CHAPTER - I

A SHORT REVIEW OF ORGANOTIN CHEMISTRY

Ia. Introduction

Organotin compounds are those which contain at least one tin-carbon bond. The first chemist to report an organotin compounds 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 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, 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 halogen 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 recently 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 (6-8), $Ph_3Sn\ Si\ Ph_3$, $Ph_3Sn\ Si(Ge\ Ph_3)$, $R_3Sn-SnR_3$ (8), $Me_3\ Si-Hg-SnR_3$, $R_3Sn-Hg-SnR_3$, (~~4~~ 9,7) $Ph_3Sn\ Zn\ Sn\ Ph_3$, $Ph_3Sn\ Cd\ Sn\ Ph_3$, 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 stabilizers of polyvinyl chloride plastics, rubber antioxidants, Ziegler type catalysts in the polymerization of olefins, food preservatives, agricultural fungicides and as active ingredients in certain veterinary medicine (10) and also an increased general scientific interest produced or striking renaissance of organotin chemistry starting about 1949 and continuing to the present day.

1B. 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 $5s^2p^2$ configuration (11). The tetra covalent 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 group IV A form organometallic compounds which are more stable and less reactive than those of Gr. III or IV B metals. The increased stability may be partly due to sp^3 hybridisation. Thus, tetravalent tin is unreactive towards air and water but Me_3In and Me_3Sb 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 (12) who observed that mean bond dissociation energies ($\bar{D}$) fall as the sub group is descended so that $\bar{D}$ (C-R) $\rangle$ $\bar{D}$ (Si-R) $\rangle$ $\bar{D}$ $\rangle$ (Ge-R) $\rangle$ $\bar{D}$(Sn-R) $\rangle$ $\bar{D}$(Pb-R). The mean values of the bond dissociation energies are C-C: 83, 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 $1.4A^0$ 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 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 (13-15) depends both in direction and magnitude on the nature of the alkyl group (16-17).

The electronegativities of Gr. IV elements have been investigated by several workers (20a-d). The results always vary in accordance 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 allowances will have to be made for the influence of all ligands.

Table - 1

Electronegativities of Gr IVB elements

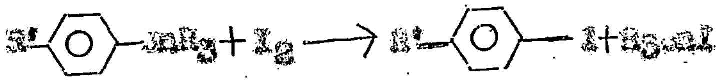
	Pauling	Sanderson	Fineman Daignault	Allred-Rochow
C	2.5	2.47	2.57	2.60
Si	1.8	1.74	1.90	1.90
Ge	1.8	2.31	2.02	2.00

Contd..

Table - 1 (Contd..)

	Pauling	Sanderson	Pineman [illegible]	Allred-Rochow
Sn	1.8	2.02	2.47	1.93
Pb	1.9	--	--	2.45

Closely related with this is the inductive effect which the tin atoms or stannyl groups exert on their surroundings. The bond polarisation $\overset{-\delta}{C}$——$\overset{+\delta}{Sn}$, which is there in principle, may be changed by substitution at C as well as at Sn. NMR data on organotin compounds (18-19) and semiempirical calculations of Majee and Gupta (20) emphasise this. According to Eaborn et al (21), 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 (A). Thus, this reaction may be marked as electrophilic aromatic substitution.



(A)

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 $>$ -Bu $>$ i-pr $>$ Et $>$ Me $>$ H $>$ Br $>$ F $>$ Cl $>$ COOH.

Electron donor porperties 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_3M CH_2 C_6H_4—SnR_3. These are : M = Si 1.00, Ge 1.36, Sn 3.21 (22). A similar sequence emerges from IR and NMR measurements (23) and also from IR studies on esters of the type $MeCOOMMe_3$ (M = C, Si, Ge) (24).

A problem which often arises in the investigations to measure relatived inductive effects is that there may be some π - character in a bond between tin and an element possessing p-electrons (25-27). 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 $\overset{+\delta}{Sn} \rightarrow \overset{-\delta}{X}$, 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 (27-30) 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 (31) 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 (32-33), IR (34), UV (34) and dipole moments (30) of Ph_3Sn compounds and the acid strengths of the substituted benzoic acids p-$Me_3MC_6H_4COOH$ (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-position indicated the absence of pπ - dπ bonding in the tin-pyridine link (36). 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 (35). There is evidence for dπ - dπ interaction in the bonds formed between tin and certain transition metals (37, 92). On the other hand Majee and Gupta has shown in a series of papers (50) that most of the properties of organotin compounds may be interpreted without assuming any dπ - pπ interaction. However, in a more recent article Majee demonstrated that the success of earlier Del Re calculations does not necessarily rule out such interactions (90).

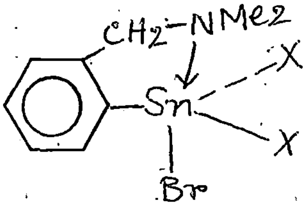
10. Organotin Complexes

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 (39), Gielen and Sprecher (51) and more recently by Ho, Zuckerman (45), P.G.Harrison (28), Bulton (33), Zoton (61), Poltsal (86).

The most interesting example is afforded by R_3SnX type compounds which form various type of adducts with Lewis bases (4). These compounds are generally penta co-ordinated (40-41). 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 (43, 93). R_3SnX and R_2SnX_2 compounds can form organotin chelates with chelating agents, viz, 8-hydroxy quinoline (45,46,94), acetyl acetone (47,48), 1,10 phenanthroline (45,49) etc, which may be five, six or sometimes even eight co-ordinated compounds.

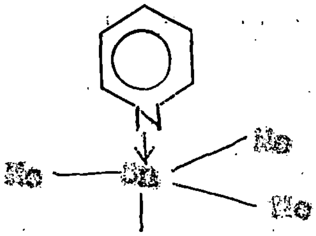
N-substituted salicylidineiminato trialkyltin derivatives have been prepared by the reaction of the trialkyltin chloride or alkoxides with the corresponding Schiff (52) bases and 5 co-ordination is proposed for Sn in these complexes. Trimethyl tin derivative of sulphur containing Schiff bases are known (53). Several triorganotin dithiocarbamates of the formula R_3SnDtc (R = Ph, n-Bu, Bz, Dtc = n-Pr, n-Bu, N-phenyl, dibenzyl etc. - dithiocarbamates) have been reported by Srivastava (64). The quarternary phosphonium cations $[\geqslant PCH_2\,Sn\,Me_3]^+$ is also known (65).

Recently a nitrate complex of organotin (IV) containing triphenyl phosphine oxide has been reported (50). The triorganotin halides which contain potentially bidentate ligand the Me_2 NCH_2 C_6H_4 group is reported. In view of the known tendency of triorganotin halides to form 1:1 complexes with Lewis bases, for novel triorganotin compounds, the trigonal bipyramidal structure I in which the tin atom is penta co-ordinate as a result of intramolecular Sn-N bond formation.

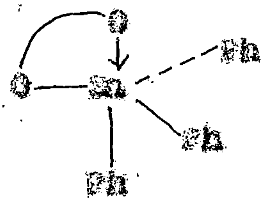


I

A well known example is the penta co-ordinated str. of 1:1 complex of trimethyl tin chloride with pyridine.

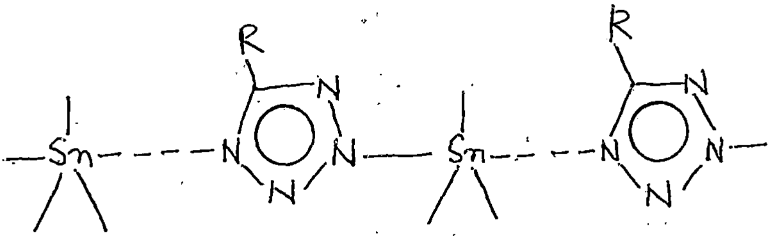


An X-ray study was reported for (1,3-diphenyl propane-1,3-dionato) triphenyl tin which established the occurrence of penta co-ordination as a result of intramolecular co-ordination with the ligand spanning axial-equatorial sets (57).



O-O = 1,3-diphenylpropane -1,3-dionato

The intermolecular associated form of 2-(tri-n-butyl stannyl) tetrazoles in benzene and chloroform is confirmed as a 1,3 structure (58).

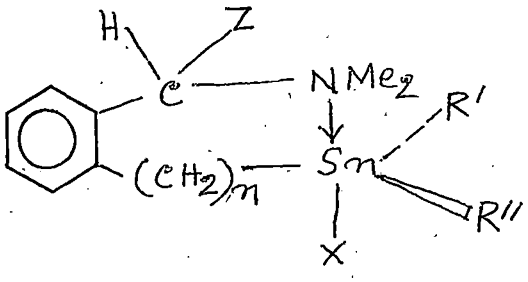


Also N-substituted N-(triphenyl stannyl)cyanamides have been reported and the tin in these complexes is shown to have a co-ordination no.> 4 by means of IR and Mossbauer spectroscopy (59). The Mossbauer parameters of N-substituted N-(triphenyl stannyl) cyanamides are given in Table 2.

Table - 2

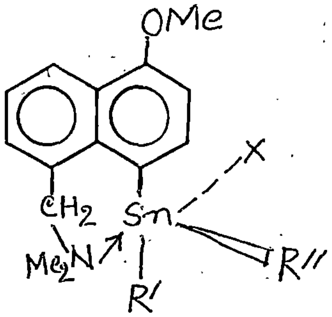
Compound	δ	ΔE	ΔE/δ
$CH_3C(OO)(CN)SSnPh_3$	1.07	4.54	4.24
$CH_3OC(O)(CN)SSnPh_3$	1.55	4.23	2.73
$PhSO_2(CN)SSnPh_3$	1.07	4.54	4.24
$MeC(O)(CN)SSnPh_3$	1.55	4.23	2.73

A compound of the formula $\left[Sn^{II}(NO_3)[(C_6H_5)_3Sn^{IV}]\right]$ containing a Sn^{IV} - Sn^{II} bond, has been reported. The environment of Sn(IV) is tetrahedral. The tin(II) atom is five coordinate by the Ph_3Sn moiety via tin and by four oxygen atoms from two adjacent nitro groups (60). The synthesis and characterization of triorganotin compounds RR'R'' SnX in which one of the organo group (R) is a potentially bidentate ligand, has been reported.

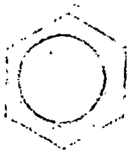


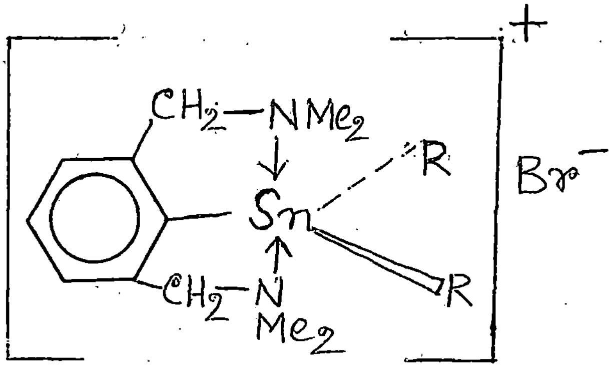
Z = H or Me ; n = 0 or 1.

R' and R'' = Me and Ph.

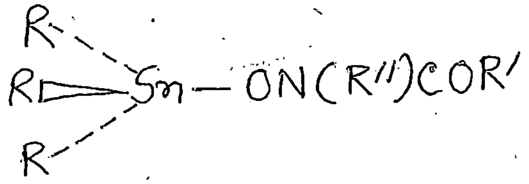


Preferential intramolecular co-ordination of the built-in ligand, C(Z) H NMe$_2$ with the tin atom which renders the Sn atom 5 co-ordinate, appears to be a common structural feature of these compounds. 2,6-bis [(dimethyl amino)methyl] phenyl group could act as a tetradentate ligand in triorganotin halides. The existence of penta co-ordinated cationic species has also been investigated (61).

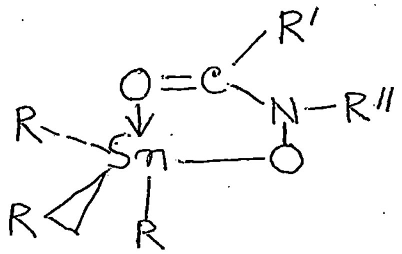




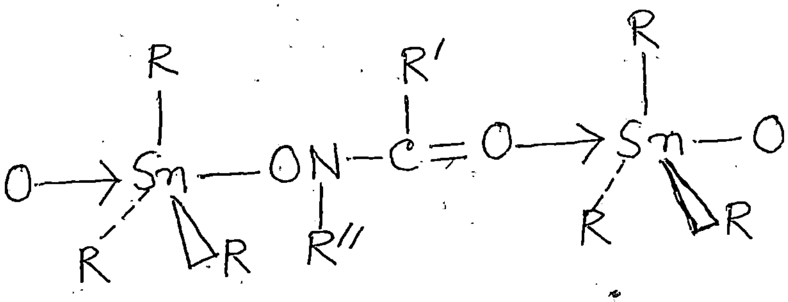
The first example of a compound containing organotin (II) and organotin (IV) in one molecule, $(Me_3Sn^{IV}\ C_5H_5)_2Sn^{II}$ has been reported recently (62). The triorganotin derivatives of N-acylhydroxyl amine, e.g. $Me_3Sn\,[ON(Ph)SO_2C_6H_4CH_3]$, $(CH_3)_3Sn\,[ON(Ph)COPh]$, $Me_3Sn\,[ON(Me)COMe]$ have been prepared. The presence of a second donor site in the N-acylhydroxyl amine ligand permits its potential function as a unidentate or a chelating a bidentate ligand; thus giving rise to the possible four co-ordinated structure (II) or the two 5-co-ordinated structures III and IV (63)



II

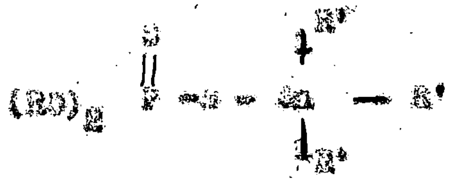


III



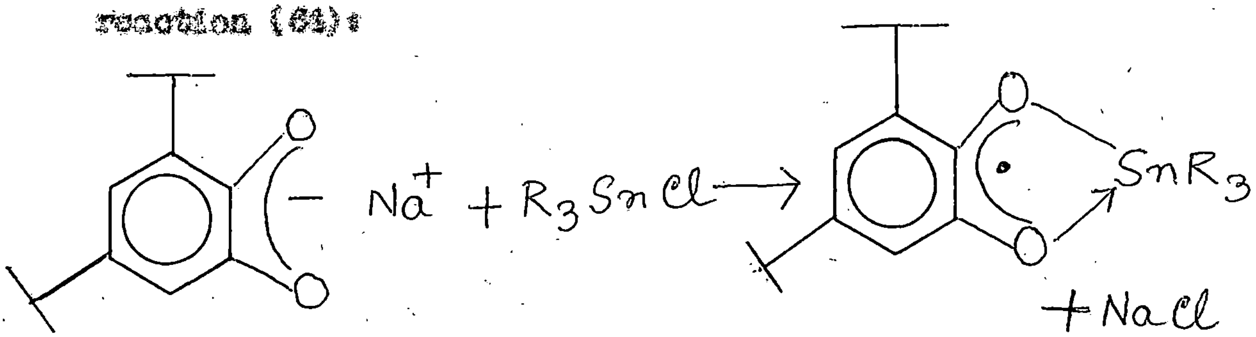
IV

Triorganotin dialkyl thiophosphates, $(RO)_2P(=S)SnR'_3$ (R = Et, i-Pr, n-Pr or Ph and R' = Me, Et, Bu or Ph) have been prepared (63). An ester type structure has been proposed for these compounds.



$$(RO)_2\overset{\overset{S}{\|}}{P}-S-\overset{\overset{R'}{|}}{\underset{\underset{R'}{|}}{Sn}}-R'$$

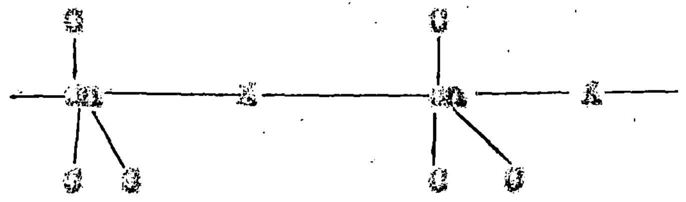
The initial E.S.R spectra observe for the reactions of O-quinones with $R_3Sn.SnR_3$ are analogous to the signals of tin containing semiquinones formed according to the reaction (64):



R_3SnCl forms 1/1, 5-co-ordinate adducts with pyridine or 4-methyl pyridine and R_3SnNCS forms adduct with 1,10-phenanthroline (co-ordination no. of tin > 5). α,α,α',α'-

tetramethyl 1,2-diamino-ethane gave either 1/1 adducts or 5-co-ordinate 1/2 adducts depending upon the group R and concentration of R_3SnNO_3 (65). A molecular adduct of nitratophenyl tin with pyridine N-oxide, [$Sn(C_6H_5)_3(NO_3)(C_5H_5NO)$] has been synthesised and characterised by IR and X-ray analysis (66). Moreover, a molecular adduct of nitratophenyl tin with triphenyl arsenic oxide [$Sn(C_6H_5)_3(NO_3)\ (C_6H_5)_3AsO$] has been synthesised. The co-ordination about tin is bipyramidal with phenyl ring in the equatorial and oxygenated ligands in the axial positions (67).

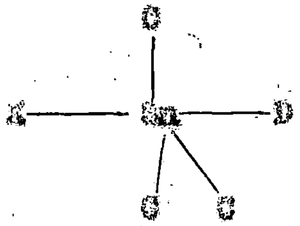
The most general feature of the penta co-ordinated tin is a polymeric str. formed by the bridging of an anionic group to the tin atom from either side of the plane of the trialkyl tin group. This kind of structure is designated as type V.



Type V

In compounds of str. type VI a donor molecule is co-ordinated to a triorganotin halide to give a trigonal bipyramidal arrangement. The best studied example is the

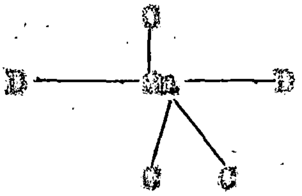
1:1 addition compounds $(CH_3)_3SnCl$ and pyridine.



(D = donor molecule)

Type VI

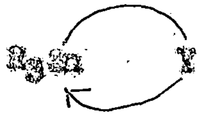
In cases where the anionic groups have no co-ordinating sites e.g., $B(C_6H_5)_4^-$, two molecules of a mono-anionic Lewis base viz, water can occupy the co-ordination sphere, giving a planar SnC_3 arrangement with a penta co-ordinated tin atom (Type VII)



Type VII

This finding may well be applied to interpret the str. of 1:2 addition compounds of formula $R_3SnX.2D$ (5) so that containing a bipyramidal [R_3SnD_2] and X^- anion, and may preclude the existence of 6-co-ordinated tin atoms in such triorganotin complexes (6).

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



Type VIII

In contrast to penta co-ordinate triorganotin compounds, examples of 6-coordinate triorganotin compounds are very few. Recently a number of 0-(5'-substituted aryl azo) benzoates of triorganotin compounds have been synthesised(96). Spectral and other studies indicate these to 6-coordinated triorganotin group.

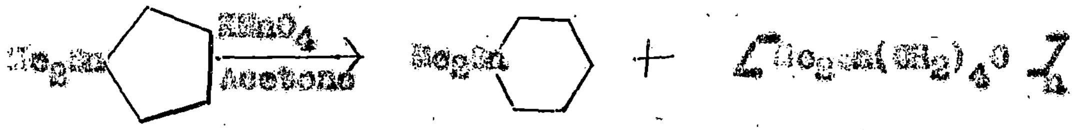
The reaction of dicyclopenta-dienyl tin and bis (methyl cyclo-pentadienyl) tin with some boron, aluminium trihalides give complexes of the composition (68 ~~[illegible]~~):

$R_2Sn:MX_3$ (R = C_5H_5, MX_3 = BF_3, BBr_3, $AlCl_3$, $AlBr_3$;
R = MeC_5H_4, MX_3 = $AlCl_3$)

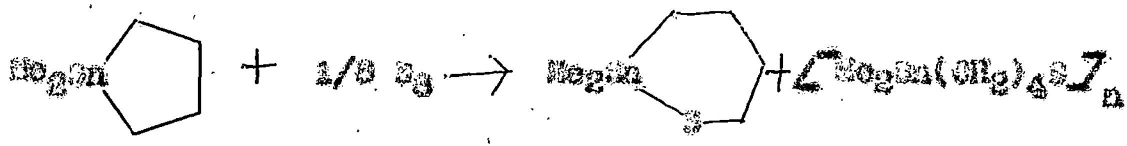
The addition of dicyclopentadienyl tin to THF solutions of the complexes $M(CO)_5$ THF (M = Cr, Mo, W) produces complexes (69 ~~[illegible]~~): $R_2Sn : M(CO)_5$, where R = C_5H_5 M = Cr; Mo, W); R = MeC_5H_4, M = Cr, W. The evidence for Cis-Bis (2,4-

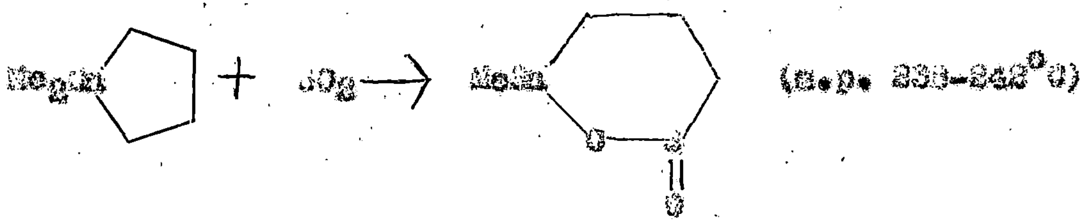
pentanedionate) dimethyl tin (IV) has been found in solution (70).

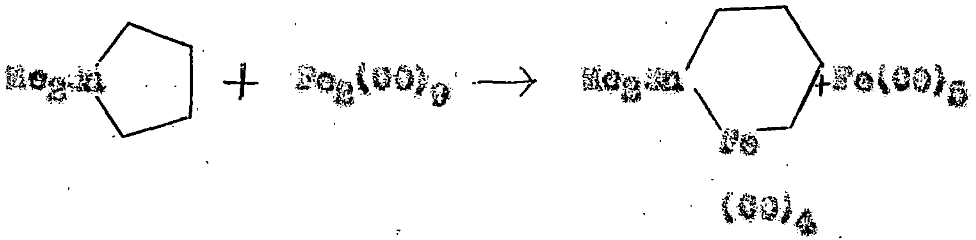
As a result of the enhanced reactivity of the endocyclic tin-carbon bond, 1,1, dimethyl-1-stannacyclopentane (DMSC-5) readily undergoes ring expansion reactions with a variety of substrates to produce new organotin heterocycles. A few examples given include ring expansion reactions with O_2, S, $SO_2Fe_2(CO)_9$ (71).



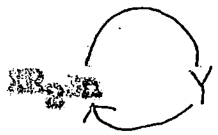
Reaction of DMSC-5 with sulphur at 200°C proceeds to give the monomeric ring expansion product.







In case of diorganotin derivatives, both penta co-ordinated and hexa co-ordinated tin compounds have been reported. Penta co-ordinated tin is observed in dialkyl tin dihalide, carboxylates, dialkyl tin halide oxinates and dimethyl (1,3- dimethyl triazeno) tin halides (72) Type (IX)



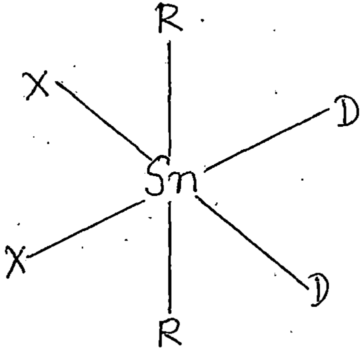
Type IX

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

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

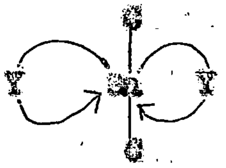
Type X

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 XI.



Type XI

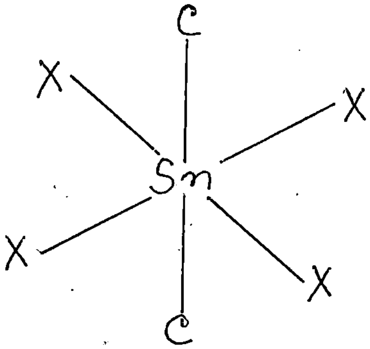
Many di-organotin bis(chelates) have been isolated (49,72,73,94) and found to contain hexa co-ordinated tin atom. Some representative compounds are acetyl acetonates, oxinates and carboxylates. The alkyl group in these compounds exists predominantly in the trans position (Type XII).



Type XII

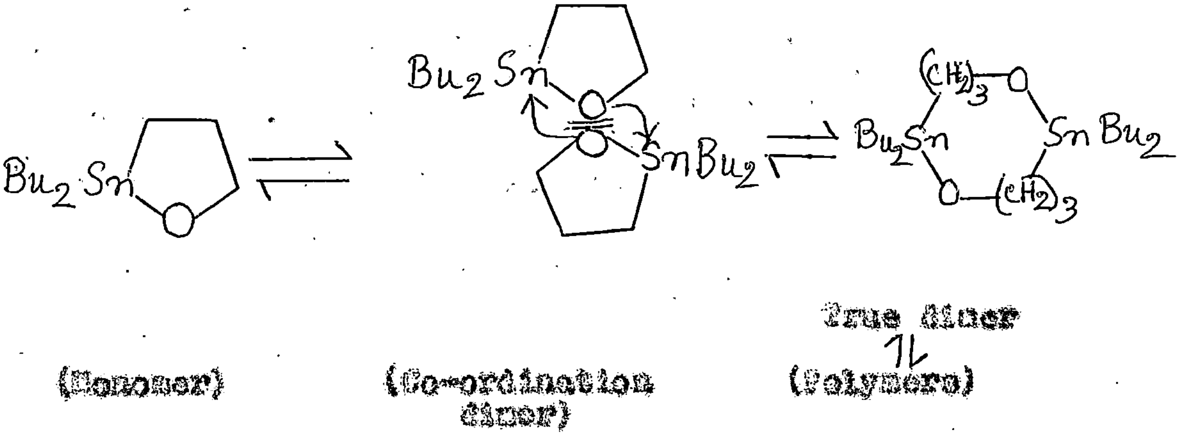
For diorganotin dioxinates such a conventional octahedral structure is however, far from correct as X-ray investigation of dimethyl tin dioxinate shows this molecule to be some what like a highly disturbed tetrahedron (91).

The most symmetric species is the $(CH_3)_2SnX_4^{-2}$ anion (X = F, Cl, NCS≡) where the structure is represented by XXII. 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 (74, 75,79).



Type XXII

An analysis of IR spectra in the 1100-900 cm^{-1} of the compounds of the type $n\text{-}Bu_2\,\overline{Sn\ CH_2\ CH\ R'CHR''\ O}$ ($R' = R'' = H$ or Me) allow us to distinguish between monomers, co-ordination dimers with large cycles or polymers (79).



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 (77) and bis oximates (78) as well as the addition compounds of formula $RSnX_2.2D$ (95) 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 (81).

$$[C_2H_5SnPd(OH)_p]^{(p-5)-} \quad \text{and}$$
$$[C_2H_5SnPd_2(OH)_{p'}]^{(p'-7)-}$$

Recently organotin complexes of strong π-acids of the type

$Me_3Sn.TCNQ$, $MePh_2Sn.TCNQ$, $MePh_2Sn.nTCNE$ (n = 1,2)
and
$SnX_4.TCNE.THF$ (X = Cl, Br) (80)

have been prepared (TCNQ = Tetracyano p-quinodimethane TCNE = tetracyano ethylene). From the detailed investigation, the complex $Me_3Sn.TCNQ$ is best represented by the canonical form $(Me_3Sn)^+(TCNQ)^-$, and provides the first example of an isolable paramagnetic organotin complex.

D. 7-Co-Ordinated Organotin Complexes

The mono-, di- and tri- organotin compounds generally exhibit a coordination 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 (82) to be monomeric in methylene chloride, suggesting a seven co-ordination around the tin. Kawakami et al (83) have concluded from UV, NMR and IR data that n-butyl tin tris-oxinate may have 7-coordinated tin atom. Ruddick and Sams (84) 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. Anhydrous methyl tin trinitrate crystallises with three chelating nitrate groups forming a pentagonal bipyramid about tin (85), Fig. XIV.

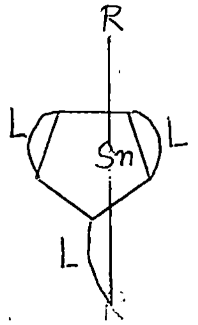


Fig. XIV

Tris(dimethyl sulphoxide) nitrato diphenyl-tin-nitrate has been characterised as a hepta co-ordinated organotin complex from IR and X-ray crystallography (66). The structure consists of monomeric hepta co-ordinated cation $[Sn(C_6H_5)_2NO_3\{(CH_3)_2SO\}_3]^+$ and NO_3^- anion. Co-ordination around tin is pentagonal bipyramid with the bidentate nitrate group and the three dimethyl sulphoxide molecules in the equatorial positions and the two phenyl ring at the apices.

The only example of a probable 7-co-ordinate triorganotin complex is provided by dimethyl di isothiocyanato (terpyridyl)-tin (IV), $[(CH_3)_2Sn(NCS)_2(C_5H_5H_{11})]$, which contain two Sn-C bonds, has recently been shown to be 7-co-ordinate (67).

The scarcity of 7-co-ordinated triorganotin complexes are, understable because of the very low Lewis acidity of the triorganotin atom attached to three carbon atoms. It is, however, possible to realise such complexes with suitable polydentate ligand where geometrical factors would favour such co-ordination. The present work will describe some examples of this type.

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