

CHAPTER-I

DONOR-ACCEPTOR CHARACTER OF TIN COMPOUNDS.

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I.1 *Introduction :*

During the last three decades the coordination chemistry of organotin compounds has experienced tremendous growth and still continues to grow, due mainly, to theoretical and structural interests as well as due to the role of these coordinated species as intermediates in various synthetic reactions and interesting biocidal properties in many of these compounds. The concept of organotin compounds as Lewis acids is of fundamental importance to an understanding of many problems of structure and reactivity.

The acceptor strength of the group IVB elements follows the sequence Sn >> Ge >Si. Tin compounds form complexes with Lewis bases much more readily, though to a lesser extent in the lower oxidation states, than Si and Ge, which behave as acceptors only when four strongly electronegative substituents are bonded to the metal atoms. The remarkable Lewis acidity of tin is attributed primarily to the availability of d-orbitals of sufficiently low energy, compared to the lighter group IVB elements. Addition complexes containing both tetravalent and divalent tin as acceptors are well characterised. Some of the important features of these compounds are discussed here in brief. Addition complexes of tin halides, though not organotin compounds in the strict sense

of the term, are also included in the discussion for the sake of completeness and comparison.

Beside the dominating acceptor character, organotin compounds often behave as interesting donors, an aspect not so well recognised.

In the bivalent state, tin should be capable of showing donor properties, at least in principle, due to the presence of the 5s-lone pair. However, the σ -donor strength of the 5s-lone pair in Tin (II) should be small, because the ability of an atom, possessing a lone pair, to act as donor, decreases with the increase in atomic number. Tin (IV), on the other hand, is devoid of any lone pair and as such the donor property in Tin(IV) compounds arises from M.O.'s delocalised over two or more atom centres. A short review on the donor abilities of organotin compounds is also presented here.

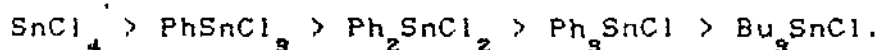
1.2.1 Tin (IV) Compounds as Acceptors :

1.2.1A. Relative Acceptor Strength :-

In the most familiar tetravalent state tin almost invariably behaves as a hard acid or class A acceptor^{1,2} because of its small size, high positive charge, absence of any outer electron easily excitable to higher states and presence of empty

5d orbitals. The d-orbitals are of sufficiently low energy for them to be frequently used in bonding so that tin can readily expand its coordination number above four. Consequently, detailed studies regarding the acceptor properties of Sn(IV) compounds have been made with R_nSnX_{4-n} (where, $n = 0,1,2,3,4$; R = alkyl/aryl groups, and X = halogen, pseudo halogen, AcO, NO_2 , etc.) and a large number of their complexes with N and O containing ligands are known⁹⁻¹⁵.

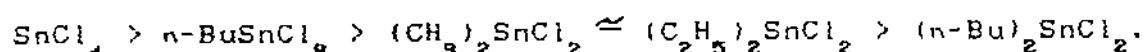
It is well known that the tin tetrahalides have a marked tendency to form thermodynamically stable six coordinate adducts. As the halogen atoms are successively replaced by less electronegative organic groups the acceptor strength of tin declines, but in general, the stability of organotin complexes seems to indicate that tin retains its class A character⁹. Using the difference between the dipole moments in dioxan and hexane as a measure of complex forming ability, the following sequence for acceptor strengths was obtained¹¹.



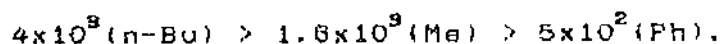
The same sequence has also been found from both potentiometric and conductometric studies of penta-coordinated anionic complexes in acetonitrile¹².

The coordinative bond strength in complexes between several alkyltin chlorides and 2,2'-bipyridyl, as derived from

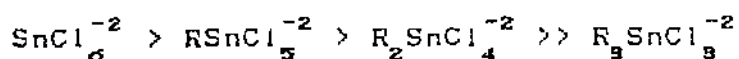
thermodynamic data is found to decrease in the order¹¹ :



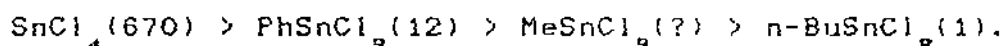
The acidity constant of SnCl_4 ¹¹ on substitution of one chlorine by an organic substituent is decreased by a factor of



The same trend is observed in the stability of the hexa-coordinate organotin anions¹¹, where the sequence



is observed and there are no reports on the existence of $\text{R}_4\text{SnCl}_2^{-2}$ ions. Anionic chloride or bromide complexes are also obtained more easily with PhSn(IV) than with MeSn(IV) ¹¹. The quantitative relative acceptor strength of three organotin trichlorides and SnCl_4 vs aniline bases¹¹ was found to be



For the tetrachlorides it was found that complexes were formed with decreasing strength as the halide changed, in the sequence¹¹ $\text{F} > \text{Cl} > \text{Br} > \text{I}$. The quadrupole splitting in the Mossbauer spectra of Me_3SnX compounds with a series of donors was also interpreted in terms of the acceptor strength of the Me_3SnX moiety and showed that the nature of the X-substituent influenced this strength in the order¹¹ $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{OH}^-$. The tendency for complex formation by organotin halide systems was also studied by paper electrophoresis and anion exchange paper chromatography. The

results indicated decreasing complex stability as a function of the halogen substituents¹¹ : $F^- \gg Cl^- > Br^- > I^-$

On the basis of the foregoing observations, the variation in the acceptor strength of the $R_n SnX_{4-n}$ compounds can be represented conveniently by the following tabular form¹⁵ :

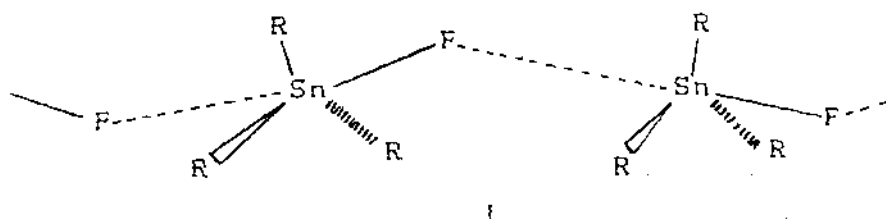
		Decreasing acceptor strength of $R_n SnX_{4-n}$					>			
X	NCS	F	\gg	Cl	>	Br	>	I		
R	Ph	>	Me	>	Et	>	Pr	>	Bu	
n	\downarrow	SnX_4	>	$RSnX_3$	>	R_2SnX_2	>	R_3SnX	>	R_4Sn

12.18. Consequences Of Acceptor Character :-

(i) Intermolecular association :

As a manifestation of this remarkable acceptor property, tin increases its coordination number above four in solid organotin halides and pseudohalides by extensive intermolecular association^{17,18}. These compounds are monomeric with tetrahedral tin atoms, only in the vapour phase or in dilute solutions in non-conducting solvents¹⁷.

X-ray and Mossbauer studies have shown that triorganotin fluorides consist of planar organic groups and fluorine atoms arranged alternately, with non-linear asymmetric Sn—F—Sn bridges [1]¹⁶.



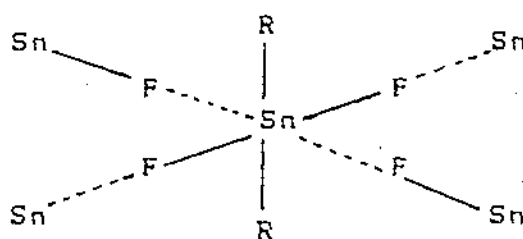
The lower alkyltin chlorides also have similar structures whereas, triphenyltin chloride contains discrete monomeric species with four coordinate tin. ^{85}Cl NQR data suggest that triorganotin chlorides with larger alkyl and aryl groups undergo phase change to associated structures at lower temperatures¹⁵.

Due to their weak Lewis acidity and large size of the halogen, triorganotin bromides and iodides favour a monomeric tetrahedral structure in the solid state. ^{119}Sn Mossbauer spectroscopy indicates that at 80°K the lower trialkyl tin bromides and iodides adopt associated structures containing penta-coordinate tin¹⁶.

In the solid triorganotin pseudohalides, the pseudohalogen group bridges planar R_3Sn units to form infinite linear or zig-zag chains¹⁶. Even R_3SnX compounds (where $\text{X} = \text{ClO}_4^-, \text{NO}_3^-, \text{BF}_4^-, \text{AsF}_6^-$), which may be thought as being ionic in the solid state are bridged polymers according to I.R. data¹². The sterically hindered triorganotin halides and pseudohalides having bulky organic groups are monomeric with tetrahedral tin atoms.

Diorganotin difluorides consist of infinite two dimensional

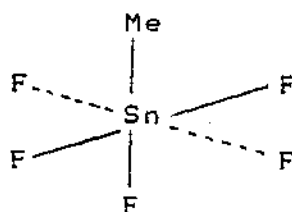
sheets of tin and fluorine atoms, with each tin linearly bridged to its four neighbours and having trans-octahedral tin atom configuration [III]¹⁶.



III

In other dialkyltin dihalides and pseudohalides the intermolecular association is weaker and the tin atom has distorted trans-R₂SnX environment¹⁶. Ph₂SnCl₂ contains distorted tetrahedral molecular species with weak or no intermolecular association¹⁹.

The I.R. and Raman spectra of methyl tin trifluoride are indicative of both bridging and terminal halogen and a polymeric structure [III] containing octahedral tin in the solid phase²⁰.



III

The vibrational and NQR (³⁵Cl and ⁸¹Br)¹⁶ spectra of the other

MeSnX_3 (X = Cl, Br, I) compounds are indicative of similar associated structures in the solid state.

(ii) Solvation :-

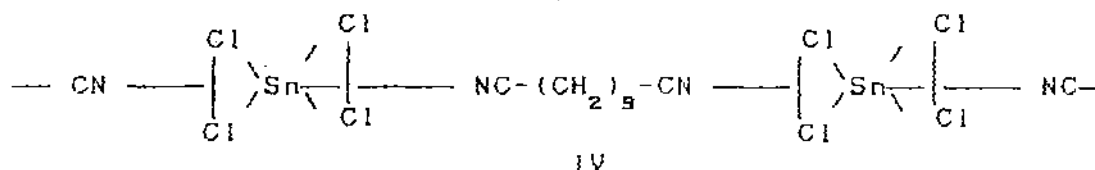
Addition of solvents to the $\text{R}_n\text{SnX}_{4-n}$ compounds usually destroy their polymeric structures and produces solvated organometallic complexes. The ability of the coordinating solvents to act as ligands has been studied mainly by PMR and Mossbauer spectroscopy. In the NMR data, the increase of the tin-proton coupling constants $J_{117/119\text{Sn-C-H}}$ was thought to be related to the changes in the hybridisation around tin on changing from the tetrahedral sp^3 state in the pure organotin compound to a trigonal bipyramidal configuration in the penta-coordinated tin complexes and to an octahedral configuration in the hexa-coordinated tin compounds¹¹. The relative nucleophilic character for a series thus established is : $\text{DMSO} \sim \text{DMF} > \text{HOH} > \text{Py} > \text{MeOH} > \text{MeCOMe} \sim \text{MeCOOMe} > \text{Dioxan} > \text{MeCN} \sim \text{MeCOOH} > \text{MeNO}_2 > \text{PhCl} \sim \text{CCl}_4$. It should be noted that O- or N-donor solvents solvate organotin compounds more efficiently than S- and P-donors, e.g., $\text{Et}_2\text{S} < \text{Et}_2\text{D}$; $\text{DMTA} < \text{DMA}$; $\text{HMTAFT} < \text{HMPTA}$; $\text{Bu}_3\text{P} < \text{Py}$ etc. This behaviour is typical for hard Lewis acids.

The quadrupole splitting observed in ^{119}Sn Mossbauer studies of the interaction between $n\text{-Bu}_2\text{SnCl}_2$ and a number of organic coordinating solvents yielded the following sequence for their

relative nucleophilicity : DMSO > DMF > HMTAP > DME > THF > DEF > Et₂O¹¹.

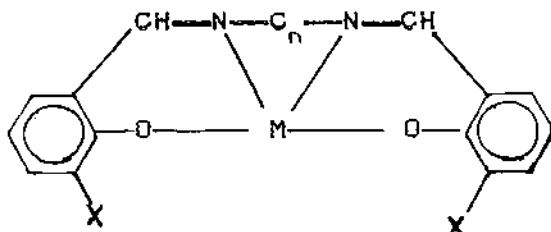
(iii) Formation of addition complexes :-

The tin tetrahalides form both ionic and neutral adducts with an enormous range of monodentate ligands and most of these have the composition SnX₄.2L, though 1:1 adducts have also been reported²¹. The 1:2 complexes have octahedral geometry²², whereas, 1:1 complexes are trigonal bipyramidal. With some monodentate ligands both 1:2 and 1:1 complexes may be obtained, e.g. SnX₄.2PBu₃ and SnX₄.PBu₃^{23,24}. Bidentate ligands generally form 1:1 complexes having octahedral tin atom geometry²⁵⁻³⁰. A bidentate ligand can also act as a bridge between SnX₄ units [IV]³¹.



However, some bidentate ligands, e.g. o-amino benzonitrile³², or amide derivatives of hydroxybenzoic and anthranilic acids³³, give SnX₄.2L complexes as well as SnX₄.L complexes. Many bidentate Schiff-bases act uniformly as monodentate ligands forming SnX₄.2L type complexes^{26b, 34, 35}. Transition metal derivatives of polydentate Schiff-bases [V] may act as bidentate ligands and add on to tin tetrachloride producing bimetallic complexes as 1:1

addition products^{95,96}.



[where, M = Cu, Ni ; C_n = -CH₂-CH₂-, X = H , -COOH.

C_n = -C₆H₄-, X =H.]

V

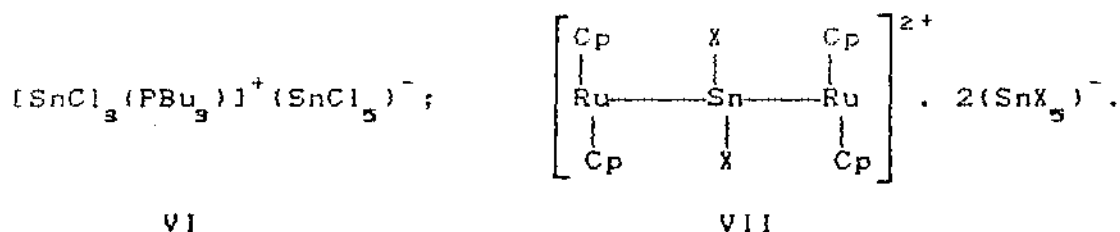
In the intra molecularly coordinated complex dichloro bis (ethyl 3-oxo butanoato)tin(IV) [Cl₂Sn(CH₃COCH₂COOEt)], the β-keto ester acts as a bidentate ligand coordinating through the carbonyl O-atoms and the environment around tin is slightly distorted octahedral⁹⁷. Pyrazole derivatives behaving as tridentate ligands can react with SnX₄ producing compounds of the type Sn(L)X₃ [where, L = tris-(3,5 dimethyl poly pyrazoly)borate ; X = Cl, Br] having hexacoordinated tin atoms^{98a, b}.

Acetate and haloacetate esters can act as monodentate ligand and add on to SnCl₄ giving trigonal bipyramidal as well as octahedral (both cis and trans) complexes⁴⁴.

In crown ether derivatives, such as, SnCl₄(18-crown-6).2H₂O, X-ray studies have shown that the tin atom environment consists of

octahedral $\text{SnCl}_4(\text{H}_2\text{O})_2$ units and the ether molecule is only hydrogen bonded to the water molecule⁴⁰⁻⁴². Additional water or other solvent molecules may be associated through hydrogen bonding⁴¹. However, Atwood et.al. have interpreted X-ray data suggesting that the ether acts as a bidentate ligand⁴³.

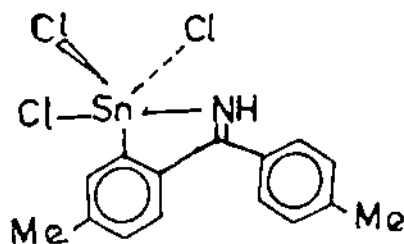
In ionic adducts the tin:ligand ratio may be other than 1:2 or 1:1,^{29,45-48} e.g., $2 \text{SnCl}_3 \cdot \text{PBu}_3$ ²⁹ or $(\text{Cp})_2\text{Ru} \cdot 1.5 \text{SnX}_4$ (where, Cp = cyclopentadiene and X = Cl, Br)⁴⁵, because these complexes contain both tetrahedral and trigonal bipyramidal tin moieties, one in the cationic and the other in the anionic part [VI, VII].



The compounds $4\text{XeF}_6 \cdot 3\text{SnF}_4$ and $3\text{XeF}_6 \cdot 4\text{SnF}_4$ are intermediate compounds with both $\text{Xe}_2\text{F}_{11}^+$ and XeF_5^+ cations present⁴⁰.

Mono-organotin compounds, RSnX_3 also show a marked tendency to increase their coordination number from 4 to 6 or even 7, the lowering in the acceptor strength of tin becoming striking only when weak donors are involved, such as alkyl sulfides, which gives adducts with SnCl_4 but not with PhSnCl_3 . With monodentate ligands there are few examples of five coordinate 1:1 complexes of the

type $RSnX_3 \cdot L$, containing a trigonal bipyramidal tin atom^{50,51,62,63,104a}, although these are far less common than the octahedral adducts $RSnX_3 \cdot L_2$ (L = monodentate donor). $MeSnBr_3 \cdot DMF$ ⁵⁰ and $(Ph_4As)^+(MeSnCl_4)^-$ ⁵¹ are examples of 1:1 complexes having trigonal bipyramidal structure with Me groups occupying an equatorial site. A similar geometry was also found in the intra molecularly penta coordinate ketiminotin trichloride [VIII]⁵² and ester tin trichlorides, $R[CO(CH_2)_2]_2SnCl_3$ (R = H, Me, Et, Bu, Ph)⁵³.



VIII

The six-coordinate complexes may be anionic, e.g., $RSnX_5^{-2}$ or neutral, e.g., $RSnX_3 \cdot bipy$ and are readily formed with a wide range of ligands^{25,40,54-62,64}, both mono and bidentate.

In some intra molecularly coordinated mono organotin complexes, such as $PhSnT_3$ (T = tropolonate)⁶⁵, $BuSn(OCOR)_3$ (R = Me, Et)⁶⁶, $MeSn(SCSNET_2)_3$ ⁶⁷, $BuSn(OX)_3$ (OX = oxinate) and $MeSn(NO_3)_3$ ⁶⁸, involving potentially polydentate ligands, the coordination number of tin is seven. In intra molecularly coordinated poly pyrazolyl

borate derivatives $\text{RSn}(\text{pz})_3\text{BH}\bar{\text{X}}_2$ [where, pz = pyrazolyl moiety, and X = halogen or pseudohalogen], however, only coordination number six is attained^{38,69}, the ligand behaving as a tridentate one (though, potentially hexadentate in this case).

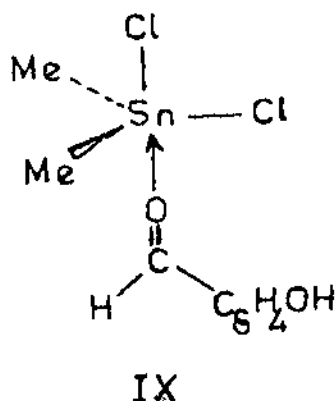
No example of mono-organotin trihalide or pseudohalide adducts with a higher coordination number than six have been demonstrated by X-ray crystallography, although a number of 1:4 adducts, such as, $\text{MeSnI}_3 \cdot 4\text{py}$ ⁶ or $\text{PhSnCl}_3 \cdot 4(\text{morpholine})$ ⁷⁰ have been synthesised.

The R_2SnX_2 compounds are able to form complexes having five, six or seven-coordinate tin atoms. Generally, coordination saturation at tin is reached at six, as $\text{R}_2\text{SnX}_2 \cdot \text{L}_2$ (L = monodentate ligand, L_2 = bidentate ligand, X = Cl, Br, I, NCS, AcO, CF_3CO_2) forming octahedral complexes with a wide range of organic donors, the R groups being usually trans to each other^{25,54,64,71-84}. Mossbauer spectroscopy has indicated that certain octahedral R_2SnX_2 adducts, e.g., $\text{R}_2\text{SnX}_2 \cdot \text{bipy}$ [where X = Cl, Br, R = furyl, thienyl⁸⁵; X = Cl, R = p-tolyl⁹⁰; X = NCS, R = Ph⁸⁶], $\text{Ph}_2\text{SnCl}_2 \cdot (2\text{-amino methyl pyridine})$ ⁸⁷ contain a cis disposition of the R groups.

However, the formation of $\text{R}_2\text{SnX}_2 \cdot \text{L}_2$ complexes must a priori proceed via a five coordinate $\text{R}_2\text{SnX}_2 \cdot \text{L}$ species⁸⁸ and the existence of a number of penta-coordinated complexes having a cis $\text{R}_2\text{SnX}_2 \cdot \text{L}$

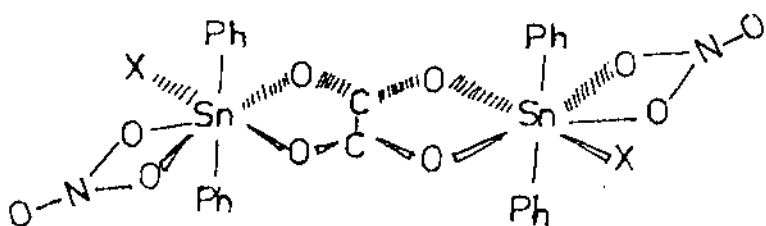
geometry have been demonstrated by X-ray crystallography. The anion in quinolinium dimethyl trichlorostannate $(C_8H_7N)^+(Me_2SnCl_3)^-$ contain a distorted trigonal bipyramidal tin atom with the two Me groups occupying equatorial positions⁸⁹. Salicylaldehyde forms a 1:1 complex with Me_2SnCl_2 , where X-ray studies revealed a similar tin atom geometry, with two Me groups occupying equatorial positions of a trigonal bipyramid [IX]⁹⁰. With some ligands both the penta-coordinated (1:1) and hexa-coordinated (1:2) complexes of diorganotin dihalides have been isolated^{76,91-93}.

Dimethyltin diisothiocyanate forms a 1:1 adduct with terpyridyl, in which the tin atom is occupying a seven coordinate



pentagonal bipyramidal geometry with trans organic groups ; the five nitrogen atoms, two from the NCS groups and three from the

tridentate ligand are situated in the equatorial plane⁹⁴. X-ray diffraction studies have shown that $\text{Ph}_2\text{Sn}(\text{NO}_3)_2 \cdot \text{L} \cdot \text{CHCl}_3$ (where, $\text{L} = \text{cis-Ph}_2\text{P}(\text{O})\text{CH}=\text{CHP}(\text{O})\text{Ph}_2$) have a pentagonal bipyramidal structure. However, $\text{trans-Ph}_2\text{P}(\text{O})\text{CH}=\text{CHP}(\text{O})\text{Ph}_2$ acts as a bidentate bridging ligand joining two six-coordinate tin atoms in $[\text{Ph}_2\text{Sn}(\text{NO}_3)_2]_2 \cdot \text{L} \cdot 2\text{H}_2\text{O}$ ⁹⁵. $[\text{Ph}_2\text{Sn}(\text{NO}_3)(\text{X})]_2 \cdot \text{C}_2\text{O}_4$ (where, $\text{X} = \text{Ph}_3\text{AsO}, \text{Pr}^n\text{SO}$), obtained by the addition of X , at room temperature under nitrogen, to an acetone-chloroform solution of $\text{Ph}_2\text{Sn}(\text{NO}_3)_2$, also have been indicated by X-ray studies, to contain a seven coordinated tin atom having a slightly distorted pentagonal bipyramidal geometry with two Ph rings in axial position and the nitrate, oxalate and X in the equatorial plane $[\text{X}]$ ^{96,97}.



X

X = $\text{Ph}_3\text{AsO}, \text{Pr}^n\text{SO}$.

Although the pyrazole derived ligands $[\text{RB}(\text{pz})_n]$, (where $\text{R} = \text{H}$ or a non coordinating substituent, $\text{pz} = \text{pyrazole}$ or its C-substituted derivative and $n = 2-4$) are potentially polydentate, (tetra-, hexa- or octa-dentate depending on the value of n), the tin atom in their di organotin derivatives, $\text{R}_2\text{Sn}(\text{L})\text{X}$ ⁹⁸, is only hexa

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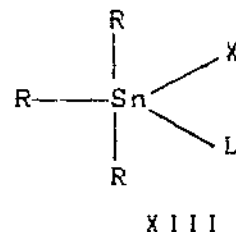
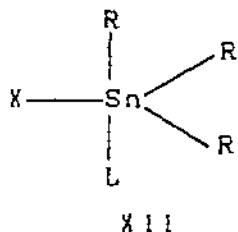
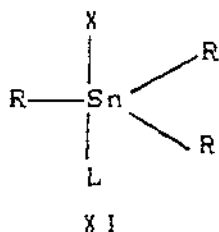
coordinated. Similar intra molecularly hexa coordinated diorganotin complexes are also formed by trihalo β -diketones⁹⁹. Diphenyltin diisocyanate is unusual in that it forms a 2:1 adduct $[\text{Ph}_2\text{Sn}(\text{NCO})_2]_2 \cdot \text{bipy}$ with bipyridyl. It is believed to contain a bridging bipyridyl group and pentacoordinated tin atoms⁹⁸.

Although organotin carboxylates unlike organotin halides or pseudohalides are reluctant to form addition complexes, diorganotin dicarboxylates are known to form 1:1 adducts in solution¹⁰⁰. A few well authenticated examples of hydrate adducts of diorganotin dicarboxylates have been reported in recent years^{101,102}. Lockhart et.al. have reported an ionic acetate adduct of dimethyl tin di acetate¹⁰³. In these complexes¹⁰¹⁻¹⁰³ the tin atom is seven coordinate with pentagonal bipyramidal environment.

The R_3SnX compounds show marked difference from their mono- and di-organotin analogues in that 1:1 adducts are formed. The generally weak acceptor strength of R_3SnX favours an increase in coordination number of the tin atom to five, by reaction with a monodentate ligand to form a trigonal bipyramidal complex in which the three organic groups are situated in the equatorial plane. X-ray studies of several $\text{R}_3\text{SnX} \cdot \text{L}$ compounds [where $\text{X} = \text{NO}_2$, $\text{L} = \text{Ph}_3\text{PO}$, Ph_3AsO , PyO ^{105,106}; $\text{X} = \text{Br}$, $\text{L} = \text{QuinO}$, Ph_3PO ^{107,108}; $\text{X} =$

Cl, L = LutO, $(Me_2N)_2CO$ ^{109,92}] have shown the tin atom to have the trigonal bipyramidal geometry [XI]. The tri organotin pseudo halides also behave like their halide analogues, producing 1:1 adducts with monodentate ligands¹¹⁰

With potentially bidentate ligands the tri organotin halides still prefer to form five coordinate adducts^{57,80-82,87,111,112} utilising only one of the donor groups as in $Ph_3SnCl, Ph_2F(O)CH=CHP(O)Ph_2$ ¹¹³. However, in some $R_3SnX.L$ complexes involving bidentate ligands X-ray studies suggest chelation and cis-geometry [XIII] around the tin atom¹¹⁴⁻¹¹⁶. A third structural possibility i.e. the meridional structure XIII has been suggested for the cationic complexes $[R_3Sn(Ch)]^+[BPh_4]^-$, (where Ch is a chelating ligand) on the basis of Mossbauer studies¹¹⁷.



The triorgano tin isocyanates and isothiocyanates are stronger Lewis acids than their halide counterparts and the IR spectra of $Ph_3SnNCX.DMO$ (where X = O, S and DMO = dimethyl oxamide)¹¹⁸ and $Me_3SnNCS.phen$ ¹¹⁹ are indicative of octahedral tin atom configuration in these complexes. The 1:1 adducts of Me_3SnCl with

2,2'-bipyridyl is also believed to contain 6-coordinate tin on the basis of IR spectra¹¹⁹. However, no example of octahedral triorgano tin halide or pseudohalide complex has yet been demonstrated crystallographically. Triethyl tin chloride is known to form the unusual $2Et_3SnCl.L$ complexes with dimethyl-, diethyl- and trimethyl amine, though the normal 1:1 adducts are also formed with the first two ligands¹²⁰.

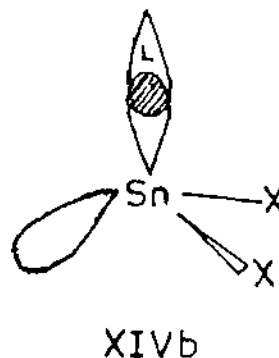
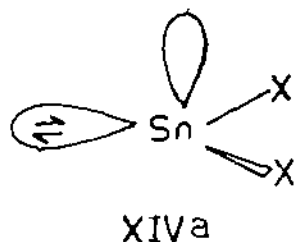
Both mono and bidentate ligands have been reported to form five coordinate adducts with triphenyl tin trihalo acetates^{121,122}. X-ray data for the polymeric adduct, triphenyl tin(IV) 8-quinolyloxyacetate hydrate¹²³ also suggest a distorted trigonal bipyramidal tin atom geometry involving coordinated water molecule.

Tetraalkyl tin compounds show no tendency to increase their coordination number owing to their weak Lewis acidity, conferred by the four electron releasing alkyl groups. However, Beattie has indicated that besides the electronegativity of the groups attached to tin other factors may affect the acceptor properties⁴ and it seems possible that compounds with four perfluoro-organic groups joined to tin, would interact with suitable donors, since it is known that the electronegativities of the CF_3 and C_6F_5 groups are comparable with that of bromine^{124,125}. A coordination

stage has been proposed for the abnormal halide ion-catalysed hydrolysis of $R_{4-n}Sn(C_6H_5)_n$ compounds¹²⁶, as also for the acid mediated additions of alkenyl tributyl stannane to aldehydes and substituted aldehydes¹²⁷⁻¹³¹. It has been claimed that trimethyl(trifluoro methyl)tin forms a 1:1 adduct with hexamethyl phosphoric triamide (HMPTA) and that this may be isolated in the solid state¹³². The addition of Sn_2Me_6 to alkenes and alkynes in the presence of $Pd(PPh_3)_4$ ^{158,159} is also most likely to involve initial donation from the π -bonding orbital of the hydrocarbons followed by cleavage of the Sn-Sn bond. The reactions of $R_3Sn-SnR_3$ with Li-metal, alkyllithium, grignard reagents and NaOR are also instances of the electron acceptor ability of the $\sigma(Sn-Sn)$ bond¹³⁵.

1.2.2. Sn(II) Compounds as Acceptors :

Covalent SnX_2 compounds, having essentially sp^2 hybridisation, have an empty p-orbital, of similar energy to those used in bonding, at right angles to the plane of the molecule [XIVa], and should act as monofunctional acceptor towards suitable monodentate ligands to form compounds of the type $SnX_2.L$, by the overlap of lone pair orbitals on the ligand with the empty p-orbital of the Sn-compound, causing a distortion towards sp^3 hybridisation [XIVb].



This acceptor tendency makes most Sn(II) compounds polymeric. Structures of the oxide, sulfide, selenide, chloride and sulfate reveal this¹⁹⁶. Although many monomeric organotin(II) compounds have been reported in the older literature, the R_2Sn compounds exist only as unstable intermediates which self react to form cyclic oligomers, unless the R group is π -cyclopentadienyl or strongly sterically hindering¹⁶. The polymerisation is caused by the overlap of the lone pair orbital on a monomer with the empty p-orbital of an adjacent tin atom.

The stannous ion with empty 5p and 5d orbitals can also act as an acceptor towards certain ligands. The complexes would be formed by overlap of lone pair orbitals on the ligands with the empty hybrid orbitals on tin. In view of the small energy separation between the s and p orbitals in the stannous ion all p orbitals should be included in the hybridisation and the sp^3

hybrid configuration should be very stable. The involvement of d-orbital in the hybridisation would appear to be less likely due to greater s-d energy separation.

Most of the available evidence does suggest that the stannous ion is a class A acceptor and the order of stability of the complexes formed with halide ligands is $F^- \gg Cl^- > Br^- > I^-$. The trifluorostannate(II) ion has been shown to be a very stable species¹⁹⁵, and to be the strongest tin(II) halide complex. IR and Raman spectra suggest that the trihalostannate(II) ions have a pyramidal structure based on sp^3 hybridisation of the tin(II) orbitals^{197,198}.

For ligands other than halides, the order of stability of complexes formed by type A acceptors $OH^- > NH_3 > RS^- > H_2O$ etc. may not be exactly followed by the stannous ion, because of the probability¹⁹⁶ that the lone pair 5s orbital is strongly antibonding with respect to certain ligands such as NH_3 , H_2O , and the CN^- ion. A spectroscopic study of the tin(II) thiocyanate complexes has shown that the nitrogen atom of thiocyanate is the donor atom and this provides further evidence for the A type acceptor behaviour of the stannous ion¹⁹⁶.

A number of adducts of tin(II) compounds with monodentate oxygen and nitrogen donors, such as, water, acetic acid, dioxan, sulfoxides, DMF, NH_3 , py, amines, amine-N-oxides etc. are

known^{136,139,140}. Spectroscopic study of dihalo bis-(p-toluidine) tin(II) compounds has suggested that the tin-nitrogen bonds are relatively weak¹³⁶. Beside the usual 1:1 addition compounds, some of these ligands may form complexes with varying tin to ligand ratio, e.g. in NH_3 adducts of SnX_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) the mole ratio may be as high as 1:9¹³⁶. In the 1:1 complexes the tin atom acts as a monofunctional acceptor making use of the empty p-orbital in its valence shell in complex formation. Often, the first material to be precipitated from the solution of a tin(II) compound in a donor solvent is a polysolvated material, from which the 1:1 complex can usually be obtained¹³⁶. This suggests that the tin is acting primarily as a monofunctional acceptor and that further donor molecules are taken up mainly for lattice packing purposes. The crystal structure of tin(II)chloride dihydrate shows that only one of the solvent molecules is bonded directly to the tin atom having a pyramidal environment [XV]¹³⁶.



The second water molecule in the structure forms hydrogen bond

with the water molecule bonded to the tin atom and can be removed by careful dehydration at 80°C .¹³⁶ Other 1:1 complexes are believed to have similar structures^{139,140}.

The only known addition compounds formed with sulfur ligands are the thiourea and tetramethyl thiourea adducts¹³⁶. From X-ray studies, diacetato bis-(thiourea)tin(II) has been shown to have a square-pyramidal structure, the tin atom being bonded to two thiourea S atoms and two carboxylate O atoms, whereas, in tetrabromo pentathiourea ditiin(II)dihydrate, $(\text{SnBr}_2)_2[\text{S}=\text{C}(\text{NH}_2)_2]_5 \cdot 2\text{H}_2\text{O}$ both the tin sites have trigonal pyramidal configuration¹⁴¹. A tin(II)fluoride-hydrofluoric acid complex, $\text{SnF}_2 \cdot 2\text{HF}$, containing a halogen donor is known¹³⁶.

4 coordinated complexes of the type $\text{SnX}_2 \cdot \text{L}_2$ (where L = monodentate and L_2 = bidentate ligand) are frequently formed by $\text{Sn}(\text{SO}_3\text{Cl})_2$ ¹⁴², tin halides and isothiocyanate^{104b,140,143-146}. 1:1 complexes with many bidentate Schiff's bases, semicarbazones and thiosemicarbazones with SnCl_2 are also known¹⁴⁷⁻¹⁴⁹. But their structures are not very well authenticated.

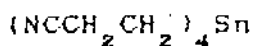
In the 2:1 addition product of SnCl_2 with 18-crown-6 ether formulated as $[\text{SnCl}(\text{L})][\text{SnCl}_3]$ and in $[\text{SnCl}(\text{L})][\text{ClO}_4]$ ¹⁵⁰, X-ray crystallography has revealed that the tin in the cationic moiety occupies a hexagonal pyramidal site, being bonded to all six crown ether oxygens and the chlorine atom in an axial position.

In the pyruvic acid thiosemicarbazone (HL) derivative $\text{Sn}^{\text{II}}(\text{L})\text{Cl}^{151}$, the tin atom is five coordinate due to intra molecular coordination by the tetradentate ligand. The tin(II) poly(1-pyrazolyl)borates $[(\text{pz})_{4-n}\text{BR}]_m\text{SnCl}_{2-m}$ (where, Hpz = pyrazole or its C-substituted derivative ; R = non coordinating substituent ; $n = 0-2$ and $m = 1,2$)¹⁵² are interesting due to the fact that in these compounds the effective coordination number of $\text{Sn}(\text{II})$, assigned on the basis of ^1H NMR data, can be five, six or even seven, obviously through the involvement in intra molecular coordination, of the N atoms of the pyrazolyl moiety.

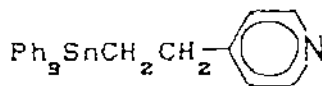
1.3 Donor Property Of Tin Compounds :

From the forgoing discussion it is apparent that tin compounds almost universally behave as acceptors, unless the substituents bonded to tin atom are donors themselves. As for example, the π -orbital of the cyclopentadienyl part in bis-(cyclopentadienyl)tin(II)¹⁵³ acts as donor, forming charge-transfer complexes with acceptors like TCNE (= tetracyano ethylene) and TCNQ (= tetracyano quinodimethane), the complexes being similar to those of iron cyclopentadienyls¹⁵⁴. Organotin bases such as tetrakis-(2-cyanoethyl)tin(IV) [XVII], or triphenyl[2-(4'-pyridyl)ethyl]tin(IV) [XVIII] have been used to form adducts with compounds of tin and other metals. Thus, XVI

forms 1:1 complexes with stannic chloride and bromide, $\text{SnX}_4 \cdot \text{L}$ ¹⁵⁵ and XVII forms stable adducts with organotin and other halides, e.g., $\text{Ph}_2\text{SnCl}_2 \cdot 2\text{L}$, $\text{Ph}_3\text{SnCl} \cdot \text{L}$, $\text{ZnCl}_2 \cdot 2\text{L}$, $\text{CoCl}_2 \cdot 4\text{L}$, $\text{NiCl}_2 \cdot 4\text{L}$ and $\text{CuCl} \cdot \text{L}$ ¹⁵⁶.



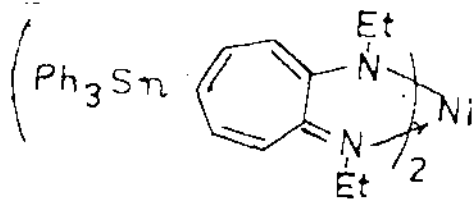
XVI



XVII

A Ni-complex of structure XVIII is also known¹⁵⁶. But the donor abilities of such compounds are almost solely the property of the organic moiety, because the tin atom is too far apart from the donor atom to modify their donor strength in any way.

These compounds are, therefore, of very little interest in the discussion of the donor properties of organotin compounds. However, not only quite a few Sn(II) molecules and complex ions containing sterically active lone pairs behave as donors¹³⁶, but also, a number of tin(IV) compounds, notably the tin tetraalkyls are known to form complexes with acceptors, although the analogous unsubstituted alkanes do not show any such tendency. In the latter compounds, the donor activity of the molecules is a direct consequence of substitution by tin, although tin(IV) itself, is not the donor. The donor properties of Sn(II) and Sn(IV) compounds are now discussed separately, because of the totally different role of the tin atoms in the two cases.

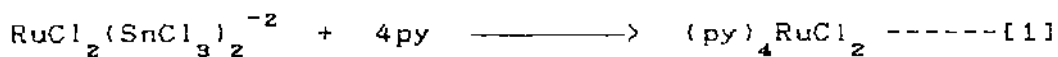


XVIII

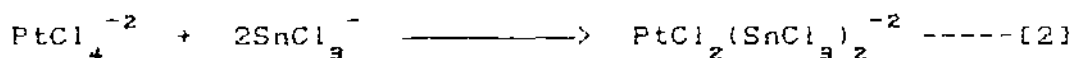
1.3.1 Sn(II) Compounds as Donors :

In Sn(II) compounds the donor property is masked because of the predominating acceptor tendency of the vacant hybrid orbital. These compounds exhibit donor property only when the vacant orbitals have been used in forming dative bonds with Lewis bases such as halide ions and the anionic halogen complexes of the type SnX_3^- possess sufficient donor strength to form a variety of complexes with suitable acceptors, particularly the platinum metal acceptors¹⁹⁶. The lone pair orbital of the pyramidal trihalostannate(II) ion must be responsible for the σ -donor properties of the group. The donor ability of the SnX_3^- ions, in contrast to the other Sn(II) complexes is presumably due to the lowering of 5s ionisation potential in the anionic species. This is supported by the absence of donor tendency in SnF^+ , SnCl^+ and SnBr^+ , where the 5s lone pair is expected to be more difficult to ionise¹⁹⁶. Similar donation by a pyramidal monosolvated tin(II) halide results in the formation of neutral complexes in some nonaqueous solutions¹⁹⁶. Examples where SnX_3^- ions act as donors include $\text{PtCl}_2(\text{SnCl}_3)_2^-$; $\text{Pt}(\text{SnX}_3)_5^{-9}$ (where X = Cl, Br); $\text{Pt}_3\text{Sn}_8\text{Cl}_{20}^{-4}$; $\text{Pd}_2\text{Cl}_2(\text{SnCl}_3)_4^{-4}$; $\text{Ir}_2\text{Cl}_6(\text{SnCl}_3)_4^{-4}$; $\text{OsCl}_2(\text{SnCl}_3)_4^{-4}$; $\text{RuCl}_2(\text{SnCl}_3)_2^{-2}$; $\text{Rh}(\text{SnCl}_3)_4^{-3}$; $\text{Rh}_2\text{Cl}_2(\text{SnCl}_3)_4^{-4}$; $\text{RhCl}(\text{CO})(\text{SnCl}_3)_2^{-2}$ etc.¹⁹⁶. Evidence for the presence of the trichlorostannate(II) ligand in $\text{Pt}_3\text{Sn}_8\text{Cl}_{20}^{-4}$ ion comes from the

strong IR band in its spectrum at 330 cm^{-1} , which is characteristic of σ -bonded SnCl_3^- .¹³⁶ The best confirmatory evidence for the existence of tin(II) donor atoms in the complexes formed with the platinum metals comes from ligand replacement reaction involving the tin(II) species. The SnCl_3^- ion can be replaced from anions containing it by strong π -bonding ligands such as py, p-toluidine, PPh_3 and CO, e.g.,



Similarly the trichlorostannate(II) ion can replace weaker π -bonding ligands such as chloride, mesityl oxide etc.



Many such replacement reactions in organic solvents result in the formation of neutral complexes crystallisable from solution, e.g., $(\text{Ph}_3\text{P})_2\text{Pt}(\text{SnCl}_3)$, $(\text{Ph}_3\text{P})_3\text{Pt}_3(\text{SnCl}_3)_2$ etc.¹³⁶

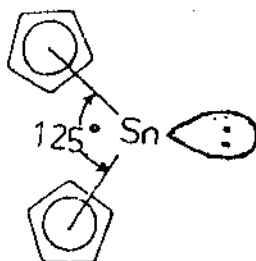
Though SnX_3^- ion is a weak σ -donor, it exhibits a large trans-effect because of its ability to form strong $d\pi-d\pi$ bonds with Pt-group metals. The π -acceptor property of SnX_3^- ion is in fact comparable to those of the two most powerful π -acceptor ligands NCS^- and CN^- .¹³⁶ The SnCl_3^- ion appears to have empty d orbitals of the correct size and symmetry to form strong π -bonds with the filled d orbitals on the platinum metals.

The trichlorostannate ion in $(\text{Et}_3\text{NH})(\text{SnCl}_3)$ acts as σ -donor towards acceptor molecules such as TCNE and TCNQ forming 1:1

complexes. The formation of the complexes of tin(II) halides with TCNE and TCBQ (= tetrachloro benzoquinone) and of bis-(β -ketoenolato)tin(II) with TCNE, TCNQ and TCBQ, also involves σ -donation from the tin(II) atom. But in the process TCNE and TCBQ completely oxidise the metal in the tin(II) halide and bis-(β -ketoenolato)tin(II) to the quadrivalent state. The TCNQ complexes of bis-(β -ketoenolato)tin(II) exhibited resonance due to both Sn(II) and Sn(IV)¹⁵⁸. Similar oxidative additions are also undergone by Sn(II) derivatives of 1,2-diols^{158,159}.

Although the π -acceptor properties of SnX_3^- ion play an important part in its donor ability, the BX_3 complexes can only involve the σ -donor properties of the ion. The formation of $\text{Cl}_3\text{SnBF}_3^-$ and $\text{Cl}_3\text{SnBCl}_3^-$ has been accounted for by σ -donation from the lone pair of the SnCl_3^- ion to the empty acceptor orbital of the BX_3 ¹⁶⁰.

Electron diffraction and X-ray crystallography has shown that the two rings in bis-(cyclopentadienyl)tin(II) are non parallel [XIX] and the bonding can be described in terms of sp^2 -hybridised tin with two orbitals involved in bonding to the cyclopentadienyl rings and the third containing unshared pair of electrons¹⁶¹⁻¹⁶³. This unshared pair can coordinate to a Lewis acid such as BF_3 .



XIX

The addition of BF_3 -etherate to a THF solution of stannocene [XIX] precipitated the complex $(\eta^5\text{-C}_5\text{H}_5)_2\text{Sn}:\rightarrow\text{BF}_3$ ¹⁶⁴. Stannocene also forms 1:1 complexes with Lewis acids such as AlCl_3 and AlBr_3 ¹⁶⁵. The Mossbauer spectra of these adducts are very similar to that of stannocene indicating that the complexation of the tin lone pair does not significantly affect the 5s electron density at the tin atom. However, the stannocene complex $(\eta^5\text{-C}_5\text{H}_5)_2\text{Sn}:\rightarrow\text{BF}_3$ has recently been shown to contain the units $(\text{BF}_4)^-$, $(\eta^5\text{-C}_5\text{H}_5)_2\text{Sn}$, $(\eta^5\text{-C}_5\text{H}_5\text{Sn})^+$ and THF by Zuckerman et.al. from X-ray crystallographic measurements¹⁶⁶.

The bonding in organostannylene complexes such as $[\text{CH}(\text{SiMe}_3)_2]_2\text{Sn.M}(\text{CO})_5$ (M = Cr, Mo) or $\text{Cp}_2\text{Sn.M}(\text{CO})_5$ (M = Cr, Mo, W)^{105b, 107, 168} and bis-naphthyl $\text{Sn}^{\text{II}}.\text{W}(\text{CO})_5$ ¹⁶⁹ can be interpreted as involving σ -donation from the lone pair of the tin atom to the transition metal and back donation from the later to the empty p

or d orbitals of the former. Base stabilised terminal complexes such as $R_2Sn(B).Cr(CO)_5$ ($R = CH_3, t-Bu$; $B = py, THF$)¹⁷⁰ involve coordination of the tin to only one metal atom but the vacant p orbital on Sn additionally coordinates a molecule of the base.

1.32. Tin(IV) compounds as Donors :

As already mentioned, the donor property of Sn(IV) compounds arises from delocalised M.O.'s involving the metal atom and its neighbours. Bond polarity and inductive effect play important role in the ability of tin atom to modify the donor activity of the substituent bonded to it. The Sn—X bonds in molecules of the type R_nSnX_{4-n} (where X = a monovalent atom or group, such as H, OH, OR, NR_2 , halogen; $n = 1-4$) acquire a large polarity due to the low electronegativity of tin as compared to the common ligands. Addition reactions of alkyltins to aldehydes and ketones demonstrate the polarity of Sn—C bond.

Closely related with this is the inductive effect which the tin atoms or stannyl groups exert on their surroundings. The bond polarisation, $Sn^{\delta+}-X^{\delta-}$, which is there in principle, may be changed by substitution at X as well as at tin. NMR data on organotin compounds^{171,172} and semi empirical calculations of Majee and Gupta¹⁷³ emphasise this. Studies of the relative rates of acid cleavage of the compounds $p-Me_3MCH_2C_6H_4SnMe_3$ ($M = Si, Ge,$

Sn^{174} and the rates of alkaline hydrolysis of $\text{R}_3\text{M}(\text{CH}_2)_n\text{COOEt}$ ($\text{R} = \text{Me, Et}; n = 1-3; \text{M} = \text{Si, Ge, Sn}^{175}$, as also, IR and NMR measurements on $(\text{Me}_3\text{Si})_2\text{N}(\text{MMe}_3)$ ($\text{M} = \text{Si, Ge, Sn, Pb}^{176}$ and IR studies on esters of the type MeCOOMMe_3 ($\text{M} = \text{C, Si, Ge}^{177}$ have established that the R_3M groups have a +I effect and the order of electron release is $\text{Me}_3\text{Pb} > \text{Me}_3\text{Sn} > \text{Me}_3\text{Ge} > \text{Me}_3\text{Si}$. The drift of electrons from the metal to its partner in the $\text{Sn}-\text{X}$ bond, therefore, makes the atom X quite rich in electron density. Unless there is back bonding between the filled orbitals of X and empty 5d orbitals of Sn, a possibility of electron donation through X arises. Although there are controversies regarding the extent of $d\pi-\pi$ back bonding in Sn(IV) compounds, it is now broadly agreed that such bonding is generally absent except in compounds having $sp^2 \text{C}-\text{Sn}$ bonds¹⁷⁸. There is evidence that the π -character in the $\text{M}-\text{X}$ bonds decreases as we go down the group IVB. Thus $\text{Si}-\text{O}$ or $\text{Si}-\text{N}$ bonds have appreciable π -character, whereas, IR and Raman studies of compounds R_3SnXR_3 ($\text{X} = \text{O, S}$) indicated that there is no π -contribution to the $\text{Sn}-\text{O}$ and $\text{Sn}-\text{S}$ bonds¹⁷⁸. It is expected that the much diffused nature of 5d orbitals on Sn (as compared to the 3d orbitals on Si) would be unsuitable for back bonding with filled $p\pi$ orbitals on the more electronegative atoms.

Depending on the nature of the substituents two types of donors may be encountered:

(i) Type A : Compounds in which the substituent X is not an electron pair donor, e.g., tetraalkyl tin compounds. The comparatively low energy of the σ -M.O. corresponding to the Sn—X bond and its polarity makes this class of compounds weak donors.

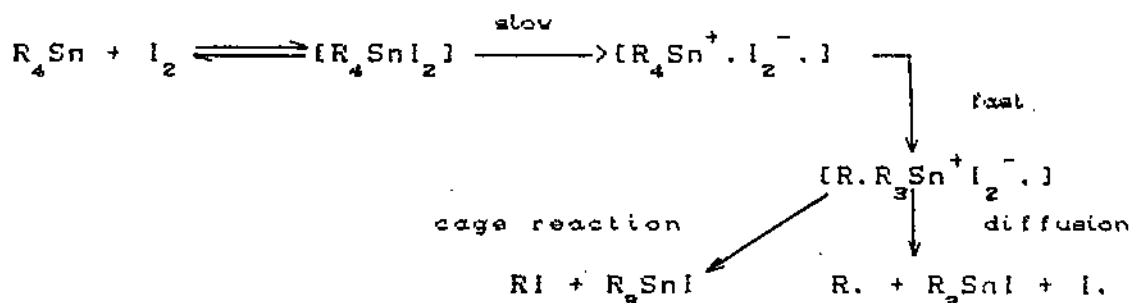
(ii) Type B : Compounds in which the substituent is an electron pair donor, e.g., $(R_3Sn)_2O$. Although the donor orbital is almost localised on the substituent in these compounds, the adjacent tin atom often profoundly modifies their donor strength through inductive effect and in some case even through σ — π conjugation.

In addition some triorgano tin(aryloxy)benzoates have been shown to form 1:1 molecular complexes of weak donor acceptor type with almost any type of molecules including unsubstituted alkanes¹⁷⁹. Electronic absorption spectral studies show the organotin molecules to be the donor. However, the role of the tin atom in these case is not yet fully understood and these compounds have been excluded from the purview of the present discussion. The above two types of Sn(IV) donors are now discussed in some details.

1.3.2A. Type A Tin(IV) Donors :

The unsubstituted alkanes do not usually possess any donor or acceptor property, presumably, due to the absence of any low lying M.O. in them. However, substitution of a hydrogen by tin

results in a relatively high energy HOMO (low I.P.) and because of this lowering in I.P., the tetraalkyl tin compounds can act as weak σ -donors¹⁸⁰. Group IVB metal alkyls have been found by Kochi et.al.¹⁸¹⁻¹⁸⁶ to form weak charge-transfer complexes with acceptors such as TCNE, I₂, HgCl₂ etc. in CCl₄ and CH₂Cl₂. These authors have interpreted the iodinolysis of R₄Sn as involving electron transfer within the charge-transfer complex as shown below¹⁸⁵.



in CT complexes of benzyl organotin derivatives, e.g., PhCH₂SnPh₃, PhCH₂SnMe₃, C₆H₄(CH₂)₂SnPh₂ etc. with TCNE^{187,188}, the organotin group is found to exert a large activity on the aromatic ring through σ - π conjugation. The magnitude of the decrease of the CT frequency in the stannyl derivatives compared to that in the corresponding carbon compounds show that the donor ability of the >Sn-CH_2 - group is comparable to that of -NR_2 group¹⁸⁷.

The metal alkyls have also been found to undergo electron transfer reactions with oxidants like IrCl₆⁻², Fe(dipy)₃⁺³ and Fe(Phen)₃⁺³. In molecular contact complexes, reported to exist in

solutions of NbF_5 , MoF_6 , WF_6 and $WF_6 \cdot OMe$ in the tetraalkyls of Ge, Sn and Pb^{180} , electron transition from the σ -M.O. of the M—C bond in R_4M to the empty antibonding M.O. of the penta/hexavalent metal is believed to take place.

The cleavage of Sn—C bonds of R_4Sn compounds by metal halides such as SnX_2 , SnX_4 , BX_3 , PX_5 , CuX_2 , PdX_2 and HgX_2 are well known^{190,191}. The disproportionation between R_4Sn and $SnCl_4$ is the basis of the Kocheshkov preparation of alkyltin chlorides, R_nSnCl_{4-n} . These reactions involve donation from the σ -M.O. of the Sn—C bond to the electrophiles, nucleophilic assistance being provided at the tin centre.

Although homopolar, the σ (Sn—Sn) bond in hexaorgano distannanes can act as σ -donor due to its low energy. Thus oxidative cleavage R_3SnSnR_3 , by various π -acceptors, e.g., TCNE, TCNQ, TCBQ, 1,4-Benzoquinone etc. gives CT complexes like $[R_3SnSnR_3]^+[TCNE]^-$ and $[Ph_3SnSnPh_3]^+[TCNQ]^-$ as well as free radicals R_3Sn -TCNE., R_3Sn -TCNQ., $[R_3Sn$ -(1,4-benzoquinone).], as shown by ESR studies^{192,193}. Stable free radicals like R_3Sn -TCNQ. (R = Me, n-Pr, n-Bu) and Me_2Sn (TCNQ.)₂ are also obtained by the reactions of the Li-salt of TCNQ with organotin(IV) chlorides¹⁹². Oxidative cleavage of the Sn—Sn bond by electrophiles, e.g., halogens, O_2 etc. has also been studied¹⁹⁵. These cleavage reactions take place through electron transfer from the σ (Sn—Sn)

bond. Complexes of polysilanes, hexamethyl disilanes and hexamethyl germane with TCNE and TCNQ also form in a similar way through σ -electron transfer to the π -acids^{194,195}.

1.3.2.B. Type B Tin(IV) Donors :

The Lewis basicity of compounds such as $(R_3M)_nX$, where X is an electron donor such as N, O, S etc. and M is a group IVB element, have been evaluated from the shift caused in $\nu(C-D)$, due to C—D ----X hydrogen bonding, in their IR spectra in $CDCl_3$. Values for the relative donor strength of some of these organometallic bases measured as $\Delta\nu$ (cm^{-1}) for $\nu(C-D)$ of 'free' and 'H-bonded' states in $CDCl_3$, are illustrated in the table-1.1. below¹⁹⁶:

Table:-1.1.

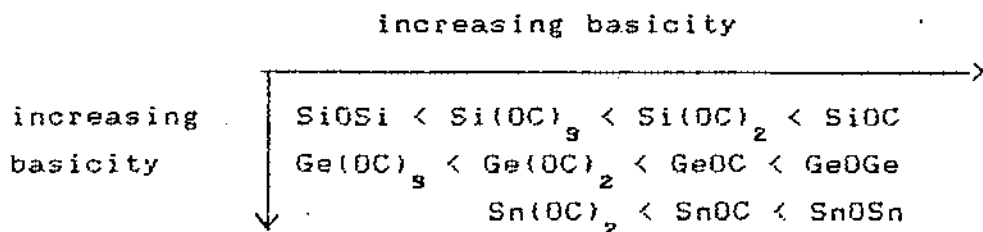
Relative Donor Strength of $(R_3M)_nX$. [as $\Delta\nu$ cm^{-1}].

M	$(Me_3M)_3N$	$(Me_3M)_2O$	$(Me_3M)_2S$
C	100	33	40
Si	0	13	29
Ge	72	55	38
Sn	106	84	43

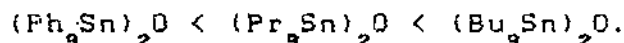
The data in the table reflect differences both in the inductive effects of the group IVB elements and also their capacity to form

$p\pi-d\pi$ bonds with N, O or S. The absence of interaction between $(Me_3Si)_3N$ and $CDCl_3$ implies complete involvement of the nitrogen lone pair in π -bonding in contrast to the strongly basic $(Me_3Sn)_3N$, which is pyramidal, and in which $N \rightarrow Sn$ multiple bonding, if present at all, does little to offset the electron releasing properties of the Me_3Sn group. As a result, the trimethyl stannyl amine is found to be more basic than the organic amine¹⁹⁷. The proton acceptor abilities of the chlorine atom in group IVB organometallic chlorides as measured by the shift of $\nu(OH)$ of phenol in CCl_4 in presence of the chlorides¹⁹⁸ also indicate the same trend. Organotin azides and organotin acylates (R_3SnCOR') also have been found to be stronger bases than their carbon analogues¹⁹⁹⁻²⁰¹.

In compounds such as R_3MOMR_3 and $R_nM(OR')_{4-n}$ (where $n = 1-3$, $M =$ Group IVB metal), the following sequence of basicity for the oxygen atom has been assigned on the basis of IR frequency shifts $\Delta\nu(OH)$ of methanol or $\Delta\nu(NH)$ of pyrrole due to hydrogen bonding with the oxygen atoms of these compounds in methanol or pyrrole solution²⁰².



The increased basicity of the oxygen atom in alkyl or aryl stannoxanes has been confirmed by the isolation of 1:1 and 1:2 adducts of μ -oxo-bis[triphenyltin(IV)] with $TiCl_4$; of $R_3SnOSnR_3$ ($R = n\text{-Pr, } n\text{-Bu}$) with $TiCl_4$ and $SnCl_4$; and 1:1 adducts of μ -oxo-bis[triphenyltin(IV)] with $SbCl_5$, as well as, adducts of di n -butyltin oxide with $TiCl_4$, $SnCl_4$ and $SbCl_5$ ^{203a,204}. μ -oxo-bis[tri n -butyltin(IV)] also react with MX_2 (where $M = Cu(II), Mn(II), Ni(II), Co(II)$; $X = Cl^-, Br^-, I^-, NCS^-$ and NO_2^-) to form compounds of general composition $MX_2.L_4$. Compounds of the type $M(ClO_4)_2.L_6$ also have been reported for $M = Ni(II), Cu(II)$ and $Mn(II)$ ^{205,206}. $(R_3Sn)_2O$ ($R = n\text{-Pr, } n\text{-Bu, Ph}$) forms complexes of stoichiometries $NiCl_2.L.EtOH$ and $Ni_2Cl_4.L.3EtOH$ with $NiCl_2$ in absolute alcohol^{203b}. Amongst these oxoorganotin compounds the donor strength varies as -

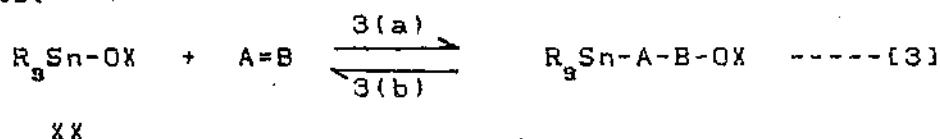


The IR spectra of all these addition products show that the ν_{as} (SnOSn) band of the free stannoxane which appears around 780 cm^{-1} suffers considerable negative shift, thereby indicating that, in all these products the organo stannoxane is coordinated to the metal through oxygen atom^{203a,205,206}.

Beside these adducts with metal halides, organotin oxides and hydroxides are known to combine with organotin halides, $R_2Sn(OH)_2$ and $R_2Sn(OAC)_2$ to form a large number of addition

products in which the oxides or hydroxides donate through the oxygen atom^{5,209a}. Some of these compounds are listed in table-1.2.

The nucleophilicity of the oxygen bonded to tin is important in the addition reactions of the Sn—O bond. Trialkyltin oxides and alkoxides [XX], (X = SnR₃ and R' respectively) often combine with a variety of multiply-bonded acceptors (A=B) to give 1:1 adducts.



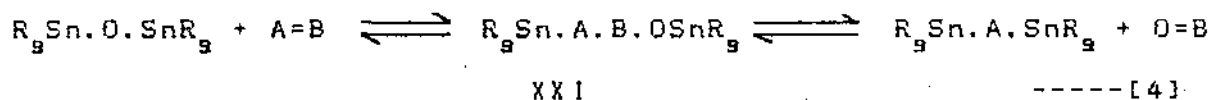
Tributyltin oxide and methoxide which are regarded as model compounds for their respective classes, add on to acceptors, such as, aldehydes and ketones, CO₂, carbodiimides (RN=C=NR), isocyanates (RNCO), CS₂, isothiocyanates (RNCS), SO₂, sulfodiimides (RNSNR), sulfinylamines (RNSO), imines (RNCR), nitriles (RCN), ketenes (CH₂=CO) etc. to give 1:1 adducts^{207,208}, examples of which are shown in the table-1.3.

Most of the additions shown in the table-1.3. occur exothermally at room temperature. The reactions are reversible and the adducts dissociate upon heating. However, the decomposition can proceed by a route other than simple retrogression [eqn. 3(b)] particularly, where oxide adducts are concerned.

Table:-1.2.

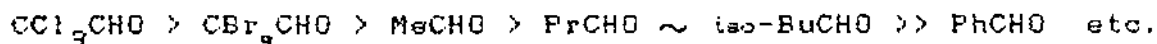
Addition compounds of organotin oxides and hydroxides
with organotin halides and acetates:

Compound type	R	R'	X
$R_2SnO \cdot R'_2SnX_2$	Me	Et, n-Pr	Br, I
	Et	Me	I
		Et	Cl, Br, I
	n-Pr	n-Pr	Br
		Et	Br
		n-Pr	Cl, Br
$(R_2SnO)_2 \cdot R'_2SnX_2$	Me	Me	Cl
$R_2SnO \cdot R'_2SnIOH$	Me, Et,	R' = R	-
	iso-Pr,	,,	-
	iso-Bu,	,,	-
	iso-Pent	,,	-
$R_2SnO \cdot R'_2Sn(OAC)_2$	Me	Me	-
$H(R_2SnO)_3 \cdot OH \cdot R'_2SnX_2$	Me	Me	Br, I
	Et	Me	I
		Et	Cl, Br, I
	n-Pr	n-Pr	I
$R'(R_2SnO)_3 \cdot OR' \cdot R'_2SnX_2$	Me	Me, Et,	Br, I
	Et	n-Pr, n-Bu	I
		Et	Cl, Br, I
	n-Pr	Et, n-Pr	I
$(R_3Sn)_2O \cdot R'_3SnX$	Me	Me	Br, I
$(R_3Sn)_2O \cdot R'_2SnX_2$	n-Bu	Et	Cl
$(R_3Sn)_2O \cdot R'_3SnX_3$	n-Bu	Et	Cl
$R_3SnOH \cdot R'_3SnX \cdot H_2O$	Me	Me	Cl, Br, I
$(R_3SnOH)_2 \cdot R'_3SnX$	Me	Me	Cl, Br, I
	Et	Et	Br

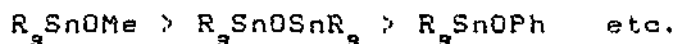


Clearly, the product XXI formed by addition of $R_3Sn.O.SnR_3$ to $A=B$ could equally arise from addition of $R_3Sn.A.SnR_3$ to $O=B$.

The multiple bond of the acceptor being polar, the tributyltin group is attached to the negative end of the dipole $A^{\delta-} = B^{\delta+}$. Hence, structural alterations within a given class of acceptors which increase the electrophilicity of B increase their reactivity. Thus, for carbonyl compounds the acceptor strength changes in the sequence-



The relative power of tin-oxygen bonded compounds to act as addenda by equation 3(a) above, decreases in the sequence-



these suggest that the principal process governing the reactivity is the nucleophilic attack by the oxygen bonded to tin upon the positive end of the dipole and that the electrophilic attack of tin upon the negative end is relatively unimportant.²⁰⁷

Dialkyltin dialkoxides undergo similar reactions²⁰⁷. Dialkyltin oxide and alkyltin trialkoxides are expected to undergo similar reaction, but have not yet been investigated.

Liquid SO_2 in CCl_4 reacts with μ -oxo-bis(triphenyl tin(IV)) in dichloromethane at $-20^\circ C$ to give a 1:1 adduct. In the IR spectrum of the adduct²⁰⁹ the $\nu_{as}(SnOSn)$ appears at 650 and 630

Table:-1.3.

Products of the reaction between Bu_3SnOX and $A=B$:

A=B	$Bu_3Sn.A.B.OX$	
	X = Me	X = $SnBu_3$
$O=CH.CCl_3$	$Bu_3Sn.O.CH(CCl_3).OMe$	$Bu_3Sn.O.CH(CCl_3).OSnBu_3$
$O=C:O$	$Bu_3Sn.O.CO.OMe$	$Bu_3Sn.O.CO.OSnBu_3$
$NpN=C:NNp$	$Bu_3Sn.N.Np.C(:NNp).OMe$	$Bu_3Sn.NNp.C(:NNp).OSnBu_3$
$MeN=C:O$	$Bu_3Sn.NMe.CO.OMe$	$Bu_3Sn.NMe.CO.OSnBu_3$
$O=S:O$	$Bu_3Sn.O.SO.OMe$	$Bu_3Sn.O.SO.OSnBu_3$
$Tol.N=S:N.Tol$	No reaction	$[Bu_3Sn.NTol.SO(=NTol).SnBu_3]$
$Ar.N=S:O$	$[Bu_3Sn.NAr.SO.OMe]^a$	b
$S=C:S$	$[Bu_3Sn.S.CS.OMe]$	c
$S=C:NPh$	$Bu_3Sn.S.C(:NPh).OMe$	d
$SO_2TolN=CHCCl_3$	$[Bu_3Sn.N(SO_2Tol)CH(CCl_3)OMe]$	$[Bu_3SnN(SO_2Tol)CH(CCl_3)OSnBu_3]$
$N=C.CCl_3$	$[Bu_3Sn.N:C(CCl_3)OMe]$	$Bu_3Sn.N:C(CCl_3).OSnBu_3$
$H_2C=C:O$	$[Bu_3Sn.CH_2.CO.OMe]$	$[Bu_3Sn.CH_2.CO.OSnBu_3]$

Notes: Np = 1-naphthyl, Tol = p-tolyl, Ar = $p-NO_2C_6H_4$.

a- The 1:1 adduct only exist in equilibrium with its precursors.

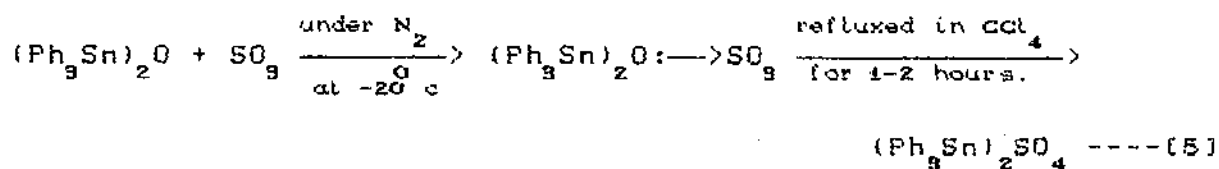
b- A 1:1 mixture of $Bu_3Sn.O.SO.OSnBu_3$ and $Bu_3Sn.NAr.SO.NAr.SnBu_3$ is obtained.

c- $Bu_3Sn.S.SnBu_3$ and $Bu_3Sn.O.CO.OSnBu_3$ are obtained.

d- oxygen-sulfur exchange occurs giving $Bu_3Sn.S.SnBu_3$ and $Bu_3Sn.NPh.CO.OSnBu_3$.

[] Compounds in parenthesis have not been obtained analytically pure.

cm⁻¹, thereby suggesting that it is formed by donor-acceptor interaction between the O atom of the stannoxane and the S atom of SO₃, the former being the donor. Subsequently, on being refluxed in dry CCl₄ for 1-2 hours the adduct undergoes intramolecular rearrangement to give bis[triphenyl tin(IV)]sulfate²⁰⁹ [eqn. 5], which can also be prepared by reacting either the organotin halide with Ag₂SO₄²¹⁰ or the oxide with H₂SO₄¹⁶.

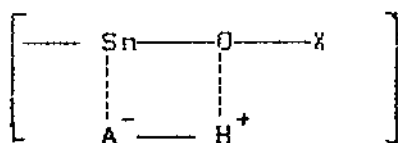


Therefore, it is evident that the adduct is formed as an intermediate in the formation of bis-[triphenyl tin(IV)] sulfate from the reaction of (Ph₃Sn)₂O with SO₃. However, no such intermediate could be detected when (R₃Sn)₂O (where R = n-Pr and n-Bu) and di-n-butyltin oxide reacted with liquid SO₃ and the corresponding sulfates were obtained directly^{209,211}.

It should be stressed that the formation of an intermediate may help a reaction by substantially decreasing the energy of the transition state, even if the intermediate is too unstable to be detected²¹².

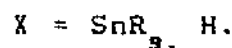
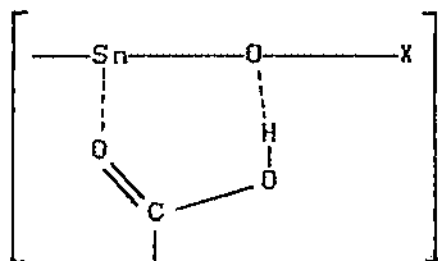
The reaction between organotin oxides/hydroxides and organic or inorganic acids, universally used for the preparation of

organotin esters, is also believed to proceed through an intermediate donor-acceptor transition state, similar to [XXII] proposed for the reaction of siloxanes with AlCl_3 ²¹² and the reaction between $(\text{Ph}_3\text{Sn})_2\text{O}$ and HgX_2 ²¹³.



XXII

The transition state involving organotin oxides/hydroxides and carboxylic acids in non-ionising solvents may be represented by



XXIII

Such a cyclic intermediate is expected to be most favourable, because the nucleophilic attack of the oxygen bonded to tin upon the H-atom and the electrophilic attack by the tin centre upon the O-atom of the carboxylic acid assist each other. Although no evidence in favour of such an intermediate, is available so far, its stability (if it does exist at all) is likely to be enhanced with the increase in the electronegativity of RCO_2^- group of the

acid. Thus, if the reaction is assumed to proceed through the formation of the cyclic intermediate, the presence of strongly electron withdrawing group and additional potential donor atom capable of forming a chelate ring, both most effective if present on the α -carbon atom within R, can create a situation conducive to the realisation of such intermediate in the isolated state.

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