CHAPTER I

A Short Review of Organotin Chemistry

IA Introduction

Organotin Compounds are substances containing 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 have remained unknown to most of his contemporaries as well as to later authors. The work of C.Lowig (3) in 1852 has usually 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:

$$R_4Sn, \quad R_3SnX, \quad R_2SnX_2, \quad RSnX_3$$

R can be identical or different, substituted or unsubstituted, aliphatic, or aromatic groups. X can be negative groups such as $-OR$, $-SR$, $-OOCR$, $-OSnR_3$, $-NR_2$, or halogen or some other acid radicals or neutral ligands such as $-H$, or electropositive ones such as Li or Na. The three series of organotin hydrides R_3SnH, R_2SnH_2 and $RSnH_3$ (4,5,6,7) have recently assumed considerable importance.

Stannyl metal compounds of the type R_3SnM and R_2SnMg (8-9), $Ph_3SnSiPh_3$, $Ph_3SnSi(GePh_3)_3$, $R_3Sn-Sn-R_3$ (9) Ph_3Sn Zn Sn Ph_3 and $Ph_3SnCdSnPh_3$ 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 stabilisers of polyvinyl chloride plastics, rubber antioxidants, Ziegler type catalysts in the polymerisation of olefins, agricultural fungicides and as active ingredients in certain veterinary medicine (10) and also an increased general scientific interest produced a striking renaissance of organotin chemistry starting about 1949 and continuing to the present day.

II Bonding in organotin compounds

The electronic configuration of tin 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 (11). The common tetra covalent state is derived from the sp^3 hybridisation by promoting one of the paired s electrons to the next higher p level. The tetra covalent state occurs much more frequently than divalent state and a great number of organotin compounds contain tetravalent tin atom. Organo derivatives of group IV A metals are generally more stable and less reactive than the corresponding compounds of Gr III or IV metals. The increased stability may be attributed to the 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 marked increase in stabilities of R_4Sn compounds over R_2Sn types also demonstrate the effect of increased hybridisation on the stability.

Carbon bond strengths have been reviewed by Skinner (12) who noted that mean bond dissociation energies ($\bar{\bar{D}}$) fall as the sub group is descended so that $\bar{\bar{D}}$ (C-R) $>$ $\bar{\bar{D}}$ (Si-R) $>$ $\bar{\bar{D}}$ (Ge-R) $>$ $\bar{D}$ (Sn-R) $>$ 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 Kcal/mole. These values are of course further dependent on the nature of the alkyl group i.e. on the stabilisation of the corresponding alkyl radical by hyperconjugation.

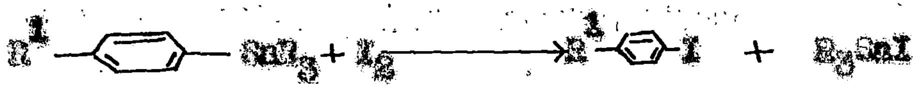
The covalent radius of the tin atom is 1.40A^{0} and is surprisingly independent of the nature of the ligands. Only when there is an accumulation of strongly negative ligands round the tin is there some decrease in bond lengths. The bonding of the tin would thus appear to be almost entirely covalent at least in crystalline solids, in non polar media and in the vapour. 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 Sn -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 (13-15) depends both in magnitude and direction on the nature of the alkyl group (16-17).

The electronegativities of the elements of group IV have been investigated extensively by different workers (20a-d). The results, a selection of which is given in Table 1, always differ according to the method of measurement and the compounds selected. This is not surprising since the electronegativity, not being a uniquely defined parameter, depends on the method of measurement and the surrounding of the atom in question. In practice, therefore, one generally works not with an 'electronegativity of tin' but with a value for tin in a particular combination i.e. allowance will have to made for the influence of all ligands.

Table 1

	Pauling	Sanderson	Fineman Daigneult	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 connected with this is the inductive effect which tin atoms or Stannyl groups exert on their surroundings. The bond polarization $C^{\delta-} - Sn^{\delta+}$, which is there in principle, may be changed by substitution at C as well as at Sn. NMR data on organotin compounds (10-19) and semiempirical calculations of Majee and Gupta (63) emphasises this. According to Eaborn et al (21) polarisation is increased by electron donor substituents R' in the p-position in a phenyl group, as shown by the increase in the rate of scission of the C-Sn bond by iodine according to reaction (I). The reaction thus belongs to the class of electrophilic aromatic substitutions (21-23).


(I)

As expected, electron attracting groups R^1 decrease the rate by lowering the nucleophilicity of the ring carbon attached to tin. The sequence of relative reaction rates is for R^1 = 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-$R_3MCH_2CH_4$-SnR_3. These are for M = Si 1.00, Ge 1.36 Sn 3.21 (23). A similar sequence emerges from IR and NMR measurements (24) and also from IR studies on esters of the type $MeCOOMMe_3$ which give M = C < Si < Ge (25).

One difficulty which often arises in experiments designed to measure relative inductive effects is that there may be some π-character in a bond between tin and an element possessing p electrons (26-27). 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 → X, there may be some overlap between a filled p-orbital on X and an empty 5d orbitals on Sn causing a transfer of electron density in the opposite direction. Despite many controversies (28-31), it is widely accepted that there are significant ($p_\pi \rightarrow d_\pi$) contributions to the Sn-N bonds in compounds such as the planar trisilyl amine (32). There is some evidence that in phenyl tin compounds, interaction occurs between the electrons of the phenyl groups and the 5d orbitals of tin. This conclusion is based on the interpretation of NMR (33-34), infrared (35), ultraviolet (35) and dipole moments (36) of phenyltin 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 pK_a values for a series of pyridine having Me_3M (M = C, Si, Ge, Sn). Substituents in the 3-position indicated the absence of p_π-d_π bonding in the tin-pyridine link (37). 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 (38). There is evidence for d_π-d_π interaction in the bonds formed between tin and certain transition metals (38-39). On the other hand Gupta & Majee has shown in a series of papers (63) that most of the properties of organotin compounds may be interpreted without assuming any $d_\pi - p_\pi$ interaction. However, in a very recent article (64) Hajee has demonstrated that the success of earlier Del Re calculations does not necessarily rule out such interactions.

1C Organotin complexes

Organotin compounds can form various types of complexes with ligands. The structural aspect of those compounds has been exhaustively reviewed by Ingham et al (8), Poller (40), Gielen and Sprecher (60) and more recently by Ho and Zukermann (67).

The most interesting example is afforded by R_3SnX type compounds which forms various types of adducts with Lewis bases (8). These compounds are generally penta co-ordinated (41-42). For X = Cl, B, or I, Me_3SnX type compounds 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 types (43-44). The aquo ion $Me_2Sn(H_2O)_4^{+2}$ has a linear C-Sn-C group, there are presumably four water molecules weakly co-ordinated in the equitorial plane (45). Similarly R_3SnX and R_2SnX_2 compounds can form organotin chelates with chelating agents such as 8-hydroxy quinoline (46-48), acetyl acetone (49-50), 1,10 phenanthroline (47,50) etc. which may be five, six or some times even eight co-ordinated compounds.

The most general feature of the penta co-ordinated tin is a polymeric structure formed by the bridging of an anionic group to the tin atom from either side of the plane of the tri-alkyl tin group. This kind of structure is designated as Type I. Type I compounds can be divided into three sub groups as shown in Table 2

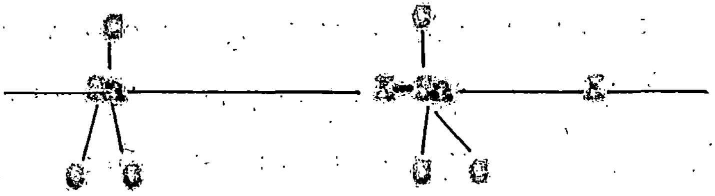
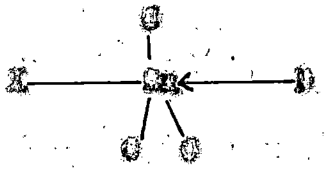


Table 2

Sub group	Compound
(a)	$(CH_3)_3SnF$, $(CH_3)_3SnOH$
(b)	$R_3SnOOCR'$, $(C_4H_9)_3Sn$(imidazole), $(CH_3)_3SnNO_3$ $(CH_3)_3SnClO_4$, $(CH_3)_3SnSbF_6$, $R_3SnAlCl_4$
(c)	$(CH_3)_3SnCl$, $(CH_3)_3SnBr$, $(CH_3)_3SnCN$ R_3SnN_3, $(CH_3)_3SnNCS$, $(CH_3)_3SnNCO$

The compounds in the (c) sub group of this classification contain tin atoms bridged by the anionic groups in the manner, -Sn-X-Z-X-, where X represents a halogen, an oxygen, or a nitrogen atom and Z represents the remainder of the resulting group. The compounds in both (a) and (b) sub group compounds are assumed to contain planar SnC_3 moieties, but in so far as they have been studied, those in the (c) sub group have no such planar arrangement.

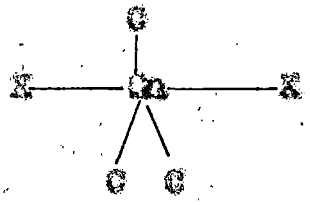
In compounds of structure type II, a donor molecule is co-ordinated to a triorganotin halide to give a trigonal bipyramidal arrangement. The best studied example is the 1:1 addition compounds of $(CH_3)_3SnCl$ and pyridine.



(D = donor molecule)

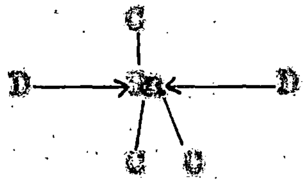
Type II

A halide ion can also act as a Lewis base to trimethyl tin halide, giving a symmetrical bipyramidal configuration of type III



Type III

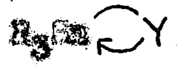
In cases where the anionic groups have no co-ordinating sities, for example, $B(C_6H_5)_4^-$, two molecules of a mono-anionic Lewis base such as water can occupy the co-ordination sphere, giving a planar SnC_3 arrangement with a penta co-ordinated tin atom (type IV)



Type IV

This finding may well be applied to interpret the structure of 1:2 addition compounds of formula $R_3SnX.2D$ (8) as that containing a bipyramidal $R_3SnD_2^+$ and X^- anion, and may preclude the existence of hexa-co-ordinated tin atoms in such triorganotin complexes.

If the X group in R_3SnX belongs to a chelating ligand, intramolecular co-ordination can occur as shown in structure (V).



Type V

In the case of di-organotin derivatives, both penta co-ordinated and hexa co-ordinated tin compounds have been reported. Penta-co-ordinated tin is observed in dialkyl tin halide, carboxylates, dialkyl tin halide oxinates and dimethyl (1,3-dimethyl triazene) tin halides (61) (Type VI).

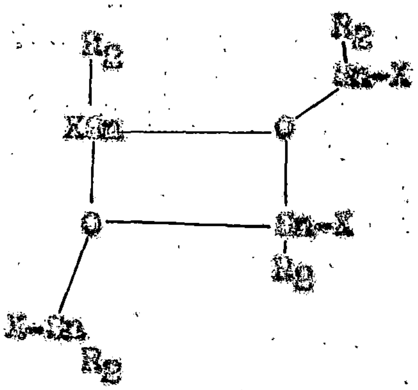
Type VI

The 2:1 addition compound of $(C_6H_5)_2Sn(NCS)_2$ and bipyridine is another type of penta co-ordinated di-organotin structure (VII)

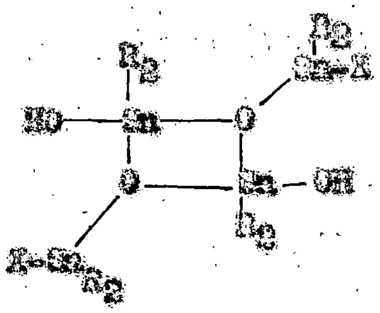
$$X_2R_2Sn \longleftarrow D \text{———} D \longrightarrow SnR_2X_2$$

Type VII

The dimeric tetraalkyl distannoxanes, $(XR_2SnOSnR_2X_2)$, $(XR_2SnOSnR_2X_2)_2$ and $(XR_2SnOSnR_2OH)_2$, are unique because they are believed to contain both tetra-co-ordinated and penta co-ordinated tin atoms (Type VIII and VIII')

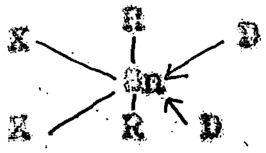


Type VIII



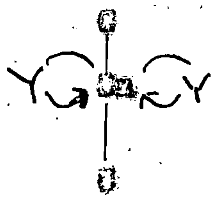
Type VIII'

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 amines in 1:1 mole ratio, are of the type IX



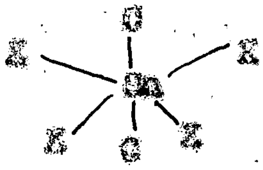
Type IX

Many di-organotin bis (chelates) have been isolated (46,47,51-57) and found to contain hexa co-ordinated tin atom. Some representative compounds are acetyl acetonates, oxinates, and carboxylates. The alkyl group in these compounds exists predominantly in the trans position (type X), though X-ray crystallography on dimethyl tin dioxinate shows this to have a very much distorted structure (63).



Type X

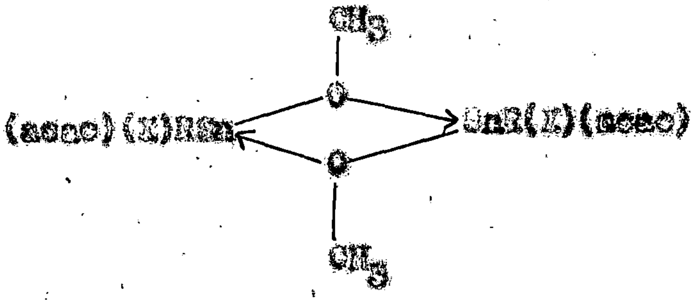
The most symmetric specie is the $(CH_3)_2SnX_4^{-2}$ anion (X = F, Cl, NCS) where structure is represented by (XI). Tobias et al have shown that there are analogous specie, $[(CH_3)_2Sn(OH)_4]^{2-}$ as well as cationic hydrated specie in aqueous solution of dimethyl tin compounds (57,58,59)



Type XI

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 acetyl acetonates (60) and bis oxinates (61) as well as the addition compounds of formula $RSnX_3 \cdot 2D$ (62) are examples of hexa co-ordinated tin compounds.

The complex compound $[(acac)XRSn(OCH_3)]_2$, obtained by the partial alcoholysis from $RXSn(acac)_2$ is unique in that it contains two bridging methoxy groups forming a four membered Sn-O ring as shown in structure XII



Type XII

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

Several organotin (IV) complexes with quadri and tetradentate anionic schiff base ligands have been prepared and investigated in the solid state (60-70). 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(N-saldap-2-O) the ligand appears to be only terdentate leading to a penta-co-ordinate structure similar to those of the R_2Sn (Sal-N-2-OC_6H_4) derivatives (R = Ph, Me).

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* H_2Salen = N,N' ethylenebis (salicylaldimine)

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

Recently organotin complexes of strong -acids of the type $Me_3Sn.TCNQ$, $MeCl_2Sn.TCNQ$, $Me\ Cl_2Sn.nTCNE$ ($n = 1,2$) and $SnX_4.TCNE.THF$ ($X = Cl, Br$) (71) 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 streching region which is assigned to the antisymmetric mode of a planar Me_3Sn moiety, with bridging TCNQ residues resulting in a trigonal bypyramidal configuration at the tin. The intese 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.

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