A SHORT DISCUSSION OF ORGANOTIN CO-ORDINATION COMPOUNDS

Introduction

The Chemistry of organotin compounds has been studied extensively during last few decades due to their unique physico-chemical, structural, biocidal and other properties.

Historically, Frankland (1-2) in 1849 first reported an organotin compound though he could not characterise it properly until 1853. Lowig (3) in 1852 isolated the first organotin compound from the reaction of sodium-tin alloy on ethyl iodide. These initial investigations soon initiated more work in the field of organometallic chemistry in general and organotins in particular.

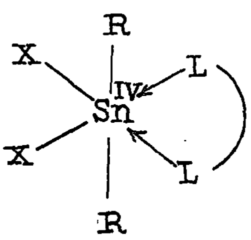
A number of review articles in this area have been published. The first comprehensive review covering the literature upto 1935 was done by Krause and Von Grosse (4). Ingham, Rosenberg and Gilman (5) extended the literature work upto 1959. The list of organotin compounds covering the literature from 1937 to 1964 was done by Weiss (6). From 1964, few literatures of organotin chemistry have been published in annual surveys (7-16). The tin annual survey covering the year 1974 has been published (17). Harrison published two reviews — one is of organotin derivatives of tin and lead (18) and another of organotin compounds in 1973 (19). Apart from these review articles, several books have been published (20-23).

After the discovery, organotin compounds long remained of purely scientific interest, but in recent years these have been put into large scale commercial exploitations. The present annual world consumption of organotin compounds is about 30,000 tons, though the production in 1948 was maximally a few tons. Most of these productions are utilised for P.V.C. Stabilisation, the remainder being shared between several biocidal and catalytic uses of organotin compounds.

The applications of organotin compounds are diverse (24-26) in nature and some of which may be indicated as follows:

For stabilisation of poly vinyl chloride (P.V.C.), di-organotin and mono organotin compounds are currently used. P.V.C. for its processing is subjected to temperature between 150-200°C. At this temperature, decomposition of P.V.C. takes place unless it is protected by appropriate stabiliser. Apart from organotins, metallic soaps and some pure organic compounds are also used as stabilisers for P.V.C. The organotin stabilisers are most powerful though it is more expensive. When a perfectly clear and colourless product is required or extreme temperature is used in processing, the organotin stabilisers are mostly used.

Apart from the use of organotin compounds for P.V.C. stabilisation, there are a large number of biological applications of organotin compounds. The biological effects of organotin compounds was systematically studied since 1950. These compounds have been found very active against a number of fungi and bacteria, marine organisms, parasitic worms, aquatic snells and insects. Investigations in these area have led to proposals for practical applications, some of which have been successfully realised. A comprehensive review of such applications has been written by Luijten (27). Recently an interesting potential use of organotin complexes have been indicated by the effectiveness of a series of organotin dihalides complexes for anti tumour activities. The compounds are of the type $R_2SnX_2 \cdot L_2$(I) where R = Me, Et, n-Pr, n-Bu, Ph; X = Cl, Br, I, NCS; L = O- or N-donor ligand have been tested for antitumour activity (28). These compounds were modelled on the original active platinum compounds (29) Cis-$Pt(NH_3)_2Cl_4$ (II) and Cis-$Pt(NH_3)_2Cl_2$ (III).



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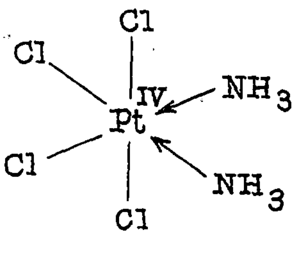

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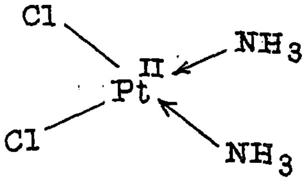


III

The diorganotin complexes chosen for test contain Cis-halogen groups and some of these compounds inhibit P388 Leukaemia in mice.

In recent years, the co-ordination chemistry of organotin compounds has been extensively studied. Tin differs from the lighter group IVA elements in that its d-orbitals are of sufficiently low energy for them to be frequently used in bonding, so that tin can readily expand its co-ordination number above four. As a consequence, many organotin compounds form stable adducts with Lewis bases. Reactions involving nucleophilic attack at tin are also facilitated by the formation of co-ordinated intermediates.

The ability of tin compounds to form complexes is largely dependent on the electronegativity of the substituents. Thus the acceptor strengths of the halides are in the order $SnCl_4 \gg SnBr_4 > SnI_4$. When the electronegative chlorine atoms of $SnCl_4$ are replaced by relatively electropositive organic group, the acceptor strength of tin declines as indicated by the sequences $SnCl_4 > RSnCl_3 > R_2SnCl_2 > R_3SnCl$; $Ph_3SnCl > Bu_3SnCl$; and $PhSnCl_3 > MeSnCl_3 > BuSnCl_3$. No adducts of tetraalkyl or aryl tin compounds have yet been reported and attempts to detect interaction between tetra ethyl- or tetra phenyl tin and dioxanes by dipole moment measurements gave negative results (30).

A large number of most commonly used ligands are those with donor atoms from the first row of periodic table particularly oxygen and nitrogen, as it is widely accepted that tin (IV) is a class A acceptor (hard acid) (31).

Kumar Das (32) has prepared complexes of the type $R_3SnX.L$ (where R = Me, Ph; X = Cl, NO_3 and L = hexamethyl phosphoric triamide (HMPA), dimethyl Sulphoxide (DMSO), 1:10 phenanthroline (Phen) etc. 1:1 complex of HMPA with Ph_3SnX (X = Cl, Br, I, N_3, CN) have been prepared (33-34) by the general reaction

$$Ph_3SnX + HMPA \xrightarrow[\text{or pet ether}]{\text{chloroform}} Ph_3SnX.\ HMPA$$

That, the $Ph_3SnNO_3.L$ (L = HMPA, DMSO and phen) complexes are relatively good electrolytes in absolute alcohol, indicate a weak co-ordination of nitrate group to the tin atom. I.R. spectral data support it and these three complexes have been found to be penta co-ordinated by Mössbauer spectral data (35).

A large number of 1:1 adducts of substituted pyridine N-oxides with triphenyl tin chloride have also been prepared (36). These compounds are precipitated by mixing together an equimolecular amount of the reactants (37). Stability constant measurements of the compounds $Me_3SnCl.L$ (L = substituted pyridine N-oxide) clearly indicate the formation of stable adducts by these ligands with Me_3SnCl.

The formation of 1:1 complexes of triorganotin chlorides and thiocyanates with some tridentate chelating agents have been reported by Smith and Liengme (38). The chelating agents are

3-[2-(1,10-phenanthrolyl)]-5,6-diphenyl-1,2,4-triazine (I) and 3-[2-(1,10-phenanthrolyl)]-5,6-dimethyl-1,2,4-triazine (II). The isolated complexes were $(CH_3)_3SnCl.L$; and $(C_6H_5)_3SnCl.L$ (L = I and II) and $(C_6H_5)_3Sn(NCS).L$ (L = I). These complexes are stable crystalline solids and behave as non-electrolytes in nitrobenzene.

A number of complexes like $Me_2SnCl_2.2Py$; Me_2SnCl_2 . phen (39,40); Me_2SnX_2. Bipy (X = Cl, Br, I); $2R_2SnX_2$. Terpy (41) (R = Me, Ph; X = Cl, Br, I) have been obtained by the action of ligands such as Pyridine (Py), bipyridyl (Bipy), Phenanthroline (Phen), terpyridyl (Terpy) etc. upon diorganotin halides.

Reutov et al have summarised a large number of crystalline complexes of the general formula $R_{4-n}MX_n$. L where L is a neutral donor ligand (31). In that summary, they also discussed the structures of such complexes containing monodentate and bidentate ligands. In recent years a large number of organotin complexes with various bidentate ligands have been extensively studied. A brief review of some representatives of these complexes may be described as follows:

<u>Organotin derivatives of oximes and Schiff Bases:</u>

The oxime derivatives of organotin compounds have been reviewed by Mehrotra and his co-workers (42). Organotin oximates are prepared either by the action of sodium or lithium Salts on organotin halides (43-45)

$$\begin{array}{c} R_{4-n}SnCl_n + nNa(Li)ON = CR'R'' \\ \downarrow \\ R_{4-n}Sn(ON = CR'R'') + nNaCl(LiCl) \end{array}$$

or by azeotropic distillation of water from a mixture of organotin oxide or hydroxide with oxime in benzene or toluene (43-45).

$$\begin{array}{c} (R_3Sn)_2O + 2HON = CR'R'' \\ \downarrow \\ 2R_3SnON = CR'R'' + H_2O \end{array}$$

$$R_3SnOH + HON = CR'R'' \longrightarrow R_3SnON = CR'R'' + H_2O$$

Reactions of alkyl tin alkoxides with oximes (42-43, 46,47) take place as

$$\begin{array}{c} R_{4-n}Sn(OR')_n + nHON = CR''R''' \\ \downarrow \\ nR'OH + R_{4-n}Sn(ON = CR''R''')_n \end{array}$$

From the action of diorganotin dichloride with the silver salt of oxime, Koheler et al (48) was able to prepare diorganotin derivatives of a dicyanoformaldehyde.

Mehrotra et al (49) have also prepared various types of butyl tin derivatives of alkanolamines. Organotin derivatives of oxime can react with acyl or benzoyl halides and o-acyl or o-benzoyl oxime (42).

$$R_{4-n}Sn(ON = CR'R'')_n + nR'''COX \longrightarrow R_{4-n}SnX_n + nR'R''C = NOCOR'''$$

Organotin halides or oxides can react with bidentate, tridentate and tetradentate Schiff bases.

$RSnCl_3$ reacts with $HOC_6H_4CH : NR'$ (where R = Et, *n*-Bu and Ph; R' = Me, Et and Ph) in cyclohexane and forms 1:2 adducts (50). Molar conductance measurements in nitrobenzene have shown the non-electrolytic nature of these adducts. Infrared and Mössbauer spectral studies suggest octahedral structures for these adducts.

$(CH_3)_2SnCl_2$ reacts with tridentate Schiff bases N-(2-hydroxyl phenyl) salicylaldimine $OH.\ C_6H_4CH = N.\ C_6H_4\ .OH$ or its derivatives to form penta co-ordinated structures (51). Triphenyl tin hydroxide reacts with N-(2-hydroxy phenyl)-salicylaldimine to form hexa co-ordinated complex. The structure of N-(2-hydroxy phenyl)-salicylaldimine has been determined and found to be heavily distorted with organic groups occupying equitorial positions (52).

Diorganotin oxides react with tetradentate Schiff Bases to yield R_2Sn(Salen), R_2Sn(aceto-salen) and R_2Sn(benzo salen) where R = *n*-Bu, *n*-octyl and benzyl ; [salen = bis-(2-hydroxy-5-methyl acetophenone) ethylene diamine; benzo salen = bis-(2-hydroxy-5-methyl benzophenone) ethylene diamine].

The compound R_2Sn (aceto salen) and R_2Sn(benzo salen) exist in trans form both in solid and in solution whereas R_2Sn(salen) exist both in cis and in trans forms (53).

Organotin Oxinates:

Organotin oxinates (oxine = 8-hydroxy quinoline) are stable and well defined compounds. These have been studied extensively. These organotin oxinates are generally of the following types:

$R_3Sn(OX)$, $R_2Sn(OX)_2$, $RSn(OX)_3$, $R_2Sn(OX)X$ and $RSn(OX)_2X$, where R = organic group, OXH = 8-hydroxy quinoline, X = halogens, isothiocyanate and carboxylates.

The simple organotin oxinates of the type $R_{4-n}SnOX_n$ (n = 1,2,3) are prepared either from the organotin halides and sodium oxinate (54)

$$R_2SnCl_2 + 2NaOX \longrightarrow R_2Sn(OX)_2 + 2NaCl$$

$$n\text{-}BuSnCl_3 + 3NaOX \longrightarrow n\text{-}BuSn(OX)_3 + 3NaCl$$

or from organotin halide and oxine, the hydrogen halide formed during the reaction is removed by neutralising with the help of a base such as ammonia (55).

$$R_2SnCl_2 + 2OXH + 2NH_3 \longrightarrow R_2Sn(OX)_2 + 2NH_4Cl$$

and organotin oxide with oxine (56,57)

$$(Ph_3Sn)_2O + 2OXH \longrightarrow 2Ph_3SnOX + H_2O$$

Triorganotin oxinates have also been prepared by the reaction of triorganotin chloride with a mixture of oxine and sodium methoxide (54).

By refluxing (58) a mixture of tetra [bis-(penta fluoro phenyl) ~~tin~~ or tris-(penta fluoro phenyl)]tin chloride and an excess of oxine in ethanol, (bis-penta fluoro-phenyl) tin bis oxinates have been prepared. The crystal structure of dimethyl tin bis-(8-hydroxy-quinolinate) has been determined (59). The compound assumes a structure with cis-dimethyl tin groups (110.7^{o}) in which the oxygen atoms appear trans (the O-Sn-O angle seems not to be listed) and the nitrogen atoms are Cis (N-Sn-N = 75.8^{o}). The nearly tetrahedral dimethyl tin groupings has tin-carbon internuclear distances that are the same as those observed for the tetrahedral tin compounds, $(CH_3)_nSnX_{4-n}$ and CH_3SnH_3. In the bonding of the oxinate ligand to tin, it seems that the tin oxygen distances are shorter by $0.25A^{o}$ than the tin-nitrogen distances.

By the reaction of diphenyl tin dichloride and oxine in benzene in absence of a base in 1:1 molar ratio, halo oxinate is formed (60,54):

$$R_2SnCl_2 + OXH \longrightarrow R_2SnCl(OX) + HCl$$

Halo oxinate compounds can also be obtained through disproportionation of a dihalide and a dioxinate in refluxing benzene or ethanol (61,54).

$$R_2SnCl_2 + R_2Sn(OX)_2 \longrightarrow 2R_2SnCl(OX)$$

or, by the reaction of dioxinate and silver halide (60).

$$R_2Sn(OX)_2 + AgX \longrightarrow R_2SnX(OX) + Ag(OX).$$

Dimethyl chlorotin oxinate have been prepared by McGrady et al. (62) by the disproportionation reaction of dimethyl tin dichloride and dimethyl tin dioxinate in refluxing benzene. Dialkyl tin isothiocyanate oxinate and acetate oxinate have similarly been prepared (60). Dialkyl tin nitrate oxinate and sulfate oxinate are prepared by the following methods (60)

$$R_2Sn(OX)_2 + AgNO_3 \xrightarrow{\text{in } CH_3OH} R_2Sn(NO_3)(OX) + Ag(OX)$$

$$2R_2SnCl(OX) + Ag_2SO_4 \longrightarrow [R_2Sn(OX)_2]SO_4 + 2AgCl.$$

In other halogen substitution reaction the product disproportionates (63) as

$$R_2SnCl(OX) + I^- \longrightarrow [R_2Sn(I)(OX)] + Cl^-$$

$$2[R_2SnI(OX)] \longrightarrow R_2SnI_2 + R_2Sn(OX)_2$$

The halogen atom of penta co-ordinated tin halo oxinate undergo ready exchange with groups such as butyl, alkoxy or even with chelating agents e.g. acetyl acetonates (54,63) which may disproportionate into diorganotin derivatives, e.g.

$$\begin{tikzcd}
R_2SnCl(OX) + Tl\text{-}OC_2H_5 \arrow[r] & R_2Sn(OC_2H_5)(OX) + TlCl
\end{tikzcd}$$

$$\begin{tikzcd}
R_2SnCl(OX) + n\text{-}BuLi \arrow[r] & R_2Sn(n\text{-}Bu)(OX) + LiCl \arrow[d, shift right] \\
& R_2Sn(OX)_2 + R_2Sn(n\text{-}Bu)_2 \arrow[u, shift right]
\end{tikzcd}$$

$$\begin{tikzcd}
R_2SnCl(OX) + Tl\text{-}acetate \arrow[r] & R_2Sn(acac)(OX) + Tlcl \arrow[d, shift right] \\
& R_2Sn(OX)_2 + R_2Sn(acac)_2 \arrow[u, shift right]
\end{tikzcd}$$

Datta (64) have prepared phenyl tin halo oxinates by the reaction of diphenyl tin dioxinate with mercuric halides in ether at room temperature.

$$Ph_2Sn(OX)_2 + HgCl_2 \longrightarrow PhSnCl(OX)_2 + PhHgCl$$

Phenyl tin acetate dioxinate has been prepared by Roy (65) by the displacement of chlorine atom from phenyl tin chloro oxinate with sodium acetate. He has also prepared $PhSn(OCOC_2H_5)(OX)_2$, $PhSn(OCOCH_2Cl)(OX)_2$ and $PhSn(OCOCF_3)(OX)_2$ complexes by similar methods.

A novel compound, $[n\text{-}C_4H_9Sn(OX)_2]S$ has been prepared from the reaction of n-butyl tin sesquisulfide and oxine in boiling toluene (66).

Mehrotra et al (67) have synthesised butyl tin-isopropoxy oxinates $[BuSn(OPr^{i})_{3-n}(OX)_{n}]$ by the reaction of butyl tin tris-isopropoxide and oxine and the isopropanol formed in the reaction was removed by azeotropic fractionation with refluxing benzene.

Ghosh and co-workers (68) have examined the action of mercuric halides on organotin oxinates and probable mechanisms of these reactions have been given. Triphenyl tin oxinate has been shown to react readily with HgX_2 (X = Cl, Br, I) at room temperatures. The hexa co-ordinated diphenyltin dioxinate is attacked by HgX_2 only when refluxed in benzene or ether. In both the cases, $PhSn(OX)_2X$ have been found. It has also been shown that $Ph_2SnCl(OX)$ can react with mercuric chloride with the complete cleavage of the tin-phenyl bond, producing $Sn(OX)_2Cl_2$, PhHgCl and Ph_2SnCl_2.

Organotin derivatives of substituted oxines, e.g., some diaryl tin bis oxinates/2-methyl oxinates and diaryl tin chloride oxinate/2-methyl oxinates have been reported by Srivastava et al (69).

Sen et al (70,71) have prepared and characterised several diorganotin bis-(mono- and disubstituted oxinates) by the reaction of diorganotin dichloride with ligands in 1:2 molar ratio in DMF or ethanol.

Gopinathan et al (72), Kumar Das et al (73), Deb and Ghosh (74) have very recently prepared oxine compounds of ester tins.

Kumar Das et al have also reported and synthesised the compounds of the type $R_2Sn(OX)_2$ and $R_2SnCl(OX)$ (where R = $MeOCOCH_2CH_2$). The former compound hase been synthesised by the method of Westlake and Martin (75) and the latter by the reaction of an equivalent amount of diorganotin bis(oxinate) with R_2SnCl_2 in benzene. The compounds were studied by U.V., I.R., P.M.R. and Mössbauer spectroscopy.

It has been proved by P.M.R. data that relative to bis oxinate, the chloro oxinate appears to involve a greater extent of chelation.

Deb and Ghosh (loc cit) have synthesised and characterised co-ordination compounds ~~of~~ β-substituted mono- and dialkyl ester tin compounds with ligands like 8-hydroxy quinoline, substituted 8-hydroxy quinolines, dithizone, alizarin etc. by the reactions of ester tin chlorides with ligands.

Organotin Tropolonates, Kojates, Dithiocarbamates and β-Diketonates:

A number of organotin tropolonate complexes of the types Ph_3SnT, Me_2SnXT, R_2SnT_2, $RSnXT_2$ (R = alkyl or Ph; X = Cl, Br, I; TH = Tropolone) have been prepared where the tropolone acts as bidentate chelating agent bonding through both oxygen atoms.

Diorganotin bis-tropolonates have been prepared (76,77) by the following reactions.

$$R_2SnCl_2 + 2NaT \longrightarrow R_2SnT_2 + 2NaCl$$

$$R_2SnCl_2 + 2TlT \longrightarrow R_2SnT_2 + 2TlCl$$

By the reaction of phenyl tin trichloride in benzene with a solution of tropolone in ether (78), the compounds phenyl tin tris tropolonate and phenyltin chloride bis tropolonate have been prepared.

Organotin complexes with kojic acid, e.g., from methyl tin chloride - and methyl tin bromide bis kojates have been prepared by Otera et al (79).

Organotin dithiocarbamates are prepared by the reaction of sodium-dithiocarbamate with an organotin chloride (80-81).

Organotin compounds can form a number of complexes with bidentate oxygen donor β-diketones. There are several organotin acetyl acetonates. They are generally of the following types: $R_3Sn(acac)$, $R_2Sn(acac)_2$, $RSn(acac)_3$, $RSnX(acac)_2$, $RSnX(OR')(acac)$ and $RSn(acac)_n(OR')_{3-n}$.

R_3SnL [R = Me, Ph; LH = acetylacetone(acac), benzoyl acetone (bzac)] compounds have also been prepared and characterised by I.R., N.M.R. and Mössbauer spectroscopy (82). These compounds have been prepared by Tl(1) salt method (83,84,85) e.g.,

$$R_3SnCl + Tl(acac) \longrightarrow R_3Sn(acac) + TlCl.$$

Diorganotin bis acetyl acetonates, $R_2Sn(acac)_2$ and diorganotin bis (β-diketones) have been prepared either by the addition of acetyl acetone to a mixture of diorganotin dichloride and sodium methoxide in methanol (86) or by direct reaction of the reactants in the presence of a base (83).

Srivastava and Saxena (87) have synthesised some diorganotin bis (acetyl acetonates), $R_2Sn(acac)_2$ (R = Ph, o-, m-, p-tolyl).

Tri and diorganotin complexes of 2-Thenoyl-trifluoro acetone of the types $R_3Sn(TTA)$ (where R = CH_3, C_2H_5, C_4H_9 and HTTA = 2-Th$\overset{e}{}$noyl trifluroacetone) have been synthesised by Bachlas and Jain (88).

$$CH_3ONa + HTTA \longrightarrow \overset{+}{Na}(TTA)^- + CH_3OH$$

$$R_3SnCl + \overset{+}{Na}(TTA)^- \longrightarrow R_3Sn(TTA) + NaCl$$

$$(R_2SnO)_x + 2XHTTA \longrightarrow XR_2Sn(TTA)_2 + XH_2O$$

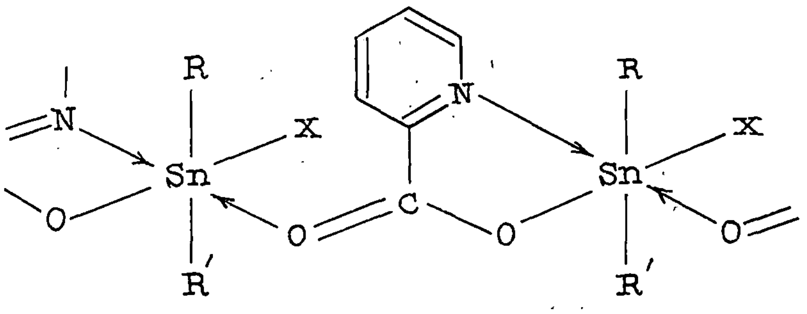
Organotin derivatives of Pyridine carboxylic acids and other ligands:

A series of diorganotin bis (pyridine carboxylates), $R_2Sn\ (O.CO.C_5H_4N\text{-}n)_2$ ($R = Me$, $n = 2\text{-}4$; $R = Ph$, $n = 2$ or 3); diorganochlorotin pyridine carboxylates, $R_2ClSn\ (O.CO.C_5H_4N\text{-}n)$ ($R = Me$ or Ph, $n = 2$; $R = Me$, $n = 4$) and monoorganochlorotin pyridine carboxylates $RCl_2Sn(O.CO.C_5H_4N\text{-}2)$ ($R = Bu$ or Ph) have been synthesised and their structures are investigated by ^{119}Sn Mössbauer and Infra red spectroscopy (89).

The spectra indicates the trans octahedral R_2SnX_4 geometry of the three dimethyl tin bis-(pyridine carboxylates) along with diphenyl tin bis-(3 pyridine carboxylate) and dimethyl chloro and diphenyl chlorotin 2-pyridine carboxylate in the solid state.

Dimethyl chlorotin 4-pyridine carboxylate, however, possesses a five co-ordinated trigonal bipyramidal Cis- R_2SnX_3 stereochemistry while diphenyl tin bis-(2-pyridine carboxylate) has an octahedral Cis-R_2SnX_4 structure, with two bidentate N-chelating pyridine carboxylate groups.

The structure of dimethyl tin bis-(2-pyridine carboxylate) most probably has both bridging and terminal carboxylate groups where co-ordination from pyridine nitrogen atom to tin occurs (Fig. 1).



Stucture of dimethyl tin bis-(2-pyridine carboxylate)
($R = R' = Me$; $X = O.CO.C_5H_4N-2$)

(Fig. 1)

Di-ethyl-, di n-octyl- and dicyclohexyl tin derivatives of 2-pyridine carboxylic acid also adopt a similar structure in solid phase as indicated by Nelson (90).

Some mixed chelate compounds of diorganotin (IV) of the type $[SnR_2L'L'')$ involving the chelate ligands N,N-dialkyl dithiocarbamate ($S_2CNR'_2$), 8-quinolinate (oxine), 2-methyl-8-quinolinate (quin) and the anion of bis (p-fluoro benzoyl methane) (fbm) has been synthesised together with the symmetrical bis-chelates $[SnR_2(quin)_2]$ ($R = Me, Ph$), and The cationic complex $[SnMe_2(PPh_3O)_2(AsPh_3O)_2]^+[BPh_4]^-_2$, containing mixed mono dentate ligands has been prepared (91).

These mixed chelate complexes were prepared according to the reaction scheme:

$$TlL' + [SnR_2ClL'') \longrightarrow [SnR_2L'L''] + TlCl$$

where $R_2 = Me_2$, Bu_2, Ph_2, BuPh and L', L" are as indicated above.

The symmetrical bis chelates, $[SnR_2(quin)_2]$ (R = Me, Ph), were prepared by the method described by Westlake and Martin (75) for the corresponding bis oxinates. The complex, $[SnMe_2(PPh_3O)_2(AsPh_3O)_2]^+[BPh_4]^-$ was obtained immediately by the addition of an ethanolic solution containing the two oxygen donor ligands to an ethanolic solution containing dimethyl tin dichloride and sodium tetraphenyl borate. The reactants were kept in stoichiometric ratio indicated below in the parenthesis:

$[SnMe_2Cl_2]$ (1), $[AsPh_3O]$ (1), $[PPh_3O]$ (3), $[NaBPh_4]$ (2).

Configurational assignments of the Sn-C bonds in the octahedral structures of these complexes have been made (91) by Mossbauer spectroscopy.

A series of air stable s-triorgano stannyl derivatives of L-cysteine and DL-homocysteine have been prepared (92b) by the reaction of appropriate triorganotin hydroxide or bis (triorganotin) oxide with the sulphydryl - containing amino acids in methanol/water at room temperature. Some tributyl stannyl derivatives of types A, B, C formed with glycine, cysteine and histidine are shown in fig. 2.

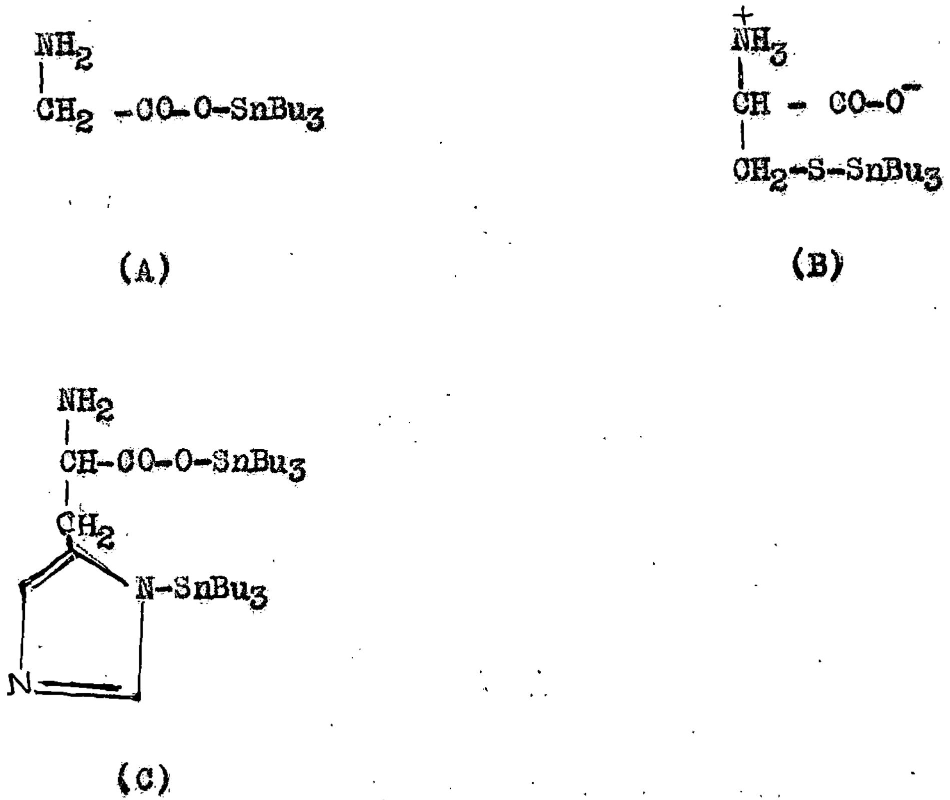


Fig. 2 Types of tributyl stannyl derivatives formed from amino acids.

$$(R_3Sn)_2O + 2HS(CH_2)_nCHNH_2COOH \longrightarrow 2R_3SnS(CH_2)_nCHNH_2COOH + H_2O$$

(n = 1, R = Np; n = 2, R = Bu or Np)

$$R_3SnOH + HS(CH_2)_nCHNH_2COOH \longrightarrow R_3SnS(CH_2)_nCHNH_2COOH + H_2O$$

(n = 1 or 2, R = Ph or Cy).

Very recently, ^{119}Sn- N.M.R spectra are reported for toluene solutions of tributyl stannyl ethers of 2,3,4,6-tetra-o-methyl-D-glucose, 1,2,3,4-di-o-isopropylidene-α-D-galactopyranose, methyl 2,3-di-o-methyl-α-D-glucopyranoside and the dibutyl stannyl ether of the last mentioned sugar (92a).

The structure of dibutyl stannylene derivative of methyl 4,6-o-benzylidene-α-D-glucopyranoside, which in solid state as well as in solution exists as a dimer as shown in (Fig. 3).

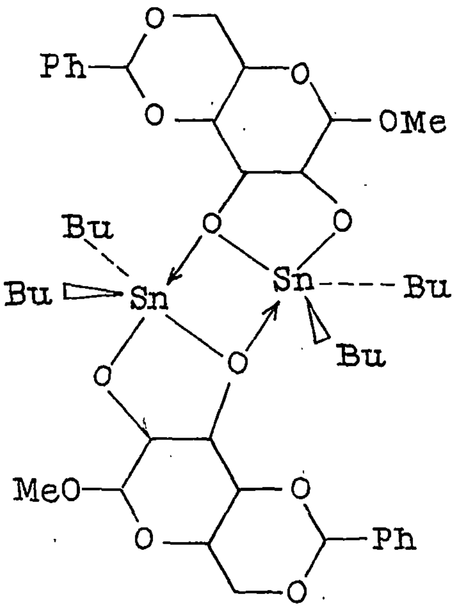


Fig. 3 Structure of dibutyl stannylene derivative of methyl 4,6-o-benzylidene α-D-glucopyranoside.

Organotin hydroxamates

A good number of metal complexes with hydroxamic acids have been prepared by many workers and these hydroxamic acids have been proved to be a very good analytical reagent (93).

Harrison (94,95) has synthesised the hydroxamic acid derivatives of organotin by the azeotropic removal of water from the mixture of appropriate hydroxylamine and the organotin oxides or hydroxides:

$$\tfrac{1}{2}(R_3Sn)_2O + HONR'R'' \text{ or } R_3SnOH + HONR'R'' \longrightarrow R_3SnONR'R'' + H_2O$$

(where R = Me, R' = R'' = Et; R = Me, R' = Ph, R'' = COPh; R = n-Pr, R' = Ph, R'' = COPh; R = Ph, R' = Ph, R'' = COPh; R = Me, R' = H, R'' = COPh; R = n-Pr, R' = H, R'' = COPh).

However, attempts to prepare $Ph_3SnONHCOPh$ by the same method only resulted in the formation of tetraphenyl tin in high yield, presumably by a disproportionation reaction, although no pure diphenyl tin derivative could be isolated.

$$Ph_3SnOH + HONHCOPh \xrightarrow{-H_2O} [Ph_3SnONHCOPh]$$
$$\longrightarrow Ph_4Sn + [Ph_2Sn(ONHCOPh)_2]$$

The organotin derivatives of N-benzoyl hydroxyl amines are extremely stable in moisture. The $Ph_3SnONPhCOPh$ is monomeric in both the crystal and solution phases, whereas the trimethyl tin derivatives are associated in the solid (96,94)

Diorganotin derivatives of N-substituted benzo hydroxamic acids have been prepared (97,98,99) according to the following reaction schemes:

$$R_2SnO + 2HONR'R'' \longrightarrow R_2Sn(ONR'R'')_2 + H_2O$$

$$R_2SnCl_2 + 2HONR'R'' \longrightarrow R_2Sn(ONR'R'')_2 + 2HCl$$

The liberated hydrochloric acid was neutralised by 25% aqueous ammonia and the precipitated ammonium chloride was removed by filtration.

Phenyl tin halide bis-(N-phenyl benzohydroxamates) have been prepared by the reaction of triphenyl tin N-phenyl benzohydroxamate with mercuric chloride, mercuric bromide and mercuric iodide (99).

Phenyl tin thiocyanate bis-(N-phenyl benzohydroxamate) has been prepared (loc. cit) from the corresponding chloride by the displacement of chloride by thiocyanate.

$$PhSnCl(PBHA)_2 + KCNS \longrightarrow PhSn(CNS)(PBHA)_2 + KCl$$

(HPBHA = N-phenyl-N-benzohydroxamic acid)

Pradhan and Ghosh (99,99a) have also prepared compounds of the type $R_2SnX(PBHA)$ (where R = Ph, X = Cl, I, SCN; R = Bu, X = SCN) through disproportional reactions.

$$R_2SnX_2 + R_2Sn(PBHA)_2 \longrightarrow 2R_2SnX(PBHA)$$

But $Ph_2Sn(SCN)(PBHA)$ has been prepared by the reaction of corresponding chloride complex with KCNS (100)

$$Ph_2SnCl(PBHA) + KCNS \longrightarrow Ph_2Sn(SCN)(PBHA) + KCl$$

It has been shown by Pradhan and Ghosh (99) that penta co-ordinated diorganotin halide N-phenyl N-benzohydroxamates, on refluxing in non-polar solvent like benzene for a long time, disproportionate to the more stable hexa co-ordinated tin compounds

$$2Ph_2SnX(PBHA) \longrightarrow PhSnX(PBHA)_2 + Ph_3SnX$$

(where X = Cl, SCN).

However, in polar solvents like methanol, ~~change was not found~~. ~~Instead~~ another hexa co-ordinated compound phenyl tin halide methoxy N-phenyl N-benzohydroxamate was formed along with the liberation of one equivalent of benzene (99).

This methoxy compound was also obtained when phenyltin halide bis-N-phenyl-N-benzohydroxamate was refluxed in methanol with the liberation of one mole of ligand.

$$Ph_2SnX(PBHA) \xrightarrow{\text{in } CH_3OH} PhSnX(OCH_3)(PBHA) + C_6H_6$$

$$PhSnX(PBHA)_2 \xrightarrow{\text{in } CH_3OH} PhSnX(OCH_3)(PBHA) + HPBHA$$

Some mono organotin derivatives of hydroxamic acids were prepared by Narula and Gupta (100).

Five, six and seven co-ordinated mono organotin derivatives of hydroxamic acids have been synthesised by them. They isolated the compounds having the general formulae $R_2Sn_2O_2L_2$, $(RSnL_2)O$

(LH = hydroxamic acid derivative).

Recently Harrison et al (98) have prepared a number of new organotin hydroxamates following the usual procedures (94, 95). These compounds are of the types: R_2SnL_2(where R = Me, nBu*, n-octyl, Ph and LH = N-benzoyl-N-phenyl hydroxylamine), R_2SnXL (where R = Me; X = Cl, Br, I) and $RSnL_3$ (where R = n-Bu)

Organotin Dithizonates

Alridge and Cremer (101) showed that on extraction with dithizone from a borate-buffer triethyl tin compound gave a yellow complex and that of diethyl tin compound gave an orange complex in solution. The complexes formed had ϵ_{max} = 23300 at 435 and

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* Reported earlier by Pradhan and Ghosh (loc. cit)

ϵ_{max} = 70500 at 510 nm respectively. Irving and Cox (102) have suggested a 1:1 complex for the former compound and 1:2 for the latter. Similar complex compound in solution of tri n-propyl- and tri n-butyl tin, dibutyl - and dioctyl tin compounds were reported.

Skeel and Bricker (103) confirmed that dibutyl tin dichloride reacts with dithizone, but noted that λ_{max} appeared to depend on the pH, the concentration, and the composition of the buffer system employed. This unexpected effect has recently been explained by Kahara and Takei (104) who showed that whereas a 1:2 complex $Bu_2Sn(HDZ)_2$ with ϵ_{max} = 63500 at 479 nm is extracted from a phosphate buffer, a 1:1 complex of $Bu_2Sn(HDZ)X$ (where X = CH_2Cl, COO^-) is extracted from monochloroacetate buffer, and a mixture of the two (X = $HCOO^-$ or $MeCOO^-$) from a formate and acetate buffer. All these mixed complexes had λ_{max} in the range 496-499 nm, with ϵ_{max} = 36600-38300. The complexes formed by Pr_2Sn^{2+} had almost identical properties.

Recently Ghosh and Ghosh (105) reported the isolation and characterisation of a number of crystalline organotin dithizonates. These are of the following types:

R_3SnHDZ (where R = Pr, Bu, Ph) and $R_2Sn(HDZ)_2$
(where R may be Me, Pr, Bu, Ph, p-tolyl, Benzyl).

These triorgano- and diorganotin derivatives were characterised by visible, I.R., P.M.R. spectroscopy and elemental analysis. In all these derivatives dithizone acts as a mono basic acid and the second hydrogen could not be replaced.

Besides these a number of diorgano halo-dithizonates ($R_2SnXHDZ$ where R = Ph, Bu, Me, Benzyl, p-tolyl; X = Cl, Br, I, SCN) and some mono organo halo mixed ligand dithizonates [$RSnXLHDZ$ where R = Ph; X = Cl, I; L = N phenyl benzohydroxamate and H_2DZ is dithizone] have been prepared (106).

All these derivatives are beautifully crystalline in nature and are highly coloured with sharp melting points.

Diphenyl carbazone (Diazene carboxylic acid, 2-phenyl hydrazide) has been used as analytical reagent for various metals for a long time.

Skeel and Bricker (107) used diphenyl carbazone as a reagent for spectrophotometric determination of dibutyltin dichloride in presence of mono-, tri- and tetrabutyltin compounds by measuring the absorbance of dibutyl tin-diphenyl carbazonate complex. They noticed that $BuSnCl_3$ interferes the determination of dibutyl tin content and suppressed the $BuSnCl_3$ by addition of ethylene diamine tetraacetic acid. By controlling the pH, they reported that 3-150 γ of Bu_2SnCl_2 can be determined spectrophotometrically.

Badoz-lamburg, Herlem and Thiebault (108) reported that diphenyl carbazone acts as a mono basic acid in liquid ammonia.

They reported that the pK value of diphenyl-carbazone is between 9.5-11.

Diphenyl carbazone forms a large number of derivatives of the metals like Zn^{2+}, Ni^{2+}, Pb^{2+}, Cd^{2+}, Cu^{2+}, Co^{2+}, Hg^{2+} etc (109, 110). Kemula and Janowski reported that the $>(C=O)$ band observed in diphenyl carbazone disappears and new intense bands at $\sim 1200\ cm^{-1}$ and $\sim 1550\ cm^{-1}$ appears. They also concluded, in metal derivatives, metal- oxygen bond is present and there is also intramolecular hydrogen bond $N—H\cdots N$ in the complexes. Van Dalen and Balt also observed disappearance of $\nu >C = O$ frequency from 5.85μ.

Though a large number of metallic derivatives of diphenyl carbazone have been prepared, so far, there is no report of any solid organotin diphenyl carbazonate.

In view of the fact, a large number of crystalline organotin dithizonates could be synthesised and characterised, it was considered desirable to attempt similar derivatives of diphenyl carbazone with organotin compounds, as we can consider diphenyl carbazone is an oxygen analogoue of dithizone. We also wanted to prepare diphenyl carbazone derivatives of organo tin compounds in order to test their fungicidal properties, since it was observed in this laboratory that triphenyltin dithizonate has excellent fungitoxicity against a number of plant pathogenic fungi (111).

From the crystal structure determination, it was observed, in dithizone, coplanar N-N-C-N-N bonds are delocalised and the presence of $>C = S$ group in dithizone could not be definitely established but the crystal structure determination conclusively showed the presence of $>C = O$ group in diphenyl carbazone and one hydrazo chain bond is delocalised and hence it was considered interesting whether the presence of $>C = O$ in organotin diphenyl carbazonates could be confirmed. Moreover, it would be highly interesting to investigate the relative stabilities of organotin dithizonates and diphenyl carbazonates so that some idea of the nature of organotin compounds in the light of HSAB concept can be obtained. It is expected that diphenyl carbazone is a harder acid than dithizone and so may form weaker complexes with organotins than dithizonates (112).