CHAPTER-II

ORGANOTIN CARBOXYLATES : A BRIEF REVIEW.

ORGANOTIN CARBOXYLATES : A BRIEF REVIEW

II.1 *Introduction :*

Organotin carboxylates constitute one of the most important classes of compounds in the ever expanding field of organotin chemistry. Theoretical and structural interests in this class of compounds continue to grow along with the tremendous growth in their industrial, agricultural and other applications.

These compounds are derivatives of tin(IV) and may be of three general types, viz. $R_3SnOCOR'$, $R_2Sn(OCOR')_2$ and $RSn(OCOR')_3$, where, the groups R and R' may either be the same or different. Many discussions on the chemistry of this group of organotin compounds with varying degrees of details are available[1-5] and as such only the more important aspects are presented here.

II.2. *Preparation :*

Organotin carboxylates are prepared through a number of routes, of which the most common and convenient one involves the reaction between organotin oxides (or hydroxides) and carboxylic acids or their anhydrides[6-14] as shown below :

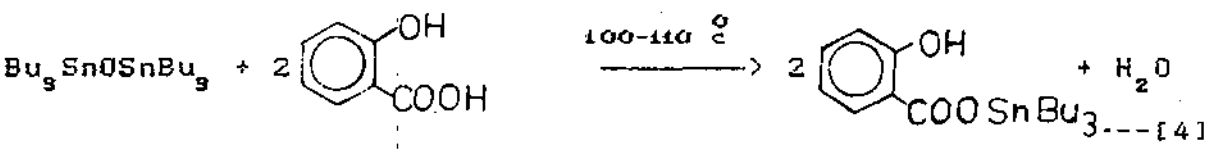
$$R_3SnOSnR_3 + 2R'COOH \longrightarrow 2R_3SnOCOR' + H_2O \text{ ------- [1]}$$

$$R_2SnO + 2R'COOH \longrightarrow R_2Sn(OCOR')_2 + H_2O \text{ ------[2]}$$

$$R_3SnOSnR_3 + (R'CO)_2O \longrightarrow 2R_3SnOCOR' \text{----------[3]}$$

The water produced in these reactions is removed, usually by

azeotropic distillation using a Dean and Stark separator or alternatively by refluxing at higher temperature[15] for example :



---[4]

Triphenyl tin carboxylates, such as, p-$ROC_6F_4COOSnPh_3$, (where, R = Me, Et), p-$(Ph_3SnOCO)_2C_6F_4.H_2O$ and o-$(Ph_3SnOCO)_2C_6F_4.H_2O$ have been prepared by the reaction of Ph_3SnOH with the appropriate polyfluoro carboxylic acids in MeOH[16].

Organotin carboxylates have also been prepared by the reaction of the corresponding organotin halides with the alkali metal or silver salts of carboxylic acids either by stirring at room temperature or by refluxing the reactants in a suitable solvent[13,17-19].

$R_nSnX_{4-n} + (4-n)\ MOCOR' \longrightarrow R_nSn(OCOR')_{4-n} + (4-n)\ MX$ ----[5]

(M = Na, K, Ag or Tl; X = halogen)

Another method for the preparation of organotin esters involves the cleavage of one or more organic groups of tetraorganotin compounds by carboxylic acids[20,21].

$R_4Sn + n\ R'COOH \longrightarrow R_{4-n}Sn(OCOR')_n + n\ RH$ -----[6]

In this acidolysis reaction, the cleavage of organic groups depends on the acid strength, nature of the groups R and R' and also on the temperature[22-24]. Vinyl groups are cleaved more readily than saturated alkyl radicals, but less readily than phenyl groups[25] and successive groups are lost with increasing

difficulty. Tetraalkyltin is more reactive than tetravinyltin[21].

A novel electrochemical method of preparation of trialkyltin carboxylates involving the cleavage of organic groups from R_4Sn (R = Me, Et, Pr, Bu) by Hg(I) carboxylates, has been described by Tagliavini et al[26]. Thus, tetramethyltin produces trimethyltin acetate when treated with Hg(I) acetate in MeOH at room temperature.

$$2Me_4Sn + Hg_2(OCOMe)_2 \longrightarrow 2Me_3SnOCOMe + 2Hg + C_2H_6 \quad \text{------[7]}$$

Organotin hydrides react with carboxylic acids to form the corresponding organotin esters[27,28] with evolution of hydrogen.

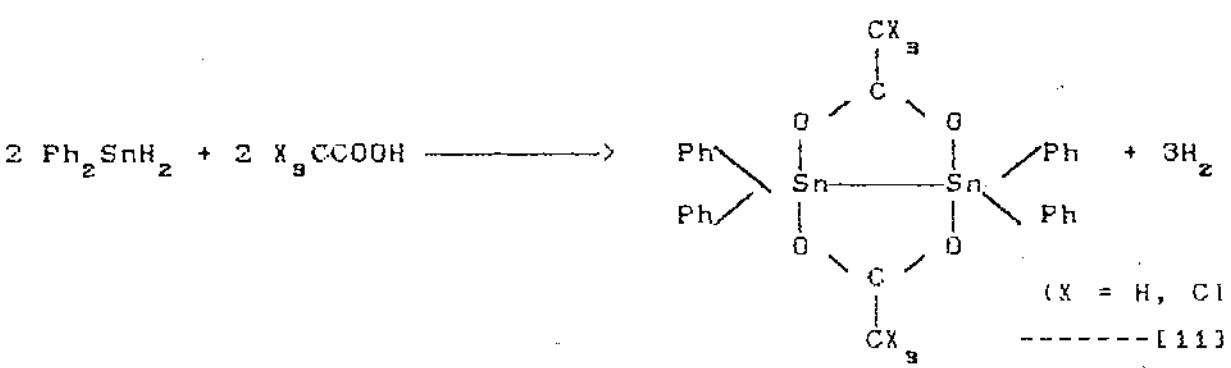
$$R_3SnH + R'COOH \longrightarrow R_3SnOCOR' + H_2 \quad \text{----------[8]}$$

$$R_2SnH_2 + 2R'COOH \longrightarrow R_2Sn(OCOR')_2 + 2H_2 \quad \text{---------[9]}$$

The initially formed dicarboxylate equilibrates with unreacted dihydride as follows[29].

$$R_2Sn(OCOR')_2 + R_2SnH_2 \rightleftharpoons 2R_2Sn(H)OCOR' \quad \text{----------[10]}$$

With di-n-butyltin dihydride the intermediate hydride carboxylate $Bu_2Sn(H)OCOR'$ decomposes to give distannane 1,2--dicarboxylates[27,90,91]. Using similar methods the acetato bridged compounds shown below have been prepared[92].



-------[11]

Halocarboxylate derivatives of organotin compounds are most conveniently synthesised by heating equimolecular mixtures of the diorganotin dicarboxylates and the diorganotin dihalides in an inert solvent[33,34].

$Bu_2SnBr_2 + Bu_2Sn(OAc)_2 \longrightarrow 2Bu_2Sn(Br)OAc$ ---------[12]

These compounds can also be prepared by the reaction of R'COOM (M = Na, K) with diorganotin dihalide as shown below[35,36].

$Bu_2SnCl_2 + KOCOR' \longrightarrow Bu_2Sn(Cl)OCOR' + KCl$ ----------[13]

At 100°C trimethyltin chloride reacts with carboxylic acids to give dimethylchlorotin carboxylate[37] which may also be prepared by the exchange reaction between dimethyltin dichloride and a triorganotin carboxylate in CCl_4 or C_6H_6 at room temperature[33] as shown below.

$Me_3SnCl + R'COOH \longrightarrow Me_2Sn(Cl)OCOR' + MeH$ ----------[14]

$R_2SnCl_2 + R''_3SnOCOR' \longrightarrow R_2Sn(Cl)OCOR' + R''_3SnCl$ --------[15]

A number of dialkylhalotin acetates have been synthesised using the following reactions[38] :

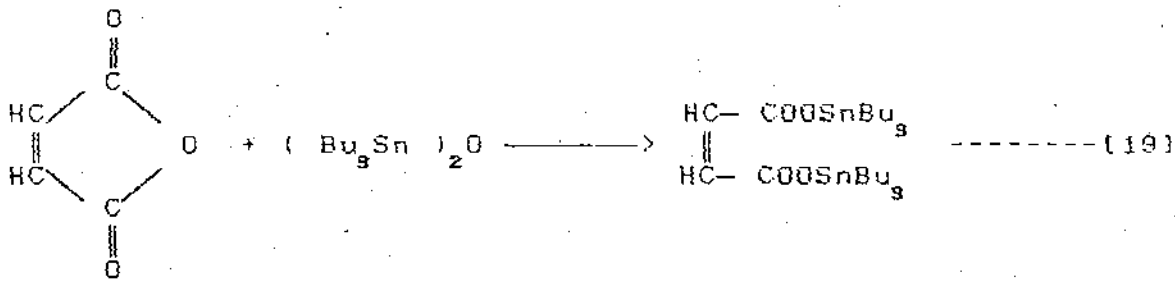
$(R_2SnCl)_2O + 2CH_3COOH \longrightarrow 2R_2(Cl)SnOCOCH + H_2O$ ------[16]

$(R_2SnCl)_2O + (CH_3CO)_2O \longrightarrow 2R_2(Cl)SnOCOCH_3$ ----------[17]

$R_2SnO + ClCOR' \longrightarrow R_2Sn(Cl)OCOR'$ ----------[18]

Anhydride of an unsaturated acid (e.g., maleic anhydride) when reacted with hexabutyl distannoxane produces disubstituted organotin esters[39].

Organotin carboxylates may also be prepared from the esters of carboxylic acids by the reactions [20] and [21][40,41], below.



$$(R_3Sn)_2O + R'COOEt \longrightarrow R_3SnOCOR' + R_3SnOEt \quad \text{----------(20)}$$

$$R_3SnOH + R'COOEt \longrightarrow R_3SnOCOR' + EtOH \quad \text{----------(21)}$$

Tricarboxylate derivatives of the type $RSn(OCOR')_3$ are usually prepared from the corresponding trichlorides by the action of the silver salts of the carboxylic acids[42].

$$RSnCl_3 + 3R'COOAg \longrightarrow RSn(COCOR')_3 + AgCl \quad \text{----------(22)}$$

II.3 *Physical Properties of Organotin Carboxylates :*

The Sn— O bond in organotin carboxylates is essentially covalent, but undergoes polar reactions depending on the solvents and attacking groups. This is why the carboxylates with small organic groups are more soluble in alcohol, ether etc. than in water[2]. The solubility of triorganotin carboxylates is low in common organic solvents because of their polymeric structures. Many of the carboxylates have low melting points indicating these to be covalent compounds.

The polymeric stannoic acids are colorless and infusible. A few of them are soluble in chloroform and carbon tetrachloride and are fairly stable towards hydrolysis. The melting/boiling points of some common organotin esters are listed in

table-II.1.[1,2,4,5,48].

Table:-II.1.

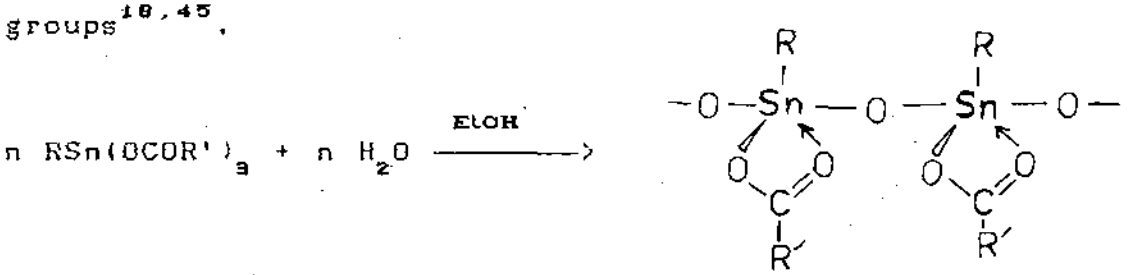
Mp./Bp. of Organotin Carboxylates :

Compound	Mp.(^{o}c) Bp.(^{o}c/mm Hg)	Compound	Mp.(^{o}c) Bp.(^{o}c/mm Hg)
$Me_3SnOCOMe$	196.5-197.5	$Bu_2Sn(OCOMe)_2$	144.5-145.5/10
$Ph_3SnOCOH$	202-203	$Ph_2Sn(OCOMe)_2$	116-117
$Ph_3SnOCOPh$	84-85.5	$Bu_2Sn(OCOCH=CHMe)_2$	34
$Bu_3SnOCOH$	120-125/0.7	$Bu_2Sn(OCOC_{11}H_{23}^{n})$	22-24
$Bu_3SnOCOMe$	85		
$Bu_3SnOCOPh$	166-168/1	$BuSn(OCOMe)_3$	46
$(Cy\text{-}hex)_3SnOCOMe$	62-63	$EtSn(OCOPh)_3$	185-188
$Ph_3SnOCOMe$	121-122	$PhSn(OCOMe)_3$	76
$Pr_3SnOCOMe$	99-100		
$Pr_3SnOCOCF_3$	88-90/1	$Et_2Sn(Cl)OCOMe$	94
$Et_3SnOCOMe$	134-135	$Bu_2Sn(Br)OCOMe$	67-68.5

II.4 *Chemical properties of Organotin Carboxylates :*

Most triorganotin carboxylates are hydrolytically stable, whereas the diorganotin derivatives undergo partial hydrolysis to produce the dimeric distannoxanes $R_2Sn(OCOR')OSnR_2(OCOR')$ and $R_2Sn(OCOR')OSnR_2OH$[4,44]. The monoorganotin tricarboxylates are readily hydrolysed in ethanol to form the monoorganotin oxycarboxylates[42] which exist as polymers or olygomers in the solid state with Sn— O— Sn bridges and chelating carboxyl

groups[18,45].



+ 2n R'COOH -----[23]

The most widely studied reactions of organotin carboxylates are decarboxylation and disproportionations. The thermal decarboxylation of triorganotin carboxylates[46] has been used for the preparation of trialkyltin hidrides[47] (equation 24), trialkyl-alkynyltins (equations 25,26)[48], triorgano cyanomethyltins (equation 27)[49] and polyfluorophenyl triphenyltins (equation 28)[16].

$$R_3SnOCHO \xrightarrow[(R = Pr,Bu)]{100\text{-}170^{o}C} R_3SnH + CO_2 \text{ ----------[24]}$$

$$R_3SnOCOC = COCOSnR_3 \xrightarrow[(R = Et,Pr,Bu)]{160^{o}C} R_3SnC = CSnR_3 + 2CO_2 \text{---[25]}$$

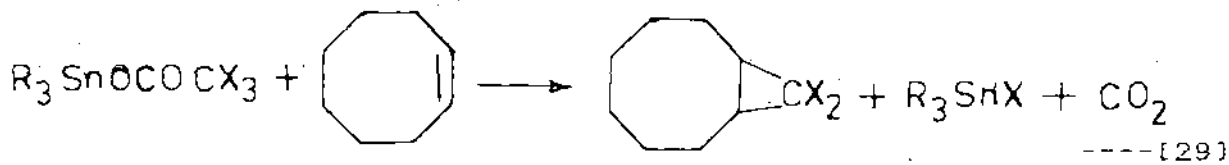
$$Bu_3SnOCOC{=}CPh \xrightarrow{60^{o}C} Bu_3SnC = CPh + CO_2 \text{ ---------[26]}$$

$$R_3SnOCOCH_2CN \xrightarrow[(R = Bu,Ph)]{140\text{-}150^{o}C} R_3SnCH_2CN + CO_2 \text{ ------[27]}$$

$$Ph_3SnOCOR \xrightarrow[(R = C_6F_5, C_6F_4OMe\text{-}4, C_6F_4OEt\text{-}4)]{\text{Boiling Py}} Ph_3SnR + CO_2 \text{ ----[28]}$$

The $Ph_3SnOCOR$ (R = C_6F_5, C_6F_4OMe-4, C_6F_4OEt-4) compounds undergo disproportionation reactions also, to form $Ph_2Sn(OCOR)_2$ and Ph_4Sn[16]. Seyferth et.al.[50] have successfully used the reaction of triorganotin carboxylates of halogen substituted carboxylic

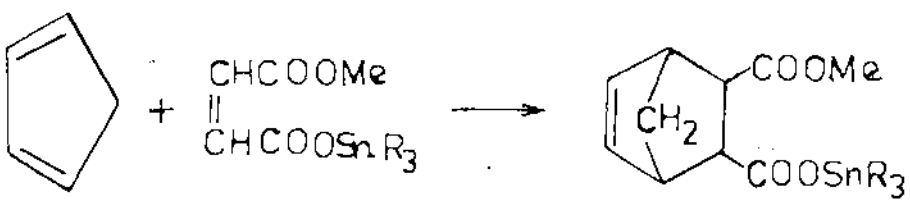
acids with cyclooctene as a carbene transfer reaction, although the reaction mechanism is not yet established.



----[29]

(R = Me, Ph; X = Cl, Br)

Diels-Alder type reactions have been carried out with organotin carboxylates and dienes[35,39].



---[30]

(R = Bu, Ph)

With thiols the following equilibrium is established and the reactions can be driven from left to right by removing the organic acid from the reaction mixtures[51].

$R_3SnOCOR' + R''SH \rightleftharpoons R_3SnSR'' + R'COOH$ ----------[31]

Action of alkoxy derivatives of metals and metalloids on organotin carboxylates produce metallostannoxanes[52,53] as shown below :

$Ph_3SnOAc + Ph_2Si(OEt)_2 \longrightarrow Ph_2Si(OSnPh_3)_2 + 2EtOAc$ ----[32]

$Bu_3SnOAc + Ti(OBu)_4 \longrightarrow Bu_3SnOTi(OBu)_3 + BuOAc$ ----------[33]

Organotin carboxylates readily undergo redistribution with other organotin compounds to form mixed organotin carboxylate derivatives (equations 10, 12, 15, 34)[4,54,55].

$$R_2Sn(OCOR')_2 + R_2SnX_2 \longrightarrow 2R_2Sn(OCOR')X \quad \text{----------[34]}$$

(X = hal.,OR,H,etc.)

In some cases carboxylate groups of the organotin ester may be exchanged with that of a free acid as shown below [17,56]:

$$AcOBu_2SnOSnBu_2OAc + 2Bu^tCOOH \longrightarrow (Bu^tCOO)Bu_2SnOSnBu_2(OOCBu^t) + 2AcOH \quad \text{-----[35]}$$

Oligomeric acetate is usually formed when a dialkyltin diacetate and a dialkyltin dialkoxide are heated at 180°C in water for 2 hours[57,58]. Oligomeric α-w diacetoxy stannoxanes are also obtained by the reaction[50]

$$Bu_2Sn(OAc)_2 + H_2O \xrightarrow{CH_2N_2} AcO(Bu_2SnO)_nSnBu_2OAc + MeOAc \quad \text{----[36]}$$

(n = 1,3,7,15)

Some triorganotin esters[60,61], most commonly the triorganotin acrylates or methacrylates, undergo polymerisation or copolymerisation under the influence of heat or free radical initiators.

$$n\ CH_2{=}\!=\!CR' \longrightarrow \left[-CH_2-CR'-\right]_n \quad \text{----[37]}$$
$$\qquad\qquad\quad CO_2SnR_3 \qquad\qquad\quad CO_2SnR_3$$

(R' = H or Me)

Generally, the organotin esters are weaker Lewis acids than organotin halides, so complex formation by esters is less extensive than by the halides. This weaker acidity appears to be essentially an inductive effect and may be related to the lower electron withdrawing power of the $ROCO^-$ group compared to the

halogen atom[62]. The presence of electron withdrawing groups attached to the tin and/or the $ROCO^-$ moiety[69] increases the Lewis acidity at tin and is expected to favour complex formation by the carboxylates. This explains why in the majority of the adducts of the di- and tri-organotin carboxylates with N, O and S containing ligands, reported so far[9,62,64-73], the organotin carboxylates are derivatives of halo carboxylic acids such as CF_3COOH or CCl_3COOH[65,66,69,72,73].

II.5. *Structure Of Organotin Carboxylates :*

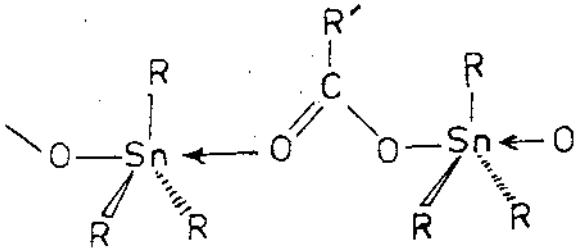
The commercial viability of organotin carboxylates has necessitated understanding of the bonding in these compounds to establish the relationship between their biocidal as well as non-biocidal activity with structure. Consequently, in recent years there has been an upsurge in the synthesis and structural elucidations of various organotin esters of well known carboxylic acids.

As early as 1961, Beattie and Gilson[74] suggested the structure involving intermolecular bridging through carboxyl oxygen atom, as an alternative to the ionic bonding previously postulated by Freeman[75] and Okawara[76]. Since then various physical methods like I.R., ^{119m}Sn Mossbauer, ^{119m}Sn NMR spectroscopy and X-ray diffraction studies have been utilised to deduce the structures of this class of compounds. The subject has been discussed and reviewed by several authors[1-5]. The salient

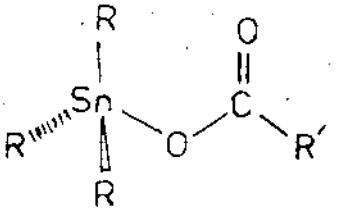
features of the structures of the three type of organotin carboxylates are discussed below.

II.5.A. Triorganotin carboxylates [$R_3SnOCOR'$] :

The triorganotin caboxylates are rich in structural possibilities. Generally, their solubilities in organic solvents are poor, because of their polymeric associated structure [1]. In the solid state the structure of trialkyltin carboxylates are polymeric involving bridging carboxylate groups and planner and near planner R_3Sn moieties[4], the geometry at the metal atom being trigonal bipyramidal [1].



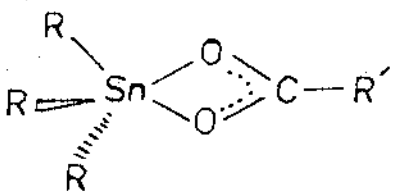
I



II

Thus IR spectrum of trimethylstannyl acetate in the solid state consist of ν_{as}(OCO) and ν_s(OCO) stretching frequencies at 1576 cm^{-1} and 1428 cm^{-1} respectively, indicating the presence of symmetrical carboxyl group as in $NaOCOCH_3$[77] . Appearance of a single Sn-C stretching band in $Me_3SnOCOMe$ is consistent with planner trimethyltin group. The associated polymeric chain

structure [I] has been demonstrated crystallographically for $Me_3SnOCOMe$, $Me_3SnOCOCF_3$[78], $Me_3SnOCOH$[9], Bz_3OCOMe[79], $(CH_2=CH)_3OCOCCl_3$[80] and $Me_3SnOCOC_4H_3S$[81].



III

On dissolving the compounds in nonpolar, noncoordinating solvents, the carboxylate absorption bands [ν_{as}(OCO) and ν_s(OCO)] are shifted to around 1650 cm^{-1} and 1300 cm^{-1} respectively, with the appearance of both ν_{as}(Sn-C) and ν_s(Sn-C) bands indicating the breakdown of polymeric structure [I] into monomers [II] with essentially tetrahedral tin atoms having ester-like carboxylate groups bonded to it. Molecular weights of the carboxylates in benzene and CCl_4 also support monomeric structure [II] in solution with the exception of trimethyltin formate. The insoluble form of the latter, when heated with cyclohexane in a sealed tube at 90^oc, is converted into a soluble form, which exists as an equilibrium of associated and unassociated forms in CCl, but monomeric in ethanol[82].

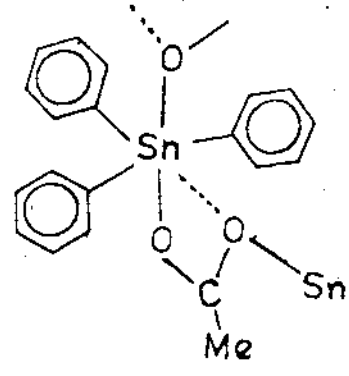
However, when the group R and/or R' is bulky or when there is branching at the carbon atom α to the tin atom (e.g., triphenyltin 2-ethyl hexoate) the compounds assume monomeric

ester-like structure [II] in the solid state, as a result of steric hindrance[18,83-87]. Thus, X-ray study on $Cy_3SnOCOMe$ showed the presence of discrete molecules, with the tin atom occupying a distorted tetrahedral geometry[85], although Majee et.al. have doubted such a representation[108]. Crystallographically authenticated claim in favour of structure [II] has also been made for tricyclohexylstannyl 1,3-indolyl acetate by Zuckerman et.al.[88]. Similar monomeric structures have been suggested for the sterically hindered trineophyltin formate and acetate on the basis of Mossbauer and I.R. spectroscopy[86,87].

In the structure of the bis-(trimethyl stannyl)ester of a dicarboxylic acid $Me_3SnOCOCH_2OCOSnMe_3$[89], each carboxyl group links planar Me_3Sn moieties intermolecularly to form a three dimensional polymeric network. In the derivatives of 2,6-pyridine dicarboxylic acids, structures [149] with trigonal bipyramidal tin atom environment involving unidentate carboxylate groups linking two different tin centres have been established recently.

Among the triphenyltin derivatives, $Ph_3SnOCOCHMe_2$ and $Ph_3SnOCOCH=CH_2$ are penta-coordinate one dimensional polymers possessing structure [I] in the solid state, whereas, $Ph_3SnOCOCMe_3$, $Ph_3SnOCOC(Me)=CH_2$, $Ph_3SnOCOCCl_3$[66,69,73] and $(p\text{-tolyl})_3SnOCOCCl_3$[90] are said to be tetra-coordinate monomers (structure [III]) in the solid state as well as in solution. The $\nu_{as}(OCO)$ band in the I.R. spectra of all these latter compounds appear above 1600 cm^{-1} both in the solid and solution state. While

the carboxylate bridged trans-C_3SnO_2 chain structure of triphenyltin carboxylates have been adequetly supported by X- ray analysis[91-95], the tetrahedral monomeric structure has been authenticated crystallographically only for a few compounds, such as the triphenyltin esters of anthranilic and salicylic acids[96,97] and the triphenyltin derivative of thiophene 2-carboxylic acid ($Ph_3SnOCOC_4H_3S$)[98]. However, triphenyltin acetate, on careful X-ray analysis appears to have a distorted six coordinate mer-Ph_3SnO_3 geometry at tin as shown below[99].



IV

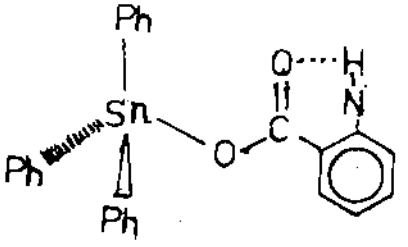
The intra molecularly chelated structure [III] involving bidentate carboxylic group has been assigned to some triorganotin esters of carboxylic acids, especially Ph_3Sn-derivatives of substituted benzoic acids, on the basis of I.R., NMR and Mossbauer spectroscopy[96,97,100-103,144]. The ν_{as}(OCO) mode in solid triphenyltin benzoate is found at 1620 cm^{-1} [104] and in

tri-n-propyl and tri-n-butyl tin benzoates, which are liquids, at 1565 cm^{-1} and 1640 cm^{-1} [105,106] respectively. Since the $\nu_{as}(OCO)$ mode is not shifted towards higher frequencies in solution, it is likely that, structures adopted in both states contain chelated benzoate groups[38]. However, examples of this geometry among trialkyl tin esters[100,101] are extremely rare, due probably, to the lower electronegativity of the alkyl than the phenyl group, which disfavours axial occupancy of the alkyl group in the trigonal bipyramidal structure.

Data for $Ph_3SnOCOC_6H_4X$ [where X = $2\text{-}NH_2$, $4\text{-}NH_2$, $2\text{-}NMe_2$, 2-OH, 4-SMe] have all been interpreted in terms of 5 coordinated structure [III], although this has been questioned[107]. From ^{119}Sn NMR and Mossbauer studies of $Ph_3SnOCOC_6H_4X$ [where X = H, 2-Me, $2\text{-}NH_2$, $2\text{-}NMe_2$, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 4-SMe, 2-OMe] in solution and in solid phases, Molloy et.al. have assigned a coordination number of four at tin in all the compounds in solution as well as in solid state with the exception of 2-Cl and 2-OH derivatives[107]. The 2-Cl and 2-OH derivatives are said to exhibit carboxylate/hydroxyl bridged polymeric structure.

On the basis of crystallographic data Holmes et.al assigned the intramolecularly five coordinate structure [III] to the 4-chloro- derivative[91], but Molloy et.al continues to prefer the tetrahedral monomeric structure[69]. The tetrahedral arrangement around tin in these compounds is supported by the X-ray diffraction studies on triphenyl tin esters of anthranilic and

salicylic acids[96,97], in which the carbonyl oxygen is only hydrogen bonded with the substituent at the ortho position of the benzene ring as shown below :



V

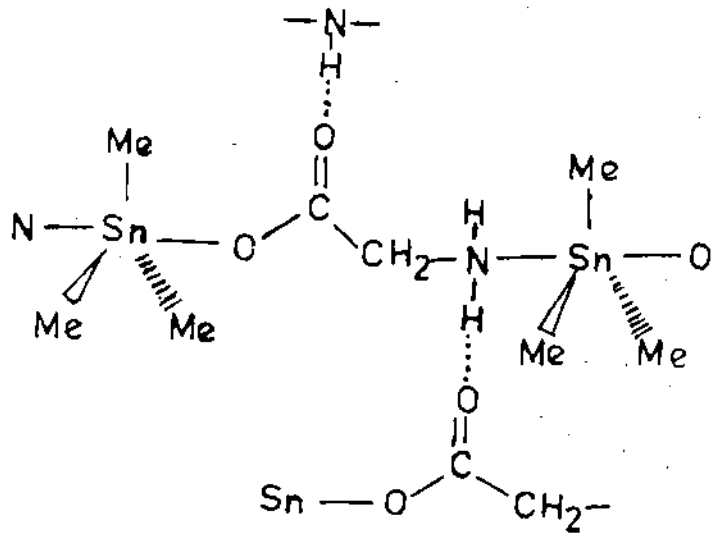
However, in the triphenyltin anthranilate and salicylate the geometry is distorted towards trigonal bipyramidal, because of the approach of oxygen of the $RCOO^-$ moiety at a tetrahedral face opposite one of the tin-phenyl groups and the Sn---O (carbonyl) distances (2.823 A^o in the anthranilate and 3.071 A^o in the salicylate) are indicative of weak interactions[96,97].

The only yet undisputed structure of type [III] has been demonstrated crystallographically for triphenyl tin o-(2-hydroxy-5-methyl phenyl azo)benzoate[108].

It should be noted here that among the $R_3SnOCOC_6H_4X$ compounds (where X is a donor group), there is no convincing evidence in favour of the involvement of the substituent X on the benzene ring in intramolecular coordination leading to chelate rings. On the other hand, there is evidence that the X group may be linked to a tin centre which is not at all carboxylated. Such

examples are provided by triorganotin derivatives of mercapto carboxylic acids[145]. However, examples of monomeric carboxylates in which the carboxylate group is part of a chelated ring formed by intramolecular coordination of N—>Sn have been provided by Majee et.al[109-111], for tri- and di-organotin derivatives of arylazo benzoic acids and arylazo phenoxy acetic acids.

Unlike the triorganotin carboxylates cited so far, the structure of trimethyl tin glycinate is unique in having lone pair donation through nitrogen giving a one dimensional amino bridged polymer and trigonal bipyramidal geometry at tin. There is hydrogen bonding between carbonyl oxygen and amino N— H between the chains[112].



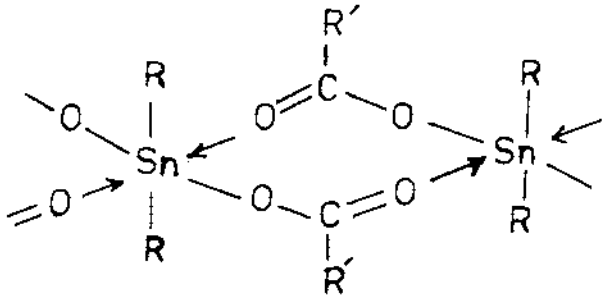
VI

This structure seems unusual since the affinity of tin for oxygen is greater, but the structure has been demonstrated crystallographically[112]. Similar structure has also been demonstrated for di-t-butyltin glycylglycinate monohydrate[146], with the exception that, the equatorial plane is composed of two Bu groups and one N atom of the tridentate ligand. The water molecule present contributes to the H-bonding net work.

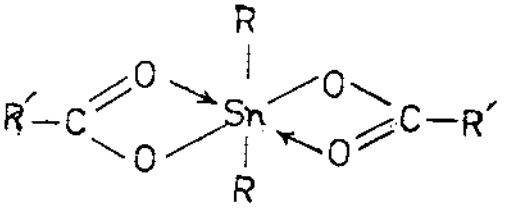
From the above observations it is apparent that in spite of accumulation of large amount of structural information on triorganotin carboxylates it is still not clear what properties of the R and R' groups determine which of the structures I, II, III is adopted in the solid state.

II.5.B. Diorganotin Dicarboxylates $[R_2Sn(OCOR')_2]$:

The structure of dialkyltin dicarboxylates was first suggested for dimethyltin diformate by Okawara[76] as consisting of a linear Me_2Sn cation and formate anion. Mossbauer[113,114] and I.R.[4,115] studies on a number of dialkyltin dicarboxylates suggest that in the neat liquid or solid states, these adopt a polymeric structure [VII] with intermolecularly bridging carboxylate groups and an octahedral trans-R_2SnX_4 tin atom geometry. X-ray crystallographic evidences in favour of this structure are, however, lacking. In solution, these compounds are monomeric and probably possess an octahedral intramolecularly chelated structure [VIII][4,115].



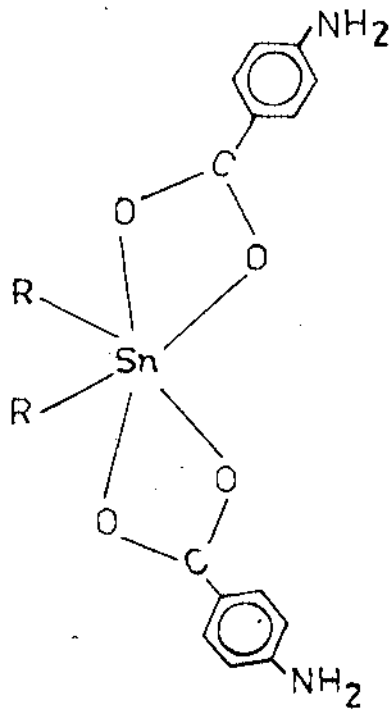
VII



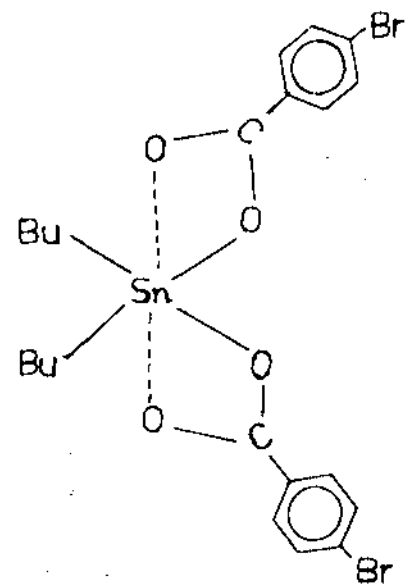
VIII

Recently, some dialkyltin dicarboxylates have been shown from crystallographic studies, to have monomeric structure in the solid state[116-119]. Thus from X-ray studies the mono nuclear $Me_2Sn(OCOC_6H_4\text{-}p\text{-}NH_2)_2$ has been assigned a distorted octahedral cis-R_2SnX_4 geometry around tin[116] as shown in structure IX. The structures of $^nBu_2Sn(OCOCH_2SC_6H_5)_2$[117], $^nBu_2Sn(OCOC_6H_4\text{-}p\text{-}Br)_2$[118], $Et_2Sn(OCOC_4H_3S)_2$[147] and $Pr_2Sn(OCOCH_2SPh)_2$[148] have been described as having a skew trapezoidal bipyramidal geometry at tin, also with a cis-R_2SnX_4 disposition as shown in figure (X). The $^nBu_2Sn(OCOC_6H_4\text{-}o\text{-}Br)_2$ has, however, been shown[120] to have, in the solid state, a distorted pentagonal bipyramidal geometry with trans Bu groups, due to dimerisation through weak interaction between a tin atom and a carboxylate-O atom linked to the other tin atom (XI). In solution the dimer dissociates.

In polymeric dimethyltin dipicolinate, where both carboxylate groups bridge successive atoms, tin is formally seven



IX

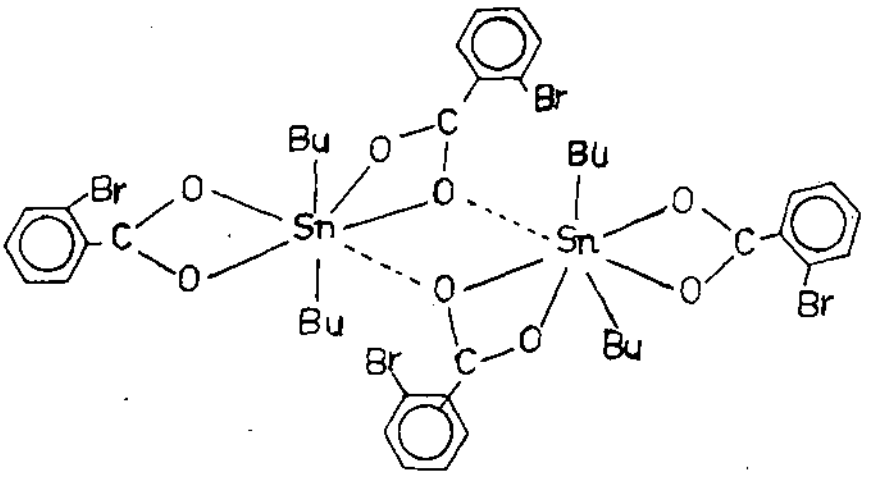


X

coordinate due to the formation of intramolecular tin-nitrogen bond[142]. Sandhu et.al. also have suggested the involvement of the N atom in intramolecular coordination in derivatives of picolinic acid [$R_2Sn(pic)_2$; where, R = Me, n-Bu, n-Oct and Bz.] on the basis of Mossbauer studies[149]. A distorted trans octahedral structure involving unidentate carboxylate groups has been suggested for these compounds. However, a weak C=O----Sn bridging interaction has not been ruled out in some compounds.

On the basis of IR, NMR, and ^{119}Sn Mossbauer studies, the intramolecularly chelated octahedral trans-R_2SnX_4 geometry around

tin [VIII] has been suggested for the diorganotin derivatives of 3-Benzoyl propionic acid[99], 2-Benzoyl benzoic acid[121] and some N-substituted amino acids[122-124].



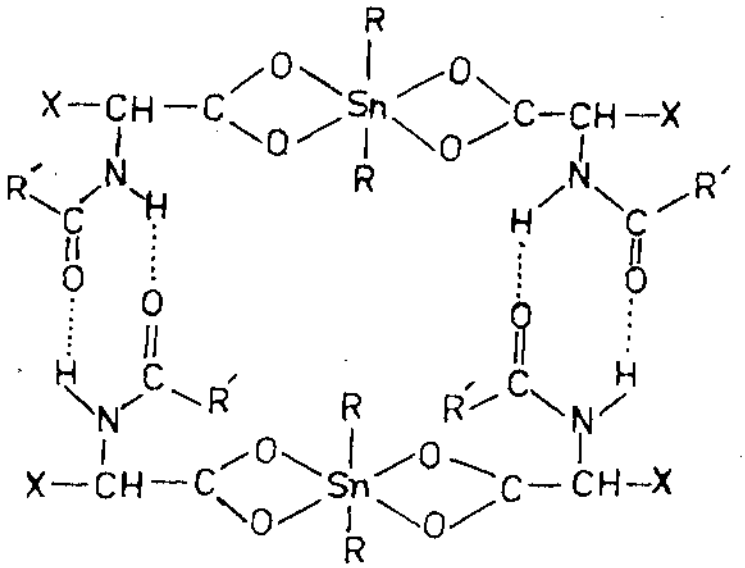
XI

The aminoacid derivatives dimerise due to H-bonding through the functional substituents on the amino N atom as shown below [XII][122,129]:

However, from X-ray studies, Sandhu et.al. have shown that [$Bu_2Sn(A)$] (where, HA = monochloro acetyl-L-phenyl alanine) has a monomeric structure with skew trapezoidal planar geometry around tin[150], instead of the octahedral geometry shown above [XII].

In addition to the 1:2 complexes shown above the aminoacids form similarly hydrogen bonded carboxy diorgano stannoxanes of the type $R_2(L)Sn\text{-}O\text{-}Sn(L)R_2$, where, the geometry around tin atom is trigonal bipyramidal trans-R_2SnX_3, involving chelating carboxylate groups[122-124,150].

In the diorganotin derivatives of mercapto carboxylic acids

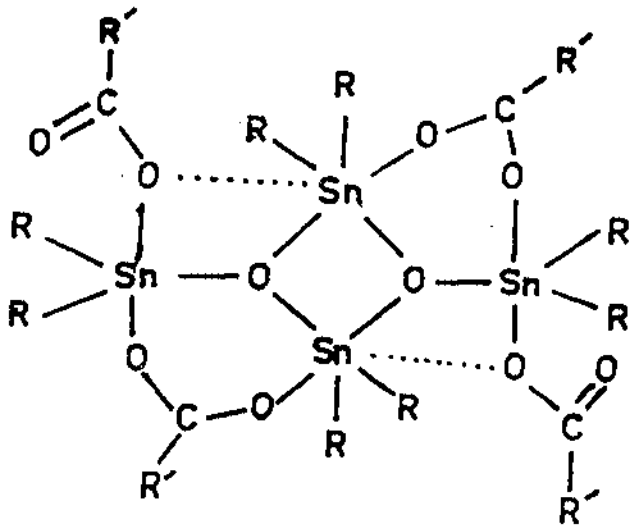


XII

also, Mossbauer[151] and X-ray[152] data indicate that the tin atom geometry is trigonal bipyramidal, nonlinear polymeric compounds being formed through the involvement of the S atom and bridging bidentate carboxylate groups.

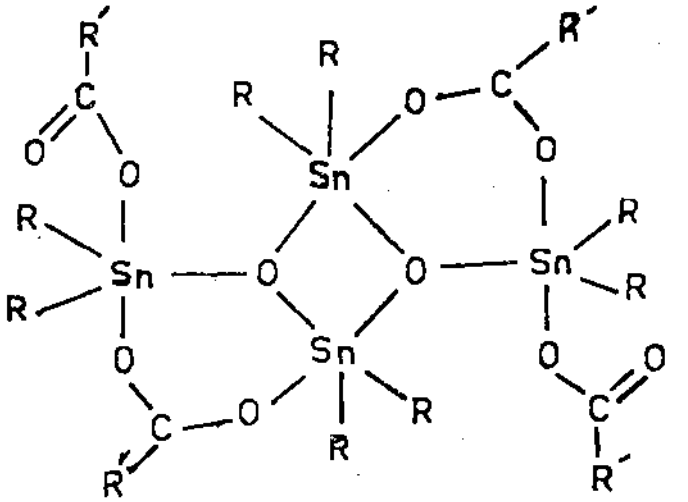
The reaction between diorganotin oxides and carboxylic acids often leads to the formation of carboxy diorgano stannoxanes, which are hydrolysed derivatives of the diorganotin carboxylates. A survey of the literature reveals that, diorganotin esters in general, and carboxy diorgano stannoxanes carrying ligands with functional substituents in particular, have not received attention commensurate with their structural possibilities[116,125-128]. As far back as in 1977, Tagliavini et.al. suggested the following dimeric structure [XIII] involving both monodentate and bidentate

carboxylate groups for tetrabutyl-1,3-trichloroacetoxy distannoxane $[(^{n}Bu_2SnOCOCCl_3)_2O]_2$ and similar compounds[125,129] in the solid state, as well as in CCl_4 solution, on the basis of IR spectra and X-ray studies. In more polar solvents like $CHCl_3$ the weak Sn----O bonds shown in structure XIII are broken and partial depolymerisation occurs and structure XIV and XV are supposed to be present[125].

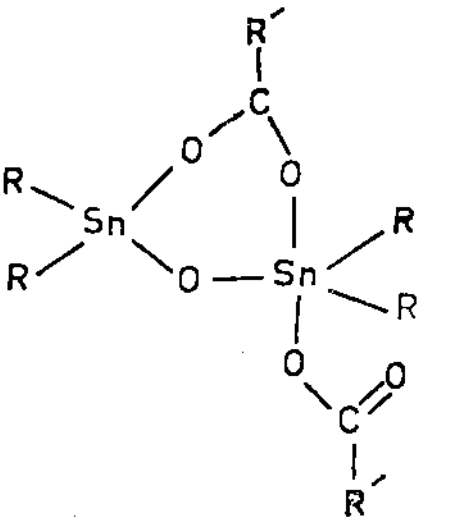


XIII

The distinctive features of these structures are the presence, in each, of two different tin atom geometries and two types of unique carboxylate groups, one of which bridges two tin centres, though weakly, via one oxygen atom only, the carbonyl oxygen remaining free. Further experimental support for the above structure XIII with a planar four membered Sn_2O_2 ring, of tetraalkyl dicarboxy



XIV

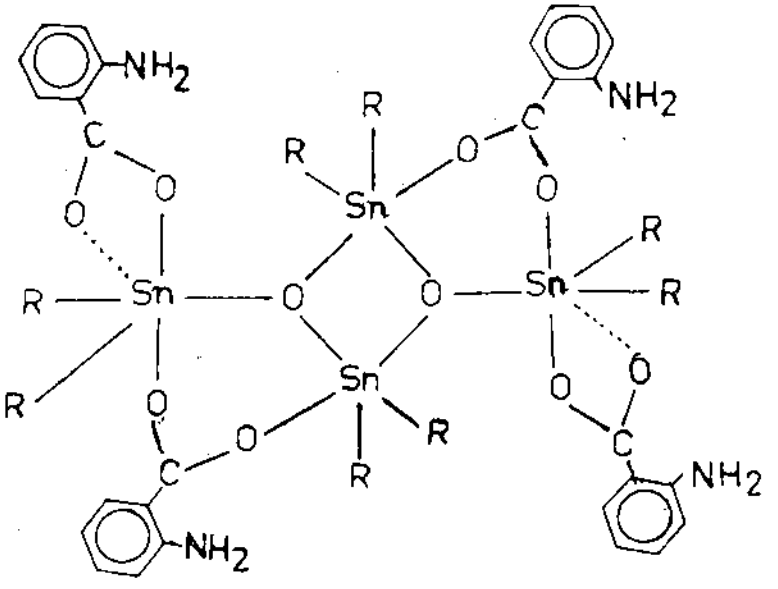


XV

distannoxane has only recently been provided from crystallographic studies of $[(Me_2SnOCOC_6H_4\text{-}o\text{-}NH_2)_2O]_2$[116], $[(^nBu_2SnOCOC_6H_4\text{-}o\text{-}NH_2)_2O]_2$[128], $[(^nBu_2SnOCOC_6H_4\text{-}o\text{-}OMe)_2O]_2$[119], $[(Bu_2SnOCOC_4H_3S)_2O]_2$[153] and other compounds[148]. However, the structure assigned to these compounds [XVI] differs slightly from structure XIII due to the involvement of the carbonyl oxygen in weak Sn----O interaction, thus rendering both the endocyclic and exocyclic tin atoms six-coordinate[116].

The tetraorgano stannoxane structure suggested for $[Me_2SnOCOC_6H_4\text{-}p\text{-}NH_2)_2O]_2$[116] differs considerably from both structures XIII and XVI in having two different tin atom geometries, but only one type of essentially monodentate carboxylate group, one oxygen atom of which bridges two tin centres through weak Sn----O interaction [XVII] . The other oxygen

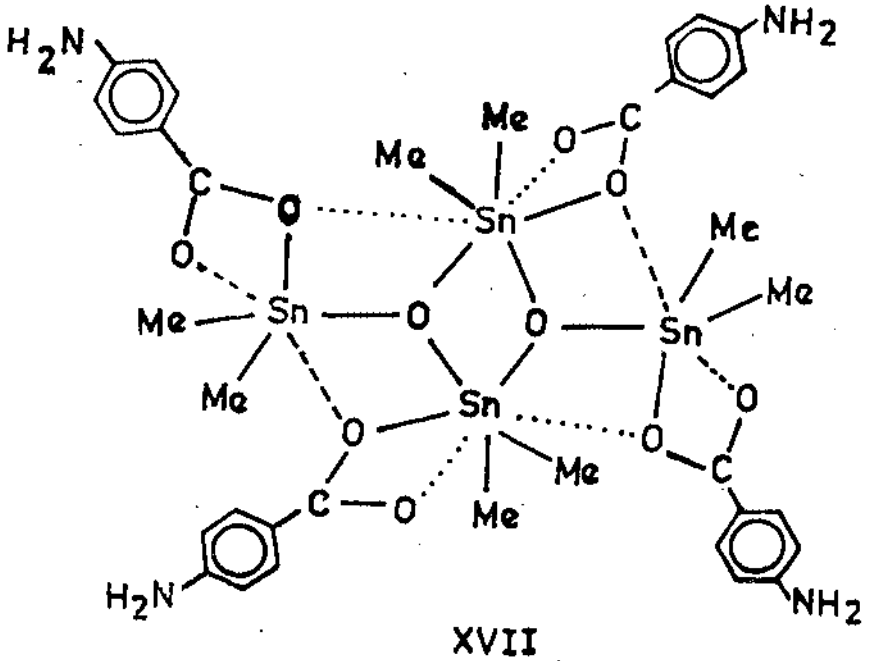
atom is also involved in weak Sn----O interaction.



XVI

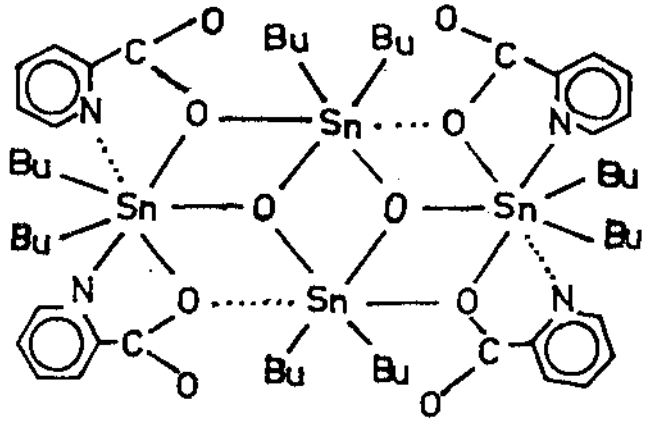
Crystal structure determination of $[Bu_2SnOCOC_5H_4N)_2O]_2$ [130] reveals that the 2-pyridine carboxylate ligand introduces a major change in the dicarboxylato tetraorgano stannoxane structure as a result of the formation of Sn—N bond [XVIII]. The centrosymmetric dimer features two unique carboxylate groups, one of which bridges two tin centres via one oxygen atom (the pendant oxygen atom is not coordinated but the N atom is weakly associated to tin).
The other carboxylate functions essentially in the monodentate mode (the carboxylate oxygen atom is involved in weak bridging interaction) and a chelate ring is formed through the formation of Sn—N bond. One tin atom is six coordinate and the other is seven coordinate by virtue of weak but significant intramolecular

interactions.



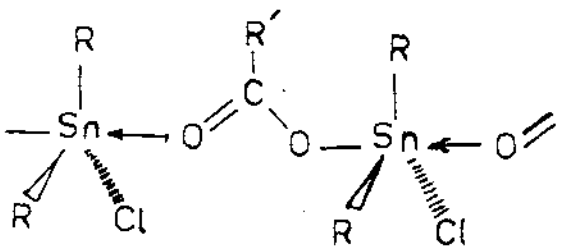
XVII

The dialkyl halotin carboxylates $R_2Sn(OCOCR')X$ are believed

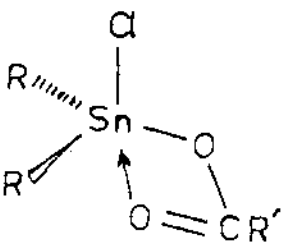


XVIII

to possess intermolecularly bridging and intramolecularly chelated structures XIX and XX, in solid state and solution respectively, with the tin atoms occupying a trigonal bipyramidal cis-R_2SnX_3 geometry[38]. These structures are quite similar to the structures I and III of the triorganotin carboxylates, the halogen atom of the former occupying the position of a R group of the latter.

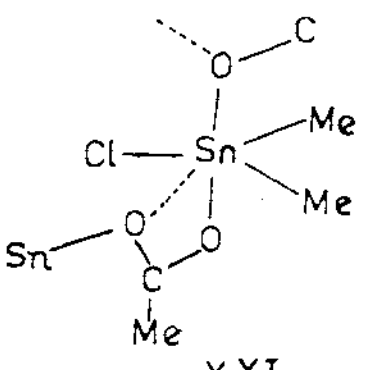


XIX



XX

X-ray studies of polymeric dimethyl chlorotin acetate[191], however, reveals that the tin atom is in a distorted trigonal bipyramidal environment, the distortion being attributed to a weak but

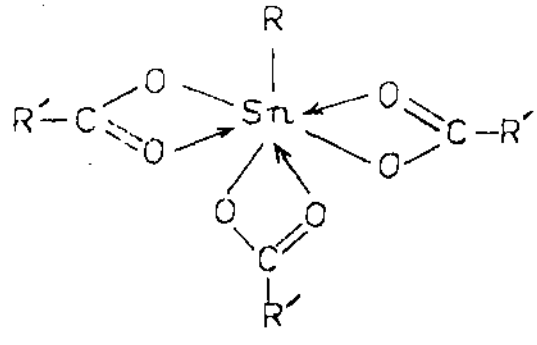


XXI

significant carbonyl O---Sn interaction resulting in the tin atom becoming six coordinate [XXI], resembling the structure of triphenyltin acetate [IV].

II.5.C. Monoorganotin Tricarboxylates [$RSn(OCOR')_3$] :

The structure of this type of organotin carboxylates have not been adequately elucidated. No X-ray studies are yet available on any monoorganotin tricarboxylate. The IR spectra of a number of monoorganotin esters in CCl_4 solution show coordinated carbonyl stretching bands, and additionally, $BuSn(OCOMe)_3$ and $BuSn(OCOEt)_3$ were found to be monomeric in camphor solution[42]. This is indicative of seven coordinated tin atom geometry for these compounds in solution [XXII].



XXII

II.6. *Organotin Keto carboxylates :*

Although triorganotin(IV) carboxylates are mostly five coordinate carboxylate-bridged polymers whose repeat units are

propagated in a zig-zag or helical manner in the crystal lattice[192], a bonding mode alternative to carboxyl bridging may become possible if the carboxylate group contains a substituent carrying a donor atom. The involvement of the additional donor atom in bonding may result in either a intramolecularly chelated ring structure or intermolecularly bridging polymeric structure. This latter option is adopted in trimethyltin glycinate [VI], where bridging occurs axially at tin along the chain through the amino nitrogen atom[112]. This seems unusual, since the affinity of tin for oxygen coordination is believed to be greater, and has generated tremendous interest in the solid state structure of organotin carboxylates containing an additional potential donor atom in the carboxylate moiety. Among many such compounds organotin esters of substituted benzoic acids and some amino acid derivatives have received much attention in recent years.

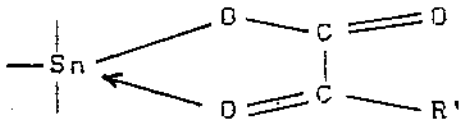
Keto carboxylic acids, though potentially polydentate, and apparently capable of forming a chelate ring, have not received adequate attention. KumarDas et.al. have investigated the tri- and diorganotin esters of some γ-keto carboxylic acids, viz, hippuric acid, succinanilic acid, levulinic acid[193] and 3-benzoyl propionic acid[98]. On the basis of IR and ^{119}Sn Mossbauer spectra the diorganotin compounds have been shown to adopt in the solid state, trans-R_2SnX_4 octahedral geometries and the triorganotin compounds, trans-R_3SnX_2 trigonal bipyramidal geometries, in which the carboxyl oxygen, rather than the ketonic oxygen, participates

in intermolecular coordination to tin. X-ray studies on the triphenyltin ester of 3-benzoyl propionic acid[93] has confirmed a carboxylate bridged rigid polymeric structure. The ketonic oxygen is not involved in coordination. The tri- and diorganotin esters of 2-benzoyl benzoic acid, which also has two carbon atoms separating the carboxyl and ketonic carbons, are also reported to have identical carboxylate bridged trans-R_3SnX_2 and six coordinate trans-R_2SnX_4 structures respectively[121]. The triorganotin acetylacetates (β-keto carboxylates) might be expected to be more rigid than the levulinates but their reported IR spectra[134] are rather similar to those of the levulinates. However, the organotin derivatives of β-keto carboxylic acids are yet to be investigated thoroughly.

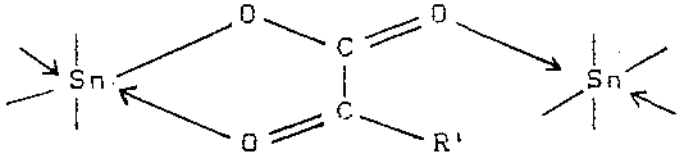
Although metal complexes, especially mixed ligand complexes of pyruvic acid, the first member of the α-keto carboxylic acid series are well known[135-140], reports on the organotin esters of α-keto acids are scanty. Only sketchy reports on the preparation[6] and IR spectra[106] of Bu_3Sn-derivatives and Mossbauer spectra of Ph_3Sn-derivative[141] of pyruvic acid have appeared so far. The ease with which the α- and β-keto carboxylic acids, as well as their metal derivatives undergo polymerisation, decarboxylation and decarbonylation may be one of the main reasons for the apparent lack of interest in organotin derivatives of keto carboxylic acids.

In comparison to the γ-keto acids studied so far[93,133] the

keto group in the α-keto acids is more suitably placed for being involved in a chelate ring in their organotin derivatives as shown below:

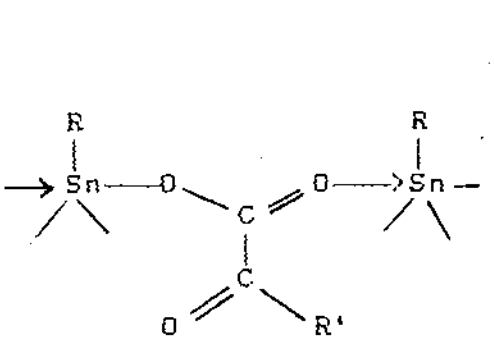


However, formation of such a chelate ring does not, in any way, preclude polymerisation, as the carboxyl C=O may be involved in bridging interaction as shown below :

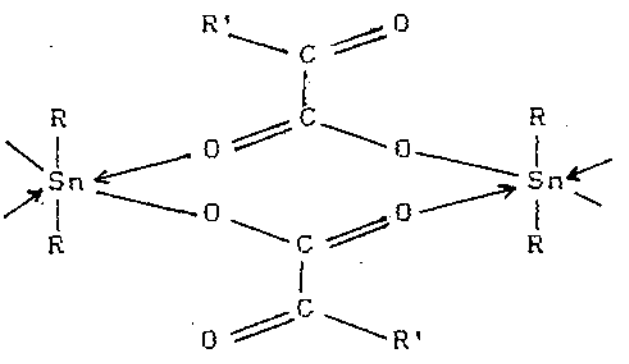


The high electronegativity of the $R'COCOO^-$ moiety is likely to increase the Lewis acidity of the tin atom, thereby helping the nucleophilic attack on it by the carboxyl C=O of another ring, leading to polymeric structure.

Besides, irrespective of the role of the keto group, polymerisation is likely to proceed through the involvement of carboxyl group in intermolecular bridging mode, which is a general feature of all compounds incorporating strongly electronegative acid ligands[63], resulting into one dimensional rigid polymeric structures, such as,



;



etc.

The ultimate demonstration of whether or not a ketonic group in the organotin esters of keto carboxylic acids is involved in coordination must await further investigation.

BIBLIOGRAPHY.

1. Poller R.C., *The Chemistry of Organotin Compounds.*, Logos Press, London, 1970, Ch-10.
2. Neuman W.P., *The Organic Chemistry of Tin.*, Wiley, London 1970, Ch-17.
3. Okawara R. and Wada M., *Advances in Organometallic Chemistry.* Academic Press, N.Y., 1967, Vol-V, P-137.
4. Okawara R. and Ohara M., *Organotin Compounds.*, Ed. A.K. Sawyer, Marcel Dekker, N.Y., 1971, Vol-II, P-253.
5. Davies A.G. and Smith P.J., *Comprehensive Organometallic Chemistry.*, Ed. G.Wilkinson., Pergamon Press, 1982, Ch-11, P-564.
6. Dunn P. and Norris T., *Austral. Comm. Dept. Suppl. Def. Std. Lab. Rept.*, 1964, No.269, P-21.
7. Vilarem M. and Maire J.C., *Compt. Rend. Ser.*, 1966, 262 C, 460.
8. Japanese Patent., *Chem. Abstr.*, 1966, 65, 2298g.
9. ,, ,, ,, ,, 12240c.
10. ,, ,, 1968, 69, 87186.
11. U.S. Patent., ,, 1966, 65, 12240b.
12. Polish Patent., ,, 1968, 68, 49776.
13. Ford B.F.E. and Sams J.R., *J. Organomet. Chem.*, 1971, 31, 47.
14. Poller R.C., Ruddick J.N.R., Taylor B. and Toley D.L.B., *J. Organomet. Chem.*, 1970, 24, 341.
15. French Patent., *Chem. Abstr.*, 1965, 62, 16296a.
16. Deacon G.B. and Farquharson G.J., *J. Organomet. Chem.*, 1977, 135, 73.

17. Frankel M., Gertner D., Wagner D. and Zilkha A., *J. Organomet. Chem.*, 1967, 9, 83.

18. Ford B.F.E., Liengme B.V. and Sams J.R., *J. Organomet. Chem.*, 1969, 19, 53.

19. Srivastava T.N. and Tandon S.K., *J. Prakt. Chem.*, 1969, 311(5), 878.

20. Clark H.C., O'Brien R.J. and Fickard A.L., *J. Organomet. Chem.*, 1965, 4, 43.

21. Peruzzo V., Plazzogna G. and Tagliavini G., *J. Organomet. Chem.*, 1972, 40, 121.

22. Anderson H.H. *Inorg. Chem.*, 1962, 1, 647.

23. Henderson A. and Holliday A.K., *J. Organomet. Chem.*, 1965, 4, 377.

24. Wiberg E. and Behringer H., *Z. Anorg. Allgen. Chem.*, 1964, 290, 329.

25. Ingham R.K., Rosenberg S.D. and Gilman M., *Chem. Rev.*, 1960, 60, 459.

26. Peruzzo V., Plazzogna G. and Tagliavini G., *J. Organomet. Chem.*, 1969, 16, 500.

27. Sawyer A.K. and Kuivila H.G., *J. Org. Chem.*, 1962, 27, 610.

28. Weber S. and Becker E.I., *J. Org. Chem.*, 1962, 27, 1258.

29. Kuivila H.G., *Adv. Organomet. Chem.*, 1964, 1, 82.

30. Hester R.E., *J. Organomet. Chem.*, 1970, 23, 123.

31. Sawyer A.K. and Kuivila H.G., *J. Org. Chem.*, 1962, 27, 837.

32. Adams S., Drager M. and Mathiasch B., *J. Organomet. Chem.*, 1987, 326(2), 173.

33. Alleston D.L. and Davies A.G., *J. Chem. Soc.*, 1962, 2050.

34. Sawyer A.K. and Kuivila H.G., *Chem. Ind.*, 1961, 260.

35. Mufti A.S. and Poller R.C., *J. Chem. Soc.(C)*, 1967, 1362; 1767.

36. Okawara R. and Rochow E.G., *J. Am. Chem. Soc.*, 1960, 82, 3285.

37. Wang C.S.C. and Shreeve J.M., *J. Organomet. Chem.*, 1972, 38, 287.

38. Honnick W.D. and Zuckerman J.J., *J. Organomet. Chem.*, 1979, 178, 133.

39. Rzaev Z.M., Kochkin D.A. and Zubov P.I., *Dokl. Akad. Nauk. SSSR.*, (Eng. trans), Consultants Bureau, 1967, Vol.-172(No-103), 364.

40. Anderson H.H., *J. Org. Chem.*, 1954, 19, 1766.

41. Biswas G., Ph.D. Thesis, North Bengal Univ., India (1977).

42. Anderson H.H., *Inorg. Chem.*, 1964, 3, 912.

43. Ingham R.K., Rosenberg S.D. and Gilman H., *Chem. Rev.*, 1960, 60, 490.

44. Alleston D.L., Davies A.G., Hancock M. and White R.F.M., *J. Chem. Soc.*, 1963, 5469.

45. Davies A.G., Smith L. and Smith P.J., *J. Organomet. Chem.*, 1972, 39, 279.

46. Deacon G.B., *Organomet. Chem. Rev.*, (A), 1970, 5, 355.

47. Okawara R. and Ohara M., *J. Organomet. Chem.*, 1965, 3, 484.

48. Luijten J.G.A. and Van der Kerk G.J.M., *Recl. Trav. Chim. Pays-Bas.* 1964, 83, 295.

49. Luijten J.G.A. and Van der Kerk G.J.M., *J. Appl. Chem.*, 1956, 6, 93.

50. Seyferth D., Armbrecht(Jr.) F.M., Prokai B. and Cross R.J., *J. Organomet. Chem.*, 1966, 6, 573.

51. Anderson H.H., *J. Org. Chem.*, 1956, 21, 869.

52. Thies C. and Kissinger J.B., *Inorg. Chem.*, 1964, 3 ,551.

53. Cohen H.J., *J. Organomet. Chem.*, 1967, 177.

54. Crowe A.J., Hill R., Smith P.J., Brooks J.S. and Formstone R., *J. Organomet. Chem.*, 1981, 204 ,47.

55. Cohen A.D. and Dillard C.R., *J. Organomet. Chem.*, 1970, 25 ,421.

56. Bloodworth A.J., Davies A.G. and Graham I.F., *J. Organomet. Chem.*, 1968, 13 ,351.

57. Zhivukhim S.M., Dudikova E.D. and Ter-Sarkisjan E.M., *J. Gen. Chem. USSR.*, 1962, 32 ,3010.

58. Zemlyanskii N.N., Panov E.N., Samagina O.P. and Kocheskov K.A., *J. Gen. Chem. USSR.*, 1965, 35 ,1034.

59. Zemlyanskii N.N., Panov E.N., Slovokhotova N.A., Samagina O.P. and Kocheskov K.A., *Proc. Acad. Sci. USSR.*, 1963, 149 ,205.

60. Henry M.C. and Davidsohn W. '*Organotin Compounds.*',Ed. A.K.Sawyer, Marcel Dekker, N.Y., 1972, Vol-III, P-975.

61. Subramanian R.V. and Garg B.K., *Polym-Plast. Technol.,Eng.*, 1978, 11 ,81.

62. Graddon D.P. and Rana B.A., *J. Organomet. Chem.*, 1977, 136 ,19.

63. Molloy K.C., Blunden S.J. and Hill R., *J.Chem.Soc. Dalton.Trans.*, 1988(5),1259.

64. Huber F., Enders M. and Kaiser R., *Z. Naturforsch.*, 1966, 21B, 83.

65. Garner C.D., Hughes B. and King T.J., *J.Chem.Soc. Dalton. Trans.*, 1975, 572.

66. Ford B.F.E. and Sams J.R., *Inorg. Chim. Acta.*, 1978, 28 ,L173.

67. Harrison P.G. and Phillips R.C., *J.Organomet.Chem.*, 1979,162 ,37.

68. Siddiqui K.S., Zaidi F.R., Khan T.A. and Zaidi S.A.A., *Bull. Soc. Chim. Fr.*, 1983, 5-6 Pt-1, 140.

69. Srivastava T.N. and Sing J.D., *Ind. J. Chem.*, 1983, 22A(2), 128 ; 1983, 22A(8), 674 ; 1986, 24A(6), 489.

70. Siddiqui K.S., Kureshi R.I., Khan P. and Zaidi S.A.A., *Ind. J. Chem.*, 1983,22A(7), 616.

71. Narula S.P., Sharma R.K., Lata S., Kapur N. and Seth R., *Ind. J. Chem.*, 1983, 22A(3), 248.

72. Midha A.and Verma R.D., *J. Ind. Chem. Soc.*, 1985, 62(6), 421.

73. Srivastava T.N., Siddiqui M.A., Sing J.D. and Srivastava S., *Ind. J. Chem.*, 1987, 26A(2), 158.

74. Beattie I.R. and Gilson T., *J. Chem. Soc.*, 1961, 2585.

75. Freeman J.P., *J. Am. Chem. Soc.*, 1958, 80 ,5954.

76. Okawara R., Webster D.E. and Rochow E.G., *J. Am. Chem. Soc.*, 1960, 82 ,3287.

77. Itoch K. and Bernstein H.J., *Can. J. Chem.*, 1956, 34 ,170.

78. Chih H. and Penford B.R., *J. Cryst. Mol. Struct.*, 1973, 3 ,285.

79. Alcock N.W. and Timms R.E., *J. Chem. Soc. (A).*, 1968, 1873.

80. Calogero S., Clemente D.A.,Peruzzo V. and Tagliavini G., *J. Chem. Soc. Dalton. Trans.*, 1979, 1172.

81. Sandhu G.K., Verma S.P. and Tiekink E.R.T., *J. Organomet. Chem.*, 1990, 393 ,195.

82. Simons P.B. and Graham W.A.G., *J. Organomet. Chem.*, 1967, 6 ,479.

83. Reichle W.T., *Inorg. Chem.*, 1966, 5 ,67.

84. Zimmer H., Homberg O.A. and Jayawant M., *J.Org.Chem.*,1966,31,3857.

85. Alcock N.W. and Timms R.E., *J. Chem. Soc. (A).*, 1968, 1876.

86. Barbieri R., Pellerito L., Bertazzi N. and Stocco G.C., *Inorg. Chim. Acta.*, 1974, 11 ,173.

87. Burke J.J. and Lauterbur P.C., *J. Am. Chem. Soc.*, 1961, 83 ,326.

88. Molloy K.C., Purcell T.G., Han E., Schumann H. and Zuckerman J.J., *Organometallics.*, 1985, 5 ,85.

89. Schubert U., *J. Organomet. Chem.*, 1978, 155 ,285.

90. Sharma C.P., Kumar N., Chandra S. and Bhide V.G., *J. Inorg. Nucl. Chem.*, 1981, 43 ,2659.

91. Holmes R.R., Day R.O., Chandrashekhar V., Vollano J.F. and Holmes J.M., *Inorg. Chem.*, 1986, 25 ,2490.

92. Holmes R.R., Day R.O., Chandrashekhar V., Holmes J.M. and Smith P.J., *Inorg. Chem.*, 1986, 25 ,2495.

93. Ng S.W., KumarDas V.G. and Syed A., *J. Organomet. Chem.*, 1989, 364(3), 353.

94. Ng S.W., Amini M.M., Fidelis K., Heeg M.J., Muchmore C.R. and Zuckerman J.J., *J. Organomet. Chem.*, 1989, 365 ,103.

95. Ng S.W., Chin K.L., Chen W., KumarDas V.G. and Butcher R.J., *J. Organomet. Chem.*, 1989, 376 ,277.

96. Swisher R.G., Vollano J.F.,Chandrashekhar V., Day R.O. and Holmes R.R., *Inorg. Chem.*, 1984, 23 ,3147.

97. Vollano J.F., Day R.O., Rau D.N., Chandrashekhar V. and Holmes R.R., *Inorg. Chem.*, 1984, 23 ,3153.

98. Ng S.W., KumarDas V.G., vanMeurs F., Schagen J.D. and Shavers L.H. *Acta. Crystallogr. C.*, 1989, 45 ,568.

99. Molloy K.C., Purcell T.G., Quill K. and Nowell I.W., *J. Organomet. Chem.*, 1984, 267 ,237.

100. Debye N.W.G., Fenton D.E., Ulrich S.E. and Zuckerman J.J., *J. Organomet. Chem.*, 1971, 28 ,339.

101. Harisson P.G., King T.J. and Molloy K.C., *J. Organomet. Chem.*, 1980, 185 ,199.

102. Sandhu G.K., Verma S.P., Moore L.S. and Parish R.V., *J. Organomet. Chem.*, 1987, 321 ,15.

103. Sandhu G.K. and Kaur G., *J. Organomet. Chem.*, 1990, 388 ,63.

104. Poller R.C., *J. Inorg. Nucl. Chem.*, 1962, 24 ,593.

105. Egorochkin A.N., Domarchev G.A., Vyazankim N.S., Khorshev S.Ya., Djachkovskaya O.S. and Bychkov V.I., *Izvest. Akad. Nauk. SSSR., Ser. Khim.*, 1971, B ,164.

106. Cummins R.A. and Dunn F., *Austral. Comm. Dept. Suppl. Def. Std. Lab. Rept.*, 1963 No-266, P-106.

107. Molloy K.C., Quill K., Blunden S.J. and Hill R., *Polyhedron.*, 1986, 5 ,959.

108. Harrison P.G., Lambert K., King T.J. and Majee B., *J. Chem. Soc., Dalton. Trans.*, 1983, 363.

109. Majee B. and Banerjee S., *J. Organomet. Chem.*, (a) 1977, 139 ,39. (b) 1977, 140 ,151.

110. Majee B., Chattopadhyay T.K. and Sengupta A., *Ind. J. Chem.*, 1982, 21A ,1090.

111. Majee B., Chattopadhyay T.K. and BasuBaul T.S., *Polyhedron.*, 1983, 2 ,635.

112. Ho B.Y.K., Molloy K.C., Zuckerman J.J., Reidinger F. and Zubieta J.A., *J. Organomet. Chem.*, 1980, 187 ,213.

113. Smith P.J., *Organomet. Chem. Rev.(A).*, 1970, 5 ,373.

114. Ruddick J.N.R., *Rev. Silicon, Germanium, Tin, Lead Compds.*, 1976, 2 ,115.

115. Maeda Y. and Okawara R., *J. Organomet. Chem.*, 1967, 10 ,247.

116. Chandrashekhar V., Day R.O., Holmes J.M. and Holmes R.R., *Inorg. Chem.*, 1988, 27(5), 958.

117. Sandhu G.K., Sharma N. and Tiekink E.R.T., *J. Organomet. Chem.*, 1989, 371(1), C-1.

118. Ng S.W., KumarDas V.G., Skelton B.W. and White A.H., *J. Organomet. Chem.*, 1989, 377 ,221.

119. Parulekar C.S., Jain V.K., Kesavadas T. and Tiekink E.R.T., *J. Organomet. Chem.*, 1990, 387(2), 163.

120. Ng S.W., KumarDas V.G., Yip W.-H., Wang R.-J. and Mak T.C.W., *J. Organomet. Chem.*, 1990, 393 ,201.

121. Ng S.W. and Zuckerman J.J., *J. Organomet. Chem.*, 1983, 249 ,81.

122. Sandhu G.K., Sandhu S.S., Gupta R. and Parish R.V., *Polyhedron.*, 1985, 4(1), 81.

123. Sandhu G.K., Sandhu S.S., Gupta R., Parish R.V. and Moore L.S., *J. Organomet. Chem.*, 1986, 311 ,281.

124. Sandhu G.K., Sandhu S.S., Gupta R., Parish R.V. and Brown K., *J. Organomet. Chem.*, 1985, 279 ,373.

125. Graziani R., Bombieri G., Forsellini E., Furlan R., Peruzzo V. and Tagliavini G., *J. Organomet. Chem.*, 1977, 125 ,43.

126. Valle G., Peruzzo V., Tagliavini G. and Ganis P., *J. Organomet. Chem.*, 1984, 276 ,325.

127. Birchall T., Frampton C.S. and Jhonson J.P., *Acta.Crystallogr. C.*, 1987, 43 ,1492.

128. Narula S.P., Bharadwaj S.K., Sharma H.K., Mairesse G., Barbier P. and Nowogrocki G., *J. Chem. Soc., Dalton. Trans.*, 1988, 1719.

129. Peruzzo V. and Tagliavini G., *J. Organomet. Chem.*, 1974, 66 ,437.

130. Parulekar C.S., Jain V.K., Das T.K., Gupta A.R., Hopkins B.F. and Tiekink E.R.T., *J. Organomet. Chem.*, 1989, 372 ,193.

131. Allen D.W., Nowell I.W., Brooks J.S. and Clarkson R.W., *J. Organomet. Chem.*, 1981, 219 ,29.

132. Ng S.W., Chen W. and KumarDas V.G., *J.Organomet.Chem.*,1988,345,59.

133. Ng S.W., Chen W., Yap C.K., KumarDas V.G. and Mak T.C.W., *J. Organomet. Chem.*, 1986, 311 ,289.

134. Chan J.K. and Marcus E., *Chem. Ind.*, 1966, 1767.

135. Leusing D. L. and Shultz D.C., *J. Am. Chem. Soc.*, 1964, 86 ,4846.

136. Leusing D.L. and Tallman D.E., *J. Am. Chem. Soc.*, 1969, 91 ,6253; 6256 ; and references cited therein.

137. Harrowfield J.M. and Sargeson A.M., *J. Am. Chem. Soc.*, 1979, 101(6), 1514.

138. Palrecha M.M. and Gaur J.N., *Ind. J. Chem.*, 1969, 7(10), 1035.

139. Ghandour M.A., Mansour H., Abu-El-Wafa M.H.M. and Khodary M., *J. Ind. Chem. Soc.*, 1988, 65 ,713 ; 827 ; and references cited therein.

140. Gaifullin A.A., Kharlampidi Kh.E., Efanova E.A., Koshkina G.M. and Lebedeva W.M., *Neftekhimiya.*, 1988, 28(3), 388.

141. Ng S.W. and KumarDas V.G., Unpublished work, cited in Ref.93.

142. Lockhart T.P. and Davidson F., *Organometallics.*, 1987, 6 ,2471.

143. Ng S.W., KumarDas V.G. and Tiekink E.R.T., *J. Organomet. Chem.*, 1991, 403(1-2), 111.

144. BasuBaul T.S. and Rivarola E., *Ind. J. Chem.*, 1993, 32A(10), 905.

145. Ng S W., Chin K.L., Wei C., KumarDas V.G. and Mak T.C.W., *J. Organomet. Chem.*, 1989, 365 ,207.

146. Preut H., Mundus B., Huber F. and Barbieri R., *Acta. Crystallogr. Sect.C. Cryst. Struct. Commun.*, 1989, C45(5), 728.

147. Vatsa C., Jain V.K., Kesavadas T. and Tiekink E.R.T., *J. Organomet. Chem.*, 1991, 410(2), 135.

148. Sandhu G.K., Sharma N. and Tiekink E.R.T., *J. Organomet. Chem.*, 1991, 403(1-2), 119.

149. Sandhu G.K. and Poparov N.S., *J. Organomet. Chem.*, 1991, 411 ,89.

150. Sandhu G.K., Hundal R. and Tiekink E.R.T., *J. Organomet. Chem.*, 1991, 412(1-2), 31.

151. Hager C.D., Huber F., Silvestri A., Barbieri A. and Barbieri R., *Gazzetta Chimica Italiana.*, 1993, 123(10), 583.

152. Lockhart T.P., *Organometallics.*, 1988, 7(6), 1438.

153. Vatsa C., Jain V.K., Das T.K. and Tiekink E.R.T., *J. Organomet. Chem.*, 1990, 396(1), 9.