CHAPTER - I

A SHORT REVIEW OF ORGANOTIN CHEMISTRY

I.A. Introduction

Organotin compounds are those which contain at least one tin-carbon bond. The first chemist to report an organotin compound seems to have been E. Frankland[1,2]. But his work appears to remain unknown to most of his contemporaries as well as to later authors. The work of C. Lowig[3] in 1852 has unusually been considered to represent the beginning of organotin chemistry. Apart from the compounds described by Lowig, many significant contributions were made in this field during the next few decades.

The vast majority of organotin compounds fall within the four classes:

R_4Sn, R_3SnX, R_2SnX_2, $RSnX_3$

R can be identical or different, substituted or unsubstituted, aliphatic or aromatic groups. X can be negative groups such as -OR, -SR, -OCOR, $-OSnR_3$, $-NR_2$ or halogens or some other acid radicals or neutral ligands such as -H or electropositive one such as Li or Na. The three series of organotin hydrides R_3SnH, R_2SnH_2, $RSnH_3$ have assumed considerable importance[4-7]. The acceptor strength of the organotin compounds generally follows the sequence; $R_3SnX < R_2SnX_2 < RSnX_3$.

Stannyl metal compounds of the type R_3SnM, R_2SnM_2[8,9], $Ph_3SnSiPh_3$, $Ph_3SnSi(GePh_3)$, $R_3Sn-SnR_3$[8], $Me_3Si-Hg-SnR_3$, $R_3Sn-Hg-SnR_3$[10], $Ph_3Sn-ZnSnPh_3$, $Ph_3SnCdSnPh_3$, are also known where R may be aliphatic or aromatic, M may be Li, Na or K.

The discovery of industrial applications of organotin compounds as rubber anti-oxidants, Ziegler type catalysts in the polymerization of olefins, food preservatives, agricultural fungicides and as active ingredients in certain veterinary medicine[11] and also an increased general scientific interest produced a striking renaissance of organotin chemistry starting about 1949 continuing to the present day.

The biocidal properties of organotin compounds have led, over the past decade, to a rapid increase in the commercial utilization of these species. Organotins are currently in use as agricultural fungicides and miticides, surface disinfectants, anthelminties and marine antifouling agents[12].

One intriguing development is the synthesis of compounds in which the organotin is bonded to ligands that exhibit biocidal activity, the effectiveness of the product being potentially greater than the sum of the components. Although several ligand systems suggest themselves for study, the oxy and thio phosphorus acids are particularly amenable. Esters of dithiophosphoric acids have, for example, found widespread use in the post war years as pesticides, being marketed under such trade names Ethion, Malathion and Thimet[13], while the importance of phosphates in in-vivo systems is well documented.[14] Moreover, specific evidence for the activity of miscellaneous organotin derivatives of the phosphorus acids is available[15,16] and provides encouragement for more detailed studies. In particular, answers to the important structure — activity questions demand the availability of

reliable structural data, the collection of which has formed the basis of many recent research efforts.

Application of fungitoxic organotin phenoxy-acetates for controlling human dermatomycosis have also been reported[17].

Diorganotin dicarboxylates are widely used in industry as homogenous catalysts for polyurethane and RTV Silicone polymerizations and for trans esterification reactions[125].

I.B. Bonding in organotin compounds

The electronic configuration of tin atom is : $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^{10}$ $4s^2$ $4p^6$ $4d^{10}$ $5s^2$ $5p^2$, the ground state being 3p state derived from s^2p^2 configuration[18]. The tetracovalent state is derived from the sp^3 hybridisation by promoting one of the 5s electrons to the 5p level. A large number of organotin compounds consist of tetravalent tin atom because of its much more frequent occurrence than the divalent atom. The metals of Gr. IVA form organometallic compounds which are more stable and less reactive than those of Gr. III or IVB metals. The increased stability may be partly due to sp^3 hybridisation. Thus, tetravalent tin is unreactive towards air and water but trimethyl indium and trimethyl antimony have a strong affinity towards these reagents. The significant increase in stabilities of R_4Sn compounds over R_2Sn types also show the effect of increased hybridisation on the stability. Metal-carbon bond strengths have been

reviewed by Skinner[19] who observed that mean bond dissociation energies ($\bar{D}$) fall as the sub group is descended so that $\bar{D}(C-R) > \bar{D}(Si-R) > \bar{D}(Ge-R) > \bar{D}(Sn-R) > \bar{D}(Pb-R)$. The mean values of the bond dissociation energies are C-C : 87, C-Si : 70, C-Ge : 60, C-Sn : 50, C-Pb : 31-37 K.Cal/mole. Moreover, these values are dependent on the nature of the alkyl group i.e., on the stabilisation of the corresponding alkyl radical by hyperconjugation etc.

The tin atom has covalent radius of 1.4Å and is independent of the nature of the ligands. There is some sort of decrease in bond lengths only when strongly negative ligands are accumulated around the tin. The bonding of the tin would thus appear to be almost entirely covalent at least in crystalline solids, in the vapour and in non-polar media. However, the electronegativity of tin being less than most of the common ligands, e.g. carbon, nitrogen, oxygen, halogen and even hydrogen, the bonds are expected to be sufficiently polar in the sense $\overset{+\delta}{Sn} - \overset{-\delta}{X}$ and dipole moments of various Sn-X bonds have also been estimated. The dipole moment of the alkyl tin bond, mostly estimated as 0.45-0.6D[20-22] depends both in direction and magnitude on the nature of the alkyl group[23].

The electronegativities of Gr. IV elements have been investigated by several workers[24a-d]. The results always vary with the method of measurement and the compounds selected. It is not surprising since the electronegativity, not being a uniquely defined parameter, depends on the method of measurement and the environment of the atom in

question. In fact, one always works not with an electronegativity of tin but with a value for tin in a particular combination and allowance will have to be made for the influence of all ligands.

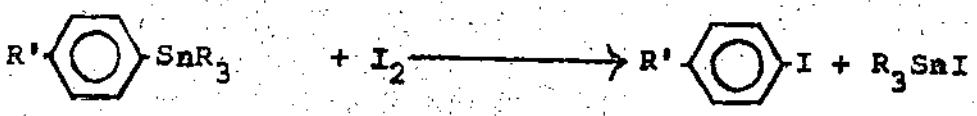
Table - 1

Electronegativities of Gr. IVA elements

	Pauling	Sanderson	Fineman Daignault	Allred-Rochow
C	2.5	2.47	2.57	2.60
Si	1.8	1.74	1.90	1.90
Ge	1.8	2.31	2.02	2.00
Sn	1.8	2.02	2.47	1.93
Pb	1.8	-	-	2.45

Closely related with this is the inductive effect which the tin atoms or stannyl groups exert on their surroundings. The bond polarisation $C^{-\delta} - Sn^{+\delta}$, which is there in principle, may be changed by substitution at C as well as at Sn. NMR data on organotin compounds[25,26] and semiemperical calculations of Majee and Gupta[27] emphasise this. According to Eaborn et al[28], polarisation is increased by electron donor substituents R' in the p-position in a phenyl group, as demonstrated by the increase in the rate of cleavage of C-Sn bond by iodine according to the reaction (1). Thus, this reaction may be

marked as electrophillic aromatic substitution.



Eqn.(1)

The electron attracting groups R' diminish the rate by lowering the nucleophilicity of the ring carbon attached to tin. The sequence of relative reaction rates is for R' = OMe > t-Bu > i-Pr > Et > Me > H > Br > F > Cl > COOH.

Electron donor properties increase in the series (R = Me) : $SiR_3 < GeR_3 < SnR_3$, as may be seen from the relative rates of acidolysis of $p\text{-}R_3M\ CH_2\ CH_4 - SnR_3$. These are : M = Si 1.00, Ge 1.36, Sn 3.21[29]. A similar sequence emerges from IR and NMR measurements[30] and also from IR studies on esters of the $MeCOOMe_3$ (M = C, Si, Ge)[31].

A problem which often arises in the investigations to measure relative inductive effects is that there may be some π -character in a bond between tin and an element possessing p-electrons[32-34]. Thus in a Sn-X bond where X is C (sp^2), N, O, S or halogen, it is possible that, opposing the inductive electron drift $Sn^{+\delta} \rightarrow X^{-\delta}$, there may be some overlap between an empty 5d orbital on Sn and a filled p-orbital on X causing a transfer of electron density in the opposite direction.

Inspite of many disputes[34-37] it is widely accepted that there are significant ($p\pi \rightarrow d\pi$) contributions to the Sn-N bonds in compounds

such as the planer triethylamine[38]. There is some evidence that in phenyl tin compounds, interaction occurs between the electrons of the phenyl group and the 5d orbitals of tin. This conclusion is based on the interpretation of NMR[39,40], IR[41], UV[41] and dipole moments[42] of Ph_3Sn compounds and the acid strengths of the substituted benzoic acids $p\text{-}Me_3MC_6H_4COOH$ (M = C, Si, Ge, Sn). It can not be assumed that other aromatic groups behave similarly since the pKa values for a series of pyridine having Me_3M (M = C, Si, Ge, Sn). Substituents in the 2-postition indicated the absence of $p\pi - d\pi$ bonding in the tin-pyridine link[43]. Calculation based upon nuclear quadrupole resonance measurements indicated π-character in the Sn-I bonds of diethyl tin diiodide whereas it was concluded from the dipole moments of organotin chlorides that the Sn-Cl bond order is close to unity[42]. There is evidence for $d\pi - d\pi$ interaction in the bonds formed between tin and certain transition metals[44,45]. On the other hand Majee and Gupta has shown in a series of paper[27] that most of the properties of organotin compounds may be interpreted without assuming any $d\pi - p\pi$ interaction.

Such apparently contradictory observations and interpretations probably originate from the fact that the overall behaviour of tin compounds is a complex function of many factors, e.g., atoms or groups to which it is joined, its coordination number, its oxidation state, the phase in which the molecule is found and even temperature and external pressure may often change the behaviour dramatically. Since tin forms a very large variety of compounds with many different atoms, groups and ligands, any attempt to interprete the properties of all

groups of tin compounds in terms of a particular criteria is fraught with grave danger of creating confusion, rather than systematisation.

Notwithstanding such wide variations, one may, however, classify tin (IV) compounds, which constitute the overwhelmingly major part of organotin literature, into the following categories[46]:

1. Ionic compounds in which tin may be considered to be in +4 oxidation state with electronic configuration $[Kr]\ 4d^{10}\ 5s^{o}\ 5p^{o}$.

2. Covalent tetrahedral compounds in which tin may be considered to be sp^3 hybridized.

3. Tin (IV) complexes where the 5d orbitals may be included in hybridisation scheme to form organotin compounds with coordination number of 5 to 8.

All compounds of the type $R_{4-n}SnX_n$ (R = organic group, X = monodentate atom, group or liand) usually belong to category 2 and characterised by tetrahedral geometry around the tin atom except when the group X is capable of forming intra or intermolecular coordination bond.

In general the X group (s) play the most dominant role in determining the bonding and structure of organotin compounds. Because of this, there has been a tremendous spurt of activity on the synthesis and structural studies of organotin complexes. In the following section a brief discussion on the organotin complexes is therefore presented.

I.C. Organotin Complexes

Organotin compounds can form various types of complexes with ligands. The structural aspect of these compounds has been exhaustively reviewed by Ingham et al[8], Poller[47], Gielen and Sprecher[48] and by Ho, Zuckerman[49], P.G. Harrison[75], Koten[51], Pelizzi[52] and latter by Zubieta and Zuckerman[53].

The structural aspects, viz., coordination number and geometry around the tin atom, of organotin complexes derived from R_nSnX_{4-n} type compounds, depend both on the number of the organic groups (R) around the tin atom and the ligand. As a general rule, R_3SnX type compounds tend to form penta coordinated complexes, while higher coordination number can be realised with R_2SnX_2 and $RSnX_3$ type compounds.

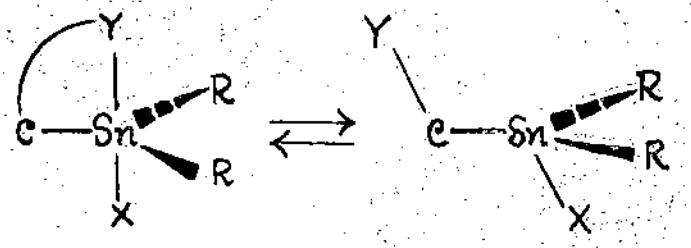
The most interesting example is afforded by R_3SnX type compounds which form various type of adducts with Lewis bases[8]. These compounds are generally penta co-ordinated[54,55]. For X = Cl, Br, I, Me_3SnX type are usually tetrahedral but for X = ClO_4^-, F^-, CO_3^{-2}, BF_4^-, NO_3^-, AsF_6^-, -OCOR, the compounds are five co-ordinate about tin where the anions are probably either bridging or chelate type[56,57]. R_3SnX and R_2SnX_2 compounds can form organotin chelates with chelating agents, viz. 8-hydroxy quinoline[58,59], acetyl acetone[60,61], 1, 10-phenanthroline[51,61] etc, which may be five or six co-ordinated compounds.

N-substituted salicylidineiminato trialkyl tin derivatives have been prepared by the reaction of the trialkyl tin chloride or

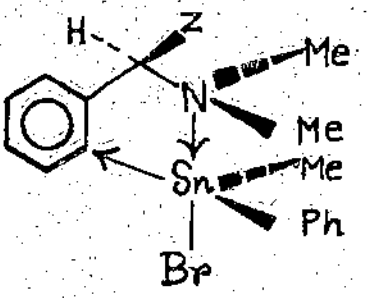
alkoxides with the corresponding Schiff[62] bases. These complexes are believed to contain 5-co-ordinate tin atom. Trimethyl tin derivatives of sulphur containing Schiff bases are also known[63]. Several triorganotin dithiocarbamates of the formula R_3SnDtc (R = Ph, n-Bu, Bz, Dtc = n-pr, n-Bu, 2-phenyl, dibenzyl etc - dithiocarbamates) have been reported by Srivastava[64]. The quaternary phosphonium cations $[\geqslant PCH_2SnMe_3]^+$ is also known[65]. Nitrate complex of organotin (IV) containing triphenyl phosphine oxide has been reported[66].

A series of triorganotin halides, RR'SnBr(C-N), and a series of tetraorganotin compounds $R_3Sn(C\text{-}N)$ have been synthesized[88] in which C-N is either monoanionic $2\text{-}Me_2NC_6H_4CH_2^-$ or novel monoanionic $2\text{-}Me_2N.C_6H_4CH(SiMe_3)^-$. ^1H and ^{13}C NMR data indicate that the tin center in the $R_3Sn(C\text{-}N)$ compounds is tetra coordinate whereas the tin atom in the RR'SnBr(C-N) derivatives is penta coordinate as a result of intramolecular Sn-N coordination. Penta coordination in a trigonal bipyramidal manner with axial N and Br atoms has also been established by the X-ray structure determination of $[2\text{-}Me_2NC_6H_4CH(SiMe_3)]SnMePhBr$.

The existence of an equilibrium in solution between two possible situations i.e. with and without intramolecular Sn-Y coordination (A and B respectively) could be monitored in many cases by following the temperature dependence of the ^1H NMR patterns of prochiral groupings present in the compounds e.g. the CH_2 and NMe_2 groups.



A B

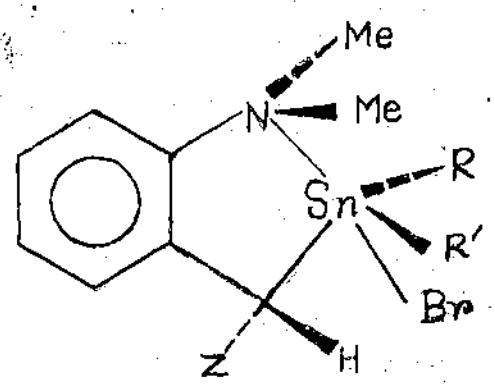


1; Z = H
2; Z = Me

I

The influence of intramolecular co-ordination (cf A) on the configurational stability of triorganotin halides is the steric bulkiness, the heteroatom-containing group represents when it is not coordinated has been explained. If one compares the stereochemistry of the coordinated and non coordinated situations A and B respectively for compounds 1 and 2, both having two sp^2 C-atoms in the five membered chelate ring, one comes to the conclusion that the non coordinated $O\text{-}CH(Z)NMe_2$ substituent represents a group with considerable steric bulkiness. This bulkiness destabilizes situation B with respect to the five-coordinate situation A. In the latter situation this bulkiness has been completely removed by the Sn-N coordination.

An X-ray crystal structure determination of one diastereomer, i.e. $[2\text{-}Me_2NC_6H_4CH(SiMe_3)SnMePhBr]$ has been described.



II

R = R' or R ≠ R'

3; Z = H

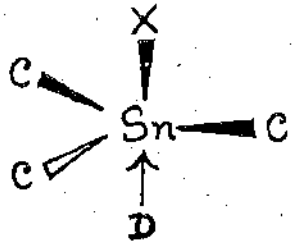
4; Z = $SiMe_3$

The structure shows that the chelate ring conformation is such that it places the bulky Me_3Si substituent both out of the plane of the aryl ring and futhermore, at the side of the less bulky methyl ligand. It is suggested that the unusual high configurational stability of the RR'SnBr(C-N) compounds arises from the rigidity of the 2-$Me_2NC_6H_4CH(Z)^-$ ligand which holds the 2-Me_2N group in close proximity of the tin centre. If Z is the bulky $SiMe_3$ group also, the SnR_2Br grouping is locked in a fixed position with respect to the N donor site.

The penta co-ordinated organotin complexes may be classified into three groups:

i) Type - I

Addition complexes, in which a donor molecule is coordinated to R_3SnX molecule to give a trigonal bipyramidal arrangement.

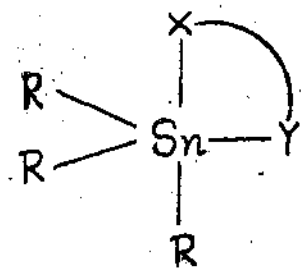


Type - I

In these complexes, R-groups occupy the equitorial positions while the electronegative group X and the ligand occupy the axial position as would be expected from the isovalent hybridisation principle. A well known example of this structure is the 1:1 addition compound of $(CH_3)_3SnCl$ and pyridine.

ii) Type - II

Organotin complexes derived from chelating agents, e.g., 8-hydroxy quinoline, acetylacetone, 1,10-phenanthroline etc., are generally intramolecularly coordinated (II)



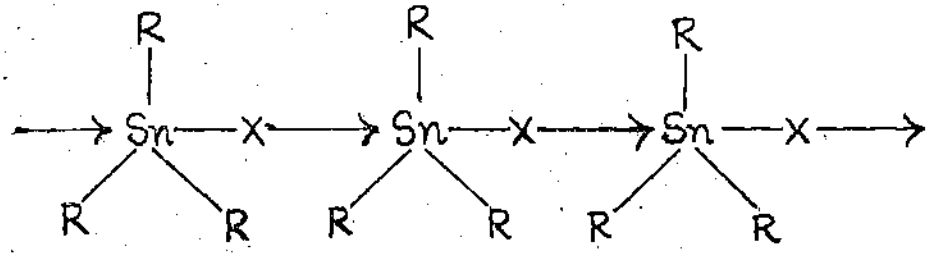
Type - II

Large number of such complexes have been synthesised and studied. Structural studies using X-ray crystallography have also been reported in many cases.

An X-ray study was reported for (triphenyltin 1,3-diphenyl-propionate) triphenyltin which established the occurrence of penta co-ordination as a result of intramolecular co-ordination with the ligand spanning axial equatorial sets[100].

iii) Type - III

In contrast to the intramolecularly coordinated organotin complexes (type II), the intermolecularly coordinated compounds are more abundant in organotin chemistry. In this case, a polymeric structure is formed by bridging of an anionic group to the tin atom from either side of the plane of R groups (III).



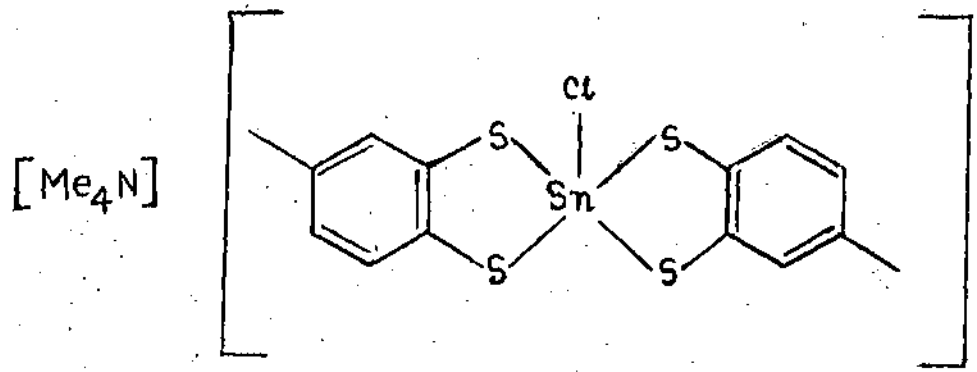
Type- III

The intermolecular associated form of 2-(tri-n-butyl stannyl) tetrazoles[67] in benzene and chloroform is well known.

The first anionic five co-ordinated tin compounds containing saturated rings has been reported[68] to be formed from the reaction of $RSnCl_3$ and $Et_4N^+Cl^-$ with sodium ethane-1, 2-dithiolate and from the partial hydrolysis of bis (ethane-1, 2-dithiolato) tin in the presence of an amine base. X-ray analysis of the new stannates and the distannates showed that the geometry of the former in terms of distortions from a square or rectangular pyramid, while geometry of the latter more closely approaches a trigonal bypyramid.

The authors[68] have reported earlier the synthesis and X-ray study of the first tin compound having a discrete square-pyramidal

geometry. The compound was a spirocyclic derivative that resulted from the reaction of bis(toluene-3, 4-dithiolato) tin (IV) with $(CH_3)_4N^+Cl^-$ at room temperature.



III

The first example of polytopal dominance of square pyramidal geometry in organotin penta coordination : crystal structure of tribenzyl (2-thiolato pyridine-N-oxide) tin (IV) has been reported[118].

The coordination geometry about the central atom in monomeric tribenzyl (2-thiolato pyridine-N-oxide) tin (IV) is a unique square pyramid, with one benzyl carbon atom occupying the apical position and the base plane containing the other two benzyl carbon atoms along with the oxygen and sulfur atoms of the chelating ligand; the tin atom is displaced out of the basal plane in the direction of the apical carbon atom by 0.64(1) Å.

Many N-substituted N-(triphenyl stannyl) cyanamides have been reported and the tin in these complexes is shown to have a co-ordination No. > 4 by means of IR and Mossbauer Spectroscopy[69].

Several organotin (IV) complexes with quadri and tetradentate anionic Schiff base ligands have been prepared and investigated in the solid state[70,71]. Mossbauer parameters derived from both zero field and magnetically perturbed spectra suggest that the R_2Sn(Salen)*, R = Me, Et, Ph and Me_2Sn (Saldap-2-OH)** complexes have distorted trans octahedral structures. However in Ph_2Sn(H-Saldap-2-O) the ligand appear to be only terdentate leading to a penta- co-ordinate structure similar to those of the $R_2Sn(Sal\text{-}N\text{-}2\text{-}OC_6H_4)$ derivatives (R = Ph, Me).

The Mossbauer parameters are given in table 2.

Table 2

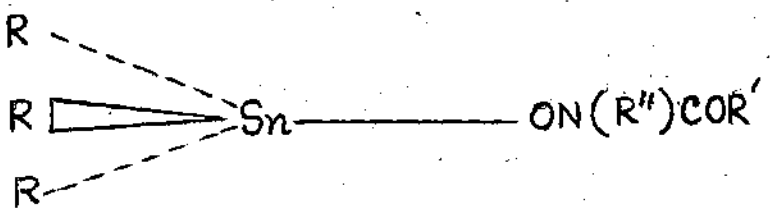
Compound	δ	ΔE	$\Delta E/\delta$
$CF_3C(CO)(CN)NSnPh_3$	1.07	4.54	4.24
$CH_3OC(O)(CN)NSnPh_3$	1.55	4.23	2.73
$PhSO_2(CN)NSnPh_3$	1.07	4.54	4.24
$MeC(O)(CN)NSnPh_3$	1.55	4.23	2.73

* H_2Salen-N,N' ethylene bis(Salicylaldimine)

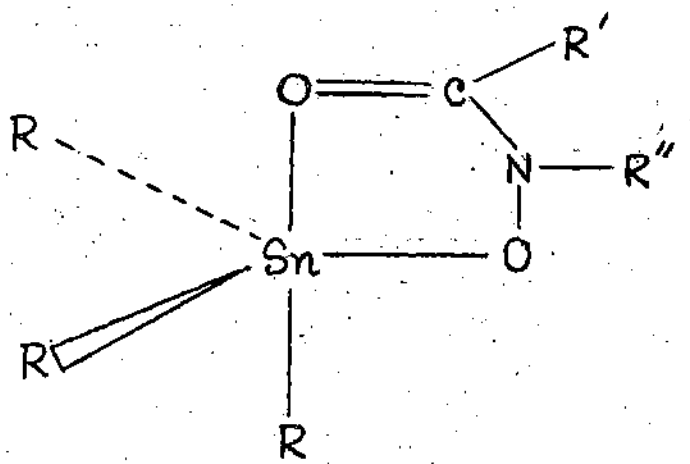
** H_2Saldap-2-OH-N,N' (2-hydroxy trimethylene)bis(salicylaldimine).

Organotin complexes of strong π-acids of the type $Me_3SnTCNQ$, $MeCP_2Sn.TCNQ$, $MeCP_2Sn.nTCNE$ (n = 1,2) and SnX_4 TCNE.THF (X = Cl, Br)[72] have been prepared (TCNQ = Tetra cyano-p-quinodimethane, TCNE = tetracyano ethylene). The infrared spectra of the complex $Me_3Sn.TCNQ$ exhibits a single band at 555 cm^{-1} in the tin-carbon stretching region which is assigned to the anti-symmetric mode of a planar Me_3Sn moiety, with bridging TCNQ residues resulting in a trigonal bipyramidal configuration at the tin. The intense colouration of the compound is indicative of the formation of $(TCNQ)^-$ radical anion on complexation. The complex is therefore best represented by the canonical form $(Me_3Sn)^+$. $(TCNQ)^-$ and thus provides the first example of an isolable paramagnetic organotin complex.

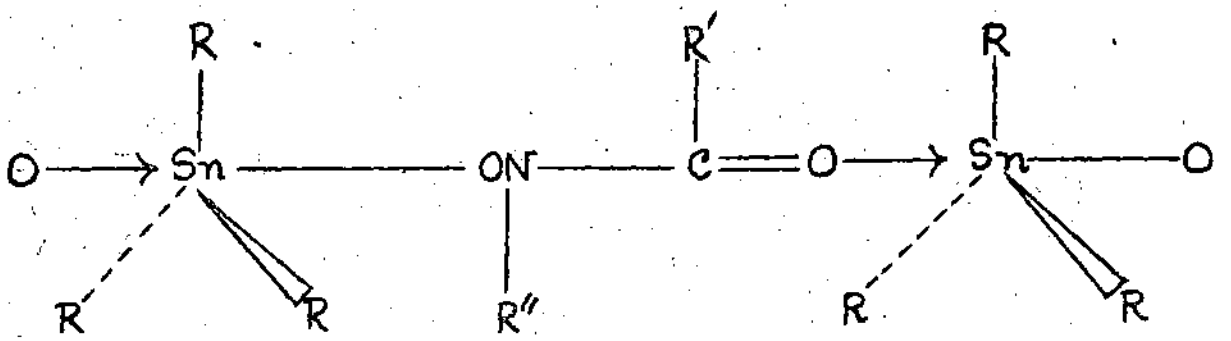
Example of a compound containing organotin (II) and organotin (IV) in one molecule, $(Me_3Sn^{IV}C_5H_5)_2Sn^{II}$ has also been reported[73]. A flat sandwich type compound, decaphenyldicyclopentadienylstannocene, involving tin (II) structure $[\eta^5 - (C_6H_5)_5C_5]_2Sn^{II}$ has been reported[74]. The triorganotin derivatives of N-acyl-hydroxylamine e.g. $Me_3Sn[ON(Ph)SO_2C_6H_4CH_3]$, $(CH_3)_3Sn[ON(Ph)COPh]$, $Me_3Sn[ON(Me)COMe]$ have been prepared. The presence of a second donor site in the N-acylhydroxylamine ligand permits its potential function or a unidentate or a chelating bidentate ligand; thus giving rise to the possible four co-ordinated structure (IV) or the two 5-co-ordinated structure (V) and (VI)[75].



Type -IV

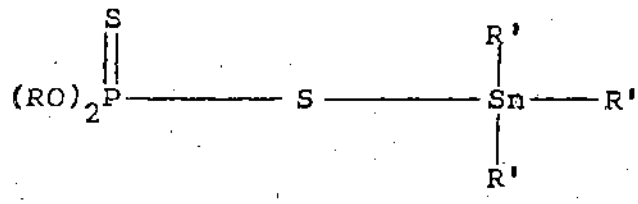


Type - V



Type - VI

Triorganotin dialkyl thiophosphates, $(RO)_2P(=S)SSnR'_3$ (R = Et, i-Pr, n-Pr or Ph and R' = Me, Et, Bu or Ph) have been prepared[76]. An ester type structure has been proposed for these compounds.

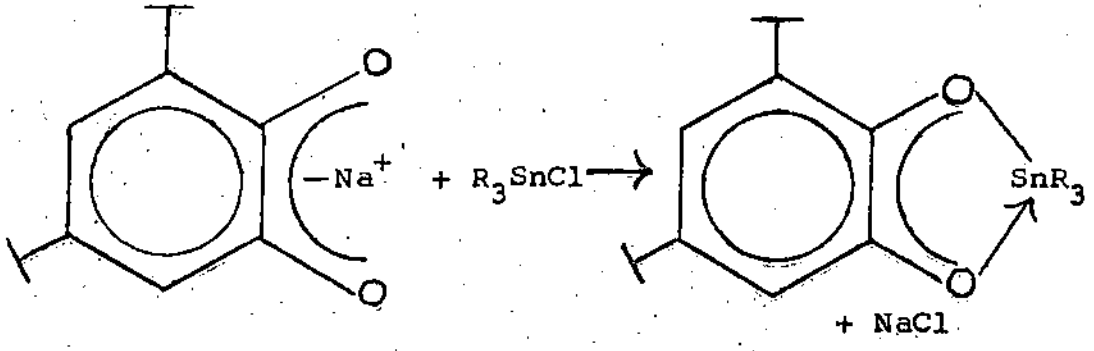


Type- VII

Works on oxy and thio phosphorous acid derivatives of tin-structural contrasts has been reported by Molloy et al[77].

The contrast between the chelating of the dithiophosphorus acid groups and the bridging of the corresponding oxygenated ligands has been reported[77], where it has been rationalized on two counts. Firstly the Sn-O bond is at least 0.2Å shorter than the corresponding Sn-S bond. Thus when chelation occurs, the angular strain within the resulting four-membered SnE_2P (E = O,S) heterocycle is greater for oxygen, rendering chelation less favourable. The relative electro-negativities of C(2.50), S(2.44) and O(3.50) underlie the second rationale. In a trigonal bipyramid, for example, competition between carbon and sulfur for p- or S-dominated orbitals on tin will be negligible. Conversely, the increased electronegativity of oxygen over carbon directs it into the axial position of the trigonal bipyramid with the ligand unable to span both axial sites in the same molecule, bridging was observed.

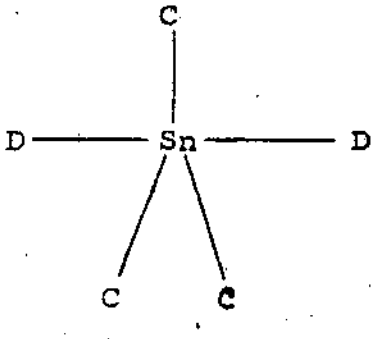
The initial ESR spectra observed for the reactions of O-quinone with R_3SnSnR_3 are analogous to the signals of tin containing semiquinones formed according to the reaction.



Eqn. (2)

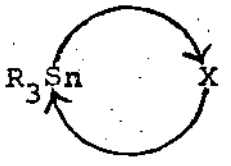
From the reaction of pyridine N-oxide with nitratotriphenyl tin in dry acetone under nitrogen, two types of crystals belonging to the monoclinic and triclinic system, respectively and having same $[Sn(C_6H_5)_3(NO_3)(C_5H_5NO)]$ stoichiometry has been reported[78]. Moreover, a molecular adduct of Nitratophenyl tin with triphenyl arsenic oxide $[Sn(C_6H_5)_3(NO_3)(C_6H_5)_3AsO]$ has also been synthesised. The co-ordination about tin is bipyramidal with phenyl ring in the equatorial and oxygenated ligands in the axial positions[79].

In cases where the anionic groups have no co-ordinating sites e.g. $B(C_6H_5)_4^-$, two molecules of a mono-anionic Lewis base viz., water can occupy the co-ordination sphere, giving a planar SnC_3 arrangement with a penta co-ordinated tin atom (TypeVIII).



Type VIII

Intramolecular coordination often results in many interesting structural variations when the X group in R_3SnX belongs to a chelating ligand. Such structures may be schematically represented as shown below (Type IX).



Type IX

Crystal structure of tribenzyl (2-pyridinethiolato-N-oxide) tin (IV) : a rare example of square pyramidal organotin (IV) compound has been reported[119].

Tribenzyl (2-pyridinethiolato-N-oxide)tin (IV), $[(C_6H_5CH_2)_3Sn(2\text{-}SC_5H_4NO)]$, crystallizes in space group $P\bar{1}$, with

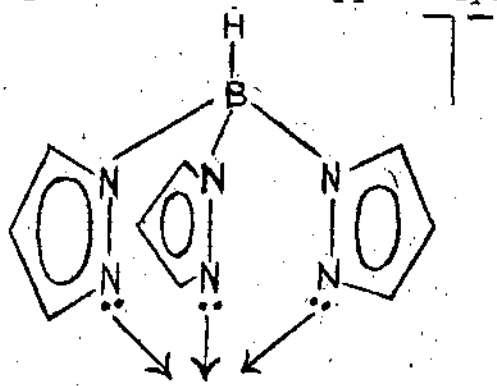
a 9.169(, b 10.498(3), c 13.511(4) Å, α 91.54(2), β 104.61(2), γ 112.49(2)° and Z = 2. The structure has been refined to R = 0.028 using 4593 observed MO-K_α reflections. The molecule adopts a configuration displaced 91% from trigonal bipyramid to a square pyramid along the Berry pseudorotation pathway. The basal plane is composed of the oxygen and sulfur atoms of the chelating 2-pyridinethiolato ligand and the carbon atoms of two benzyl groups [Sn-O 2.261(2), Sn-S 2.577(1), Sn-C 2.189(3), 2.196(3) Å]. The apical tin-carbon bond [Sn-C 2.167(3) Å] is shorter than the other two tin-carbon bonds. The tin atom is placed 0.64(1) Å from the basal plane in the direction of the apical carbon [sum of the basal angles = 341.7(4)° and the C apical - Sn L basal angles are in range 100.1(1)-110.1(1)°.

The unusual geometry of tribenzyl (2-pyridinethiolato-N-oxide) tin (IV) provides the first example of polytopal dominance of the square pyramidal configuration in penta coordinated organotin compounds.

In contrast to the penta co-ordinated triorganotin compounds, examples of 6-coordinate triorganotin compounds are very few. The Mossbauer recoil free fraction and structure of triorganotin aryl-azobenzoates has been reported[82]. Spectral and other studies indicate some of these to be 6-coordinated triorganotin compounds.

The synthesis and X-ray structures of Tris(Pyrazolyl)borate (Trimethyl)tin : A six coordinate Trialkyltin complex has been reported[120].

Reaction between Me_3SnCl and $K[HB(PZ)_3]$ (PZ = 1-pyrazolyl, $C_3H_3N_2$) affords $[HB(PZ)_3]SnMe_3$ which was shown by a full X-ray structure determination (Trigonal space group $P\bar{3}$, a = b =11.722(3) C = 8.211(2)Å, Y = 120°, Z = 2) to contain six coordinate tin bonded to three methyl groups and to three pyrazolyl groups.



IV

The infrared and mass spectra of $HB(pz)_3SnMe$, were fully consistent with the assumed formulation and the ^1H NMR spectra showed that all three pyrazolyl rings were equivalent between-60 and +30°C, suggesting that all three were coordinated to the tin atom, or that rapid exchange of the rings of a partially co-ordinated ligand was occurring.

The invariance of the ^1H NMR spectrum of $HB(pz)_3SnMe_3$ over the range - 60 to +30°C suggests that a six coordinate structure with equivalent pyrazolyl rings is maintained in solution, although a lower coordination system with rapid exchange of rings cannot be ruled out.

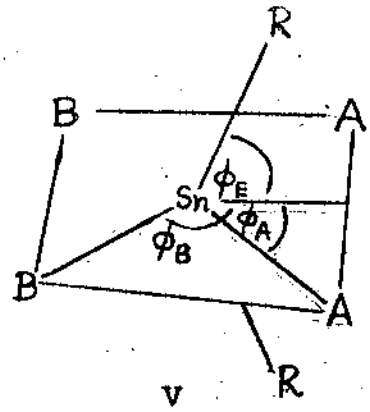
Skew-trapezoidal bipyramidal diorganotin (IV) bis chelates. Crystal structure of dimethyl-bis(2-pyridinethiolato-N-oxide)tin(IV) has been reported[121].

Dimethyl bis (2-pyridinethiolato-N-oxide)tin (IV), $Me_2Sn(2\text{-}SPyO)_2$, crystallizes in space group $P2_1/C$ with a 9.877(3), b 11.980(4), C 13.577(3)Å, β 109.1(2)° and Z = 4. The structure was refined to R_F = 0.036 for 2263 MO-K_α observed reflections.

The coordination geometry at tin is a Skew-trapezoidal bipyramid, with the oxygen [Sn-O 2.356(3), 2.410(4) Å] and sulphur [Sn-S 2.536(1), 2.566(1) Å] atoms of the chelating groups occupying the trapezoidal plane and the methyl groups [Sn-C 2.106(6), 2.128(7) Å] occupying the apical positions. The methyl-tin-methyl skeleton is bent [C-Sn-C 138.9(2)°]. The S-Sn-S angle is 77.8(1)°, but the O-Sn-O angle is opened to 136.7(1)° to accommodate the intruding methyl groups. The carbon-tin-carbon angles predicted from quadrupole splitting (^{119m}Sn Mossbauer) and one-bond $^{119}Sn\ ^{13}C$ coupling constant (solution ^{13}C NMR) data agree closely with the experimental value.

In the idealized case of a six coordinated diorganotin bis-chelate the carbon-tin-carbon angle is 90° for the cis and 180° for the trans isomer. The angle of 138.9(2)° found for the title compound is close to the average of the two extremes.

The geometry of the co-ordination polyhedron around the tin in $Me_2Sn(2\text{-}SPyO)_2$ is best described as a Skew-trapezoidal bipyramid (STB). A schematic representation of this is shown in Fig.



V

The first X-ray crystal structure of a diorganotin dicarboxylate as well as the first X-ray structural study of a 7-coordinate organotin anion, a diorganotin tricarboxylate has also been reported[122].

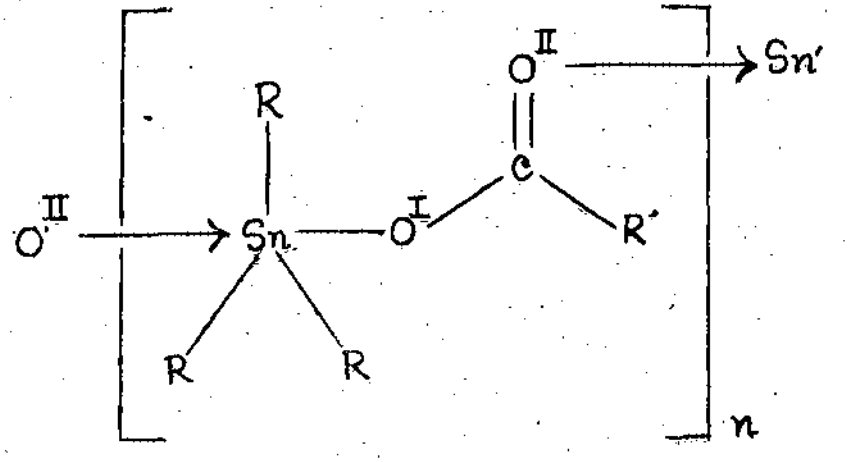
The X-ray crystal and molecular structure of $Me_2Sn(OAc)_2$ has been reported[122] and compared with previous predictions based on other structural methods. The molecule is found to be monomeric and 6 - coordinate at tin in the solid state. The Me-Sn-Me angle of 135.9(2)° is in close agreement with the value predicted from solid-state and solution NMR studies.

The most striking result of this study is the discovery that 6-coordinate $Me_2Sn(OAc)_2$ is capable of adding a third acetate group, giving rise to a diorganotin (IV) anion with a coordination number of 7. Solution and solid-state NMR data for $Me_2Sn(OAc)_3^- NMe_4^+$ provide evidence that the complex is thermodynamically stable in solution relative to dissociation and indicate that, in addition to the well characterized penta substituted di- and triorganotin (IV) halide anions, organotin (IV) compounds bearing other, less strongly electron withdrawing ligands can give rise to stable, isolable anionic complexes.

A clear implication of the results obtained for the reaction of $Me_2Sn(OAc)_2$ with $NMe_4^+OAc^-$ is that nucleophilic substitution reactions of even 5- and 6- coordinate tin compounds can, and may frequently, proceed by associative mechanisms involving anionic tin intermediates of high coordination number. Such mechanisms may in fact be the rule for many industrially important reactions catalyzed by diorganotin dicarxoylates.

It has been reported[123] that an analysis of X-ray data for seventeen polymeric triorganotin (IV) carboxylates gives a repeat distance of 5.19 ± 0.21 Å for the carboxylate-bridged $R_3SnO.C(O)R'$ unit that defines the crystal lattice. The repeat distance is insensitive to the organic substituents on either the tin or carboxylate group. Tricyclohexyltin acetate and tricyclohexyltin trifluoroacetate are reclassified as weakly associated polymers.

In the cyrstal lattice, the $Sn-\overset{I}{O}-C$ angle is generally 120° bu the $C-\overset{II}{O}-Sn'$ angle can open up to accommodate more bulky R' groups[124].



VI

The reaction of dicyclopenta-diethyl tin and bis-(methyl cyclo-pentadienyl) tin with some boron, aluminium trihalides give complexes of the composition[83].

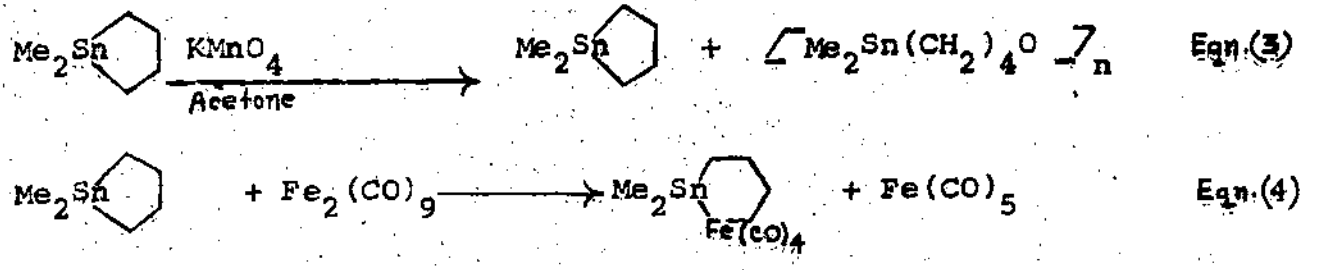
$R_2Sn{:}MX_3$ ($R = C_5H_5$, $MX_3 = BF_3$, BBr_3, $AlCl_3$, $AlBr_3$;

$R = MeC_5H_4$, $MX_3 = AlCl_3$)

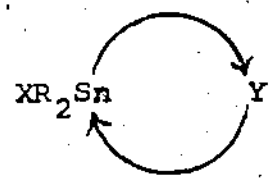
The addition of dicyclopentadienyltin to THF solution of the complexes $M(CO)_5THF$ (M = Cr, Mo, W) produces complexes[84] :

R_2Sn ; $M(CO)_5$ (where $R = C_5H_5$, M = Cr, Mo, W), $R = MeC_5H_4$, M = Cr, W. The evidence for cis-Bis(2,4-pentanedionates) dimethyl tin (IV) has been found in solution[85].

As a result of the enhanced reactivity of the endocyclic tin-carbon bond, 1,1, dimethyl-1-stannacyclopentane (DMSO-5) readily undergoes ring expansion reactions with a variety of substrates to produce new organotin heterocycles. A few examples of ring expansion involving O_2, S, $SO_2Fe_2(CO)_9$[86] are given below.

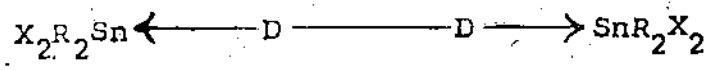


In case of diorganotin derivatives, both penta co-ordinated and hexa-coordinated tin compounds have been reported. Penta co-ordinated tin is observed in dialkyltin dihalide, carboxylates dialkyl tin halide oxinates and dimethyl (1, 3-dimethyl triorgasono) tin halides[87] are of (type-X)



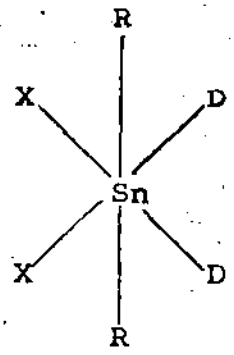
Type-X

The 2:1 addition compound of $(C_6H_5)_2Sn(NCO)_2$ and bipyridine in another type of penta-co-ordinated di-organotin structure of (type-XI).



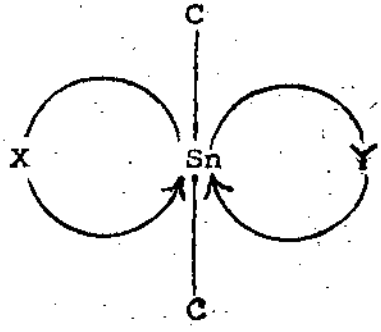
Type-XI

Infrared spectroscopic investigations have shown that the addition compounds of R_2SnX_2 (X = halogen) and monodentate amines in 1:2 mole ratio or bidentate amine in 1:1 mole ratio are of the (type-XII).



Type XII

Many di- organotin bis(chelates) have been isolated[54,59,87,89] and found to contain hexa co-ordinated tin atom. Some representative compounds are acetylacetonates, oxinates and carboxylates. The alkyl group in these compounds exists predominantly in the trans-position (Type-XIII).

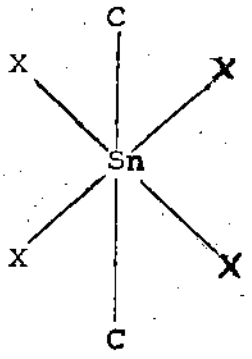


Type XIII

For diorganotin dioxinates, such a conventional octahedral structure is, however, far from correct as X-ray investigation of dimethyl tin dioxinate shows this molecule may be interpreted in terms of distorted tetrahedron formed through 3-centre bonds involving sp^3-

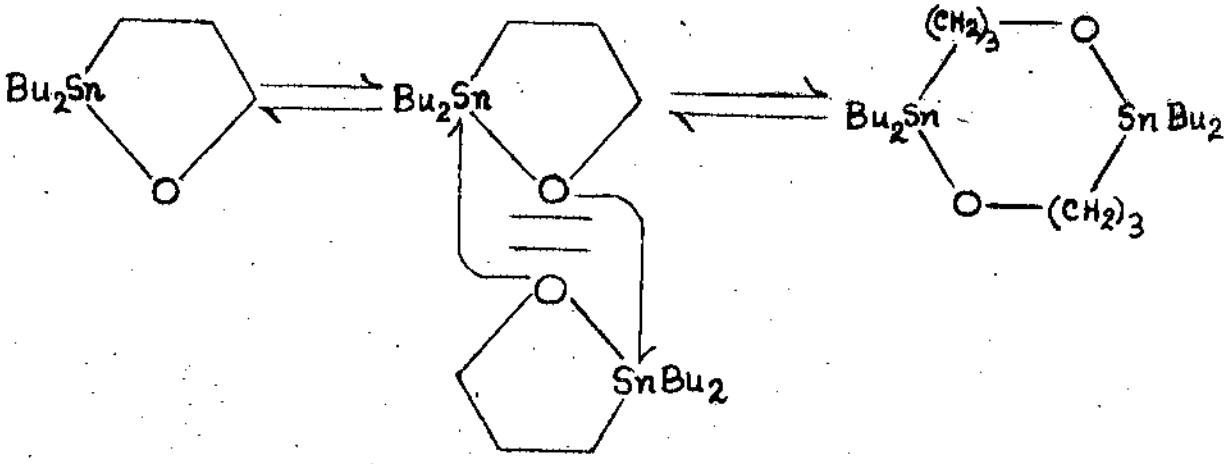
orbital of the tin atom and the valence orbitals of the donor atoms (oxygen and nitrogen) of the oxinate group[90].

The most asymmetric species is the $(CH_3)_2SnX_4^{-2}$ anion (X = F, Cl, NCS) where the structure is represented by typeXIV. Tobias et al have shown that there are analogous species $[(CH_3)_2Sn(OH)_4]^{-2}$ as well as cationic hydrated species in aqueous solution of dimethyl tin compounds[91-93].



TypeXIV

An analysis of IR spectra in the 1200-900 cm^{-1} of the compounds of the type $n\text{-}Bu_2Sn[CH_2CHR'CHR''O]$ (R' = R'' = H or Me) have been used to distinguish between monomers, co-ordination dimers and cyclic polymers[94].



Monomer Co-ordination dimer True dimer

VII

Polymers

Reports on mono organotin compounds indicate that some of these might have hexa-co-ordinated and even hepta co-ordinated tin atoms. However little work has been done on their detailed configurations. Mono-organotin halide bis acetylacetonates[95] and bis-oxinates[96] as well as the addition compounds of formula $RSnX_2 \cdot 2D$[97] are examples of 6-co-ordinated tin compounds.

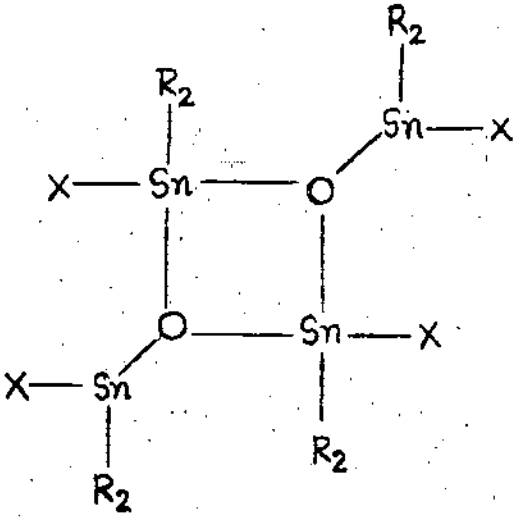
In basic aqueous media the derivatives of ethyl tin (IV) and Palladium (II) ions give two mono organotin complexes[98].

$$\left[C_2H_5SnPd(OH)_p\right]^{(P-5)^-}$$

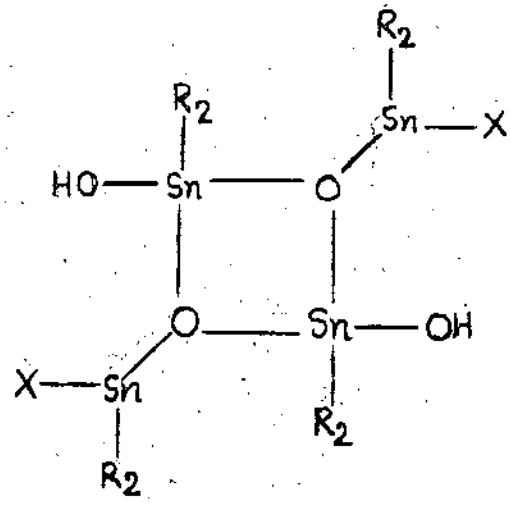
and

$$\left[C_2H_5SnPd_2(OH)_{p''}\right]^{(P''-7)^-}$$

T) dimeric tetraalkyl distannoxanes[53] $(XR_2SnOSnR_2X)_2$ and $(XR_2SnOSnR_2OH)_2$ are unique because they are believed to contain both tetra-co-ordinated and penta-co-ordinated tin atoms (Type-XVandXVI)



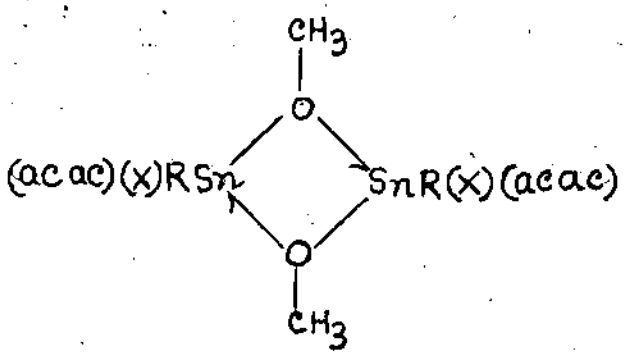
Type-XV



Type-XVI

A hepta-co-ordinated tin is observed in phenyl tin tris (tropolonate) and probably in mono organo tin tris (carboxylates).

The complex compound $[(acac)XRSn(OCH_3)]_2$ obtained by partial alcoholysis from $RXSn(acac)_2$[53] is unique in that it contains two briding methoxy gr ups forming a four membered Sn-O ring as shown in structure(XVII).



Type-XVII

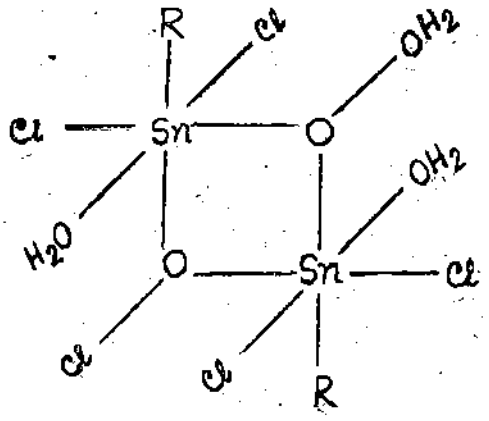
The mono-, di- and tri- organotin compounds generally exhibit a co-ordination number from 4-6. However, not many organotin compound have been found to possess hepta-co-ordinated tin, the geometry of which is expected to be pentagonal bipyramidal one. Phenyl tin tris-tropolonate has been reported[99] to be monomeric in methylene chlorice, suggesting a seven co-ordination around the tin. P.G. Harrison[75] have concluded from UV, NMR and IR data that n-butyl tin tris-oxinate may have 7-co-ordinated tin atom. Ruddick and Sams[101], from Mossbauer spectroscopy, determined the co-ordination number around tin in $BuSn(OX)_3$ which is consistent with seven co-ordination, with three equivalent bidentate oxine groups. A new structural interpretation[102], based on solid-state and solution ^{13}C NMR data for $Me_2Sn(OAc)_2$ was put forth for diorganotin di-carboxylates. The first X-ray structural study of a 7-coordinate organotin anion, a diorganotin tri-carboxylate has been reported[122].

The structure of polymeric mono-organo-stannoic acids and the crystal structures of their carboxylate derivatives has been reported[103,104] where it has been shown that polymeric tin compounds are most likely to show a Mossbauer effect at ambient temperature.

The synthesis and X-ray crystal structure of hexameric phenyltin oxycyclohexanecarboxylate, $[PhSn(O)O_2CC_6H_{11}]_6$ has been reported[105]. The x-ray characterisation shows tin (IV) present in a new structural environment appearing as a drum shaped molecule containing hexa coordinated tin atoms.

The synthesis of hexameric n-butyloxotin benzoate $[n\text{-}BuSn(O)O_2CC_6H_4NO_2\text{-}2]_6 \cdot 3C_6H_6$ and the dimeric methyloxotin cyclohexanoate, $[(MeSn(O)O_2CC_6H_{11})_2MeSn(O_2CC_6H_{11})_3]$ by condensing the stannoic acid with the respective carboxylic acid as well as synthesis of dimeric n-butyloxotin carboxylate, by reacting n-butyltin trichloride with the silver salt of the respective carboxylic acid have been reported[106]. These substances, as found by X-ray analysis, form a new structural class of organotin compounds having "unfolded drum" or "ladder" structures.

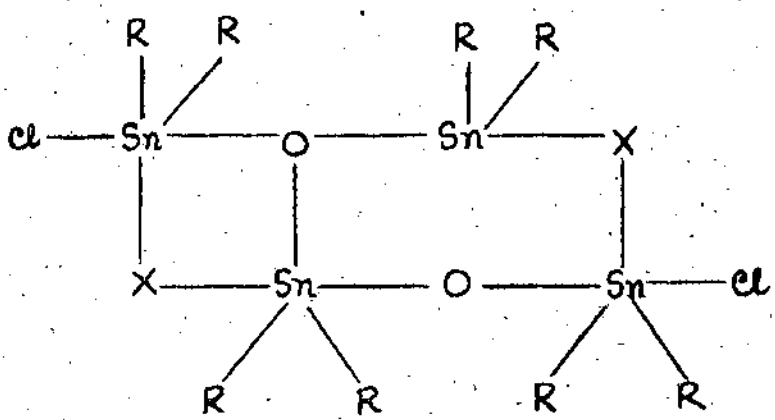
Formation of distannoxane rings seems to be an integral component of hydrolysis products of many organotin compound[107]. For example, monoalkyltin halides hydrolyze to give distannoxanes- of the type



R = n-Bu, Et

VIII

whereas diorganotin halides give dimeric distannoxanes as end products. These possess "ladder"[107-109] or "stair case"[110,111] structures. Here the tin atoms are penta-coordinated.



IX

where X = Cl, OH

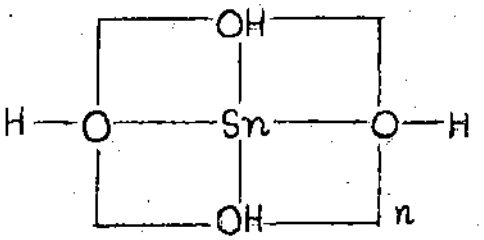
R = Ph, alkyl

The synthesis of a soluble drum compound, containing cyclopentane units, $[n\text{-}BuSn(O)O_2CC_5H_9]_6 \cdot C_6H_6$ and the formation of a novel chloro derivative $[(n\text{-}BuSn(O)O_2CPh)_2(n\text{-}BuSn(Cl)(O_2CPh)_2]_2$ having "ladder" or "open drum" structures has been reported[112]. Interconversion of the drum and ladder structures has been established

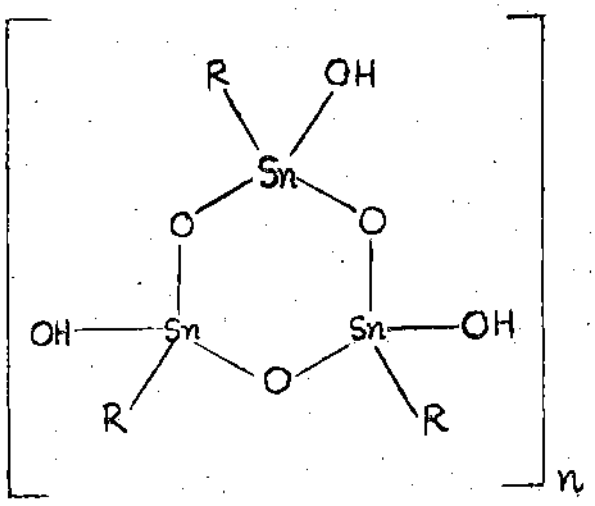
in solution by ^{119}Sn NMR along with a possible mechanism of hydrolysis of a ladder to a drum formulation has been reported[112].

Chandrasekhar et al[112] employed a variation of the original reaction by Lambourne[113] in exploring condensation products leading to the drum composition as well as to a mixed oxocarboxylate-tricarboxylate formulation, $[(R'Sn)(O)O_2CR)_2R'Sn(O_2CR)_3]_2$. The latter was identified as having an unfolded drum or ladder structure[106]. The reaction consists of a condensation of an organostannanoic acid with a carboxylic acid.

The stannoic acids are infusible powders for which a polymeric structure (X) have been proposed[114,115]. For the partially dehydrated material structure (XI) has been proposed by Platt et al[116].



X



XI

In both (X) and (XI), tin atom is 4-co-ordinated and is enclosed within the tetrahedra formed by the three oxygen atoms and the organic group R.

From the values of quadrupole splitting (EQ = 1.29-1.83 mm/sec) in organo stannoic acids Davies et al[117] have suggested a tetrahedral geometry at tin, though the possibility of association has not been completely excluded. The isomer shift value (δ = 0.40-0.78 mm/sec) are very small because of the very low 'S' electron density at the tin atom resulting from electron attraction by the surrounding oxygens.

R E F E R E N C E S

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