3$) are obtained by the reaction of triorganotin chloride and thallium acetylacetonate (38,73,74). Other triorganotin β-diketonates R_3SnL [where L = benzoylacetone (bzac) and dibenzoyl methane (bzbz)] have also been prepared in a similar way. These compounds have been characterised by I.R., N.M.R. and Mossbauer spectroscopy (75).

$$R_3SnCl + Tl(acac) \longrightarrow R_3Sn(acac) + TlCl$$

$R_3Sn(p\text{-}Br\ C_6H_4COCHCOCH_3)$ (where R = Me, Et, Pr, Bu, Ph) have been prepared by refluxing a mixture of equimolecular quantities of triorganotin chloride and sodium salt of the P-bromobenzoyl acetone in dry methanol (76).

Diorganotin-bis-acetylacetonates, $R_2Sn(acac)_2$ (acac = $CH_3COCHCOCH_3$) (77) have been prepared by the reaction of diorganotin dichloride and sodium methoxide in methanol, followed by the addition of acetylacetone.

$$R_2SnCl_2 + 2CH_3ONa \xrightarrow{\text{in } CH_3OH} R_2Sn(OCH_3)_2 + 2\ NaCl$$

$$R_2Sn(OCH_3)_2 + 2acacH \xrightarrow{\text{in } CH_3OH} R_2Sn(acac)_2 + 2CH_3OH$$

Dimethyl tin-bis-acetylacetonate is also prepared by refluxing dimethyl tin oxide in acetylacetone for several hours (109).

$$Me_2SnO + 2Hacac \longrightarrow Me_2Sn(acac)_2 + H_2O$$

Other dialkyl tin-bis-acetylacetonates and substituted β-diketonates have similarly been obtained (74-76). These diorganotin bis β-diketonates can also be obtained by the reaction of diorganotin dichloride and Tl(I) chelate or by the direct reaction of diorganotin dichloride and a β-diketone in presence of a base (38, 74).

$$R_2SnCl_2 + 2TlCh \longrightarrow R_2SnCh_2 + 2TlCl$$

$$R_2SnCl_2 + 2ChH \longrightarrow R_2SnCh_2 + 2HCl$$

(where ChH = acetylacetone, benzoylacetone etc.).

Organohalogenotin bis-acetyl acetonates, $RSnX(acac)_2$ (X = Cl, Br) have been prepared by the reaction of acetylacetone with organotin trihalide in water (77).

The iodides, $(CH_3)ISn(acac)_2$, can be prepared by the reaction of methyl tin triiodide with sodium acetyl acetonate in chloroform (77,81).

$$RSnX_3 + 2acacH \xrightarrow{\text{in } H_2O} RSnX(acac)_2 + 2HX$$

$$CH_3SnI_3 + 2acacNa \xrightarrow{\text{in } CHCl_3} (CH_3)ISn(acac)_2 + 2NaI.$$

Oxidative-addition reactions of tin (II)-bis-(β-diketonate) with organic halides have been applied to obtain organo halogenotin-bis-(β-diketonates) (78-80) e.g., for acetylacetone:

$$Sn(acac)_2 + RX \longrightarrow RSnX(acac)_2$$

(where RX = MeI, $BrCH_2CH=CH_2$, $PhCH_2Br$).

Mehrotra et al.(115) have prepared compounds of the type $RSn(R'COCHCOR'')_n(OPr^i)_{3-n}$ (where R = Et, R' = CH_3, R'' = C_6H_5

and n = 2; R = Bu, R' = R'' = CH_3, R' = CH_3, R'' = C_6H_5, R' = R'' = C_6H_5 and n = 1 and 2) by the reflux of a mixture of alkyl tin-tris-isopropoxide and β-diketones in benzene. Alkyltin mono-, bis- and tris-β-diketonates were resulted when the alkyl tin tris isopropoxide and β-diketones were taken in 1:1, 1:2 and 1:3 molar ratio respectively. All these compounds are brown viscous liquids and are decomposed on attempted distillation under reduced pressure. Their molecular weights suggest that $BuSn(OPr^i)_2$(acac) and $BuSn(OPr^i)_2$(bzac) in the neat form are probably dimeric. The tri- and diorganotin derivatives are all monomeric in benzene solution and are non-ionic in nitrobenzene (82,76).

Kawasaki et al.(83) have synthesized alkyl tin halide methoxy acetylacetonates, $RSnX(OMe)(acac)$, and suggested the compound to be dimeric through methoxy bridges. A mixture of $Bu_2Sn(acac)_2$ and $Bu_2Sn(OMe)_2$ disproportionates in hexane forming a dimer (84).

$$Bu_2Sn(acac)_2 + Bu_2Sn(OMe)_2 \longrightarrow [Bu_2Sn(acac)(OMe)]_2$$

Bachlas and Jain (85) have prepared tri- and diorganotin complexes of 2-thenoyl trifluoroacetone of the type $R_3Sn(TTA)$ (where R = CH_3, C_2H_5, C_3H_7 and C_6H_5) and $R_2Sn(TTA)_2$ (where R = CH_3, C_2H_5, C_4H_9 and HTTA = 2-thenoyl trifluoro acetone). These compounds have been prepared by the following reactions:

$$CH_3ONa + HTTA \longrightarrow Na^+(TTA^-) + CH_3OH$$

$$R_3SnCl + Na^+(TTA^-) \longrightarrow R_3Sn(TTA) + NaCl$$

$$(R_2SnO)_x + 2xHTTA \longrightarrow xR_2Sn(TTA)_2 + xH_2O.$$

These compounds are monomeric in benzene solution and non-ionic in nitrobenzene.

Organotin Oximates and Hydroxamates:

Oxime and hydroxylamine derivatives of organotin compounds have been reviewed by Mehrotra and his co-workers (86). Organotin oximates have generally been prepared either by the action of sodium or lithium salts of oximes with organotin halides (87-89) or by azeotropic distillation of water from a

$$R_{4-n}SnCl_n + nNa\ (Li)ON{=}{=}CR'R'' \longrightarrow$$

$$R_{4-n}Sn(ON{=}CR'R'')_n + nNaCl\ (LiCl)$$

mixture of organotin oxide or hydroxide with oximes in benzene or toluene (105, 86-88, 90-94) and reaction of alkyltin

$$(R_3Sn)_2O + 2HON{=}{=}CR'R'' \longrightarrow 2R_3SnOH{=}CR'R'' + H_2O$$

$$R_3SnOH + HON{=}{=}CR'R'' \longrightarrow R_3SnOH{=}CR'R'' + H_2O$$

alkoxides with oximes (105, 86, 87, 90, 95).

$$R_{4-n}Sn(OR')_n + nHON \rightleftharpoons CR''R''' \longrightarrow nR'OH + R_{4-n}Sn(ON = CR''R''')_n$$

Koehler et al.(96) have prepared diorganotin derivatives of a dicyano formaldehyde oximes by reacting diorganotin dichloride with the silver salt of the oxime. Various types of butyltin derivatives of alkanolamines have been obtained by Mehrotra et al.(97) during the investigation of the reaction of butyl tin tris-(isopropoxide) with alkanolamines in different molar ratios.

Organotin derivatives of oximes react with acyl or benzoyl halides forming organotin halides and O-acyl or O-benzoyl oximes (86)

$$R_{4-n}Sn(ON = CR'R'')_n + nR'''COX \longrightarrow R_{4-n}SnX_n + nR'R''C = NO.COR'''.$$

Organotin derivatives of oximes are generally volatile and readily hydrolysed by water to give parent oximes (86,87).

$$R_{4-n}Sn(ON = CR'R'')_n + nH_2O \longrightarrow R_{4-n}Sn(OH)_n + nR'R''C = N.OH$$

The organotin hydroxylamine derivatives have been synthesised by Harrison (98,99) by the azeotropic removal of water from

the mixture of appropriate hydroxylamine and the organotin oxide or hydroxide:

$$\tfrac{1}{2}(R_3Sn)_2O + HONR'R'' \xrightarrow{-H_2O} R_3SnONR'R''$$

or

$$R_3SnOH + HONR'R'' \xrightarrow{-H_2O} R_3SnONR'R''$$

(where R = Me, R' = R'' = Et; R = Me, R' = Ph, R'' = COPh; R = n-Pr, R' = Ph, R'' = CO.Ph; R = Ph, R' = Ph, R'' = CO.Ph; R = Me, R' = H, R'' = CO.Ph; R = n-Pr, R' = H, R'' = CO.Ph).

However, Harrison in 1972 (98) reported few triorganotin derivatives of N-substituted and unsubstituted benzohydroxamic acids. Extensive works have been done in this field by Ghosh and Pradhan (100). They have been able to synthesised five types of organotin N-substituted benzohydroxamate derivative; R_3SnL, R_2SnL_2, R_2SnXL, $RSnXL_2$ and $\left[RSnX(OCH_3)L\right]_2$.

(Where R = Ph, Bu; L = N-phenyl benzohydroxamic acid, N-phenyl para chlorobenzohydroxamic acid, N-phenyl para nitrobenzohydroxamic acid, N-ortho tolyl benzohydroxamic acid, N-para chlorophenyl benzohydroxamic acid; X = Cl, Br, I, SCN).

Triphenyltin N-substituted benzohydroxamates and diorganotin bis-N-substituted benzohydroxamates have been prepared by the two methods (99, 100).

Azeotropic distillation of water from a mixture of organotin oxide and N-substituted benzohydroxamic acid in 1:2 molar ratio

in benzene:

$$(Ph_3Sn)_2O + 2R'.CO.NOHR'' \longrightarrow Ph_3Sn(R'.CO.NOR'') + H_2O$$

$$R_2SnO + 2R'.CO.NOHR'' \longrightarrow Ph_2Sn(R'.CO.NOR'')_2 + H_2O$$

and reaction of one mole of organotin chloride with one or two moles of N-substituted benzohydroxamic acids. The liberated

$$Ph_3SnCl + R'CO.NOHR'' \longrightarrow Ph_3Sn(R'CO.NOR'') + HCl$$

$$R_2SnCl_2 + R'CO.NOHR'' \longrightarrow R_2Sn(R'CO.NOR'')_2 + 2HCl$$

hydrochloric acid was neutralised with 25% aqueous ammonia and removed as precipitated ammonium chloride.

It has been reported (101) that the triphenyltin N-phenyl benzohydroxamate is moisture stable, crystalline solid which is monomeric in benzene. The crystal structure of this compoud has been determined (101). The $Ph_3SnONPhCOPh$ possesses a trigonal bipyramidal arrangement of groups about Sn, with two equatorial and one axial phenyl group. The hydroxylamine residue is covalently bound at an equatorial site, and the carbonyl group co-ordinates intramolecularly to the tin atom via the remaining axial site.

Phenyltin halide bis-N-phenyl benzohydroxamates have been prepared by the reaction of triphenyl tin N-phenyl benzohydroxamate with mercuric chloride, mercuric bromide or mercuric iodide (100).

Phenyl tin thiocyanato bis-N-phenyl benzohydroxamate has been prepared (100) from the corresponding chloride by the displacement of chloride by thiocyanate.

$$PhSnCl(PBHA)_2 + KCNS \longrightarrow PhSn(SCN)(PBHA)_2 + KCl$$

Diorganotin halide-N-phenyl benzohydroxamates, $R_2SnX(PBHA)$ have also been prepared by Ghosh and Pradhan (100) (where R = Ph, X = Cl, I, SCN and R = Bu, X = SCN), through the disproportion reaction.

$$R_2SnX_2 + R_2Sn(PBHA)_2 \longrightarrow 2R_2SnX(PBHA).$$

But $Ph_2Sn(SCN)(PBHA)$ has been prepared by the reaction of corresponding chloride complex with KCNS (100).

$$Ph_2SnCl(PBHA) + KSCN \longrightarrow Ph_2Sn(SCN)(PBHA) + KCl$$

Ghosh and Pradhan (100) have shown that penta co-ordinated diorganotin halide-N-phenyl benzohydroxamates disproportionate to the more stable hexa co-ordinated tin compounds when refluxed in non-polar solvent like benzene for a long time.

$$2Ph_2SnX(PBHA) \longrightarrow PhSnX(PBHA)_2 + Ph_3SnX$$

(where X = Cl, SCN).

However, in polar solvent like methanol, $Ph_2SnX(PBHA)$ was found not to give any triphenyl tin halide and $PhSnX(PBHA)_2$.

instead another hexa co-ordinated compound phenyl tin halide methoxy N-phenyl benzohydroxamate was formed along with the liberation of one equivalent of benzene (100). This methoxy compound was also obtained when phenyltin halide bis-N-phenyl benzohydroxamate was refluxed in methanol with the liberation of one mole of ligand (100).

$$Ph_2SnX(PBHA) \xrightarrow{\text{in } CH_3OH} PhSnX(OCH_3)(PBHA) + C_6H_6$$

$$PhSnX(PBHA)_2 \xrightarrow{\text{in } CH_3OH} PhSnX(OCH_3)(PBHA) + HPBHA$$

Organotin Oxinates

Organotin derivatives of 8-hydroxy quinoline (oxine) have extensively been studied. They are stable, well defined compounds which have given a great impetus in the studies of organotin complex compounds. These organotin oxinates are principally of the types $R_3Sn(Ox)$, $R_2Sn(Ox)_2$, $R_2Sn(Ox)X$, $RSn(Ox)_2X$ and $RSn(Ox)_3$, where R = organic group, OxH = 8-hydroxyquinoline and X = halogen or isothiocyanate.

The simple organotin oxinates of the type $R_{4-n}SnOx_n$ (R = organic group, OxH = 8-hydroxyquinoline, n = 1,2,3) are prepared either from the organotin halides and sodium oxinate (102)

$$R_2SnCl_2 + 2NaOx \longrightarrow R_2Sn(Ox)_2 + 2NaCl$$

$$n\text{-}BuSnCl_3 + 3NaOx \longrightarrow n\text{-}BuSn(Ox)_3 + 3NaCl$$

or oxine itself is used, the hydrogen halide formed being removed by treatment with a base such as ammonia (103) and organotin

$$R_2SnCl_2 + 2OxH + 2NH_3 \longrightarrow R_2Sn(Ox)_2 + 2NH_4Cl$$

oxide with oxine (104, 105).

$$(Ph_3Sn)_2O + 2OxH \longrightarrow 2Ph_3SnOx + H_2O$$

Bis(penta fluorophenyl) tin bis oxinates have been prepared from a mixture of tetrakis(penta fluorophenyl) tin or tris-(penta fluorophenyl) tin chloride and an excess of oxine in ethanol under reflux (106). Triorganotin oxinates have also been prepared by reacting triorganotin chloride with a mixture of oxine and sodium methoxide (102).

Diphenyl tin dichloride and oxine react in benzene in the absence of a base to give diphenyl tin dioxinate. If a dihalide and oxine are allowed to react in a 1:1 molar ratio in the absence of a base the halo-oxinate is formed (107, 102).

$$R_2SnCl_2 + OxH \longrightarrow R_2SnClOx + HCl$$

These compounds can also be obtained through disproportionation of a dihalide and a dioxinate in refluxing benzene or ethanol (108, 102),

$$R_2SnCl_2 + R_2Sn(Ox)_2 \longrightarrow R_2SnCl(Ox)$$

or by reaction between a dioxinate and silver halide (107).

$$R_2Sn(Ox)_2 + AgX \longrightarrow R_2SnX(Ox) + Ag(Ox)$$

McGrady et al.(109) have prepared dimethyl tin chloride oxinate through the disproportionation of dimethyl tin dichloride and dimethyl tin di-oxinate in refluxing benzene. Dialkyl tin isothiocyanate oxinate and acetate oxinate have similarly been prepared (107). Dialkyl tin nitrate oxinate and sulfate oxinate are propered by the following methods (107).

$$R_2Sn(Ox)_2 + AgNO_3 \xrightarrow{\text{in } CH_3OH} R_2Sn(NO_3)(Ox) + Ag(Ox)$$

$$2R_2SnCl(Ox) + Ag_2SO_4 \xrightarrow{\text{in } CH_3OH} [R_2Sn(Ox)_2]SO_4 + 2AgCl$$

In other halogen substitution reaction the product disproportionates (110).

$$R_2SnCl(Ox) + I^- \longrightarrow [R_2SnI(Ox)] + Cl^-$$

$$2[R_2SnI(Ox)] \longrightarrow R_2SnI_2 + R_2Sn(Ox)_2$$

The halogen atom of penta co-ordinated tin halo oxinate undergo ready exchange with groups such as butyl, alkoxy or even with chelates e.g.,acetyl acetonates (102, 110) which may disproportionate into diorganotin dioxinates, eg.,

$$R_2SnCl(Ox) + Tl\text{-}OC_2H_5 \longrightarrow R_2Sn(OC_2H_5)(Ox) + TlCl.$$

$$R_2SnCl(Ox) + n\text{-}BuLi \longrightarrow R_2Sn(n\text{-}Bu)(Ox) + LiCl$$

$$\downarrow$$

$$R_2Sn(Ox)_2 + (n\text{-}Bu)_2SnR_2$$

$$R_2SnCl(Ox) + Tl\text{-}acac \longrightarrow R_2Sn(acac)(Ox)$$

$$\downarrow$$

$$R_2Sn(Ox)_2 + R_2Sn(acac)_2$$

Organotin halide bis-oxinates, $RSnX(Ox)_2$ (R = CH_3, n-Bu, Ph; X = Cl, Br) have been prepared by reacting organotin trihalides with oxine (1:2 mole) in ethanol followed by neutralisation with aqueous ammonia or sodium acetate (102, 111).

$$RSnX_3 + 2OxH \longrightarrow RSnX(Ox)_2 + 2HX.$$

Phenyltin halo dioxinates have also been prepared by reacting diphenyl tin dioxinate with mercuric halides in ether at room temperature (112).

Roy (113) has prepared phenyl tin acetate dioxinate by the displacement of chlorine atom from phenyl tin chloro oxinate with CH_3COONa. He also has prepared $PhSn(OCOC_2H_5)(Ox)_2$, $PhSn(OCOCH_2Cl)(Ox)_2$ and $PhSn(OCOCF_3)Ox_2$ complexes by similar method. A novel compound, $[n\text{-}C_4H_9Sn(Ox)_2]_2S$, has been prepared from n-butyl tin sesquisulfide and oxine in boiling toluene (114).

A few organotin trisoxinates have been prepared (104, 115), good yields were obtained by using either of the following reactions.

$$R_2SnO + 6OxH \xrightarrow[\text{benzene}]{\text{boiling}} 2RSn(Ox)_3 + 3H_2O$$

$$RSnCl_3 + 3NaOx \longrightarrow RSn(Ox)_3 + 3NaCl$$

(R = Et, Bu, Ph).

Methyl tin tris oxinate has also been prepared by prolonged heating of methyl tin sesquisulfide with oxine, in a 1:3 molar ratio, in boiling toluene (114).

Butyl tin isopropoxy oxinates of the formula $BuSn(OPr^i)_{3-n}(Ox)_n$ have been prepared by Mehrotra et al.(115) by reacting butyl tin tris isopropoxide with oxine and removing isopropanol by azeotropic fractionation with refluxing benzene; the products depend upon the mole ratio of the reactants used. Thus $EtSn(Ox)_3$ has been obtained by the reaction of $EtSn(OPr^i)_3$ with oxine in 1:3 molar ratio.

Organotin derivatives of substituted oxines have also been reported. Srivastava et al.(116) have prepared some diaryltin bis oxinates/2-methyl-oxinates and diaryl tin chloride oxinate/2-methyl-oxinates. Son et al.(117,118) have synthesised and characterised several diorganotin bis-(mono- and di-substituted-oxinates). These compounds have been prepared by the reaction of

diorganotin dichloride with ligand in 1:2 molar ratio in DMF or ethanol.

Of the three types of oximates, the dioximate derivatives appear to be significantly more stable than the mono and tri oximate derivatives. For example, n-BuSn(Ox)$_3$ is easily hydrolysed to n-BuSn(Ox)$_2$OH which is resistant to further hydrolysis (41). Similarly, the solvolysis of $Ph_3Sn(Ox)$ has been shown to be quite facile.

Ghosh and his co-workers (119) have examined the action of mercuric halides on organotin oximates and probable mechanisms of these reactions have been given. Whereas the penta co-ordinated compound triphenyl tin oximate has been shown to react readily with HgX_2 (X = Cl, Br, I) at room temperature, the hexa co-ordinated compound diphenyl tin dioximate is attacked by HgX_2 only when refluxed in benzene or ether. In both the cases quantitative amount of $PhSn(Ox)_2X$ is obtained. It has also been shown by them that $Ph_2SnCl(Ox)$ can react with mercuric chloride with the complete cleavage of the tin-phenyl bond producing $Sn(Ox)_2Cl_2$, PhHgCl and Ph_2SnCl_2.

Organotin Tropolonates, Kojates, Dithio-Carbamates and Xanthates:

A number of organotin tropolonate complexes are known such as Ph_3SnT, Me_2SnXT, R_2SnT_2, $RSnXT_2$ (R = alkyl or phenyl; X = Cl, Br, I; TH = tropolone) where the tropolone acts as a

bidentate chelating agent bonding through both oxygen atoms. Dimethyl tin bis tropolonate (120) $(CH_3)_2Sn(C_7H_5O_2)_2$, is obtained by the reaction of dimethyltin dichloride and sodium tropolonate (mole ratio 1:2) in methanol.

$$Me_2SnCl_2 + 2NaT \longrightarrow Me_2SnT_2 + 2NaCl.$$

Phenyltin trichloride in benzene added to a solution of tropolone in ether, followed by addition of dimethoxyethane gives phenyltin chloride bis-tropolonate (121). Reflux of a mixture of $C_6H_5SnCl(C_7H_5O_2)_2$, sodium tropolonate and acetonitrile followed by the addition of water and methanol yields phenyl tin tris - tropolonate, $C_6H_5Sn(C_7H_5O_2)_3$ (121).

Kojic acid can form complexes with organotin compounds. Thus treatment of an aqueous solution of dimethyl tin dichloride and kojic acid in a 1:2 molar ratio by aqueous ammonia gives dimethyl tin-bis-kojate (122). Methyl tin chloride and methyl tin bromide bis-kojates have been prepared upon addition of kojic acid to a solution of methyl tin oxide and either aqueous hydrochloric or hydrobromic acid (122).

Organotin dithiocarbamates are frequently prepared by the reaction of organotin chloride and sodium dithiocarbamate (123, 124).

$$R_3SnCl + R'_2NCSSNa \longrightarrow R_3SnSCSNR'_2 + NaCl$$

$$R_2SnCl_2 + 2R'_2NCSSNa \longrightarrow R_2Sn(SCSNR'_2)_2 + 2NaCl$$

They can also be prepared by the following reactions (123, (124).

$$(R_3Sn)_2O + 2R'_2NH + 2CS_2 \longrightarrow 2R_3SnSCSNR'_2 + H_2O$$

$$R_2SnO + 2R'_2NH + 2CS_2 \longrightarrow R_2Sn(SCSNR'_2)_2 + H_2O$$

When $PhSnCl_3$ and KS_2CNEt_2 (1:3 molar ratio) were reacted in methanol, colourless crystals of $PhSnCl(S_2CNEt_2)_2$ were obtained (125). When $Ph_2Sn(S_2CNPh_2)_2$ was heated in air one of the products was diphenyl tin oxide (124).

Organotin Xanthates are frequently prepared by treatment of organotin halides and potassium xanthate (126).

$$R_2SnCl_2 + R'OC(S)SK \longrightarrow R_2Sn[SC(S)OR']_2 + 2KCl$$

They can also be prepared by the reaction of organotin alkoxides and oxides with carbon disulphide (126).

$$R_3SnOCH_3 + CS_2 \longrightarrow R_3SnSC(S)OCH_3$$

<u>Organotin derivatives of (arylazo) benzoic acids and Schiff bases:</u>

Tri-organotin derivatives of some (arylazo) benzoic acids have been prepared by Majee and Banerjee (127). These compounds

have been prepared either by (a) stirring the organotin halide with the sodium salt of the carboxylic acid in methanol or ethanol or (b) refluxing the hexa organo distannoxanes with the carboxylic acid in benzene.

The tri organotin (O-arylazo) benzoates are generally penta co-ordinated, but those containing a hydroxyl group in the 2-position e.g., triorganotin O-(2-hydroxy-5-methyl benzene azo) benzoate, are hexa co-ordinated. The tetra carboxyl derivatives contain two different types of tin-carboxylate bonds, as shown by I.R. absorption.

Organotin halide or oxide react with bidentate, tridentate and tetradentate schiff bases to form complex.

$RSnCl_3$ reacts with $HOC_6H_4CH{:}NR'$ (where R = Et, n-Bu, and Ph; R' = Me, Et and Ph) to form 1:2 adducts in cyclohexane (128). Molar conductance measurement in nitrobenzene indicate that the adducts are non-electrolytes. On the basis of infrared and Mossbauer spectral studies, these adducts have been assigned octahedral structures.

$(CH_3)_2SnCl_2$ reacts with tridentate schiff bases N-(2-hydroxy phenyl) salicylal diimines $OH.C_6H_4CH = N.C_6H_4.OH$ or its derivative to form penta co-ordinated complexes (129).

Triphenyl tin hydroxide also react with N(-2 hydroxy phenyl) salicylaldimine to form hexa co-ordinated complex.

Diorganotin oxide react with quardridentate (ONNO) schiff bases to yield R_2Sn (Salen), R_2Sn(aceto-salen) and R_2Sn(benzosalen)

where R = n-butyl, n-octyl, and benzyl; Salen = bis-(salicylidehyde) ethylene diamine, acetosalen = bis-(2-hydroxy-5-methyl acetophenone) ethylene diamine; benzosalen = bis-(2-hydroxy-5-methyl benzo phenone) ethylene dimine. The compound R_2Sn (acetosalen) and R_2Sn (benzosalen) exist in trans form in solid and as well as in solution whereas R_2Sn(salen) exist both in cis and transform (130).

Mixed Organotin Chelates

Although many organotin chelates have been well studied, there are few reports on mixed chelate, in which two kinds of ligands co-ordinate to one tin atom. Westlake and Martin (110) tried to prepare various diorganotin mixed chelates using thallium β -diketonates and they could assume only $(C_6H_5)_2Sn(OX)(C_6H_5COCHCOC_6H_5)$ as a pure compound. Komura et al. have synthesised a mixed chelate dimethyl oxinate tropolonate (131) by refluxing a solution of dimethyl tin bis-oxinate and dimethyl tin bis-tropolonate in ethanol for 3 hours. The crystals are air stable and soluble in common organic solvents. The infrared spectrum in Nujol, the X-ray powder pattern, and the sharp melting point of this product are quite different from that of the reactants. Thus it is shown that the product is not a mixture of the reactants in the solid state. The existance of the mixed chelate in solution is also supported by the N.M.R. studies.

$$(CH_3)_2Sn(OX)_2 + (CH_3)_2SnT_2 \longrightarrow 2(CH_3)_2Sn(OX)(T).$$

Dimethyl tin kojate tropolonate (132) has been obtained by the reaction of methanol solutions of dimethyl tin dichloride and dimethyl tin bis-kojate with sodium tropolonate in methanol. The compound obtained differs from the original reactants as shown by its I.R. spectrum, X-ray powder pattern and sharp melting point.

Some Structural Aspects of Organotin Complexes:

Due to the availability of d-orbitals, organotin compounds can form various types of complexes with ligands. The stereochemistry of some of these complexes have also been established. A review of the structure of these organotin complexes have been published by Okawara and Wada (40), Bokii et al.(133), Ingham et al.(1), Poller (134), Gielen and Sprecher (135). Ho and Zuckerman (136) have critically reviewed the organotin compounds studied by microwave and diffraction techniques covering the literature upto middle of 1972. Harrison (Loc-cit) has reviewed some structural aspects of organotin compounds covering the year 1972-74.

It is expected that the presence of the lone pair (Sp^2) in the low oxidation state [Sn(II)] would result in lower co-ordination numbers compared to the higher oxidation state of the element [Sn(IV)]. But there is no definite correlation between

valence state and the maximum co-ordination number. Co-ordination number greater than four (in most cases penta or hexa co-ordination) are usually displayed by organotin (IV) compounds. In the present discussions, only the organic compounds of tetravalent tin would be considered.

The most interesting example is afforded by R_3SnX (X = Cl, Br, I, N_3, CN) type compounds which form 1:1 adducts with various lewis bases. These are apparently five co-ordinated trigonal bipyramidal molecules. Thus the complex formed from trimethyl tin chloride and pyridine provided one of the first conclusive structural evidences for five co-ordination at tin in 1962 (137, 145) and the structure has been shown to be trigonal bipyramidal with the three methyl group occupying the equatorial positions as shown in fig. (1a).

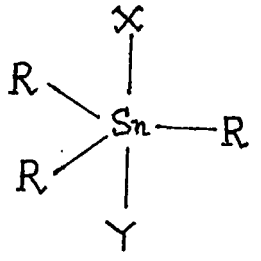
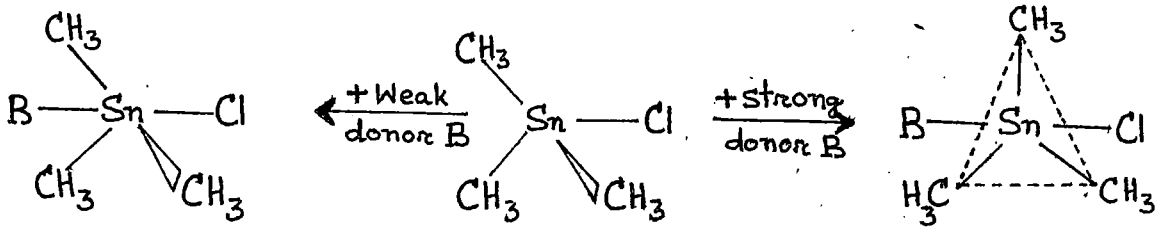


Fig - 1(a).

The NMR and UV spectra of $(CH_3)_3SnX.Py$ (138, 139) in solution show evidence for dissociation, thus suggesting that the donor-acceptor bond strength is rather low. Solution of the compound R_3SnCl in pyridine (140), DMSO, DMA and DMF (141) respectively, are non-conducting, which proves that the molecular complexes present do not have an ionic structure. These data can only be explained by assuming a co-ordination number of five around tin. The relationship between the NMR coupling constants $J_{119Sn-C-H}$ of a complex $(CH_3)_3SnCl.$ B and formation enthalpy (142,143) of the complex allowed Dolles and Drago (144) to derive the following scheme:



A strong donor causes a profound hybridisation of the tin aton and the structure of the complex approaches a trigonal

bipyramid with a $CH_3-\widehat{Sn}-Cl$ angle of about 90^0. A weak donor however forms an addition compound wherein the $CH_3-\widehat{Sn}-Cl$ angle is about equal to the tetrahedral angle of $109^028'$. As a result, it is observed that generally, with weak donors in the system steric hindrance occurs between the methyl group bonded to tin and the donor molecule. This theory is supported by a series of experimental observations. In the IR spectra of the system $(CH_3)_3SnCl.B$, remarkable differences are to be noted when compared with the spectra of the free $(CH_3)_3SnCl$ molecule; the absorption band corresponding to the symmetrical Sn-C stretching vibration disappears and the frequency of the Sn-Cl vibration is drastically decreased. A trigonal bipyramidal structure with a planar $(CH_3)_3Sn$ group with the base molecule B and the chlorine atom both in axial position, perpendicular to this plane, explain these data fairly well. Moreover detailed X-ray analysis (145) has confirmed this geometry. The hybrid orbitals in the trigonal plae should then be nearly sp^2 type orbitals. On the other hand the axial bonds are supposed to result either by using hybrid tin orbitals of the type $(P_z + d_{z^2})$ or by using three-center, four electron molecular orbital having essentially P_z character. The most general feature of the R_3SnL type compounds which are penta co-ordinated about tin is the polymeric nature which is an approximate trigonal bipyramidal structure with planar equatorial organic groups; the more electronegative group forming bridges in the apical position as shown in fig. (1b). Examples are provided by trimethyl tin nitrate monohydrate (146), trimethyl tin

hydroxide (147), trimethyl tin cyanide (148), trimethyl tin isothiocyanate (149), trimethyl tin dicyanamide (150), tribenzyl tin acetate (151).

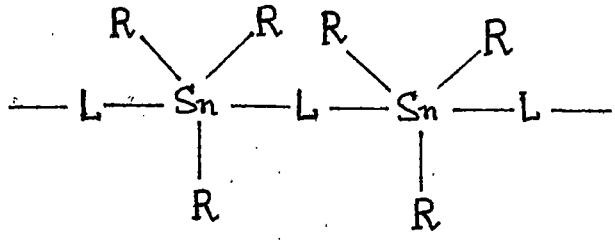


Fig. 1(b)

The Infrared spectra of trimethyl tin carboxylate in the solid state consist of two C-O stretching bands at about 1570 cm^{-1} and 1410 cm^{-1} indicating a symmetrical OCO group (134). Appearance of a single Sn-C stretching frequency in $Me_3SnOCOMe$ is consistent with a planar trimethyl tin group. Allock and Timms (151) have studied the structure of tribenzyl and tricyclohexyltin acetate by X-ray diffraction method. This study confirms that the majority of organotin carboxylateshave polymeric structure in the solid state. But with larger organic groups, the structure may become less polymeric and ultimately become monomeric.

Again in R_3SnX type compound when X = Cl, Br, I the compounds are simple tetrahedral but when X = ClO_4^-, F^-, CO_3^{-2}, BF^-, NO_3^-, AsF_6^- the compounds are five co-ordinated about tin where the anions are either bridging or chelate types (152-153).

In the case where the anionic groups have no co-ordinating sites, for example, $B(C_6H_5)_4^-$, two molecules of mono-anionic Lewis base such as water can occupy the co-ordination sphere, giving a planar SnC_3 arrangement with a penta co-ordinated tin atom (fig. 1c)

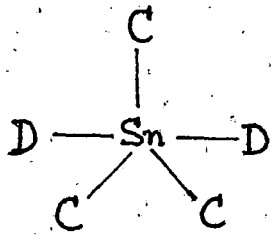


Fig- 1(c)

This findings may well be applied to interpret the structure of 1:2 addition compounds of formula $R_3SnX.2D$ (1) as that containing a bipyramidal $[R_3SnD_2]$ and X^- anion, and may preclude

the existence of hexa co-ordinated tin atoms in such tri-organotin complexes. Thus trimethyl tin chloride and-Bromide give unstable diammoniates that lose one ammonia molecule spontaneously. In these compounds the IR absorption corresponding to the Sn-C symmetrical stretching vibration is not observed, so that the diammoniates are to be formulated as ionic compounds $[(CH_3)_3Sn(NH_3)_2]^+X^-$ and the mono ammoniates as molecular compounds $(CH_3)_3SnX.NH_3$ (154).

For 1:1 complexes of trimethyl tin and triphenyl tin chloride with DMSO, it was found that the S = O stretching vibration frequency in their spectrum is lowered with respect to free DMSO; an observation which has been interpreted as indicating that co-ordination proceeds with the oxygen atom instead of sulphur atom (155).

The flattened tetrahedron structure fig (1d) with an open angle to accept a potential donor is a feature for the triorganotin compounds containing a bidentate ligand and which in favourable conditions can assume a more nearly trigonal bipyramidal shape fig (1e). Thus flattened tetrahedron structure which approximates to a trigonal bipyramidal one, with intramolecular carbonyl tin co-ordination have been proposed (99) for N-acyl substituted hydroxylamine derivatives of triorganotin moiety. Full details of crystal structure of $Ph_3SnONPh.CO.Ph$ have been published (101) in which tin atom has been shown to be five co-ordinated with a

distorted cis-Ph_3SnX_2 configuration with two phenyl groups occupying equatorial sites and the third an axial site at a longer distance. The hydroxyl amine residue is covalently bound at an equatorial site, and the carbonyl group co-ordinates intramolecularly to the tin atom via the remaining axial site. This is consistant with the lowering of the IR carbonyl stretching frequency from 1620 cm^{-1} in parent hydroxamic acid to 1540 cm^{-1} in the triphenyl tin derivative (156).

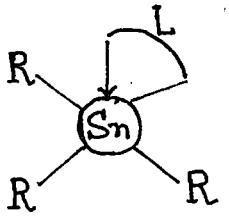


Fig- 1(d).

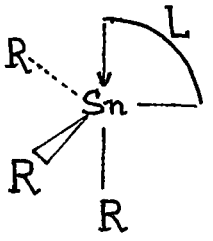


Fig- 1(e).

The electronic spectra (157) of the triphenyl tin oxinate are characterised by the presence of an absorption band at about

360 nm in cyclohexane, benzene, carbon tetrachloride and ether which corresponds to those of various chelated metal oxinates at 370-430 nm. This has been considered as an evidence for the presence of chelated oxinate ring in the molecule in these solvents, while in 95% aqueous ethanol and even in dry methanol triphenyl tin oxinate undergo solvolysis (158). Ruddick and Sams (159) have shown from magnetically perturbed Mossbauer spectroscopy that triphenyl tin oxinate and triphenyl tin acetate possess intramolecular five co-ordination stereochemistry. They have also shown that $R_2SnCl(Ox)$ (R = Me, Ph, HOx = oxine) and the Me_2Sn (Sal-N-$2OC_6H_4$) have penta co-ordinated structure. NMR, IR and UV studies of $R_2SnX(Ox)$ type compounds in general have been interpreted (102, 107, 110) as indicating monomer in solution containing a penta co-ordinated tin atom having a probable trigonal bipyramidal configuration with the R groups in trans position (fig. 1f), though $Ph_2SnX(Ox)$ (X = Cl, SCN) have been suggested to have a trigonal bipyramidal structure (116) with cis-

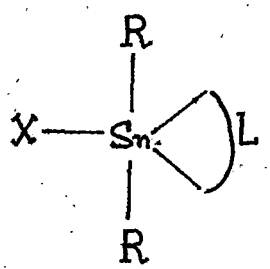


Fig- 1(f)

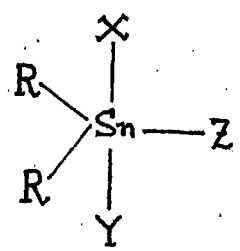


Fig- 1(g).

arrangement of the phenyl groups (160) as revealed by dipole moment data on the thiocyanate compound in benzene solution. The all-cis-structure has been confirmed for $Ph_3Sn(bzbz)$ (bzbz = dibenzoyl methane anion) by a single crystal X-ray diffraction study; the co-ordination about the tin atom being essentially a distorted trigonal bipyramid. The phenyl groups occupy one axial and two equatorial co-ordination sites with the chelating ligand bonded to one equatorial and one axial site (75). Lorberth and Lange (161) from IR, Raman and Mossbauer data have indicated the presence of trigonal pyramidally co-ordinated tin with bridging ligands for the type of compound $R_3SnONOR'R''$.

The dimeric tetraalkyl distannoxanes $(XR_2SnOSnR_2X)_2$ and $(XR_2SnOSnR_2OH)_2$ are unique in that they are believed to contain both tetra co-ordinated and penta co-ordinated tin atoms (162). Another interesting example is the terpyridyl adduct of dimethyl tin dichloride, which crystallises as a double salt $[(CH_3)_2SnCl.terpy]^+[(CH_3)_2SnCl_3]^-$. This compound contains a five co-ordinated, axially most electronegative trigonal bipyramidal anion (fig. 1g) and a six co-ordinated distorted octahedral cation (163,164). Organotin complexes of strong π-acids e.g., $Me_3Sn.TCNQ$ (TCNQ = Tetracyano P-quinodimethane) exhibits a single band at 555 cm^{-1} in the tin-carbon stretching region in the IR spectrum, which is assigned to the antisymmetric mode of planar Me_3Sn moiety, with bridging TCNQ residue resulting in a trigonal bipyramidal configuration at the tin atom (165). The

intense colouration of the compound is indicative of the formation of $(TCNQ)^-$ radical anion on complexation. The complex is therefore best represented by a canonical form $(Me_3Sn)^+ . (TCNQ)^-$ and thus provides the first example of an isolable paramagnetic organotin complex.

A number of diorganotin bis chelates have been isolated (57, 109, 103, 166-171) and found to contain hexa co-ordinated tin atom. Some representative compounds are acetyl acetonates, oximates and carboxylates. Since $Me_2Sn(acac)_2$ is the simplest of all of the complex structurally, it is discussed in detail. In the Raman spectra, lines are observed at 567 cm^{-1} in the crystal spectrum and at 560 cm^{-1} in the solution spectrum, but these lines are tentatively assigned to an out of plane vibration of the ligand. No line attributable to the antisymmetric $Sn-O_2$ stretch was therefore observed. The symmetrical stretch is observed as a strong, polarised line at 514 cm^{-1} in the crystalline sample and at 510 cm^{-1} in the solution. Examination of the IR spectra shows that all of the dimethyl tin complexes have a band at 570 to 578 cm^{-1} which is absent in diphenyl tin chelate, and this is assigned to the antisymmetrical tin carbon stretch. In addition, the ligand out of plane vibration gives a band at 550 to 560 cm^{-1} in the spectra of acetylacetone complexes. There is no band which can be assigned logically to the symmetrical stretch. The Raman and IR spectra thus indicate that $(CH_3)_2Sn(acac)_2$ has trans arrangement of methyl groups. The NMR spectra

of $Me_2Sn(acac)_2$ and $Ph_2Sn(acac)_2$ show only a single methyl signal indicating that these complexes have the trans configuration and that the phenyl groups probably are rotating freely.

For the diorganotin dioximates, a trans-octahedral configuration was favoured by McGrady and Tobias (109) from their IR, Raman and NMR studies. Nelson and Martin (38) attempted resolution of some $R_2Sn(Ox)_2$ type compounds into optically active isomers. Since optically active antipodes would be expected for a cis-octahedral configuration. The failure to resolve such compounds was suggested to be an evidence for the trans geometry. The structure of $Me_2Sn(Ox)_2$ has been determined completely by three dimensional X-ray technique by Schlemper (172) recently. This compound has a highly distorted octahedral structure (fig. 2a). The bond angles in the octahedron range from 73.4° to 110.70°.

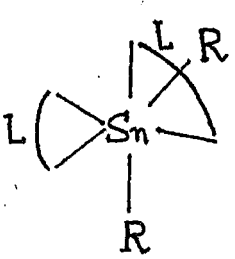


Fig- 2(a)

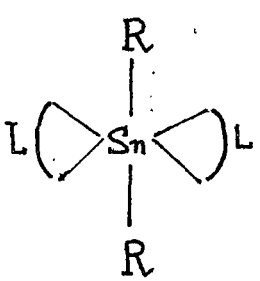


Fig- 2(b).

Though the tin atom in $Me_2Sn(Ox)_2$ is six co-ordinated, the C-$\widehat{Sn}$-C angle is nearly tetrahedral. The tetrahedral disposition of the two methyl groups around the tin atom has been considered by Schlemper (172) to indicate the involvement of two sp^3 hybrid orbitals of tin to the carbon atoms. This is also supported by the value of tin proton spin-spin coupling constants of 67.9 cps (J_{117} Sn-C-H) and 71.2 cps (J_{119} Sn-C-H) (109). The remaining two sp^3 hybrid orbitals may then be involved to form two three center bonds to the oxinate groups. Although no other tin oxinate has been investigated by X-ray so far, a highly distorted octahedral structure may be a general feature of six co-ordinated organotin oxinate derivative. Dimethyl tin dinitrate (173, 174) is an octahedral complex with trans-methyl groups and unsymmetrical bidentate chelating nitrate groups (fig. 2b). Diphenyl tin bis-(N-N'-diethyldithiocarbamate) possesses a distorted cis - octahedral geometry (175). The angle subtended at the tin atom by the group is 101.4(6)°, with the two Sn-C bond distances equal (2.176(17)A°). The Sn-S bond distances of one ligand are approximately equal but differ significantly in the other.

R_2SnCl_2 and $RSnCl_3$ (R = CH_3, C_2H_5) form 1:1 addition compounds with 1,10 phenanthroline and 2,2'-bipyridyl (56,57) but yield 1:2 adducts with pyridine (139,176), DMSO(177-179). The Sn-Cl stretching absorption bands in the IR for the Me_2SnCl_2 complexes are shifted to below 250 cm^{-1}; in the $MeSnCl_3$ complexes the corresponding frequencies are found at about 320 and

280 cm^{-1} (179). A study of the IR absorption spectra of a series of adducts between alkyl tin dichlorides with either 1,10 phenanthroline or 2,2'-bipyridyl showed that the Sn-Cl stretching vibration frequency was lowered by about 80-100 cm^{-1} with respect to the free dichloride (180). A careful examination of these results yielded the conclusion that in all these addition compounds the co-ordination number of tin is increased from 4 to 6. Absorption bands due to symmetrical stretching Sn-C vibration are not found in the IR spectra of the Me_2SnCl_2 complexes, suggesting that the methyl groups should be present in an octahedral trans position (51). The dipole moment, UV and Mossbauer spectral data confirmed the above structure (103, 181, 182). The IR spectra of a series of complexes $Me_2SnCl_2.2B$ [B = pyridine, DMSO etc.] can also be interpreted in terms of octahedral structures around tin where methyl groups are in trans positions and the other ligands in cis positions. In $(CH_3)_2SnCl_2.2DMSO$, the values of the SO stretching frequencies observed in IR spectra suggest that the oxygen atom is the donor in DMSO (155), and the single Sn-Cl stretching vibration shows evidence for a trans arrangement (183). Nevertheless the data of a far IR spectroscopic study of the DMSO (184) complexes of R_2SnX_2 (R = Me, Et, Ph and X = Cl, Br) are consistent with a cis-arrangement for all except for $(CH_3)_2SnBr_2.2DMSO$. The two dimensional lattice of dimethyl tin bis-fluorosulphate crystals contain polymeric sheets with

fluorosulphate groups acting as bridges between linear (trans) dimethyl tin units so that the tin atoms are co-ordinated octahedrally (185). The dimethyl dicyano compounds of group IVb are all associated in the solid state (186). In the tin compounds stronger bridging gives rise to planar sheets in which the molecules are distorted to a nearly octahedral arrangement with trans-dimethyl tin groups perpendicular to the sheets. Mossbauer spectra of $Bu_2Sn(CNS)Ox$ is consistent with the structure of a hexa co-ordinated tin (115). The dipole moment indicates a cis arrangement of the hydrocarbon groups for the compound in benzene solution (160). The cryotal and molecular structure of PhSnCl $(S_2CNEt_2)_2$ has been determined (125). The tin atoms are hexa co-ordinated in a distorted octahedral fashion by the phenyl groups, chlorine atoms, and two chelating diethyldithiocarbamate residues, the phenyl group and the chlorine atom occupying mutually cis-position (fig. 2c). The NMR spectra of $PhSnX(acac)_2$ (X = Cl, Br) compounds indicated an octahedral configuration at tin with phenyl and halogen above and below the plane of acetyl acetonate rings (fig. 2d) (187).

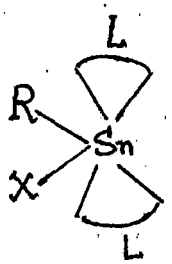


Fig- 2(c)

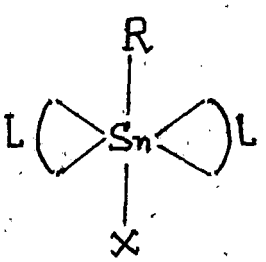


Fig- 2(d).

The novel type of compounds methoxy (acetylacetonato) tin dihalide were shown to be dimeric and their configurations have been interpreted (183) from IR studies in which each tin atom is hexa co-ordinated (fig. 2e). Dibutyltin bismethoxide and dibutyl

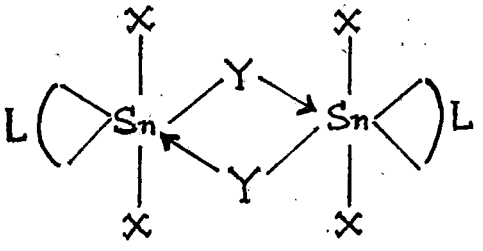


Fig- 2(e).

tin bis-acetylacetonate disproportionate in hexane and form dimers(84), which are believed to have configurations analogous to $Bu_2Sn(SCN)OX$ dimer (fig. 2e) with hexa co-ordinated tin atom. Ruddick and Sams (159) have suggested from Mossbauer spectra for $RSnCl(Ox)_2$ compounds a cis-$RSnXY_4$ octahedral structure which had been assumed by Faraglia et al.(111). Similar hexa co-ordinated tin atom has been assumed for mono-organotin halide bis-acetylacetonates (77). Bis-(pentane 2,4-dionato) dimethyl tin is a

regular octahedron with linear C-Sn-C grouping, which consists of discrete monomeric unit (139).

Not many organotin compounds have been found to possess hepta co-ordinated tin, the geometry of which would be petagonal bipyramidal one (fig. 3). Phenyl tin tris-tropolonate has been reported (121) to be monomeric in methylene chloride, which

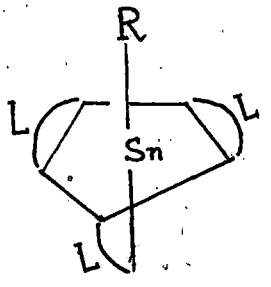


Fig-3

suggested a seven co-ordination around tin. Kawakami et al.(41) have concluded from UV, NMR and IR data that n-butyltin tris-oxinate may have hepta co-ordinated tin atom. Ruddick and Sams (159) from Mossbauer spectroscopy determined the co-ordination number around tin in $BuSn(Ox)_3$ which is consistent with a seven co-ordination with three equivalent bidentate oxine groups. Anhydrous methyl tin trinitrate crystallises with three chelating nitrate groups forming a pentagonal bipyramid about tin (190).

Tris-(dimethyl sulfoxide) nitratodiphenyl-tin-nitrate has been characterised as a hepta co-ordinated organotin complex from IR and X-Ray crystal structure of the compound (191). The structure consists of monomeric hepta-co-ordinated cation $\left[Sn(C_6H_5)_2NO_3\{(CH_3)_2SO\}_3\right]^+$ and NO_3^- anion. Co-ordination around tin is pentagonal bipyramid with the bidentate nitrate group and the three dimethyl sulfoxide moleculesin the equatorial positions and the two phenyl rings at the apices.