CHAPTER 3

SYNTHESIS, CHARACTERIZATION AND BIOCIDAL PROPERTIES OF ORGANOTIN(IV) CARBOXYLATES OF CYCLOPROPANE CARBOXYLIC ACID AND 3-CYCLOHEXYLPROPANOIC ACID

3.1 A brief review of organotin carboxylates

In the recent years [1-5], organotin compounds have been the subject of study due to their diversified biological [6-9] and non-biological [10-12] applications along with their interesting structural diversities. The structure of the molecule, coordination number, extent of alkylation and nature of organic groups attached to the tin atom are the main factors deciding the biological activity of the organotin compounds [13-15].Organotin carboxylates comprise one of the most important class of organotin compounds.The chemistry of Organotin carboxylates has attracted much attention owing to their industrial and agricultural importance [16-19] and more recently to their antitumour activity [20]. Consequently there has been considerable interest in their structural characteristics. These compounds may adopt a variety of structural modes depending on the nature of the organic substituent on the Sn atom and/or the carboxylate ligand [21]. The carboxylates are of following types which may either be monomeric or polymeric in the solid state, namely, $R_3SnOCOR'$, $R_2Sn(OCOR')_2$ and $RSn(OCOR')_3$ where R and R' may be same or different alkyl or aryl groups.

3.1.1 Synthesis of organotin carboxylates

Organotin carboxylates are readily synthesized by several routes. The reactions involved in these synthetic routes are extremely general and there does not appear to be any instance where a particular carboxylic acid failed to react with the organotin precursors. Here, attempt has been made to outline the general synthetic methods for the carboxylates of organotins. Attempts are also made to indicate some of the preparatory routes of interesting organotin carboxylates. The review, however, is not comprehensive.

The most general procedure for the synthesis of organotin carboxylates involve the reaction of carboxylic acid with organotin oxides (or hydroxides) [22-24].The reaction is achieved by azeotropic dehydration of the reactants in boiling benzene or toluene, using Dean-Stark apparatus.

$R_3SnOSnR_3 + 2R'COOH \xrightarrow{benzene} 2R_3SnOCOR' + H_2O$ ..... (1)

$R_3SnOH + R'COOH \xrightarrow{toluene} R_3SnOCOR' + H_2O$ .....(2)

$R_3SnOSnR_3 + (R'CO)_2O \xrightarrow{toluene} 2R_3SnOCOR'$ .....(3)

$R_2SnO + 2R'COOH \xrightarrow{toluene} R_2Sn(OCOR')_2$ .....(4)

In a particular synthesis, for example, the water produced in these reactions was alternatively produced by refluxing the reaction mixtures at higher temperatures [25].

$Bu_3SnOSnBu_3 + 2o\text{-}HOC_6H_4COOH \longrightarrow Bu_3SnOCOC_6H_4OH + H_2O$ .....(5)

One of the most convenient and frequently employed method for the synthesis of organotin carboxylates is the reaction between metal carboxylates and organotin halides[26,27] in suitable solvent usually acetone or methanol or CCl_4 or $CHCl_3$.

$R_nSnX_{4-n} + (4\text{-}n)MOCOR' \longrightarrow R_nSn(OCOR')_{4-n} + (4\text{-}n)MX$ ..... (6)

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

The carboxylates can also be prepared by the reaction of silver salts of carboxylic acids and organotin sulphides [28].

$R_2SnS + 2AgOCOR' \longrightarrow R_2Sn(OCOR')_2 + Ag_2S$ ..... (7)

The cleavage of one or more organic groups from tetraorganotin compounds by carboxylic acids [29] or Hg(I) carboxylates also produces organotin carboxylates.

$R_4Sn + nR'COOH \longrightarrow R_{4-n}Sn(OCOR')_n + nRH$ ..... (8)

$2Me_4Sn + Hg_2(OCOMe)_2 \longrightarrow 2Me_3SnOCOMe + 2Hg$ ..... (9)

In these acidolysis reactions, the cleavage depends on the acid strength, the nature of the organic groups being cleaved and also on the temperature [29, 30]. Vinyl groups are more readily cleaved than the saturated alkyl radicals, but less readily than phenyl [31], and successive groups are lost with increasing difficulty.

An organotin carboxylate $RBu_2SnOCOCH_3$, with different alkyl groups was synthesized by the reaction of $(Bu_2SnX)_2O$ (X=Cl, Br) with Li and subsequent alkylation with RX' (R=Me, Bu; X = Br, I) and $(CH_3CO)_2O$ [32].

Halocarboxylate derivatives of organotin compounds are most conveniently prepared by heating equimolecular proportion of diorganotin dihalides and diorganotin dicarboxylates in an inert solvent (Eq.10) [33] or by the reaction between a diorgaotindihalide(Eq.11) and a metal carboxylate[34].

$$Bu_2SnBr_2 + Bu_2Sn(OAc)_2 \longrightarrow 2Bu_2SnBr(OAc) \quad \text{.....(10)}$$

$$Bu_2SnCl_2 + R'COOK \longrightarrow Bu_2SnCl(OCOR') + KCl \quad \text{.....(11)}$$

Organotin tricarboxylates, $RSn(OCOR')_3$ (R=n-Bu and Ph) are usually prepared from the corresponding organotin trichlorides by the action of Silver salts of carboxylic acids[35].

$$RSnCl_3 + 3R'COOAg \longrightarrow RSn(OCOR')_3 + 3AgCl \quad \text{..... (12)}$$

Organotinhydrides react with carboxylic acids to form the organotin esters with evolution of hydrogen [36]. This reaction is not, however used extensively to prepare organotin esters.

$$Bu_2SnH_2 + 2MeCOOH \xrightarrow{4.5\ hours} Bu_2Sn(OCOMe)_2 + 2H_2 \quad \text{.....(13)}$$

The triorganotin derivatives of 3-ureidopropionic acid of the general formula, $R_3SnOCOCH_2CH_2NHCONH_2$ (R=Ph, n-Bu, c-Hex and *p*–tolyl) have been synthesized by the heating the mixture of Ph_3SnOH and 3-ureidopropionic acid in 1:1 molar ratio in ethanol [37].

The reaction of one molar equivalent of bis(tributyltin)oxide with two molar equivalents each of 2,6-pyridine dicarboxylic acid and dicyclohexylamine in ethanol

solution gave an precipitate of $[(c\text{-}C_6H_{11})_2NH_2][(n\text{–}C_4H_9)_3Sn(O_2C)_2C_5H_3N]$ [38] immediately. The triphenyltin analogue $[(c\text{-}C_6H_{11})_2NH_2][(C_6H_5)_3Sn(O_2C)_2C_5H_3N]$ was prepared from the equimolar reaction between Ph_3SnOH, the acid and the amine.

S.W. Ng *et al.* synthesized monohydrated carboxylate [n-Bu_3Sn(*N*-phthaloylglycin –ate)(OH_2)] and [n-Bu_3Sn(*N*-phthaloylalaninate)(OH_2)] by the condensation of bis(tributyltin)oxide with *N*-phthaloylglycine and *N*-phthaloylalanine respectively in 1:2 molar ratio in the absence of solvents [39].

Triphenyl and tributyltin carboxylates of crotonic acid, 2, 4-hexadienoic acid and 4-nitrocinnamic acids have been prepared by treatment of bis-tributyltin oxide or bis-triphenyltin oxide with one molar proportion of the corresponding acid. Reactions were carried out in benzene or toluene with azeotropic removal of water [40].

μ-oxalatobis(tricyclohexyltin), $\mu\text{-}(O_2CCO_2)[(c\text{-}C_6H_{11})_3Sn]_2$ was obtained is an attempt to prepare $[(CH_3)_4N]^+[(c\text{-}C_6H_{11})_3SnO_2ClO_2]^-$ by the reaction of $[(CH_3)_4N]Cl]$, $(c\text{-}C_6H_{11})_3SnCl$ and $Ag_2O_2CCO_2$ in ethanol by stirring in hot condition [41].

C. Deb and coworkers have shown that alkyl or aryl esters (carbonyl group attached to 1° or 3° carbon atom) may be transesterified to triorganotin carboxylates [42].

$$R'COOR'' + (R_3Sn)_2O \longrightarrow R'COOSnR_3 + R''OSnR_3 \quad \text{.....(14)}$$

Two types of diorganotin(IV) complexes i.e. $[R_2Sn(O_2CCH_2SPh)_2]$ and $\{[R_2Sn(O_2CCH_2SPh_2)_2O\}_2$, R = Me, Et, n-Pr, n-Bu and n-Oct, have been prepared in 1:2 and 1:1 molar ratio (tin : ligand) by refluxing diorganotin(IV) oxide with thiophenoxy acetic acid [43] in a dry benzene – ethanol mixture (3/1 v/v) with azeotropic removal of water.

Recently, a mixed chelate diorganotin compound has been prepared in the reaction with di-n-butyltin oxide with 2,6-pyridinedicarboxylic acid followed by reaction with bis(dicyclohexylammonium) oxalate [44].

The reaction of $RSn(O)OH$ with an excess of carboxylic acid leads to the formation of the hydrolytically sensitive tricarboxylate $RSn(O_2CR')_3$ which under goes hydrolysis to afford the ladder $[(RSn(O)O_2CR')_2\ (RSn(O_2CR')_3]_2$ [45]. In contrast a 6:6 reaction of $RSn(O)OH$ with a carboxylic acid R'COOH afforded a hexametric drum $[RSn(O)O_2CR']_6$ [46].The drums and ladders are also obtained in reactions with diorganotin and triorganotin precursors with carboxylic acids or silver salts of carboxylic acids by Sn-C cleavage reactions [47].

An interesting 2:3 (tin:carboxylate) product, $(n\text{-}Bu_2SnO_2CCCl_3)_2(\mu_2\text{-}OH)(O_2CCl_3)$ has been obtained in 1:2 reaction between $n\text{-}Bu_2SnO$ and CCl_3COOH[48]. In the product, the two Sn units are bridged by a hydroxyl group and a isobidentate carboxylate group. The complex $SnPh_3(O_2CCCl_3).MeOH$ has been prepared by the reaction of Ph_3SnOH and the carboxylic acid in methanol [49]. Synthesis of $SnPh_3(O_2CCl_3)$ without the attached solvent molecule seems to be unusually difficult, although well known for other carboxylates [50,51].In particular, recrystallization of $SnPh_3(O_2CCCl_3)$ in a non-coordinating solvent leads to the diphenyltin compound, $\{[SnPh_2(O_2CCCl_3)]_2O\}_2$.

A compound of the same formulation was also formed by the dearylation of $(SnPh_3)_2O$ with trichloroacetic acid [49].

$$(SnPh_3)_2O \xrightarrow[\text{(ii) recrystallization from dichloromethane - light petroleum}]{\text{(i) trichloroacetic acid, MeOH}} \{[SnPh_2(O_2CCCL_3)]_2O\}_2 \quad \text{.....(15)}$$

However, the product that is formed under the above mentioned condition has different structure. It is not clear whether this is due to solvent effects in the recrystallization or due to the different reaction routes.

The $Bu_2Sn(IV)^{2t}$ complexes formed with ligands containing a carboxylate group(s) are easily prepared by a one-pot method described by Davies *et al.* [52]. In a first step, tetra-n-butyl-di-n-propoxydistannoxane is prepared from Bu_2SnO and n-propanol by refluxing in benzene or in toluene. This distannoxane subsequently reacts at room

temperature with carboxylates. This method [53,54] appears to have two advantages over that in which Bu_2SnO reacts with the carboxylic in refluxing ethanol/ toluene, methanol/toluene; first as the carboxylic acid is added at room temperature, organotin(IV) carboxylates that are unstable at higher temperatures can also be prepared; second, tetra-n-butyl-di-n-propoxydistannoxane is synthesized in water-free medium because the H_2O is eliminated through a H_2O/propanol/benzene azeotrope; hence water- sensitive organotin(IV) carboxylates can be conveniently prepared.

[n-Bu_2Sn(pyridine-2-phosphonate-6-carboxylate)]$_2$ was prepared in very high yield by the reaction of tetra-n-butyl-di-n-propoxydistannoxane, [n-Bu_2Sn(O-Pr-n)OSn(OPr-n)n-Bu_2] (generated *in situ* by the reaction of n-Bu_2SnO with isopropanol in refluxing benzene) with dihydrogen pyridine-2-phosphonate–6–carboxylate in a 1:1 tin/ligand molar ratio at room temperature[55].

A series of diorganotin(IV) compounds were obtained by the reaction of diorganotin(IV) dichloride with 2- pyrazinecarboxylic acid (Hpca) in the presence of sodium ethoxide or triethylamine [56]. Using a 1:1:1 molar ratio of R_2SnCl_2: Hpca: EtONa, trinuclear macrocyclic compounds of the type $[R_2Sn(pca)Cl]_3$ R=Me, n-Bu, Ph, Bz were obtained. With a 1:2:2 ratio, monomeric or polymeric compounds with the general formula $R_2Sn(pca)_2(mH_2O).nH_2O$, m=1 : R=$CH_3$, n=2; m=0: R=n-Bu, n=0 etc. were obtained. Using a 1:2:2 molar ratio of R_2SnCl_2: Hpca: Et_3N, stannate compounds of the type $[Et_3NH]^+[R_2Sn(pca)_2Cl]^-.mH_2O$,m=0 : R=Me; m=0: R= n-Bu etc. were obtained.

The reaction of bis(triphenyltin)oxide, $Ph_3SnOSnPh_3$ and 2,4,6–tris(trifluoromethyl) -benzoic acid, 2,4,6–$(CF_3)_3C_6H_2COOH$ in a 1: 2 stoichiometry, in benzene under reflux conditions afforded the distannoxane $[Ph_2Sn(OH)OC(O)R_f)]_2$, R_f=2,4,6-$(CF_3)_3$ -C_6H_2, in about 94% yield, by means of a facile Sn-C bond cleavage process [57]. The facile Sn-C bond cleavage process occurs as a result of special electronic and steric requirements of the perfluoromesityl carboxylate unit. This is the first example of a Sn-C bond cleaved product in the reaction of $Ph_3SnOSnPh_3$ with carboxylic acid. In contrast, analogous reaction of $Ph_3SnOSnPh_3$ with mesityl carboxylic acid leads to the formation of the normal product, Ph_3SnO_2C-2,4,6-$Me_3C_6H_2$. Also the reaction of

perfluorobenzoic acid C_6F_5COOH with $Ph_3SnOSnPh_3$ leads to the normal product [24]; $Ph_3SnO_2CC_6F_5$.

X-ray quality crystals of the Bis-[(1,7-dicarba-*closo*-dodecaborane-1-carboxylato)-di-n-butyltin]oxide, $\{[1,7\text{-}C_2B_{10}H_{11}\text{-}1\text{-}COO)Bu_2Sn]_2O\}_2$ were synthesized in benzene from a 1:1 condensation of $n\text{-}Bu_2SnO$ with m-carborane-1-carboxylic acid[58].

Reactions of diorganotin(IV) oxides with *o*-anisic acid in a 1:1 and 1:2 stoichiometry in benzene with azeotropic removal of water using Dean-stark trap afforded complexes of the type $\{[R_2Sn(2\text{-}MeOC_6H_4COO)]_2O\}_2$ and $[R_2Sn(2\text{-}MeOC_6H_4COO)_2]$ R=Me, Et, n-Pr, n-Bu respectively[59].

Bis(pentafluorophenylacetato)tetra-n-butyldistannoxane, $\{[n\text{-}Bu_2Sn(O_2CCH_2C_6F_5)]_2O\}_2$; bis(*p*-fluorophenylacetato)tetra-n-butyldistannoxane, $\{[^nBu_2Sn(O_2CCH_2C_6H_4F\text{-}p)]_2O\}_2$ were prepared by the reaction of Bu_2SnO with pentafluorophenylacetic acid and *p*-fluorophenylacetic acid respectively in 1:1 molar ratio by refluxing in 4:1 toluene-ethanol mixture. The water produced in both the reactions was distilled off using a Dean-stark apparatus [60].

The product of the reaction of both ethylene-vinyl acetate copolymers (EVA) and ethylene-methyl acrylate copolymers (EMA) with Bu_2SnO at 200 °C, which leads to the cross-linking of the polymer matrix, is shown to be a dimeric 1-alkoxy-3-acyloxy-distannoxane. The reaction mechanism was studied using model esters(n-octylacetate, n-octadecyl acetate and methyl nonanoate) in absence of solvent at 200 °C. The formation of the main reaction product, $(R\text{-}CO\text{-}O\text{-}(C_4H_9)_2Sn\text{-}O\text{-}(C_4H_9)_2Sn\text{-}OR')_2$ is complete after heating for 25 minutes [61].

Base hydrolysis of $[t\text{-}Bu_2Sn(O_2CCH_3)_2]$ with NaOH yielded hydroxy bridged dinuclear complex $[t\text{-}Bu_2Sn(O_2CCH_3)(\mu\text{-}OH)]_2$, which could also be prepared by the reaction of $(t\text{-}Bu_2SnO)_3$ with acetic acid in 1 : 1 stoichiometry in benzene [62].

Organotin compounds with the general formula $R_2(X)SnL$ (where R= Me, Et, n-Bu, Ph; L= *trans*-3-(2-furanyl)-2-propenoate anion or the *trans*-3-(3-methylphenyl)-2-

propenoate anion; X=Cl) have been prepared by redistribution reactions between R_2SnL_2 and R_2SnX_2 compounds [63].

1,2,3,4-Di-μ-*o*-aminobenzoato-*O*-*O*'-1, 3-bis(*o*-aminobenzoato-*O*)-1,2,4;2,3,4-di-μ_3-oxotetrakis[di-n-butyltin(IV)] was obtained by azeotropic removal of water from the reaction between Bu_2SnO and *o*-aminobenzoic acid in the molar ratio 1:1 in benzene [64].

The complexes $[Me_2(Indo)SnOSn(Indo)Me_2]_2$ and $[Bu_2(Indo)SnOSn(Indo)Bu_2]_2$ were obtained by the azeotropic removal of water produced by the reaction between the respective diorganotin oxide and indomethacin (Hindo) in the molar ratio 1:1 [65].

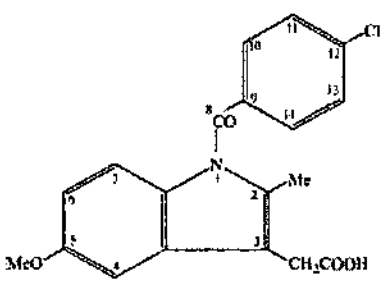


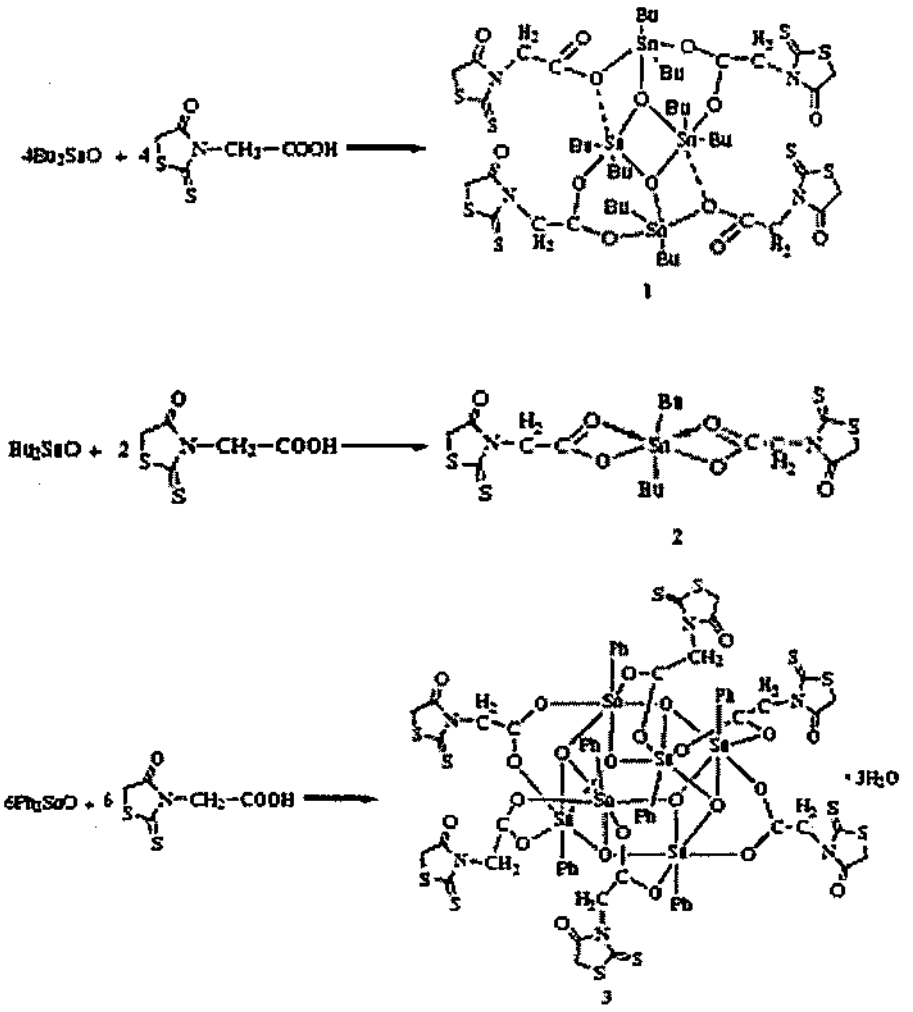
Fig. 3.1 Structure of indomethacin (Hindo) [65].

Diorganotin(IV) derivatives $[R_2Sn(A)_2]$ and $\{[R_2Sn(A)_2]_2O\}_2$ (where A is the dianion of *N*-phthaloyl-**DL**-valine and R= Me, n-Bu, n-Oct) were obtained in moderate yield by the reaction between dialkyltin(IV) oxides with *N*-phthaloyl-**DL**- valine in 1:1 and 1: 2 (Sn: ligand) molar ratio in mixture of dry benzene and absolute ethanol on a water bath by azeotropic removal of water by refluxing for 3-4 hours [66].

The hydrothermal reaction of nitroterephthalic acid, H_2NTPA or diphenic acid (H_2DPA) with 4, 4'-bipyridine and trimethyltin chloride in a molar ratio 1:1:2 at 140 °C for 3 days produced a one-dimensional chain polymer $[(Me_2Sn)_2(\mu_3\text{-NTPA})(\mu_3\text{-O})]_n$ or a two-dimensional corrugated sheet polymer $[(Me_2Sn)_4(\mu_3\text{-DPA})(\mu_4\text{-DPA})(\mu_3\text{-O})_2]_n$ respectively [67].

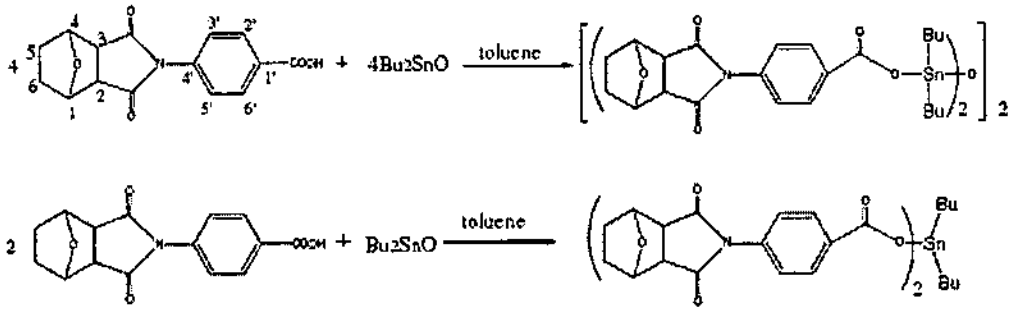
Di-*n*-butyltin oxide react with rhodanine–*N*-acetic acid in 1:1 and 1:2 molar ratios to form $\{[n\text{-}Bu_2Sn(O_2CC_6H_4NOS_2)]_2O\}_2$ (**1**), and $n\text{-}Bu_2Sn(O_2CC_6H_4NOS_2)_2$ (**2**)

respectively. Complex $[PhSn(O)O2CC_6H_4NOS_2)_6].3H_2O$ (**3**) is however produced through the dearylation reaction of diphenyltin oxide and rhodanine–*N*-acetic acid in 1:1 molar ratio [68] .The synthetic procedures are shown in the Scheme 3.1.



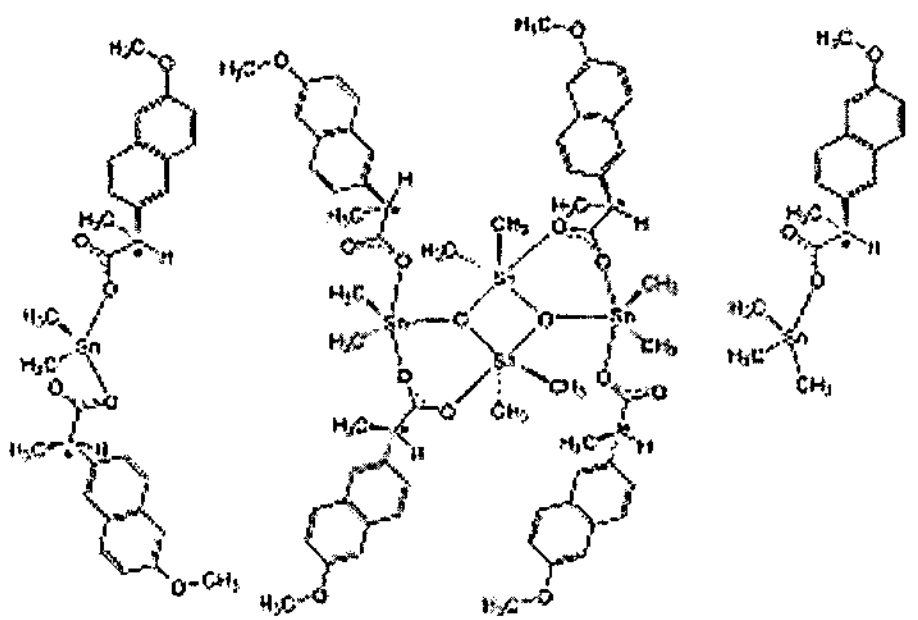
Scheme 3.1

The carboxylic acid 4'-(7-oxabicyclo[2,2,1]-5-heptane-2,3-dicarboximide)benzoic acid (A) reacts with di-*n*-butyltin oxide yielding two different compounds (Scheme 3.2) depending on molar ratio of acid/tin engaged in the reaction: bis[di-*n*-butyl(carboxylato)tin]oxide (**1**) for a 1:1 ratio and di-*n*-butyltin di(carboxylato) (**2**) for a 2:1 ratio [69].



Scheme 3.2

To prepare enantiomerically pure methyltin(IV) naproxenates, dimethyltin dichloride , dimethyltin oxide and trimethyltin chloride were allowed to react with (*S*) – naproxen or its sodium salt. The reactions gave the $Me_2Sn(nap)_2$ (**1**), {[$Me_2Sn(nap)_2]_2O_2$ (**2**) and $Me_3Sn(nap)$ (**3**) complexes (where nap = (*S*)-(+)-6-methoxy-α-methyl-2-naphthaleneaceto anion) [70] .



(1) (2) (3)

Fig. 3.2 Structure of methyltin(IV) naproxenates [70].

A number of distannoxanes have been isolated as the products either from the condensation of a diorganotin oxide with two molar equivalents of the carboxylic

acid, or from the metathetical reaction of a diorganotin dihalide with a metal carboxylate [21, 71].

3.1.2 Structure of organotin carboxylates

The structural investigations of organotin carboxylates are carried out by IR, NMR (^{1}H, ^{13}C, ^{119}Sn) and ^{119m}Sn Mössbauer spectroscopy and by X-ray Crystallography. The structure of organotin carboxylates have been studied extensively by Okawara and Wada [72]. The possibility of chelation through weak coordination of oxygen atoms of carboxylate groups to tin atoms was pointed out by Beattie and Gilson [73] against the postulation of ionic nature of bonding by Freeman [74].

A vast literature on the structure of organotin carboxylates were covered in the review written by Davies *et al.* [16] and on ^{119}Sn–NMR spectroscopy by P. J. Smith and A.P. Tupciauskas [75] and by B. Wrackmeyer [76].

Recently an excellent review by Chandrasakhar *et al.* [77] dealing with the structural diversity of organotin assemblies containing Sn-O bonds was published. The X-ray crystal structures of several organotin carboxylate have been elucidated. This aspect has been critically and quite exhaustively dealt in literatures [21, 71].

3.1.2.1 Structure of triorganotin(IV) carboxylates

Triorganotin carboxylates are known to exist in several structural forms, depending on the physical state and the nature of the substituents on the tin and the carbonyl group. These compounds can exist as monomeric compounds with four-coordinate Sn sites , as monomeric compounds with bidentate carboxylate groups producing a five-coordinate tin, or as polymeric compounds with bridging carboxylate groups that generally produces five-coordinate Sn sites [15].

Based on the studies of the X-ray crystal structures of several triorganotin carboxylate, the structures of these can be divided into two major structural types viz.; (a) discrete and (b) polymeric structures.

Steric effects associated with Sn- and/or ligand-based substituents have been found to be responsible for dictating the nature of structure in the solid state [78].

In the triorganotin carboxylates R_3SnO_2CR' having discrete structures, the tin is bound covalently to three carbons and one oxygen and is present in a distorted tetrahedral geometry [79-81].

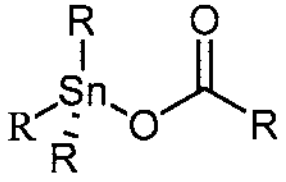


Fig. 3.3 Discrete structural form (no intramolecular coordination).

An X-ray crystal study on tricyclohexyltin acetate, $Cy_3SnOCOMe$ showed the presence of discrete molecules, with the tin atom occupying a distorted tetrahedral geometry.The compound was suggested to be a tetra-coordinated monomer probably due to steric hindrance arising from bulky organic groups [82].

Q. Xie and J. Zheng [83] in 1991 on the basis of IR, ^1H HMR and ^{13}C NMR studies have shown that compounds of the type $ROCH_2COOSnR'_3$ (R'=Ph, Substituted Ph) adopt a distorted tetrahedron containing four-coordinated Sn atom.

The crystal structure of trimesityltin(IV) benzoate, $(C_{27}H_{33})_3Sn(O_2CC_6H_5)$ is monomeric with tin atom in a distorted tetrahedral environment defined by a C_3O donor set as the carboxylate ligand coordinates in a monodentate mode [84].

Even in discrete form, participation of carbonyl oxygen in an intramolecular coordination would lead to approximate trigonal bipyramidal geometry around tin (Fig. 3.4).

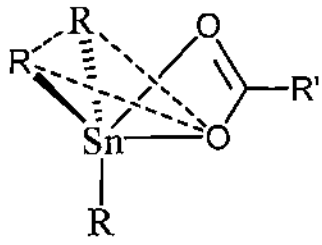


Fig. 3.4 Discrete structural form with intramolecular coordination.

The extent of intramolecular coordination in a complex depends also upon the presence of intramolecular hydrogen bonding. Thus among the $Ph_3SnO_2CC_6H_4$–2–NH_2, $Ph_3SnO_2CC_6H_4$–2–NMe_2 & $Ph_3SnO_2CC_6H_4$-4-NH_2, the anthranilic acid derivative in which the NH_2 group is intramolecularly hydrogen bonded to the C=O has the longest Sn-O distance[85].

The participation of the carbonyl group in intermolecular coordination would give rise to a polymeric associated structure (Fig.3.5) [24].

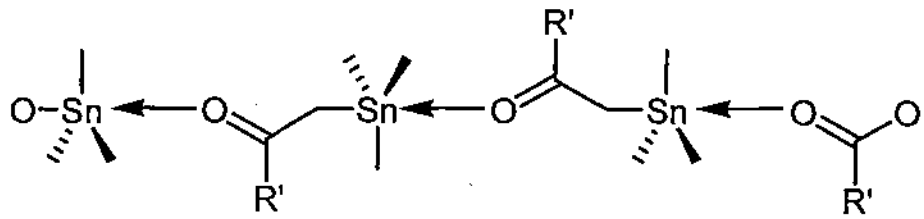


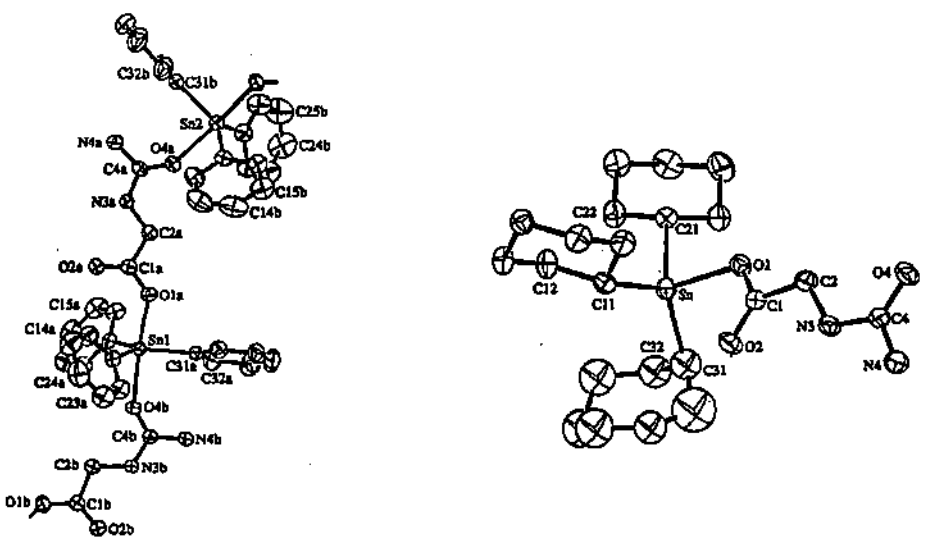
Fig. 3.5 Polymeric form of triorganotin(IV) carboxylates.

These chain polymers, involving bridging carboxylate groups are well documented in literature [86, 87].The coordination polyhedron around Sn is essentially a trigonal bipyramidal with the equatorial positions being occupied by the carbon substituents and the axial positions being occupied by the two oxygens. The Sn–O distances are non-equivalent and because of this variation of the bond distances in the triorganotin carboxylates the Sn is displaced from the equatorial plane towards the covalently bonded oxygen.

The preference for the chain structures seems to be the natural consequence of the principles of penta-coordination. However, the formation of chain structures for

$Ph_3SnO_2CC_6H_4$-2-Cl [88] and for $Ph_3SnO_2CCH_3$ [16] suggests that the factors such as pK_a of the acid and crystal packing may tilt the balance from one structure to another [89].

The structure of $[Ph_3Sn(O_2CCH_2N(H)C(O)NH_2]$ is polymeric in consequence of the bridging property of the carboxylate group. Each ligand coordinates to one Sn atom via one of the carboxylate 'O' atoms and to a symmetry-related Sn atom via a carbonyl group at the other end of the molecule (Fig. 3.6). The structure is distorted trigonal bipyramidal around the Sn atom, with a trans–R_3SnO_2 motif characteristic of triorganotin(IV) complexes. The structure of $[c\text{-}Hex_3Sn(O_2CCH_2N(H)C(O)NH_2]$, by contrast is monomeric with monodentate carboxylate group [90].



(a) (b)

Fig. 3.6 Structure of (a) $[Ph_3Sn(O_2CCH_2N(H)C(O)NH_2]$ and (b) $[c\text{-}Hex_3Sn(O_2CCH_2N(H)C(O)NH_2]$ [90].

$Ph_3Sn(IV)^+$ compounds of *p*-ethoxybenzoic acid and acetylsalicylic acid contain molecular units with Sn-O bonds and distorted tetrahedral tin centres. The phthalic acid derivative contains two tetra-coordinated tin atoms with a phthalic acid unit bridging them. The salicylaldehydato compound is polymeric with trigonal bipyramidal tin centres in which Ph group takes equatorial positions [91].

Khoo *et al.* studied the sarcosine $Ph_3Sn(IV)^+$ complexes with composition $[Ph_3Sn(OCOCH_2NH_2CH_3)_2]X$ ($X=Cl^-$, SCN^-). Sarcosine reacts in a zwitterionic form and behaves as a monodentate ligand via coordination through the carboxylate 'O'. All data support the trans–R_3SnO_2 (tbp) structure of the complexes [92].

The preparation and spectroscopic characterization of $[R_3Sn(O_2CCH_2SC_5H_4N\text{-}4)]$ (R=Ph, Bz, c-Hex and n-Bu) and $[R_3Sn(O_2CCH_2SC_4H_3N_2\text{–}2,6)]$ (R=Me, Ph, n-Bu) have been reported. The 2-pyrimidyl complexes have tbp Sn centres with trans–R_3SnO_3 geometry as confirmed by X-ray diffraction studies on $[Ph_3Sn(O_2CCH_2SC_4H_3N_2\text{–}2,6)]$. By contrast, 4–pyridyl complexes have tbp geometry in the solid state arising from the intermolecular Sn....N interactions and T_d structure in solution [93].

Triorganotin(IV) and diorganotin(IV) halides and pseudohalides form molecular adducts with zwitterions such as picolinic acid [94,95] and quinaldic acid [96]. With carboxylic acids, hydrated complexes are generally obtained. The acid in its Zwitterionic form binds to the $Ph_3Sn(IV)^+$ moiety and generates trigonal bipyramidal geometry around tin. Hydrogen bonding involving non-coordinated water molecules serves to bind the penta-coordinated units together in the form of a dimer. Such compounds display unusual structure [94-96].

V.G. Kumar Das and his coworkers [97] analyzed X-ray data for a number of polymeric triorganotin carboxylates which gave a repeat distance of 5.19 ± 0.21 Å for the carboxylate-bridged R_3SnO_2CR' unit that defines the crystal lattice. The repeat distance is sensitive to organic substituents on either the Sn or the carboxylate group.

Complexes with the formula R_3SnH_2Or (Or = Orotic acid, R= Me, n-Bu) were obtained with the $R_3Sn(IV)^+$ moieties, in which orotic acid (Or) behaves as a monoanionic bidentate bridging ligand and furnishes trigonal bipyramidal complexes [98].

An X-ray analysis of $[(c\text{-}C_6H_{11})_2NH_2]$ $[n\text{-}Bu_3Sn(O_2C)_2C_5H_3N)]$ compound shows that the structure is polymeric with neighbouring triorganotin centres being linked by dicarboxylate ligands [38]. Each carboxylate moiety is involved in coordination to a

Sn atom via one 'O' atom only which has the result that the Sn atoms are five-coordinate and exist in trigonal bipyramidal geometries with the 'O' atoms in axial positions. The pyridine 'N' atom is not involved in co-ordination to Sn.

The crystal structure of $[Me_3SnL]$, L=2',4'-difluoro- 4- hydroxyl-[1,1']-biphenyl-3-carboxylic acid, $C_{13}H_8O_3F_2$, indicates that the tin atom in the asymmetric unit exists in a trigonal bipyramidal geometry, with an orthorhombic crystal system [100].

The structural aspects of triorganotin carboxylates in the solid state and in the solution phase have been investigated by several workers by IR and far-IR spectroscopy [100,101]. The investigations showed that upon dilution of the associated triorganotin esters in organic solvents oligomeic and finally monomeric species containing tetrahedral tin atom and free ester carbonyl functionality is produced [100, 102].

The compound $[Sn(CH_3)_3(C_{15}H_9Cl_2O_2)]_n$ forms polymeric chain involving both O atoms of the carboxylate group.The coordination geometry around the Sn atom is distorted trigonal bipyramidal. The three methyl C atoms occupy the equatorial positions and two O atoms are at axial positions [103].

Several new triorganotin(IV) derivatives of L-homocysteic acid (LCAH) with formula $R_3Sn(LHCA)$ (R= Me, n-Bu, Ph) have been synthesized. Their solid state configurations were determined by IR and Mössbauer spectroscopy. The tin(IV) atom is five-coordinated in all the complexes, with the L-homocysteic acid behaving as a monoanionic bidentate ligand coordinating the tin(IV) through a chelating or bridging carboxylate group. The sulphonate $(SO_3)^-$ and NH_3^+ groups of L-homocysteic acid maintain their free acid configuration and hence do not participate to the coordination of the tin(IV) atom [104].

The crystal structure of *catena*-poly[[tri-n-butyltin]-μ-*N*-(1-naphthylmaleamato] is composed of polymeric chains wherein the metal centre exhibits a distorted trigonal bipyramidal geometry, with three n-Bu groups defining the trigonal plane and the axial positions being occupied by the carboxylate oxygen atoms of two different *N*-(1-naphthyl)maleamate ligands with inequivalent Sn-O distances. The *N*-(1-

naphthyl)maleamate fragment forms an essentially planar seven-membered ring involving an intramolecular N-H....O hydrogen bond [105].

The X-ray diffraction study of μ-oxalatobis(tricyclohexyltin) μ-(O_2CCO_2) [(c-$C_6H_{11})_3Sn]_2$ has revealed the presence of two symmetry – independent molecules, each of which contains a pair of tin atoms in a isomeric *cis* -, *trans* – C_3SnO_2 trigonal bipyramidal configuration arising from the quadridentate (chelating and bridging) behaviour of the oxalato ligand [41].

Some triorganotin carboxylates crystallize with a solvent molecule. These carboxylates show regular five-coordinate discrete structures [n-Bu_3Sn(*N*-phthaloylglycinate)OH_2] [39] is one such example. In all compounds of this type the tin is in trigonal bipyramidal geometry with the equatorial positions being taken up by the aryl or alkyl substituents on tin and the axial position being occupied by the oxygen of the solvent molecule and the covalently bonded oxygen of the Sn-O-C bond.

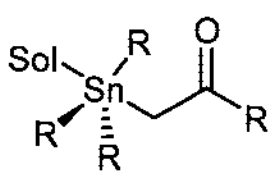


Fig. 3.7 Structure of triorganotin(IV) carboxylates crystallizing with a solvent molecule.

N.W. Alcock and S.M. Roe [49] established the structure of some phenyltin trichloroacetate complexes by X-ray crystallography. The complex $SnPh_3(O_2CCl_3)(MeOH)$ is a five -coordinated monomer. Two isomers of $\{\{[SnPh_2(O_2CCCl_3)]_2\ O\}_2$ are centrosymmetric dimers with all their carboxylate groups bridging and with half of them unidentate respectively. The complex $Sn_2Ph_8(O_2CCCl_3)_6.(OH_2)$ is a linear chain connected by hydroxy and acetate bridges. The hexatin complex $[SnPh(O_2CCCl_3)_3]_6$.$3C_6H_6$ has a drum structure.

3.1.2.2 Structure of diorganotin(IV) dicarboxylates

The dicarboxylates $R_2Sn(O_2CR')_2$ are monomeric and the Sn is hexa-coordinate in a skew-trapezoidal bipyramidal geometry resulting from a chelating anisobidentate coordination mode of the two dicarboxylate ligands[106-108]. The ^{119}Sn-NMR of the dicarboxylates show a single resonance [108].

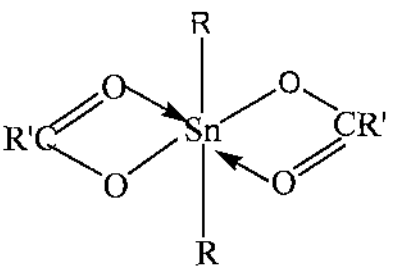


Fig. 3.8 Structure of diorganotin dicarboxylates.

For example, the crystal structure of $[n\text{-}Bu_2Sn(O_2CC_6H_4NOS_2)_2]$ is seen to be comprised of discrete molecules with tin atom hexa-coordinated [68].

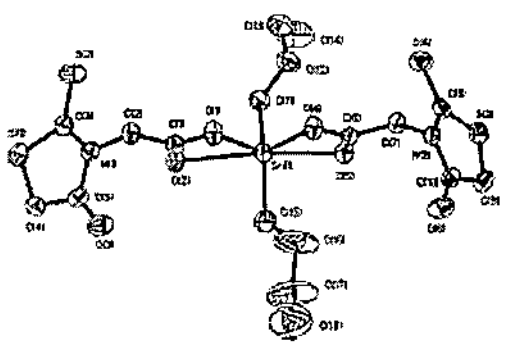


Fig. 3.9 Structure of $[n\text{-}Bu_2Sn(O_2CC_6H_4NOS_2)_2]$ [68].

The crystal structure of $[n\text{-}Bu_2Sn(5\text{-}Cl\text{-}2\text{-}OH\text{-}C_6H_3CO_2)_2]$ shows that in the monomeric species the hexa-coordinated tin atom exists in a skew-trapezoidal geometry in which the four {O} donor atoms, derived from two asymmetrically chelating carboxylate ligands, define the basal plane [109].

The di(n-butyl)tin(IV) bis(dihydroxybenzoate)s have skew-trapezoidal-bipyramidal or bicapped tetrahedral structures in the solid state[110] comparable with those of dimethyltin(IV) diacetate [111] and di(n-butyl)-bis(o-amino benzoate)tin(IV) [109].

Diphenic acid (A) forms diorganotin(IV) complexes, which are tetrahedral with two monodentate carboxylic groups. On the other land, soluble dinuclear triorganotin(IV) complexes (where the organo moieties are Me and Ph) contain symmetrically bound carboxylates, while the less soluble compound $(Cyh_3Sn)_2A$ has two asymmetrically bonded carboxylates. All have trigonal bipyramidal structures with $R_3Sn(IV)^+$ units remote from each other [45].

Orotic acid coordinates $R_2Sn(IV)^{2+}$ moieties to yield two different classes of derivatives with formulae $R_2SnHOr.nH_2O$ and $R_2Sn(H_2Or)_2.nH_2O$ (R=Me, n=0; R=Bu ,n=1) .In $R_2SnHOr.nH_2O$, the orotic acid behaves as a dianionic tridentate ligand [98].In $R_2Sn(H_2Or)_2.nH_2O$ two different Sn(IV) sites have been evidenced by Mössbauer spectroscopy in the solid state, and by ^1H and ^{13}C-NMR in DMSO-d_6 solution.

The diorganotin dicarboxylates also adopt polymeric structures (in the solid state) with intermolecularly bridging carboxylate groups and an octahedral *trans* $R_2Sn(O_2CR')$ tin atom geometry. For instance, the crystal structure of *catena*-poly[[di-n-butyltin(IV)]-μ-glutarato], $[Sn(C_4H_9)_2(C_5H_6O_4)]$, is composed of polymeric chains formed by the coordination of glutarate , through both ends to di-n-butyltin. The hexa-coordinated Sn atom is surrounded by four glutarate 'O' atoms forming an almost square base, with the n-butyl groups occupying the two axial positions. The geometry around the tin atom is a highly distorted octahedral, and may be best described as based on a skew-trapezoidal planar geometry. The symmetry-related glutarate ligands are asymmetrically coordinated to the Sn atoms with two unequal Sn-O distances [112].

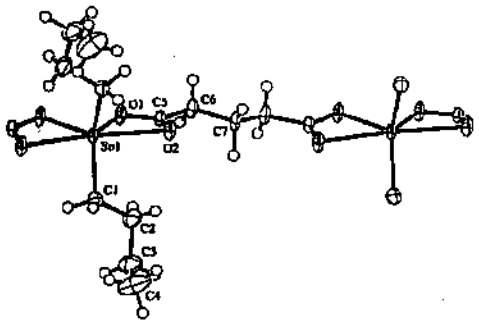


Fig. 3.10 Structure of $[Sn(C_4H_9)_2(C_5H_6O_4)]$ [112].

A crystal structure study of $[n\text{-}Bu_2Sn(O_2CCH_2SC_6H_5)_2]$ reveals the compound to be monomeric with the tin atom situated on a crystallographic two-fold axis in a skew-trapezoidal bipyramidal geometry. The carboxylate groups coordinate in an asymmetric mode forming both short Sn-O and long Sn-O bonds. The sulphur atoms do not participate in any significant interactions to the tin atom [113].

The X-ray diffraction study of the polynuclear compound $[Bu_2Sn(picolinate)_2]_n$ revealed that the central Sn atom is in a pentagonal bipyramidal environment with bond distances characteristic of organotin(IV) compounds. One of the picolinate moieties serves as bridge between Sn atoms by chelating to one Sn through one carboxylate O and the heterocyclic N atom, and binding monodentately through the other carboxylate O to the neighbouring Sn. There are hence two crystallographically distinct picolinate moieties in the structure, one bridging and the other terminal (chelating to the Sn through one carboxylate O and one N). The two butyl groups are located in axial positions. The ^{119}Sn NMR measurements in DMSO solution indicated that the polymeric structure of the complexes is not retained in the solution [114].

The crystal structure of $[t\text{-}Bu_2Sn(O_2CCH_3)(\mu\text{-}OH)]_2$ shows the presence of asymmetrically bridging hydroxyl groups leading to a planar Sn_2O_2 unit. Each Sn atom is also coordinated by an O atom of a monodentate carboxylate ligand and two C atoms of the t-Bu groups so that the environment around Sn is based on a trigonal bipyramid [62].

The crystal structure of the compound di-n-butylbis(2',4'-difluoro-4-hydroxybiphenyl-3-carboxylato-*O*,*O*')tin(IV), $[Sn(C_4H_9)_2(C_{13}H_7F_2O_3)_2]$, contains

discrete molecules in which the central Sn atoms are asymmetrically coordinated to two carboxylates and by two C atoms of two n-butyl groups. The geometry around Sn is highly distorted octahedral, that may be best described as one based on a skew-trapezoidal planar geometry. The hydroxyl groups and the carboxylate O atoms are hydrogen bonded, forming six-membered rings [115].

Several structures exhibiting similar geometry around Sn and an anisobidentate mode of coordination of the carboxylate ligand as stated above have been reported in literature [111,116-118].

The crystal structure of diphenyltin(IV) *N*-(2-hydroxy-5-ethylacetophenone) glycinate was investigated. The authors proposed trigonal bipyramidal geometry around the Sn atom with the ligand behaving as a dinegative tridentate one [119].

3.1.2.3 Structure of diorganodicarboxylato tetraorganodistannoxanes

There have been numerous crystallographic studies of the diorganodicarboxylato tetraorganodistannoxanes, of formula $\{[R_2Sn(O_2CR')]_2O\}_2$, and there are atleast five distinct types of structure known for them [21].

Structure type A, (Fig. 3.11) is by far the predominant structural form that involves a centrosymmetric structure built up around a four-membered cyclic Sn_2O_2 core in which the two endocyclic tin atoms are five-coordinate. Each of the two exocyclic five-coordinate tin atom is bound to one bridging oxygen atom of the four-membered ring, making these 'O' atoms tri-coordinate. The two independent carboxylate groups are characterized by two distinct ligating modes. One ligand is unidentate and is coordinated exclusively to the exocyclic Sn atoms. The other ligand is bidentate, one 'O' atom of the carboxylate group being coordinated to the exocyclic Sn atom and the other 'O' atom being coordinated to the endocyclic Sn atom. There are numerous examples of this common structural mode in literature [58, 60, 69,120-124].

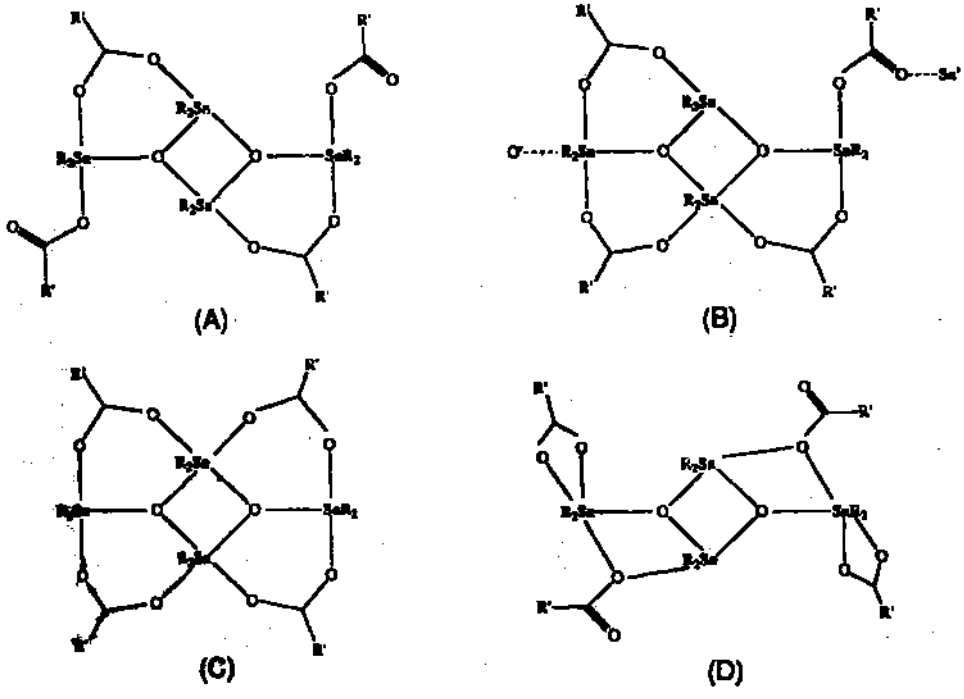


Fig. 3.11 Different types of dimeric structures of tetraorganodistannoxanes [49,108,120-124].

Variations on this basic structure are shown in B, C and D structural forms (Figure 3.11). In B three of the carboxylate ligands are bridging (e.g. R=Me, R'=Me [124]) and in C each of the four carboxylate ligands bridge a pair of Sn atoms (e.g. R=Me, R'=CCl_3 [49] and R=Me, R'= t-Bu [1]). A fourth structural type (D) is found for R=Me, R'=$C_6H_4NH_2$-*p* complex [108], in which two ligands are bridging and two ligands are chelating.

In type E, Sn_2O_2 core of the type A structure is retained, but the two bidentate, bridging carboxylate ligands of the type A now each utilize only one 'O' atom in bridging the two Sn centres. The structure of {[n-$Bu_2Sn(O_2CC_5H_4N$-2)]$_2O_2$} [2] is an example of type E. In this structure there are also interactions between the pyridyl 'N' atoms and the exocyclic Sn atom for two of the carboxylate ligands, so that these ligands may also be considered as chelating.

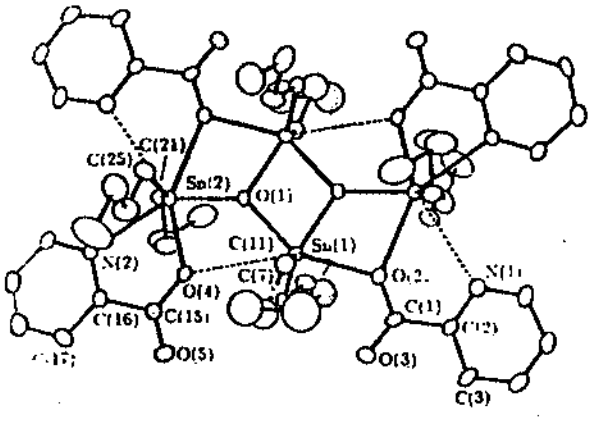


Fig. 3.12 Structure of $\{[n\text{-}Bu_2Sn(O_2CC_5H_4N\text{-}2)]_2O_2\}$ [2].

The crystal structure of $[Bu_2LSnOSnLBu_2]_2$ (where L= tolfenamic acid) has been determined by Demertzi and his coworkers [125]. Three distannoxane rings are present to the dimeric tetraorganodistannoxanes of planar ladder arrangement with distorted trigonal-bipyramidal geometry about the five-coordinated tin centers. The structure, which has two-fold symmetry, features a central Sn_2O_2 unit with two additional tin atoms linked at O. Pairs of tin atoms are bridged by bidentate carboxylate ligands and the external tin atoms have their coordination geometry completed by a monodentate carboxylate ligand. The tin atom geometries are similar and are based on trigonal bipyramidal arrangement [125].

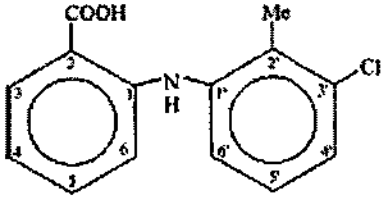


Fig. 3.13 Structure of tolfenamic acid [125].

3.1.3 Biological properties of organotin carboxylates

Organotin(IV) compounds have a range of pharmacological applications. They are used to a limited but significant extent as biocidal agents in agriculture and technology [126, 127]. The toxicology of tin compounds was reviewed in1959 [128] and 1964 [126].

One of the most important uses of organotin compounds is their ability to act as effective agrochemicals. For instance, triphenyltin compounds, including triphenyltin acetate, have received commercialization as agricultural fungicides [16,129-132]. Tributyltin, in the form of halides, oxides and acetates, are used extensively as wood preservatives [133]. Aquatic organisms such as fish, molluscs, crustaceans, algae are sensitive to tri-n-butyltin, and tricyclohexyltin compounds leading to the incorporation of these triorganotin moieties in anti-fouling paints for marine transport vessels [134], although there has been considerable environmental concern about the use of tributyltin compounds as anti-fouling paints [135]. However, the tributyltin compounds have not been shown to be neurotoxins, mutagens or carcinogens in humans [135].A full listing of reports which have evaluated organotin compounds in agriculture is to be found in a two-part review by Crowe [130,136].

The fungicidal activity of organotin complexes is strikingly dependent on the extent of alkylation of the Sn atom, being at a maximum in compounds with 3 Sn-C bonds [137] and also on the nature of the organic groups attached to Sn. In the case of tributyltin compounds, Bu_3SnX, the fungicidal activity is found to be largely independent on the nature of the group 'X' [138].

The application of multicriteria decision-making methods to the results of *in vitro* antifungal properties of organotin compounds of the type Ph_xSnX_z (n =2 or 3; X=$O_2CC_6H_4OH$, $O_2CC_6H_4OCOCH_3$, Cl or O_2CCH_3; z =1 or 2) and of free 2-hydroxybenzoic acid 2-acetoxybenzoic acids against *Aspergillus niger*, *Aspergillus flavus*, *Candida albicans*, *Penicillium citrinum*, *Trichophyton rubrum and tricbophyton violaceum* have been described. [139]. Ranking information necessary to select one toxicant in preference to others and to assess the properties influencing the preference has been obtained. Patterns in the multivariate analyses suggest that cationic and anionic moieties of the toxicant play some role in their fungicidal activities. The triphenyltin compounds were generally more active than their diphenyltin analogues, the acetoxybenzoates were more active than the corresponding hydroxybenzoates, acetates or chlorides. Thus, triphenyltin acetoxybenzoate is upto 7.5 times as active as the corresponding acetate, which is commercially marketed a fungicide. The results of the analyses have been discussed in the light of the mechanism of antifungal activity of organotin compounds and the potential of

multivariate analysis techniques to facilitate the screening and ranking of antifungal agents.

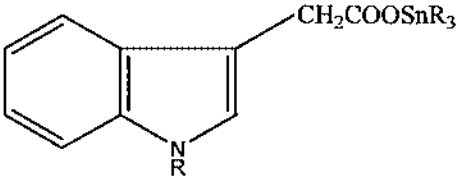
Fungitoxicity and phytotoxicity studies of $[R_3Sn(O_2CCH_2N(H)C(O)NH_2]$ (hydantoic acid) (R= Ph, c-Hex, n-Bu) indicated that the n-Bu derivative was the most active compound [90].

$Ph_3Sn(IV)^+$ compounds of *p*-ethoxybenzoic acid and acetyl salicylic acid have significant activity against a range of fungi [140].

The fungicidal activity of a number of ArSn(IV) compounds, $(p\text{-}ZC_6H_4)_3SnX$ [where X = OAC, OH or Z =F, Cl, CH_3, C_2H_5 or $(CH_3)_3C$] are reported. The results are compared with those on the Ph_3SnOAC and Ph_3SnOH archetypes. It was found that in most cases, para-substitution reduces the biocidal activity only slightly, but with p-OCH_3 the ArSn(IV) is completely ineffective. A model for the fungicidal action was proposed [141].

Q. Xie and coworkers reported the fungicidal activity of about 30 butyl tin carboxylates [142].

Molloy *et al.* [7] showed that triorganotin indolyl acetates of the type



(where R = Me, H, c-Hex) possesses fungicidal, bactericidal and insecticidal activity.

The triorganotin compounds, R_3SnX have been known for several years as having a specific action on mitochondrial oxidative phosphorylation; the activity is independent of the 'X' group but dependent on the R group [143]. Triorganotin (IV) compounds appear to inhibit the mitochondrial function in at least three ways : by (i) causing large-scale swelling at high concentrations, (ii) mediating Cl^-/OH^- exchange

across membranes, and (iii) inhibiting oxidative phosphorylation or ATP hydrolysis, like oligomycin [144]. The last process is usually assumed to be the most significant one, although binding of $Ph_3Sn(IV)^+$ to the cell wall was concluded to be responsible for the toxicity of *Ceratocystis ulmi* (*C. ulmi*)[145]. Dutch elm disease continues to devastate the diminishing population of American elm trees. The pathogenic fungus responsible for the disease is *C. ulmi*. The incorporation of the biologically active entities into a triorganotin (IV) system leads to the formation of potent biocides [146]. A number of $Ph_3Sn(IV)^+$ carboxylates were synthiszed and investigated spectroscopically. These complexes were found to be effective inhibitors of *C. ulmi* [147].

Tributyltin compounds are active against Gram-positive bacteria [136,148]. Their combination with a second chemical which combats Gram-negative bacteria produces a highly effective disinfectant which may be used on open areas posing a risk of infection, such as hospital floors and in sports pavilions. One such formulation (Incidin, Henkel) contains a mixture of tributyltin benzoate and formaldehyde [149].

Biological activity tests of the di-and tri-organotin carboxylates of 4-*p*-(chlorophenyl)-2-phenyl-5-thiazoleacetic acid (R=Me, Et, n-Bu, Ph, Bz) were carried out against various bacteria and fungi by the agar diffusion technique. All the complexes were screened for antibacterial and antifungal activity. The screening test shows that the n-Bu- and Ph- tin carboxylates are the most potent biocides against the tested bacteria. The activity of the other derivatives varies according to their R groups. However, they found that all of these compounds were active against *E. Coli* [27].

Organotin(IV) compounds are also a widely studied class of metal based antitumour drugs [132,150]. In recent years many tri- and di- organotin carboxylates have been tested for their *in vitro* activity against a large variety of tumour lines and have been found to be as effective as or better than traditional heavy metal anticancer drugs such as cisplatin [69,151,152].

In recent years, much work on organotin carboxylates containing other donor atoms (N, S) and functional groups have been reported [153-155]. Since the present work

deals with the interactions of organotin precursors with simple carboxylic acids (containing no other donor atoms except 'O'), the author has tried to confine this discussion around the organotin derivatives of very simple carboxylic acids.

3.2 Scope and Objective

The biocidal properties of organotin carboxylates are very rich [7, 156,157] and in addition these compounds show an interesting range of structural variations [21] leading to the proposal of some structure-activity relationships [14].These latter studies have shown that triorganotin carboxylates that have either isolated tetrahedral tin centres or *trans*-R_3SnO_2 tin geometries (arising from bridging carboxylate ligand) possess significantly greater activity than the compounds with the monomeric *cis*-R_3SnO_2 structural type [7,14,158].

The above led the author to study the structural behaviour and biocidal activity of a new series of organotin carboxylates, with varying R groups (alkyl or aryl). This chapter deals with the preparation, spectroscopic characterization and biological activity of the organotin(IV) carboxylates of cyclopropane carboxylic acid and 3-cyclohexyl propanoic acid and the X-ray crystal structure determination of dimethyltin(IV) derivative of cyclopropane carboxylic acid.

3.3 Experimental

3.3.1 Materials

Cyclopropane carboxylic acid (Lancaster, USA) and 3-cyclohexylpropanoic acid (Lancaster, USA) were used as received from commercial sources. Triphenyltin- (Fluka, Germany), tricyclohexyltin- (Aldrich, USA), tri-n-butyltin- (Merck,Germany), trimethyltin- (Merck, Germany) chlorides, dimethyltin- (Fluka, Germany), di-n-butyltin- (Merck,Germany) dichlorides were used after purification wherever necessary. Triphenyltin hydroxide was prepared by alkaline hydrolysis of the triphenyltin chloride. Tribenzyltin chloride and dibenzyltin dichloride were prepared using the method of Sisido *et al.* [159]. All the solvents used in the reactions were of AR grade and obtained from commercial sources (Merck, Germany). The solvents were dried using standard literature methods before use.

3.3.2 Measurements

The ^{1}H and ^{13}C NMR spectra were carried out in $CDCl_3$ solution using TMS as an internal standard on a Bruker DPX 300 spectrophotometer. The solution ^{119}Sn NMR spectra were measured in $CDCl_3$ solution at 149.05 MHz using a Jeol Eclipse Plus 400 spectrometer and were referenced against $SnMe_4$. IR spectra in the range 4000-400 cm^{-1} were obtained on an FTIR-8300 Shimadzu spectrophotometer with samples investigated as KBr discs. Thermogravimetric measurements was carried out from room temperature upto 800 °C, with a Mettler Toledo Star System operating in a pure nitrogen atmosphere in alumina crucible and at heating rate of 13 °C per minute using alumina as reference. Microanalysis were performed at RSIC, NEHU, Shillong, India and at IACS, Jadavpur, Kolkata. Tin was estimated gravimetrically as SnO_2 using standard procedure in our laboratory.

3.3.3 Synthetic procedures

The preparation of sodium salt of the ligand acids cyclopropane carboxylic acid (L^1H) and 3-cyclohexylpropanoic acid (L^2H) are described in section 3.3.3.1 and 3.3.3.2 respectively. The synthesis of organotin (IV) complexes of cyclopropane carboxylic acid (L^1H) and 3-cyclohexylpropanoic acid (L^2H) are described in section 3.3.3.3-3.3.3.16.Their characterization, analytical and spectroscopic data are given in section 3.4. All reactions were carried out under inert atmosphere of nitrogen.

3.3.3.1 Preparation of sodium salt of cyclopropane carboxylic acid (L^1H)

To a solution of cyclopropane carboxylic acid (2.5 g, 29.04 mmol) in methanol (40 ml) was added dropwise with continuous stirring 0.5 N methanolic NaOH (1.161 g, 59.2 ml, 29.02 mmol) in the presence of phenolphthalein as an indicator. The reaction system was stirred for half an hour. It was then evaporated to dryness leaving behind the sodium salt of cyclopropane carboxylic acid (L^1Na) as the product. The sodium salt thus prepared was recrystallized from methanol and then dried in an air oven at 105 °C for 48 hours.

L^1Na : Yield: 2.8 g, 76.5 %. M.p. : >245 °C

Elemental analysis (Calcd. for $C_4H_5O_2Na$) :

Calcd.: C, 44.31 ; H, 4.63 %.

Found: C, 44.39 ; H, 4.61 %.

IR (cm^{-1}) : $\nu(COO)_{asym}$, 1554; $\nu(COO)_{sym}$, 1414.

3.3.3.2 Preparation of sodium salt of 3-cyclohexylpropanoic acid (L^2H)

To a methanolic solution (35 ml) of 3-cyclohexylpropanoic acid (L^2H) (3 g, 19.23 mmol) was added dropwise with continuous stirring 0.5 N methanolic NaOH (0.769 g, 38.84 ml, 19.23 mmol) in the presence of phenolphthalein as an indicator. The reaction system was stirred for half an hour. It was then evaporated to dryness leaving behind the product of sodium salt of 3-cyclohexylpropanoic acid (L^2Na). The sodium salt thus prepared was recrystallized from methanol and then dried in an air oven at 105 °C for 48 hours.

L^2Na : Yield: 2.73 g, 72.4 % , M.p.: >245 °C .

Elemental analysis (Calcd. for $C_9H_{15}O_2Na$) :

Calcd.: C, 60.67 ; H, 8.42 %.

Found: C, 60.63 ; H, 8.41 %.

IR (cm^{-1}) : $\nu(COO)_{asym}$, 1570; $\nu(COO)_{sym}$, 1418.

3.3.3.3 Synthesis of tri-n-butyltin cyclopropylcarboxylate (1)

Tributyltin chloride (0.500 g, 1.536 mmol) in 30 ml of methanol was added to a hot methanol solution (30 ml) containing sodium salt of cyclopropane carboxylic acid (L^1-Na) (0.166 g, 1.536 mmol). The reaction mixture was heated under reflux for five hours and then the volatiles were removed by distillation. The dry mass was extracted thoroughly with hot petroleum ether (b.p. 60-80 °C) in quantities of 2-3 ml for 6 times. The crude product obtained was recrystallized from the same solvent to yield crystals of the desired product.

3.3.3.4 Synthesis of triphenyltin cyclopropylcarboxylate (2)

The compound was prepared by reacting Ph_3SnCl (0.700 g, 1.82 mmol) and L^1Na (0.196 g, 1.82 mmol) in dry methanol (65 ml) under reflux conditions for 5 h. The reaction mixture was filtered while hot and the filterate was evaporated to dryness. The residue was extracted with hot petroleum ether (b.p. 60-80 °C). The crude product obtained was recrystallized from benzene to yield crystals of **2.**

3.3.3.5 Synthesis of tricyclohexyltin cyclopropylcarboxylate (3)

$(c\text{-}Hex)_3SnCl$ (0.630 g, 1.56 mmol) in 35 ml of methanol was added to a hot methanolic solution of L^1Na (0.168 g, 1.56 mmol).The reaction mixture was heated at reflux temperature for 5 h, and then the solvent was removed by distillation. The dry mass was extracted with hot petroleum ether (b.p. 60-80 °C) in quantities of 2-3 ml for 10 times. The crude product obtained was recrystallized from the same solvent to yield the desired product.

3.3.3.6 Synthesis of trimethyltin cyclopropylcarboxylate (4)

Trimethyl cyclopropyl carboxylate (**4**) was prepared by heating at reflux for 5h the methanolic solution (35 ml) of Me_3SnCl (0.300 g, 1.505 mmol) with L^1Na (0.163 g, 1.508 mmol).The reaction system was cooled to room temperature. The sodium chloride formed was filtered off and the filterate was evaporated to dryness on a water bath. The residue obtained was extracted with hot petroleum ether (b.p. 60-80 °C) (35 ml) and kept undisturbed. Shiny white crystals of **4** were obtained the next day.

3.3.3.7 Synthesis of tribenzyltin derivative of cyclopropyl carboxylate (5)

Tribenzylltin chloride (0.500g, 1.170 mmol) in 45 ml of methanol was added to a hot methanol solution (30 ml) containing sodium salt of cyclopropane carboxylic acid (L^1-Na) (0.126 g, 1.170 mmol). The reaction mixture was heated under reflux for five hours and then the volatiles were removed by distillation. The dry mass was extracted thoroughly with hot petroleum ether (b.p. 60-80 °C) in quantities of 2-3 ml for 10 times. Shiny white crystals were obtained on cooling the petroleum ether solution.

3.3.3.8 Synthesis of dimethyltin(IV) derivative of cyclopropane carboxylic acid, $\{[Me_2Sn(cyclo\text{-}CH_2)_2CHCOO)]_2O\}_2$ *(6)*

The dimethyltin(IV) derivative of cyclopropane carboxylic acid (**6**) was obtained during an attempted synthesis of dimethyltin(IV) dicyclopropylcarboxylate. Me_2SnCl_2 (0.700g, 3.186mmol) in 40 ml of methanol was added to a hot methanol solution (45 ml) containing sodium salt of cyclopropane carboxylic acid, L^1Na (0.688g, 6.366 mmol). The reaction mixture was heated under reflux for six hours and then the solvents were removed by distillation. The dry mass was extracted thoroughly with hot petroleum ether (60-80 °C) in portions of 2-3 ml for 7 times. The product was recrystallized from methanol to yield crystals of **6**.

3.3.3.9 Synthesis of di-n-butyltin(IV) derivative of cyclopropane carboxylic acid, $\{[n\text{-}Bu_2Sn(cyclo\text{-}CH_2)_2CHCOO)]_2O\}_2$ *(7)*

The di-n-butyltin(IV) derivative of cyclopropane carboxylic acid (**7**) was obtained in an attempt to synthesize the di-n-butyltin(IV) dicyclopropylcarboxylate. $n\text{-}Bu_2SnCl_2$ (0.800 g, 2.63 mmol) in 45 ml of methanol was added to a hot methanolic solution (30 ml) containing sodium salt of cyclopropane carboxylic acid, L^1Na (0.569g, 5.26 mmol). The reaction mixture was heated under reflux for six hours and then the solvents were removed by distillation. The dry mass was extracted thoroughly with hot petroleum ether (60-80 °C) (40 ml). The product was recrystallized from methanol to yield crystals of **7**.

3.3.3.10 Synthesis of dibenzyltin(IV) dicyclopropyl carboxylate (8)

Bz_2SnCl_2 (0.500 g, 1.345 mmol) in 30 ml of methanol was added to a hot methanolic solution (25 ml) of L^1Na (0.291 g, 2.69 mmol).The reaction mixture was heated at reflux temperature for 6 h, and then the solvent was removed by distillation. The dry mass was extracted with hot petroleum ether (60-80 °C, 35 ml).The solution was concentrated and kept. White crystals of **8** were obtained the next day from the petroleum ether solution. The crystals were filtered and recrystallized from the same solvent.

3.3.3.11 Synthesis of tri-n-butyltin derivative of 3-cyclohexylpropanoic acid (9)

To a methanolic solution (35 ml) of sodium salt of 3-cyclohexylpropanoic acid (L^2Na) (0.273 g, 1.536 mmol) was added methanolic solution (30 ml) of tributyltin chloride (0.500g, 1.536 mmol). The reaction mixture was heated under reflux for five hours and then the volatiles were removed by distillation. The dry mass was extracted thoroughly with hot petroleum ether (b.p.60-80°C, 40ml). The product obtained was recrystallized from the same solvent to yield shiny crystals of **9**.

3.3.3.12 Synthesis of triphenyltin derivative of 3-cyclohexylpropanoic acid (10)

Triphenytin hydoxide (0.500 g, 1.363 mmol) in 45 ml benzene was added to the solution of the 3-cyclohexylpropanoic acid (0.212 g, 1.363 mmol) in benzene. The reaction was performed under reflux for 4 hours with water being produced removed azeotropically using a Dean-Stark trap. The volatiles were removed by distillation. The dry mass was extracted thoroughly with hot petroleum ether (60-80 °C) in quantities of 3-4 ml for 15 times. The product obtained was recrystallized from benzene to give **10**.

3.3.3.12 Synthesis of tricyclohexyltin derivative of 3-cyclohexylpropanoic acid (11)

$(c\text{-}Hex)_3SnCl$ (1 g, 2.48 mmol) in 40 ml of methanol was added to a hot methanolic solution of L^2Na (0.441 g, 2.48 mmol).The reaction mixture was heated at reflux temperature for 5 h, and then the solvent was removed by distillation. The dry mass was extracted with hot petroleum ether (b.p. 60-80 °C) in quantities of 2-3 ml for 10 times. The crude product obtained was recrystallized from the same solvent to yield the desired product.

3.3.3.13 Synthesis of trimethyltin derivative of 3-cyclohexylpropanoic acid (12)

The compound was prepared by reacting Me_3SnCl (0.300 g, 1.505 mmol) and L^2Na (0.268 g, 1.505 mmol) in dry methanol (40 ml) under reflux conditions for 5 h. The reaction mixture was filtered while hot and the filterate was evaporated to dryness.

The residue was extracted with hot petroleum ether (b.p. 60-80 °C). The crude product obtained was recrystallized from benzene to yield shiny white crystals of **12.**

3.3.3.14 Synthesis of dimethyltin(IV) derivative of 3-cyclohexylpropanoic acid, $\{[Me_2Sn(C_6H_{11}CH_2CH_2COO)]_2O\}_2$ *(13)*

The dimethyltin(IV) derivative of 3-cyclohexylpropanoic acid (**13**) was obtained during an attempt to synthesize the dimethyltin(IV) dicarboxylate of L^2H. Me_2SnCl_2 (0.500 g, 2.27 mmol) in 35 ml of methanol was added to a hot methanol solution (40 ml) containing L^2Na (0.810 g, 4.55 mmol). The reaction mixture was heated under reflux for six hours and then the solvents were removed by distillation. The dry mass was extracted thoroughly with hot petroleum ether (60-80 °C, 50 ml). The product was recrystallized from methanol to yield shiny crystals of **13.**

3.3.3.15 Synthesis of di-n-butyltin(IV) dicarboxylate of 3-cyclohexylpropanoic acid (14)

n-Bu_2SnCl_2 (0.700 g, 2.303 mmol) in 45 ml of methanol was added to a hot methanolic solution (30 ml) containing L^2Na (0.820 g, 4.607 mmol). The reaction mixture was heated under reflux for six hours and then the solvents were removed by distillation. The dry mass was extracted thoroughly with hot petroleum ether (60-80 °C) (40 ml). The product obtained was a viscous liquid.

3.3.4 X-ray Crystallography

A suitable single crystal of the compound **6** was selected under a polarizing microscope and glued to a thin glass fiber with cyanoacrylate (super glue) adhesive. Single crystal structure determination by X- ray diffraction was performed with a Siemens smart CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (MoKα radiation, λ = 0.71073 A^0) operating at 50 kV and 40mM. A hemisphere of intensity data was collected at room temperature at 1321 frames with ω scans (width of 0.300 and exposure time 20 s per frame) in the 2θ range 2.5-46.50. The structure was solved by direct methods using SHELXS-86[160], which readily

established the heavy atom positions (Sn) and facilitated the identification of the light atoms (O, C) from different Fourier maps. An empirical absorption correction based on symmetry equivalent reflections was applied using SADABS program [161]. All the hydrogen positions were initially observed in the Fourier maps, but for the final refinement the hydrogen atoms were placed geometrically and held in the riding mode. The last cycle refinement included atomic positions for all the atoms, anisotropic thermal parameters for all the non- hydrogen atoms and isotropic thermal parameters for all the hydrogen atoms. Seven carbon atoms (C5, C7, C15, C16, C19, C20 and C23) were refined only isotropically because of their poor thermal parameters. Full-matrix-least-squares structure refinement against F^2 was carried out using SHELXTL-PLUS package of program [162]. The details of final refinements are given in Table 3.1.

3.3.5 Biological Studies

The newly synthesized compounds were tested for their antifungal activity and antibacterial activity. The compounds were also tested for their phytotoxicity on healthy wheat seeds. Compounds which were highly phytotoxic would be of no use in the practical field of application.

3.3.5.1 Fungicidal activity

The biocidal activity of a few selected organotin carboxylates against four fungal pathogens (*Curvularia eragrostidis, Macrophomina phaseolina, Dreschlerea oryzae, Alternaria porri)* of four different crops were investigated. The fungal strains used in the study were gifts from the Plant Pathology Laboratory, Dept. of Botany, North Bengal University.

Table 3.1 Crystal data and structure refinement for the compound $\{[Me_2Sn(cyclo\text{-}CH_2)_2CHCOO)]_2O\}_2$ (**6**)

Identification code	sad
Empirical formula	$C_{24}H_{44}O_{10}Sn_4$
Formula weight	967.35
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	*P*-1
Unit cell dimensions	a = 10.18060(10) Å α=84.4540(10)°.
	b = 11.3774(2) Å β= 83.6480(10)°.
	c = 15.9447(3) Å γ = 74.23°.
Volume	1762.11(5) Å^3
Z	2
Density (calculated)	1.823 Mg/m^3
Absorption coefficient	2.845 mm^{-1}
F(000)	936
Crystal size	0.28 x 0.08 x 0.08 mm^3
Theta range for data collection	1.29 to 23.25°. -11<=h<=10, -12<=k<=12, -14<=l<=17.
Reflections collected	7328
Independent reflections	4923 [R(int) = 0.0245]
Absorption correction	SADABS
Max. and min. transmission	1.000000 and 0.437669
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4923 / 0 / 310
Goodness-of-fit on F^2	1.036
Final R indices [I>2sigma(I)]	R1 = 0.0391, wR2 = 0.1017
R indices (all data)	R1 = 0.0562, wR2 = 0.1112
Extinction coefficient	0.0009(2)
Largest diff. peak and hole	0.888 and -0.754 e.Å^{-3}

Materials and Methods

3.3.5.1.1 Fungal strains used for the study[a]

Species	Identification code	Host of origin
Curvularia eragrostidis	ITCC[b] No. 4150 2k	Tea *(Camellia sineusis)*
Macrophomina phaseolina	Identified by Dr. A. Saha, Dept. of Botany, N.B.U	Brinjal *(Solanum melongena)*
Dreschlerea oryzae	ITCC[b] No. 1849	Rice (*Oryzae sativa*)
Alternaria porri	Identified by Dr. A. Saha, Dept. of Botany, N.B.U	Niger (*Guizotia abyssinica*)

[a]Source of isolate: Plant Pathology Laboratory, Dept. of Botany, North Bengal University.

[b]ITCC- Indian Type Culture Collection, IARI, New Delhi.

3.3.5.1.2 Preparation of culture media

Fungi were grown on potato-dextrose-agar (PDA) medium at 28±1°C. The PDA medium was prepared as described below.

Materials required for preparing 100 ml PDA: 40 g potato (peeled), 2 g agar-agar (SRL), 2 g dextrose (Merck).

Method: 40 g of peeled potato was boiled in double distilled water and the volume was reduced to 100 ml. Then 2 g dextrose followed by 2g of agar-agar was added and the mixture was boiled just to dissolve the agar-agar and obtain a homogeneous solution. The solution was then autoclaved for 20 minutes. Now slants for culture of fungi were prepared with this media by pouring about 2 ml of this molten media in each test tubes, subsequently the test tubes were kept in a slanting condition till the media solidified. Then the media was impregnated with the spore and kept in the incubator at 28 ±1 °C. Average age of spores used for the study was 15 days.

3.3.5.1.3 Preparation of spore suspension

After average time period of 15 days, spore suspension was prepared by sterile double distilled water and the concentration was adjusted to 30-40 spores per field and used subsequently for experiments.

3.3.5.1.4 Study of the biocidal effects

The fungicidal activities were determined following spore germination bioassay as described by Rouxel *et al.* [163]. Purified eluents (10μl) were placed on two spots 3 cm apart on a clean, grease-free slide and the solvent was allowed to evaporate. One drop of spore suspension (0.02 ml per drop) prepared from 15-day-old cultures of the fungi was added to the treated spots. In this way, sets for various concentrations of the compounds were prepared. The slides were incubated at 27±1°C for 24 hours under humid conditions in Petri plates. Finally, after proper incubation period, one drop of a Cotton Blue-lactophenol mixture was added to each spot to fix the germinated spores. The number of spores germinated compared with the germinated spores of control (where no chemicals were used) was calculated using an average of 300 spores per treatment. The minimum inhibitory concentration required for complete inhibition was recorded in units of μg/ml.

3.3.5.2 Bactericidal activity

Some of the newly synthesized organotin(IV) carboxylates were screened for their antibacterial activity against *Pseudomonas fluorescens*, a fish-pathogenic, Gram-negative bacteria. The bacterial strain used in the study was kind gift from Dr. A. Saha, Plant Pathology Laboratory, Dept. of Botany, North Bengal University.

3.3.5.2.1 Preparation of culture media (Supplement nutrient agar)

Materials required for preparing 100 ml supplement nutrient agar: 1 g of beef extract (Himedia), 1 g of peptone (Himedia), 0.300 g of NaCl (SRL), 0.100 g of glucose (Merck), 2 g of agar powder (SRL).

Method: All the above except agar were boiled in double distilled water and the volume was reduced to 100 ml. Then the agar was added and the mixture boiled just to dissolve the agar. pH of the medium was adjusted to 7.4. The solution was autoclaved for 20 minutes.

3.3.5.2.2 Study of the biocidal effects

The bactericidal activities were determined using the agar well diffusion method [164]. The wells were dug in the media with the help of a sterile metallic borer with centers at least 24 mm apart. Two to eight hours old bacterial inoculums containing approximately 10^4 -10^6 colony forming units (CFU)/ml were spread on the surface of a nutrient agar with the help of a sterile cotton swab. Concentration of the test samples (1 mg/ml in methanol) was introduced into the respective wells. Other wells were supplemented with methanol serving here as control. The plates were incubated immediately at 37°C for 20 h. Activity was determined by measuring the diameter of the zones showing complete inhibition (mm). Each experiment was repeated in triplicate. All apparatus and materials used were sterilized where necessary using standard procedures.

3.3.5.3 Phtotoxicity studies

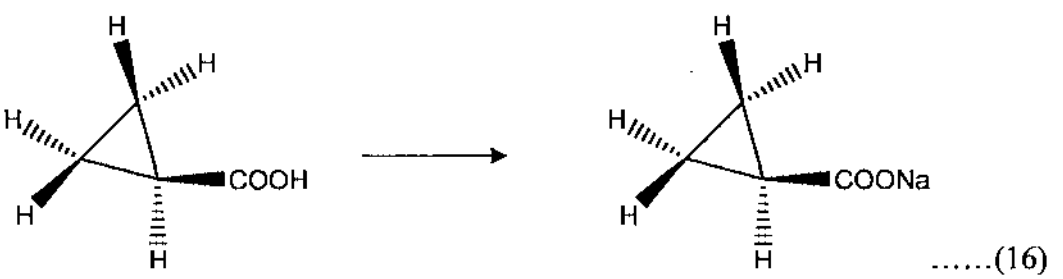
Phytotoxicities of these new organotin compounds were determined [165] on healthy wheat seeds (variety-Sonalika) purchased from Anup Seed Company, Bidhan Market, Siliguri, West Bengal. These healthy seeds were dipped in acetone-water suspensions of the compounds of different concentrations (25, 50, 100 μg/ml) for 1, 4 and 8 hours. The treated seeds were allowed to germinate sown over a mat of moist filter papers arranged in covered Petri plates. One hundred seeds were treated for each experiment. After two days, the germinated seeds (treated with compounds) were counted against the germinated seeds of the control (where no compounds were used) and those seeds, which had produced coleoptiles, were considered to have germinated. Each experiment was repeated in triplicate. All apparatus and materials used were sterilized where necessary using standard procedures.

3.4 Results and Discussion

In the previous section the synthetic recipe for the preparation of sodium salt of the ligand acids and their organotin(IV) complexes are described. A discussion of the synthetic methods adopted is carried out in this section in detail, regarding the yields obtained and the general physical characteristic of the compounds.

3.4.1 Synthesis of sodium salt of cyclopropane carboxylic acid (HL^1)

The sodium salt of cyclopropane carboxylic acid was prepared by titrating the acid with 0.5 M methanolic NaOH in the presence of phenolphthalein as an indicator.



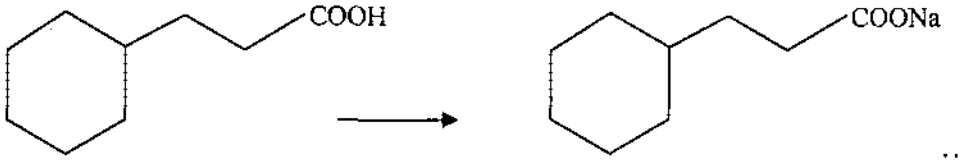
.....(16)

L^1H L^1Na

L^1Na was first obtained as a colourless liquid after titrating the acid with 0.5 M methanolic NaOH; upon concentration and cooling it slowly solidified to give an amorphous form of L^1Na. It was recrystallized from methanol and then dried in the oven at 105 °C for 48 hours. The yields were greater than 65%.The salt was found to be soluble in water, methanol, ethanol but insoluble in benzene, CCl_4 and CH_2Cl_2. L^1Na neither melted nor decomposed up to 245 °C in the melting point bath (Sulphuric acid bath).The sodium salt of the ligand was found to decompose after two to three days when kept in contact with the atmosphere. Hence, it was stored in a dessicator and the reactions of the salt carried out within 15 days of its preparation. The synthetic details and characterization data are described in section 3.3.3.

3.4.2 Syntheses of sodium salt of 3-cyclohexylpropanoic acid (HL^2)

Among all reported methods for the preparation of organotin carboxylates as discussed in section 3.1.1, the reactions of alkali metal salts with the organotin precursors is found to be one of the most straightforward and productive method.



.....(17)

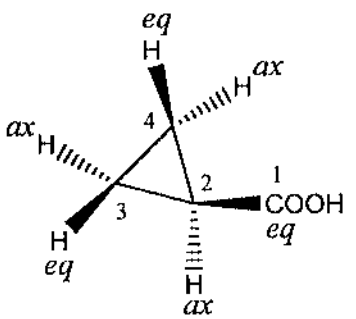
L^2H L^2Na

The ligand acid was titrated with 0.5 M methanolic NaOH. The reaction system was concentrated on a water bath, which upon cooling solidified to give L^2Na .The sodium salt of L^2H was obtained as an amorphous solid. It was recrystallized from methanol and then dried in the oven for 48 hours. Generally the yields were greater than 70%.The salt synthesized was soluble in water, methanol, ethanol and was insoluble in benzene, petroleum ether (60-80 °C) and carbon tetrachloride. The salt was found to slowly decompose when in contact with the aerial moisture and hence was stored in a dessicator. The reactions with the salt were carried out within 10-15 days of its synthesis. In the melting point bath the salt neither decomposed nor melted till 245°C. The synthetic details and characterization data are described in section 3.3.3.

3.4.3 Triorganotin(IV) and diorganotin(IV) complexes of cyclopropane carboxylic acid (L^1H)

The tri- and di- organotin (IV) complexes of cyclopropane carboxylic acid (L^1H) were prepared in moderate yields. The complexes were characterized by UV, IR, multinuclear (^1H, ^{13}C) NMR spectroscopy and elemental analyses. Thermogravimetric analysis were carried out for some selected compounds of L^1H. The numbering

scheme of the ligand and the abbreviations of the complexes are presented in the Scheme below.



(a) cyclopropane carboxylic acid (L^1H) (*ax*- axial, *eq* – equatorial)

1	Bu_3SnL^1
2	Ph_3SnL^1
3	$(c\text{-}Hex)_3SnL^1$
4	Me_3SnL^1
5	Bz_3SnL^1
6	$[Me_2Sn(L^1)_2]_2.[Me_2SnO]_2$
7	$[n\text{-}Bu_2Sn(L^1)_2]_2.[n\text{-}Bu_2SnO]_2$
8	$Bz_2Sn(L^1)_2$

Scheme 3.3

3.4.3.1 Triorganotin(IV) complexes of cyclopropane carboxylic acid, R_3SnL^1 (R=Ph, n-Bu, c-Hex, Me, Bz)

3.4.3.1.1 Synthesis of R_3SnL^1 (R=Ph, n-Bu, c-Hex, Me, Bz)

The triorganotin complexes were obtained in moderate to good yields by the reaction between the respective triorganotin chloride(R_3SnCl) and the sodium salt of the acid (L^1Na) in stoichiometric amounts in methanol.

$$R_3SnCl + L^1Na \longrightarrow R_3SnL^1 + NaCl \quad \text{.....(18)}$$

1: R= n-Bu; **2**: R= Ph; **3**: R= c-Hex; **4**: R= Me; **5**: R= Bz.

The triorganotin complexes can also be prepared by the reaction between R_3SnOH and the parent acid in benzene by the azeotropic removal of the water being produced during the reaction. But, the method using alkali metal salt of the ligand was preferred due to the ease of handling of the salt when compared to the acid. The reaction mixture was evaporated to dryness and then extracted in petroleum ether (b.p.60-80 °C) to remove NaCl produced during the reaction. The petroleum ether extract was concentrated to yield the crude product. The products were subsequently recrystallized from the appropriate solvents. The solubility of the triphenyltin analogue was poor in petroleum ether (b.p.60-80 °C) and a large amount of petroleum ether was required to extract the same. The synthetic details and analytical results are compiled in Table 3.2.

3.4.3.1.2 IR and UV spectra of R_3SnL^1 (R=Ph, n-Bu ,c-Hex, Me ,Bz)

Important IR bands for structural elucidation and their tentative assignments are presented in Table 3.3. The assignments of IR bands for all the complexes were done by comparing the IR spectra of the free acid, its sodium salt, and similar organotin compounds [16].The cyclopropane carboxylic acid display band at 1695 cm^{-1} which is assigned to the $\nu(OCO)_{asym}$ stretching vibration [166].The considerable shift of this vibration in the organotin (IV) complexes is owing to the coordination through the carbonyl oxygen atom [167]. Since the magnitude of the $\nu(OCO)_{asym}$ - $\nu(OCO)_{sym}$ (*i.e*, $\Delta\nu$) separation is of interest , therefore, the $\nu(OCO)_{sym}$ stretching frequencies[168-170] have also been identified for the compounds. The observed value of $\Delta\nu$, which are in the range 151-158 cm^{-1} indicate a bidentate bonding mode for the carboxylate moiety [27]. This suggests a penta-coordination [171] around the tin atom in the synthesized triorganotin(IV) carboxylates likely through intermolecular coordination [24]. In complex **3**, the observed value of $\Delta\nu$ (231 cm^{-1} respectively) indicates that the carboxylate moiety is behaving as a free organic ester type, in this case probably due to the bulky nature of the c-Hex groups around the tin atom [172-174]. The ν(Sn-C) stretching frequencies appear in the range of 440-511 cm^{-1} which is consistent with the literature data [12].

Table 3.2 The Physical and analytical data for **1-4**[a,b]

Complex	Crystallization Solvent	Yield (%)	M.p.(°C)	Elemental Composition[a] (%)		
				C	H	Sn
1	Petrolcum ether (b.p.60-80 °C)	92	93-94	51.19 (51.24)	8.50 (8.54)	31.58 (31.67
2	Benzene	85	136	60.64 (60.73)	4.84 (4.60)	27.28 (27.30)
3	Petroleum ether (b.p.60-80 °C)	80	139-142	58.29 (58.31)	8.44 (8.39)	26.14 (26.22)
4	Petroleum ether (b.p.60-80 °C)	84	124-126	33.60 (33.77)	5.60 (5.62)	47.34 (47.72)

[a]Calculated values in parentheses; [b]Reaction time was 5-6 h. All compounds are white.

Table 3.3 Characteristic IR absorption bands (cm^{-1}) for **1-4**[a]

Complex	$\nu(OCO)_{asym}$	$\nu(OCO)_{sym}$	$\Delta\nu(OCO)$	ν(Sn-C)
1	1566(s)	1415(m)	151	511(m), 457(w)
2	1571(m)	1413(m)	158	489(w), 451(s)
3	1635(m)	1404(m)	231	486(m), 442(w)
4	1569(m)	1418(m)	151	486(s), 440(w)

[a]s, strong; w, weak; m, medium.

The UV spectra of **1 - 4** were recorded in methanol (Table 3.4). The spectra of the complexes exhibited bands in the range of 210-213 nm, which may be due to the forbidden $n \rightarrow \pi^*$ transitions of the carboxylate group [175].

Table 3.4 UV spectral data for **1-4**

Complex	λ_{max} (nm)
1	210
2	211
3	213
4	Below 200

3.4.3.1.3 NMR spectra of R_3SnL^1 (R=Ph, n-Bu, c-Hex, Me, Bz) (1-5)

The ^1H NMR spectral data of the new triorganotin carboxylates (**1-5**) and the free acid have been recorded in $CDCl_3$ solution. The ^1H and ^{13}C NMR spectrum of **4** is presented in Fig. 3.14. The ^1H and ^{13}C NMR spectral data for the compounds (**1-4**) are reported in Table 3.5 ad 3.6 respectively.The observed resonances of protons have been assigned on the basis of their integration and multiplicity pattern. In the ^1H NMR spectra of L^1H, it is observed that the axial (H-3) and (H-4) protons in the cyclopropyl ring appear as multiplet at δ1.08-0.98 ppm and equatorial (H-3) and (H-4) protons appear as multiplet at δ0.96-0.82 ppm .The H-2 proton of the ligand (L^1H) appears as a septet at δ1.60 ppm. In the tri-n-Bu- and tri-c-Hex- organotin(IV) derivatives of L^1H the ligand protons overlap with the signal of the organic groups(n-Bu and c-Hex) attached to the tin atom, which makes the identification of the individual protons in the carboxylic acid ligand part difficult. The different R groups (Me, Ph, n-Bu, c-Hex) attached to the tin atom gave signals in the respective expected region [27, 99, 170,176].In the triphenyltin complex, the proton signals of the Ph groups appear as triplet and multiplet at δ 7.43 and 7.72-7.69 respectively. The $^3J(^{119}Sn-\ ^1H)$ for the triphenyltin complex is 63 Hz, which agree well with the data found for similar triphenyltin carboxylates [177-179].In the trimethyltin derivative of cyclopropane carboxylic acid, H-2 proton of the ligand appears at δ 1.56 as a septet. The $(H\text{-}3,4)^b_{axial}$ and $(H\text{-}3,4)^b_{equatorial}$ protons in **4** appear at δ 0.99-0.84 ppm and 0.83-0.70 ppm. The Sn-Me protons appear as a sharp singlet at δ 0.52. The $^2J(^{119}Sn-^1H)$ coupling constant = 58.8 Hz falls in the range of tetrahedral geometry in solution [180].

Table 3.5 ^{1}H NMR data (in ppm) for **1-4** [a,b,c]

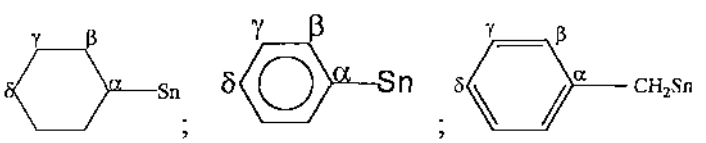
	1	2	3	4
(H-2)$^{b}_{axial}$	1.59 (s,1H)	1.69 (s,1H)	1.77-1.63 (m,1H)	1.56 (s,1H)
(H-3,4)$^{b}_{axial}$	1.07-0.88 (m,2H)	1.06-0.97 (m,2H)	1.02-0.85 (m,2H)	0.99-0.84 (m,2H)
(H-3,4)$^{b}_{equitorial}$	0.79-0.76 (m,2H)	0.93-0.82 (m,2H)	0.79-0.76 (m,2H)	0.83-0.70 (m,2H)
H–α	1.70-1.52 (m,6H)	-	1.45-1.31 (m,3H)	0.52 (m,9H) [58.8,56.4][e]
H–β	1.25-1.08 (m,6H)	7.72-7.69 (m,6H) [63 Hz][d]	1.91-1.81 (m,12H)	-
H–γ	1.49-1.29 (m,6H)	7.43 (t,9H)	1.77-1.63 (m,12H)	-
H–δ	0.90 (t,9H)	7.43 (t,9H)	1.45-1.31 (m,6H)	-

[a] Spectra recorded in $CDCl_3$, downfield to TMS, multiplicity is given as t, triplet; s, septet; m, multiplet.

[b] Refer to Scheme 3.3 for numbering scheme in the ligand skeleton.

[c] Numbering scheme for Sn-R skeleton as shown below:

$^{\alpha}CH_3$-Sn; $^{\delta}CH_3$-$^{\gamma}CH_2$-$^{\beta}CH_2$-$^{\alpha}CH_2$-Sn;



[d] $^{3}J(^{119}Sn-{}^{1}H)$ Hz.

[e] $^{2}J(^{119}Sn-CH_3)$ Hz, $^{2}J(^{117}Sn-CH_3)$ Hz.

The ^{13}C NMR spectral data reveals expected signals within the specified range [175]. The number of signals found in the spectra matches well with the number of magnetically non-equivalent carbon atoms. The R groups attached to the tin atom have their signals in different specific regions in correspondence with the literature [27, 99, 170, 176]. The assignment of the ^{13}C resonances of the tri-n-butyltin and

triphenyltin moieties follows from the $^{n}J(^{119/117}Sn - ^{13}C)$ coupling constants. In the triphenyltin complexes, the coupling constants $^{n}J(^{119/117}Sn - ^{13}C)$, especially the values of $^{1}J(^{119/117}Sn - ^{13}C)$ can be used to assign these compounds to two groups. Values of $^{1}J(^{119}Sn - ^{13}C)$ of 550-660 Hz are observed for the four-coordinate compounds and values of 750-850 Hz are observed for the five-coordinate compounds [169]. The triphenyltin complex of cyclopropane carboxylic acid **2**, exhibited $^{1}J(^{119}Sn-^{13}C) = 650$ Hz, falling in the range of four-coordinated triphenyltin(IV) species[178] in solution. In compound **4**, $^{1}J(^{119}Sn - ^{13}C)= 400$ Hz was observed which is in agreement with the previous literature report [181] and indicates a tetrahedral geometry around the Sn in solution.

Table 3.6 ^{13}C NMR data [a,b] (in ppm) of **1-4**

	Ligand skeleton			Sn-R skeleton			
	C-1	C-2	C-3	C-α	C-β	C-γ	C-δ
1	180.2	13.21	8.26	16.36 [360.0][d]	27.78 [28.3][e]	26.98 [66.7][f]	13.62
2	181.7	12.82	9.06	138.5	136.8 [47][e]	128.8 [62.2][f]	130.0 [13.5][g]
3	180.02	13.36	8.26	33.6	31.01 [14.2][e]	28.88 [63][f]	26.89 [59.2][g]
4	180.2	13.15	8.28	-2.43 [400.0 /382.8][d]	-	-	-

[a] Spectra recorded in $CDCl_3$, downfield to TMS; [b] For numbering scheme of the ligand, see Scheme 3.3; [c] For numbering scheme of Sn-R skeleton see footnotes of Table 3.5; [d] $^{1}J(^{119/117}Sn-^{13}C)$ in Hz; [e] $^{2}J(^{119}Sn-^{13}C)$ in Hz; [f] $^{3}J(^{119}Sn-^{13}C)$ in Hz. [g] $^{4}J(^{119}Sn-^{13}C)$ in Hz.

In order to gain further information about the possible coordination geometries in solution, a close examination of the $^{2}J(^{119}Sn-^{1}H)$ and $^{1}J(^{119}Sn-^{13}C)$ coupling constants was undertaken, as structural details, such as the determination of C-Sn-C bond angles, can be obtained by the use of literature methods [181, 182]. In the complex **1**, with the $^{1}J(^{119}Sn-^{13}C)$ value being 360.0 Hz and by the use of the Holecek and Lycka

equation [182], a C-Sn-C value of 112° was calculated , which corresponds to a tetrahedral geometry in $CDCl_3$ solution. Applying Lockhart's equation [181] the C-Sn-C angle for **4** was calculated as 111°, which confirms the tetrahedral geometry of tin in solution.

The ^{119}Sn chemical shifts of triorganotin(IV) complexes (**1-4**) in $CDCl_3$ solution are listed in Table 3.7.The spectrum of **1** is presented in Fig. 3.15. The chemical shift data are unambiguously characteristic for four-coordinate tin atoms in solution [79,170,183, 184].

Table 3.7 ^{119}Sn NMR data [a] (in ppm) of **1-4**

Complex	$\delta(^{119}Sn)$
1	104.68
2	-117.09
3	7.52
4	129.35

[a] Spectra recorded in $CDCl_3$ with Me_4Sn as an external reference.

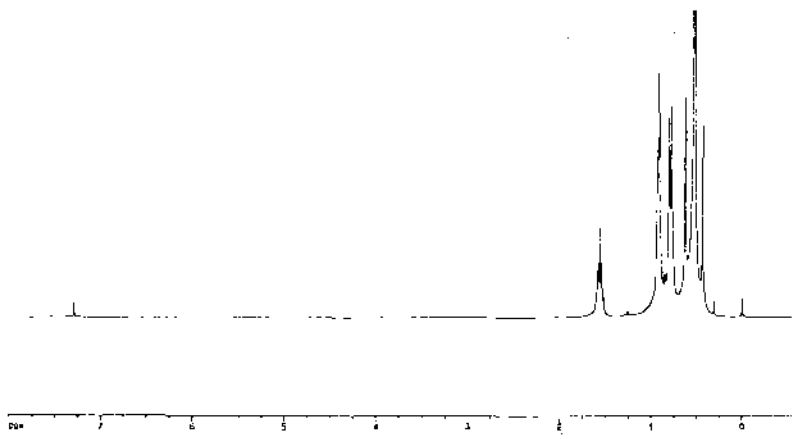
Inconclusive characterization of 5

The author was unable to characterize the complex **5**, with the help of NMR and IR spectroscopies. The compound is pure as indicated by its sharp melting point.

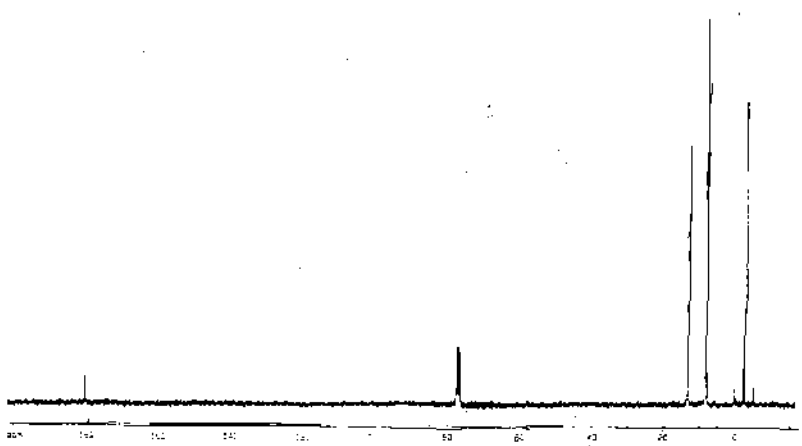
Yield: 65%, M.pt.: 116-117 °C, IR(cm^{-1}): $\nu(OCO)_{asym}$: 1570 cm^{-1}.

As the complex was unstable and decomposed within 2-3 days of its preparation on bench so the elemental analyses couldn't be done. The NMR though, revealed interesting features.

^1H NMR ($CDCl_3$, ppm): Ligand skeleton: H-2, 1.53-1.51; (H-3,4) $^b{}_{axial}$, 0.87-0.82; (H-3,4) $^b{}_{equitorial}$, 0.79-0.77; Sn-benzyl skeleton: aromatic protons, 7.34-6.74. In the ^1H NMR spectra of **5**, two types of tin-benzyl ($Sn-CH_2$) protons are identified one at δ 2.56 [$^2J(^{119}Sn-^1H)$ =72 Hz] and the other at δ 2.93 [$^2J(^{119}Sn-^1H)$ =90 Hz].The aromatic protons of the benzyl group and the presence of the ligand protons in the complex gave signals in the expected range indicating the binding of the ligand to the organotin precursor (Bz_3SnCl).



(a)



(b)

Fig. 3.14 (a) ^{1}H NMR spectrum of **4** (b) ^{13}C NMR spectrum of **4**.

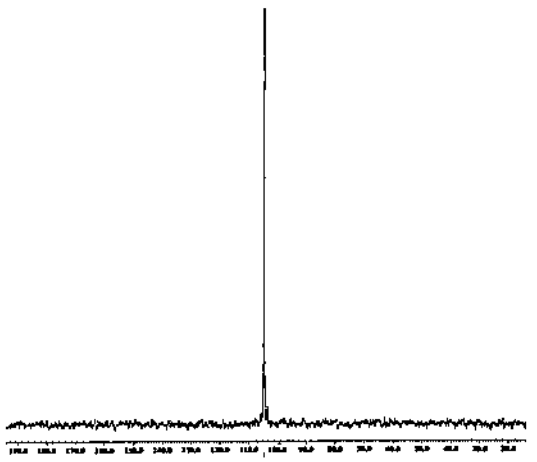


Fig. 3.15 ^{119}Sn NMR spectrum of **1**.

^{13}C NMR ($CDCl_3$, ppm) of **5** : Ligand skeleton: C-1, 182.4; C-2, 12.83; C-3, 8.80; Sn-benzyl skeleton: ring carbon atoms, 138.63, 135.89, 128.87, 128.55, 128.39, 128.33, 127.77, 124.34. Two Sn-CH_2 resonances were observed at δ 23.85 [$^1J(^{119}Sn\text{-}^{13}C)$ = 625.5 Hz] and δ 31.86 [$^1J(^{119}Sn\text{-}^{13}C)$ =367.5 Hz] in the ^{13}C NMR of **5**. Also, eight different phenyl carbons were seen in the ^{13}C NMR of **5**. Further studies and attempts to grow single crystals are in progress to establish the identity of the compound.

3.4.3.2 Diorganotin (IV) complexes of L^1H (R=Me, n-Bu, Bz)

3.4.3.2.1 Synthesis of diorganotin (IV) derivatives of L^1H (R=Me, n-Bu, Bz)

The dicarboxylato tetraorganodistannoxane derivatives (R=Me, n-Bu) of cyclopropane carboxylic acid were obtained during an attempted synthesis of diorganotin(IV) dicyclopropylcarboxylates. These were obtained in moderate yields by the reaction between the respective diorganotin dichloride(R_2SnCl_2) and the sodium salt of the ligand acid (L^1Na) in 1: 2 stoichiometric amounts in methanol. The attempt to synthesize diorganotin(IV) dicyclopropylcarboxylates (R=Me, n-Bu) using the reaction between R_2SnO (R=Me, n-Bu) and the ligand acid in benzene by

refluxing for 4 hours (water produced during the reaction being removed azeotropically) also gave the dicarboxylato tetraorganodistannoxanes (R=Me, n-Bu).

Dicarboxylato tetraorganostannoxanes are the hydrolysis products of diorganotin dicarboxylates [1,62,185] and the references of these compounds in literature are available [21]. This made the author to presume that the traces of moisture or alkali present as impurities might have caused the hydrolysis of the initially formed dicarboxylates as these compounds are very susceptible to hydrolysis [1,21, 62,124].

However, we could successfully isolate dibenzyltin dicyclopropylcarboxylate by the reaction between the dibenzyltin dichloride and the sodium salt of the ligand acid (L^1Na) in 1: 2 stoichiometric amounts in methanol.The analytical data for these complexes are presented in Table 3.8.

$$R_2SnCl_2 + 2\,L^1Na \longrightarrow [R_2Sn(L^2)_2]_2\,[R_2SnO]_2 + 2NaCl \quad .....(19)$$

6 : Me ; **7** : n-Bu

$$R_2SnO + 2\,L^1H \longrightarrow [R_2Sn(L^2)_2]_2\,[R_2SnO]_2 + H_2O \quad .....(20)$$

6 : Me ; **7** : n-Bu

$$R_2SnCl_2 + 2\,L^1Na \longrightarrow R_2Sn(L^2)_2 + 2NaCl \quad .....(21)$$

8 : Bz

Table 3.8 The Physical and analytical data for **6-8**[a,b]

Complex	Crystallization Solvent	Yield (%)	M.p. (°C)	Elemental Composition[a] (%)		
				C	H	Sn
6	Methanol	72	216-217	29.75 (29.79)	4.59 (4.55)	49.05 (49.10)
7	Petroleum ether (b.p.60-80°C)	77	130-132	44.19 (44.21)	7.05 (7.06)	36.40 (36.44)
8	Petroleum ether (b.p.60-80°C)	60	113-115	56.05 (56.08)	5.08 (5.09)	25.20 (25.21)

[a]Calculated values in parentheses.

[b]Reaction time was 5-6 h. All compounds are white.

3.4.3.2.2 IR spectra of diorganotin (IV) derivatives of L^1H (R=Me, n-Bu, Bz)(6- 8)

Important IR bands for structural elucidation and their tentative assignments are presented in Table 3.9. The assignments of IR bands for all the complexes were done by comparing the IR spectra of the free acid, its sodium salts, and similar organotin compounds [16,125]. In the dicarboxylato tetraorganodistannoxanes, two types of carboxylate stretching bands are identified in the same compound. In compound **6**, the difference Δ, [ν $(OCO)_{asym}$ - ν $(OCO)_{sym}$] between these frequencies is close to that found for monodentate (307 cm^{-1}) and bridging bidentate carboxylato groups (154 cm^{-1}) [125]. A strong band around 632 cm^{-1} can be assigned to the ν(Sn-O-Sn) mode [59, 66]. Similarly, in compound **7**, the difference [ν $(OCO)_{asym}$ - ν $(OCO)_{sym}$] corresponds to that found for monodentate (301 cm^{-1}) and bridging bidentate carboxylato groups (141 cm^{-1}) [185, 186]. In compound **8**, Δν(OCO) = 143 cm^{-1} indicates the presence of a bidentate carboxylato group [99].

Table 3.9 Characteristic IR absorption bands (cm^{-1}) for **6-8**[a]

Complex	$\nu(OCO)_{asym}$	$\nu(OCO)_{sym}$	Δν(OCO)	ν(Sn-C)	ν (Sn-O-Sn)
6	1560(m) 1616(m)	1406(m) 1309(m)	150 307	525(m) 503(m)	634(s)
7	1548(m) 1614(m)	1407(m) 1313(m)	141 301	532(m) 482(m)	632(s)
8	1604(m)	1461(s)	143	493(m) 455(m)	-

[a]s, strong; w, weak; m, medium.

3.4.3.2.3 NMR spectra of diorganotin(IV) derivatives of L^1H (R=Me, n-Bu, Bz)(6- 8)

The ^1H NMR and ^{13}C NMR spectral data of tetraorganodistannoxanes of cyclopropane carboxylic acid are presented in Table 3.10 and 3.11 respectively. The ^1H NMR and ^{13}C NMR spectrum of **7** is shown in Fig. 3.16. In the dimethyltin complex of L^1H the H-2 proton of the ligand appears as a multiplet at δ1.45-1.36 ppm. The (H-3) and (H-4) protons of the ligand appear along with the Sn-methyl

protons at δ1.01-0.52 ppm. Two Sn-methyl resonances (δ0.74 ppm, $^{2}J(^{119}Sn\text{-}^{1}H)$ 85 Hz, *exo*-cyclic and δ0.79 ppm, $^{2}J(^{119}Sn\text{-}^{1}H)$ 89 Hz, *endo*-cyclic) are observed as expected for tetraorganodistannoxanes [1,123,185,187].

In the ^{13}C NMR spectra, the diorganotin derivatives of the ligand acids displayed two sets of R-Sn resonances, as expected for the dicarboxylato tetraorganodistannoxanes [49], with high field resonances for the *exo*-cyclic R_2Sn carbon atoms and down field resonances for the *endo*-cyclic R_2Sn carbon atoms. In compound **6**, the Sn-Me resonances appeared at (δ5.94 ppm, $^{1}J(^{119/117}Sn\text{-}^{13}C)$ 753/720 Hz, *exo*-cyclic and δ8.65 ppm, $^{1}J(^{119/117}Sn\text{-}^{13}C)$ 800/763 Hz, *endo*-cyclic) as expected [1,123,185,187].

In the dibenzyltin derivative of $L^{1}H$ (**8**), methylene protons are observed as singlet (with tin satellites) at δ 2.95. The value of $^{2}J(^{119}Sn\text{-}^{1}H)$ is found to be 90 Hz [99]. This value is comparable with the value of dimethyltin chlorides confirming the tetrahedral environment around tin [188].In the dibutyltin complex of $L^{1}H$, the presence of two sets of ^{13}C, and in part ,^{1}H butyl resonances(due to non-equivalence of the *exo*- and *endo*-cyclic n-Bu_2Sn moieties), is in agreement with previous NMR data on dicarboxylato tetraorganodistannoxanes [99,185,187].

The C-Sn-C bond angles calculated for **6** from $^{1}J(^{119}Sn\text{-}^{13}C)$ values using Lockhart and Mander's equation [181] corresponds to 142.8° and 146.9° respectively and are nearer to the values obtained from the X-ray crystallographic study of **6** (142.6° and 147.9° respectively, see Table 3.13).

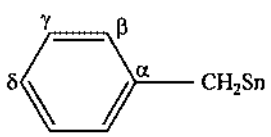
The ^{119}Sn NMR data for **6** and **7** in $CDCl_3$ are given in Table 3.12. The ^{119}Sn NMR spectra of **7** is shown in Fig. 3.17. The ^{119}Sn NMR spectra shows two well-separated high- and low- frequency ^{119}Sn resonances in accordance with the previous literature reports [117,121]. These data confirm the usual non-equivalence of the Me_2Sn and n-Bu_2Sn moieties in solution in these types of complexes reported earlier in literatures [60,189].

Table 3.10 ^{1}H NMR data (in ppm) for **6-8** [a,b,c]

Complex	Ligand skeleton	Sn-R
6	H-2 - 1.45-1.36 (s,2H) $(H\text{-}3,4)_{ax,eq}$ - 1.01-0.52 (m,8H)	H-α (12H): *exo*-cyclic 0.74 [85][d] *endo*-cyclic 0.79 [89][d]
7	H-2 - 1.71-1.57 (m,2H) $(H\text{-}3,4)_{eq}$ - 0.76(m, 8H) $(H\text{-}3,4)_{ax}$ 0.94-0.87	H-α- 1.71-1.57(m,8H) H-β,γ -1.45-1.28 (m,16H) H-δ - 0.92(t), 0.90(t) (12H)
8	H-2 - 1.44-1.45 (m,2H) $(H\text{-}3,4)_{ax,eq}$ - 0.82-0.78 (m,8H)	Sn-CH_2 - 2.95 (s, 4H) [90 Hz] H-α,β,γ,δ- 7.25-7.05 (m, 8H)

[a] Spectra recorded in $CDCl_3$,downfield to TMS, multiplicity is given as t, triplet; s, septet; m, multiplet; [b] For numbering scheme of the ligand see Scheme 3.3.

[c] Numbering scheme for Sn-R skeleton as shown below:



$^{\alpha}CH_3$-Sn; $^{\delta}CH_3$-$^{\gamma}CH_2$-$^{\beta}CH_2$-$^{\alpha}CH_2$-Sn;

[d] $^{2}J(^{119}Sn\text{-}H)$ Hz.

Table 3.11 ^{13}C NMR data (in ppm) for **6-8**[a,b,c]

	Ligand skeleton			δ(Sn-R)
	C-1	C-2	C-3	
6	181.2	14.3	8.08	5.94[753/720][d] 8.65[800/763][d]
7	180.6	14.4	7.99	α -28.67 β- 27.55[37.5][e], 27.30[n.o.][e] γ - 26.92[n.o.][f], 26.77[123.4][f] δ- 13.64
8	184.88	12.4	9.04	Sn-CH_2 – 31.94 [562.49][d] α-136.05, β- 128.3, γ-128.7, δ- 125.3

[a] Spectra recorded in $CDCl_3$,downfield to TMS.

[b] For numbering scheme of the ligands see Scheme 3.3.

[c] For numbering scheme of Sn-R skeleton see footnotes of Table 3.10.

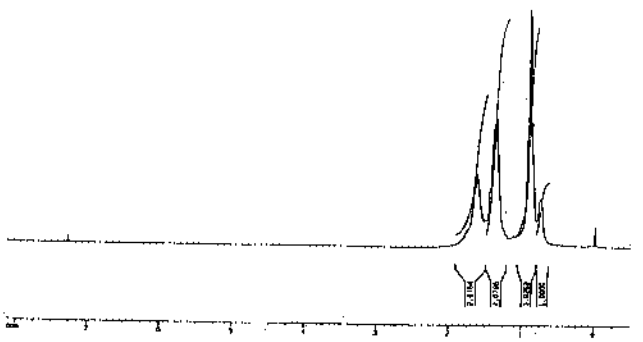
[d] $^{1}J(^{119/117}Sn\text{-}^{13}C)$ Hz ; [e] $^{2}J(^{119}Sn\text{-}^{13}C)$ in Hz; n.o. not observed.

[f] $^{3}J(^{119}Sn\text{-}^{13}C)$ in Hz; n.o. not observed.

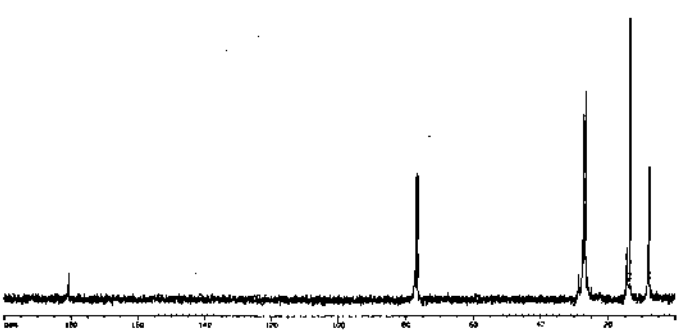
Table 3.12 ^{119}Sn NMR data (in ppm) for **6** and **7**[a]

	6	**7**
$\delta(^{119}Sn)_{exo}$	-179.1	-209.6
$\delta(^{119}Sn)_{endo}$	-190.8	-218.7

[a] Spectra recorded in $CDCl_3$ with Me_4Sn as an external reference.



(a)



(b)

Fig. 3.16 (a) ^{1}H NMR spectrum of **7** (b) ^{13}C NMR spectrum of **7**.

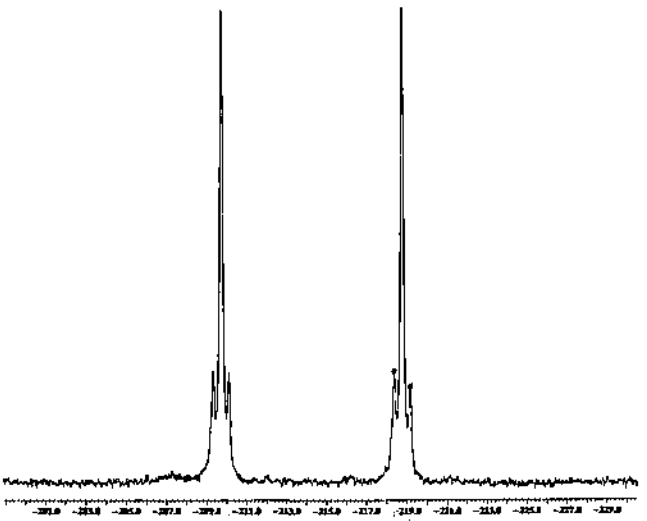


Fig. 3.17 ^{119}Sn NMR spectrum of **7**.

3.4.3.2.4 X-ray crystal analysis of 6

The author was able to successfully isolate suitable single crystals of **6** for X-ray crystallography. The selected geometric parameters of **6** are presented in Table 3.13. The atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) are presented in Table 3.14. The X-ray diffraction analysis of **6** reveals that the complex has a one-dimensional chain motif constructed from a secondary building unit of approximately rectangular Sn_2O_2 rings (Fig. 3.18). The rings are made up of a central planar $(Me_2Sn)_2O$ four-membered aggregates and two other peripheral (*exo*-cyclic) Me_2Sn units attached to two μ_3-oxygen atoms. The penta-coordinated Sn atoms have a bent C_2Sn skeleton C2-Sn1-C1 = 147.9(3) *exo*-cyclic and C7-Sn4-C8 = 144.8(4) *endo*-cyclic respectively. All the Sn atoms in the dimer are in five-coordinated environment. It is interesting to note that there are two different carboxylate ligands in the structure. One is bidentate bridging linking *endo*- and *exo*-cyclic Sn centres invoking two different Sn-O bond distances *e.g.* Sn4-O8 = 2.317(6) and Sn1-O3 = 2.224(6). The second carboxylate group bind the *exo*-cyclic Sn atom in a monodentate mode (free organic ester type) [1,123]. The pendant O atom, O9 is far removed from Sn1 atom which is reflected by the C9-O9 bond distance of 1.254(7)

indicative of the presence of substantial multiple bond character in it and is significantly shorter than the O2-C9 of 1.270(8).Slightly distorted axial angles of the trigonal bipyramidal geometry - O2-Sn1-O3 (*exo*-cyclic Sn) and O4-Sn4-O8 (*endo*-cyclic Sn) are 168.9(2) and 166.6(2) respectively. The distance between the two Sn atoms in the four membered ring is Sn3-Sn4 = 3.2761(7) which is smaller than the sum of the vander waals radii of Sn (II) (3.40 Å).This suggests that there exists possibly a weak metal-metal interaction in the ring. More over the non-covalent weak interactions via Sn1A-O10B; Sn2B- O9A; Sn1B-O10C; O9B-Sn2C etc allow the linear polymeric chain to propagate (Fig. 3.19). This work brings out the use of a carboxylic acid containing a strained ring as ligand for the synthesis of distannoxane not demonstrated earlier.

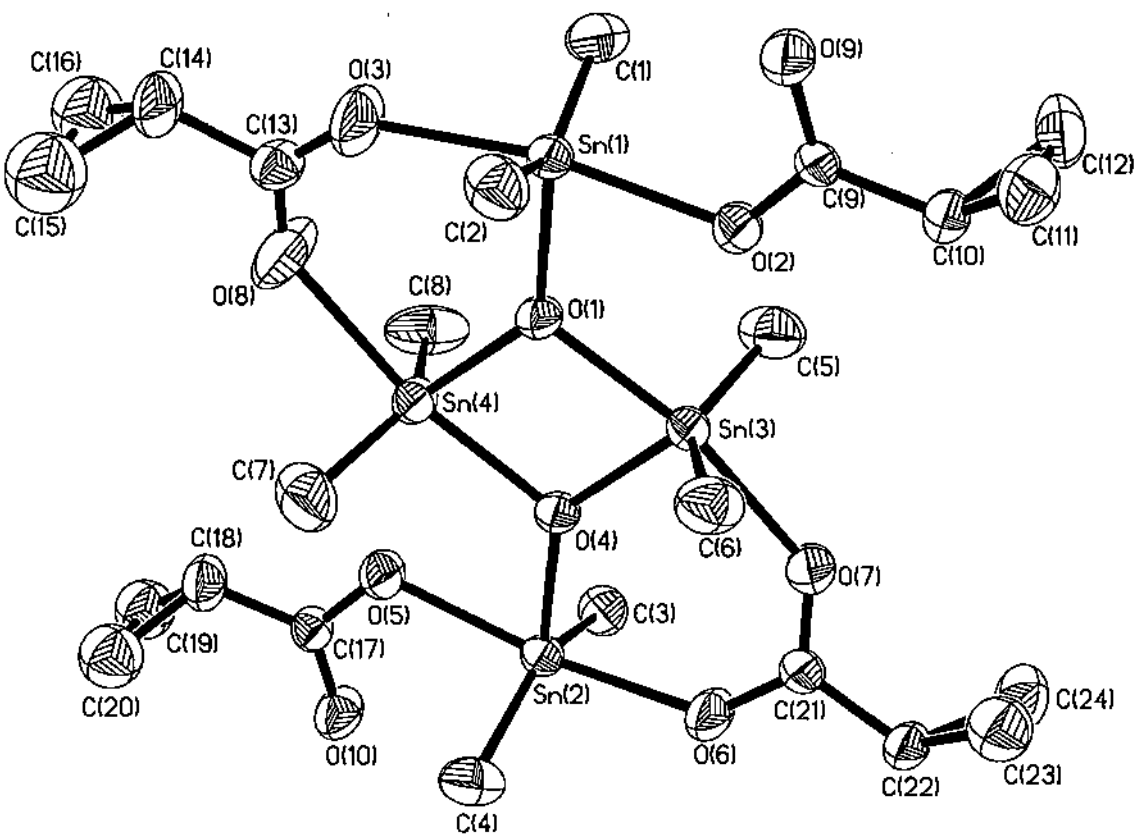


Fig. 3.18 ORTEP plot with atom labeling scheme of the molecular structure of $\{[Me_2Sn(cyclo\text{-}CH_2)_2CHCOO)]_2O\}_2$ **(6)**

Table 3.13 Selected geometric parameters – bond distances (Å) and angles (°).

Sn(1) - C(1)	2.090(7)	Sn(3) - O(1)	2.141(4)
Sn(1) - C(2)	2.083(7)	Sn(3) - O(7)	2.302(5)
Sn(1) - O(1)	2.032(4)	Sn(3) - O(4)	2.039(4)
Sn(1) - O(3)	2.224(6)	Sn(3) - Sn(4)	3.2761(7)
Sn(1) - O(2)	2.202(5)	O(2) - C(9)	1.270(8)
Sn(3) - C(5)	2.088(8)	C(9) - O(9)	1.254(7)
Sn(3) - C(6)	2.089(8)		
Sn(1) - O(10)	3.037	Sn(2) - O(9)	2.941
O(9) - Sn(2)	2.941	O(10) - Sn(1)	3.037

[Short non-hydrogen inter-molecular contacts contacts for inter-molecular clusters/or networks].

C(2)-Sn(1)-C(1)	147.9(3)	C(6)-Sn(3)-O(7)	87.0(3)
C(1)-Sn(1)-O(3)	89.5(3)	C(6)-Sn(3)-O(1)	99.9(3)
C(1)-Sn(1)-O(2)	94.3(3)	O(4)-Sn(3)-C(6)	106.7(3)
O(1)-Sn(1)-C(1)	106.7(3)	O(1)-Sn(3)-O(7)	164.4(2)
C(2)-Sn(1)-O(3)	87.9(3)	O(4)-Sn(3)-O(7)	88.2(2)
C(2)-Sn(1)-O(2)	94.3(3)	O(4)-Sn(3)-O(1)	76.5(2)
O(1)-Sn(1)-C(2)	105.3(3)	Sn(1)-O(1)-Sn(3)	121.7(2)
O(2)-Sn(1)-O(3)	168.9(2)	Sn(1)-O(1)-Sn(4)	135.1(2)
O(2)-Sn(1)-O(3)	91.0(2)	Sn(4)-O(1)-Sn(3)	103.2(2)
O(1)-Sn(1)-O(2)	77.9(2)	Sn(3)-O(4)-Sn(4)	103.5(2)
C(5)-Sn(3)-C(6)	142.6(4)	Sn(1)-Sn(4)-O(4)	76.7(2)
C(5)-Sn(3)-O(7)	83.0(3)		
C(5)-Sn(3)-O(1)	99.2(3)		
O(4)-Sn(3)-C(5)	108.8(3)		

Table 3.14 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for sad. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
Sn(1)	898(1)	2351(1)	7629(1)	50(1)
Sn(2)	2224(1)	-3632(1)	7259(1)	50(1)
Sn(3)	3021(1)	-555(1)	6894(1)	52(1)
Sn(4)	60(1)	-696(1)	7875(1)	59(1)
O(1)	1196(5)	528(4)	7532(3)	54(1)
O(2)	2960(5)	1835(4)	6958(3)	61(1)
O(3)	-1156(7)	2487(6)	8316(5)	122(3)
C(1)	-45(8)	3245(7)	6558(5)	77(2)
C(2)	1607(9)	2492(7)	8782(5)	79(2)
O(4)	1928(5)	-1790(4)	7304(3)	53(1)
O(5)	72(5)	-3023(4)	7792(3)	67(1)
O(6)	4408(6)	-3851(5)	6819(5)	97(2)
C(3)	1743(8)	-3812(7)	6048(4)	72(2)
C(4)	2902(9)	-4433(7)	8431(5)	81(3)
O(7)	4650(6)	-2110(5)	6255(4)	88(2)
C(5)	2631(9)	60(8)	5646(5)	89(3)
C(6)	4408(9)	-672(7)	7790(5)	85(3)
O(8)	-1703(8)	850(7)	8444(6)	160(4)
C(7)	316(10)	-1300(9)	9126(6)	103(3)
C(8)	-1196(10)	-515(8)	6889(7)	114(4)
C(9)	3606(7)	2655(6)	6823(4)	46(2)
O(9)	3049(5)	3726(4)	7028(3)	71(1)
O(10)	26(6)	-4935(5)	7917(4)	79(2)
C(10)	5028(7)	2309(7)	6450(5)	69(2)
C(11)	6038(8)	2901(8)	6693(6)	88(3)
C(12)	5560(9)	3191(8)	5870(5)	84(3)
C(13)	-1903(8)	1882(7)	8568(5)	61(2)
C(14)	-3215(9)	2424(9)	9083(6)	95(3)
C(15)	-3833(14)	1680(12)	9745(8)	150(5)

C(16)	-4478(12)	2058(10)	9023(7)	121(4)
C(17)	-527(7)	-3860(6)	8063(4)	50(2)
C(18)	-1886(9)	-3475(8)	8510(5)	84(3)
C(19)	-2879(11)	-4212(9)	8500(6)	102(3)
C(20)	-2241(11)	-4266(10)	9229(6)	109(3)
C(21)	5116(7)	-3213(6)	6428(4)	52(2)
C(22)	6555(7)	-3800(7)	6154(5)	69(2)
C(23)	7597(10)	-3140(9)	6181(5)	93(3)
C(24)	7235(9)	-3324(8)	5391(5)	89(3)

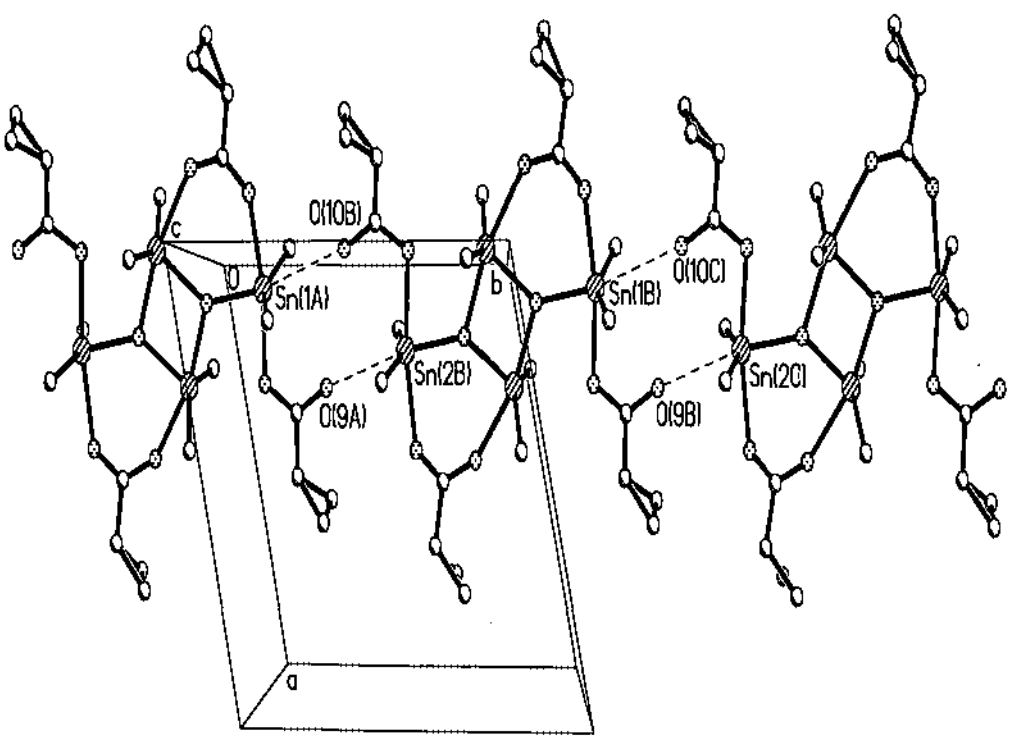
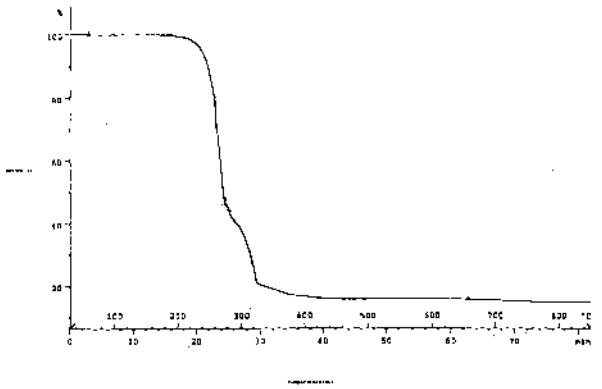


Fig. 3.19 Crystal packing in $\{[Me_2Sn(cyclo\text{-}CH_2)_2CHCOO)]_2O\}_2$ **(6)**.

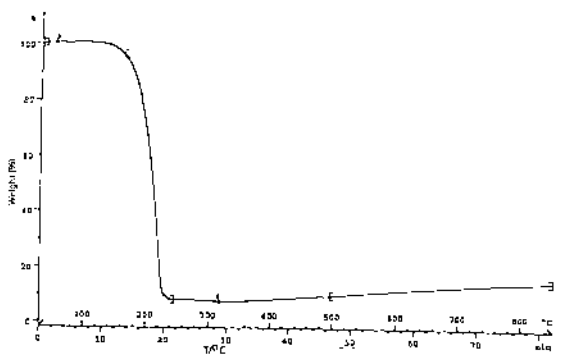
3.4.3.2.4. Thermogravimetric analysis

The thermogravimetric (TG) analysis of di- and tri- organotin(IV) derivatives of the ligand acids L^1H reveal that decomposition of the complexes occur as the temperature

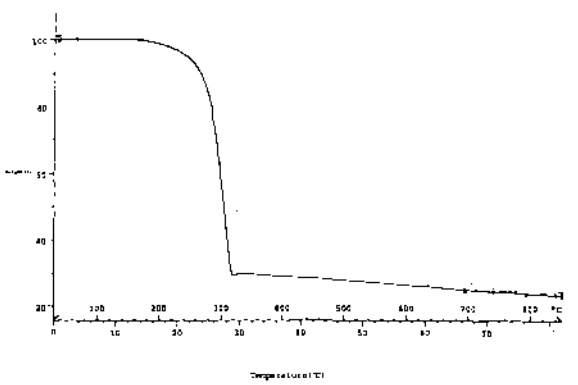
increases. The TG curves of the triorganotin(IV) and diorganotin(IV) complexes of L^1H are shown in Fig.3.20 and 3.21 respectively.



(a)



(b)



(c)

Fig. 3.20 (a) TG Curve of **1** (b) TG Curve of **2** (c) TG Curve of **3**.

The degradation pattern of the triorganotin complexes is different from those of the diorganotin complexes. In the case of the triorganotin complexes the ligand

decomposes in one step, while in the diorganotin complexes the ligand decomposes in two steps. Powder XRD analysis of the final product of **6** obtained at 800 °C shows this to be SnO_2 (mineral name-Cassiterite, JCPDS: 41-1445).

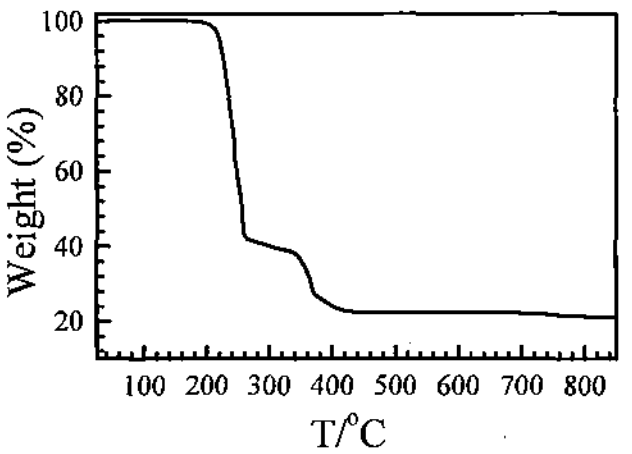
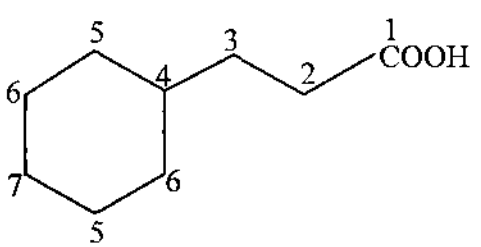


Fig. 3.21 TG Curve of **6**

3.4.4 Triorganotin(IV) and diorganotin(IV) complexes of 3-cyclohexylpropanoic acid(L^2H)

The tri- and di- organotin(IV) complexes of 3-cyclohexylpropanoic acid (L^2H) were obtained in moderate yields by heating at reflux the stoichiometric amount of L^2H or its sodium salt with the corresponding organotin hydroxide or chloride in benzene or methanol as solvents respectively . The complexes were characterized by IR, multinuclear (^1H, ^{13}C and ^{119}Sn) NMR spectroscopy and elemental analyses. Thermogravimetric analysis were carried out for some selected compounds of L^2H. The numbering scheme of the ligand and the abbreviations of the complexes are presented in the Scheme 3.4.



3-cyclohexylpropanoic acid (L^2H)

9	Bu_3SnL^2
10	Ph_3SnL^2
11	$(c\text{-}Hex)_3SnL^2$
12	Me_3SnL^2
13	$[Me_2Sn(L^2)_2]_2\text{-}[Me_2SnO]_2$
14	$n\text{-}Bu_2Sn(L^2)_2$

Scheme 3.4

3.4.4.1 Synthesis of triorganotin(IV) complexes of 3-cyclohexylpropanoic acid(L^2H), R_3SnL^2 (R=Ph, n-Bu, c-Hex, Me) (9-12)

The reaction between R_3SnOH and the parent acid in benzene by the azeotropic removal of the water produced during the reaction using a Dean-Stark apparatus produces the triorganotin(IV) carboxylates. But, the method using alkali metal salt of the ligand was preferred due to the ease of handling of the salt when compared to the acid. Only the triphenyltin complex of the acid (L^2H) was synthesized by the reaction of Ph_3SnOH and L^2H in benzene using a Dean-Stark trap. The aim was to compare the yields obtained via two different synthetic methodologies. In this case, it was found that **10** was obtained in much higher yields by the reaction of Ph_3SnOH and L^2H in benzene than by the method using alkali metal salt of the ligand and Ph_3SnCl.

$$Ph_3SnOH + L^2H \longrightarrow Ph_3SnL^2 + H_2O \quad \text{.....(22)}$$

10: Ph_3SnL^2

The other triorganotin(IV) complexes of 3-cyclohexylpropionic acid(L^2H), were obtained in moderate yields by the reaction of the respective triorganotin chloride(R_3SnCl) and the sodium salt of the ligand acid (L^2Na) in stoichiometric amounts in methanol.

$$R_3SnCl + L^2Na \longrightarrow R_3SnL^2 + NaCl \quad \text{.....(23)}$$

9: R=n-Bu; **11** :R=c-Hex; **12**: R=Me

The reaction mixture obtained by either of the above two methods was evaporated to dryness and then extracted in petroleum ether (b.p.60-80 °C).The petroleum ether extract was concentrated to yield the crude product. The products were subsequently recrystallized from the appropriate solvents. The solubility of the triphenyltin analogue was poor in petroleum ether(b.p.60-80 °C)and a large amount of petroleum ether was required to extract the same. The reaction conditions for each of the above mentioned complexes are listed in Table 3.15.

Table 3.15 Characterization and analytical data for **9-12**[a,b,c]

Complex	Crystallization Solvent	Yield (%)	M.p.(°C)	Elemental Composition[a](%)		
				C	H	Sn
9[b]	Petroleum ether (b.p.60-80°C)	88	96	56.14 (56.22)	9.30 (9.44)	26.61 (26.69)
10[c]	Benzene	73	111-112	63.46 (64.19)	5.35 (5.94)	23.42 (23.51)
11[b]	Petroleum ether (b.p.60-80°C)	67	168-170	61.72 (61.98)	9.10 (9.18)	22.59 (22.70)
12[b]	Petroleum ether (b.p.60-80°C)	79	130-131	45.35 (45.61)	6.61 (6.65)	37.47 (37.59)

[a]Calculated values in parentheses.

[b] Reflux in methanol ; reaction time was 5-6 h. All compounds are white.

[c] Reflux in benzene for 4 hours.

3.4.4.1.1 IR spectra of triorganotin (IV) derivatives of L^2H (R= n-Bu, Ph, c-Hex, Me) ***(9- 12)***

The IR spectra of all the compounds were scanned in the range 4000-250cm^{-1}. The coordinating mode of 3-cyclohexylpropionic acid towards organotin(IV) moieties can be inferred by comparing the IR spectra of the free acid, its sodium salt and the organotin compounds. Frequencies assigned to ν_{asym}(OCO) and ν_{sym}(OCO) have been

identified for all species and are reported together with bands tentatively assigned to ν(Sn-C) in Table 3.16.

For a bridging or chelating carboxylate group, $\Delta\nu \leq 150$ [190] as widely observed in the IR spectra of triorganotin carboxylates [191]. It is clear from the tabulated values that in all compounds (except the tri-c-Hex tin analogue) have Δν in the range 123-150 cm^{-1} indicating that these organotin carboxylates are carbonyl bridged polymers in the solid state [192]. The observed value of $\Delta\nu = 231$ cm^{-1} for the tricyclohexyl tin analogue [193] have been found to be comparable to those found for the mono-coordinated triorganotin carboxylates, indicating that the carboxylate group acts as a monodentate ligand [194, 195].The appearance of medium to weak intensity bands in the range 560-453 cm^{-1} due to ν(Sn-C) further confirms the formation of the complexes.

Table 3.16 Characteristic IR absorption bands (cm^{-1}) for **9-12**[a]

Complex	$\nu(OCO)_{asym}$	$\nu(OCO)_{sym}$	Δν(OCO)	ν(Sn-C)
7	1572(m)	1449(m)	123	560(w), 485(w)
8	1583(m)	1428(w)	155	554(w),454(w)
9	1614(m)	1384(w)	230	551(m),453(w)
10	1560(m)	1420(w)	140	547(m),455(m)

[a]s, strong; w, weak; m, medium.

3.4.4.1.2 NMR Spectra of ***9 – 12***

The ^1H NMR spectral data (Table 3.17) further support the composition of the new complexes suggested by IR spectral data. ^1H NMR spectra were recorded for the free ligand acid and its complexes in $CDCl_3$. The ^1H NMR spectrum of the ligand exhibits the chemical shifts for the ligand protons as follows: H-1, 11.40 (s, 1H); H-2, 2.35 (t, 2H); H-3, 1.57-1.49(m, 2H); H-4,5, 1.71-1.63 (m,5H); H-6, 1.32-1.06 (m,4H); H-7, 0.94-0.83 (m,2H). All the signals in the pure ligand were observed in the organotin(IV) complexes with slight shifts.

In the tri-n-Bu and tri-c-Hex derivatives the ligand protons overlap with the Sn-alkyl protons making the identification of individual protons difficult. All the CH_2 signals of the butyl groups are multiplets, therefore the determination of $^{n}J(^{119/117}Sn\text{-}^{1}H)$ coupling constants was not possible.

In the tri-Ph tin complex, **10**, the Sn-phenyl protons appear at 7.69 and 7.41 as multiplets. A coupling value $^{3}J(^{119}Sn\text{-}^{1}H)$ of 57 Hz was observed. Both the chemical and shifts and coupling constants for the triphenyltin complex, agree well with the data found for the other reported triphenyltin compounds [176,196].

In the trimethyltin complex of L^2H, the Sn-Me protons resonate at δ0.53. The percentage s-character of the tin-methyl orbital has been related to the $^{2}J(^{119}Sn\text{-}^{1}H)$ coupling constants[197]. For **12**, the $^{2}J(^{119}Sn\text{-}CH_3)$ coupling value was observed to be 57 Hz in agreement with the previous literature data[198,199]. This value of $^{2}J(^{119}Sn\text{-}CH_3)$ indicates that the tin atom has an approximately 25% s-character. In addition, a C-Sn-C bond angle of was calculated using the Lockhart's equation. Both these observations indicate that the methyl derivative is four-coordinated in solution.

^{13}C NMR data of the investigated compounds are given in Table 3.18. The number of signals found correspond with the presence of magnetically non-equivalent carbon atoms, which were assigned by comparison with other related organotin complexes [200, 201]. The ^{1}H and ^{13}C NMR spectrum of **12** is presented in Fig. 3.22. The carboxylate carbon shifts to a lower field in all the complexes, indicating participation of the carboxylic group in coordination to tin(IV) [201]. The $^{1}J(^{119}Sn\text{-}^{13}C)$ coupling constants have been used to infer the coordination number of the tin atom in these organotin compounds. As can be seen from Table 3.18, the $^{1}J(^{119}Sn\text{-}^{13}C)$ coupling constants range from 340.5 to 398.6 Hz for the alkyl compounds. These values are consistent with the values for similar compounds with a tetrahedral geometry [182,200,201] in solution.

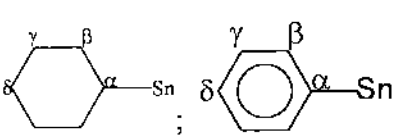
Table 3.17 ^{1}H NMR data (in ppm) for **9 - 12**[a,b,c]

	9	**10**	**11**	**12**
H-2	2.30 (t,2H)	2.41 (t,2H)	2.37-2.17 (m,2H)	2.29 (t,2H)
H-3	1.68-1.47 (m,2H)	1.63-1.50 (m,2H)	2.37-2.17 (m,2H)	1.54-1.46 (m,2H)
H-4	-	-	1.32-1.19 (m,H)	-
H-5	-	-	1.98-1.95 (m,H)	-
H-4,5	1.68-1.47 (m,5H)	1.63-1.50 (m,5H)	-	1.71-1.67 (m,5H)
H-6	1.39-1.16 (m,4H)	1.11-1.09 (m,4H)	1.42-1.19 (m,4H)	1.26-1.10 (m,4H)
H-7	0.98-0.83 (m,2H)	0.89-0.82 (m,2H)	0.94-0.87 (m,2H)	0.93-0.83 (m,2H)
H-α	1.68-1.47 (m,6H)	-	1.98-1.94 (m,3H)	0.53(t,9H) [57][e]
H-β	1.39-1.16 (m,6H)	7.69(m,6H) [57][d]	1.87-1.46 (m,12H)	-
H-γ	1.39-1.16 (m,6H)	7.41 (m,6H)	1.87-1.46 (m,12H)	-
H-δ	0.90 (t,9H)	7.41 (m,3H)	1.42-1.19 (m,6H)	-

[a] Spectra recorded in $CDCl_3$, downfield to TMS, multiplicity is given as t, triplet; m, multiplet.

[b] Refer to Scheme 3.4. for numbering scheme in the ligand skeleton.

[c] Numbering scheme for Sn-R skeleton as shown below:

$^{\alpha}CH_3$-Sn; $^{\delta}CH_3$-$^{\gamma}CH_2$-$^{\beta}CH_2$-$^{\alpha}CH_2$-Sn; 

.

[d] $^{3}J(^{119}Sn-^{1}H)$ in Hz.

[e] ^{2}J (^{119}Sn-CH_3) in Hz.

Table 3.18 ^{13}C NMR data [a,b] (in ppm) of **9 - 12**

	Ligand skeleton							Sn-R skeleton			
	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-α	C-β	C-γ	C-δ
9	179.82	37.40	33.26	32.45	33.04	26.60	26.30	16.36 [357.7 /342.1][d]	27.84 [19.5][e]	27.02 [64.5][f]	13.63
10	181.27	37.33	33.06	31.71	32.94	26.51	26.21	138.45	136.85 [47.2][e]	128.83 [62.2][f]	130.03 [15][g]
11	184.40	37.37	32.56	28.52	29.45	26.55	26.30	32.99 [340.5][d]	29.76 [18.7][e]	28.85 [56.25][f]	26.48 [45][g]
12	179.8	37.40	33.08	32.39	32.97	26.54	26.23	-2.50 [398.62 /381.0][d]	-	-	-

[a] Spectra recorded in $CDCl_3$, downfield to TMS.

[b] For numbering scheme of the ligands see Scheme 3.4.

[c] For numbering scheme of Sn-R skeleton see footnotes of Table 3.17.

[d] $^1J(^{119/117}Sn-^{13}C)$ in Hz; [e] $^2J(^{119}Sn-^{13}C)$ in Hz; [f] $^3J(^{119}Sn-^{13}C)$ in Hz.

[g] $^4J(^{119}Sn-^{13}C)$ in Hz.

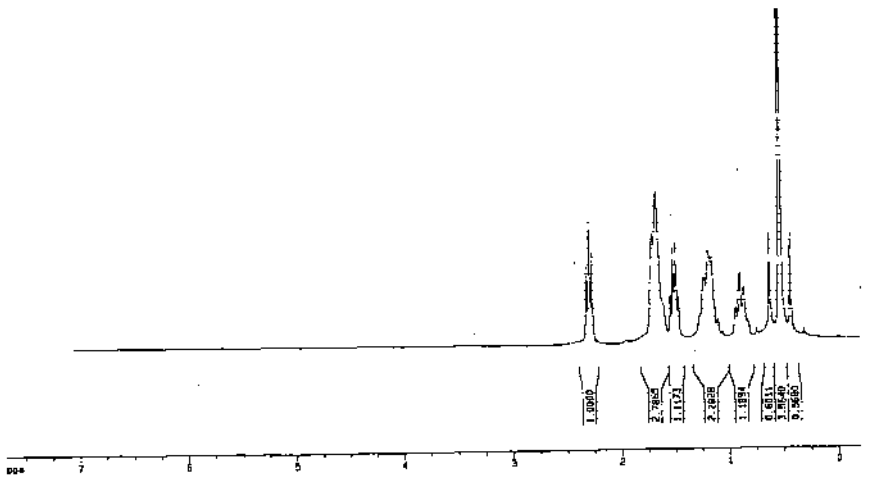
The ^{119}Sn NMR spectra of **9-12** were recorded in $CDCl_3$ solution with Me_4Sn as an external reference. The spectrum of **10** is shown in Fig. 3.23. The data for all the compounds are tabulated in Table 3.19. The chemical shifts obtained for the triorganotin(IV) derivatives lie in the range expected for a tetrahedral geometry [182, 201].

Table 3.19 ^{119}Sn NMR data [a] (in ppm) of **9-12**

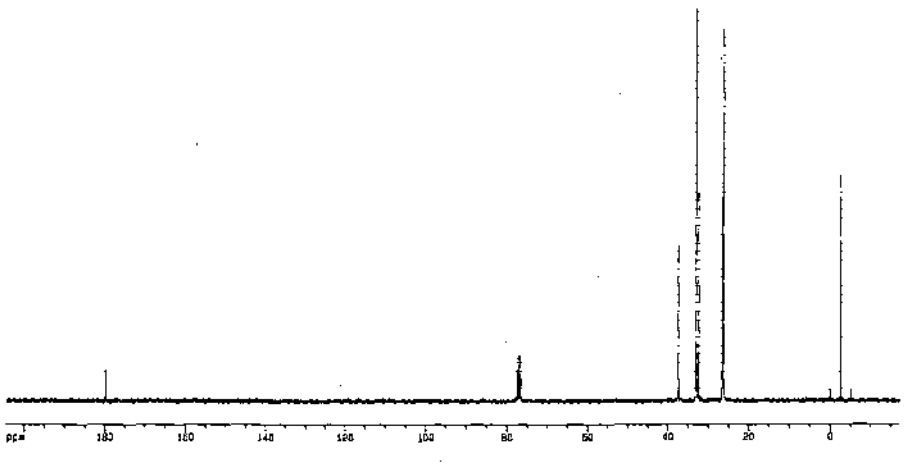
Complex	$\delta(^{119}Sn)$
9	103.73
10	-115.18
11	n.m.[b]
12	128.82

[a] Spectra recorded in $CDCl_3$ with Me_4Sn as an external reference.

[b] n.m. = not measured.



(a)



(b)

Fig. 3.22 (a) ^{1}H NMR spectrum of **12** (b) ^{13}C NMR spectrum of **12**.

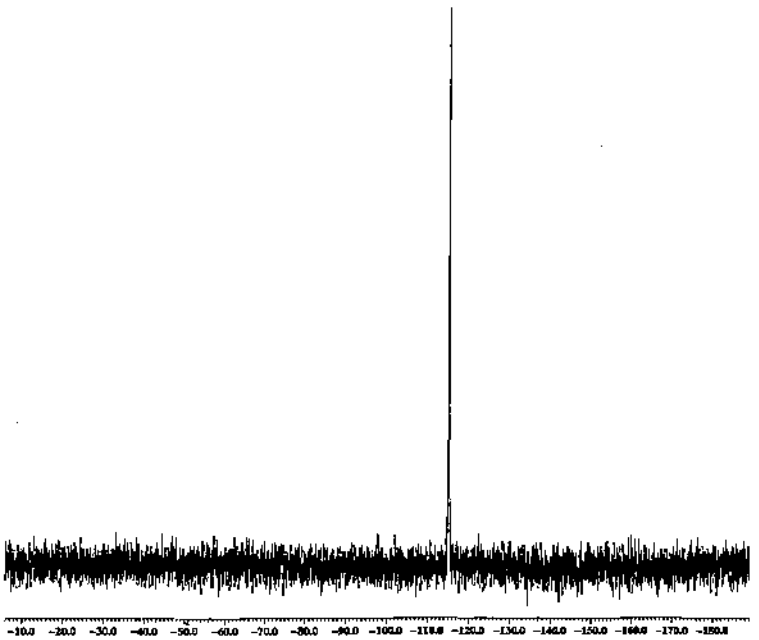


Fig. 3.23 ^{119}Sn NMR spectrum of **10.**

3.4.4.2 Diorganotin (IV) complexes of L^2H (R=Me and n-Bu)

3.4.4.2.1 Synthesis of diorganotin (IV) derivatives of L^2H (R=Me, n-Bu) (13,14)

The diorganotin derivatives of L^2H (R=Me, n-Bu) were obtained in moderate yields by the reaction between the respective diorganotin dichloride(R_2SnCl_2) and the sodium salt of the ligand acid (L^2Na) in 1: 2 stoichiometric amounts in methanol. As in the case of the diorganotin derivatives (R=Me, n-Bu) of cyclopropane carboxylic acid, the author was unable to isolate dimethyltin dicarboxylate of L^2H , instead, dicarboxylato tetraorganostannoxane was obtained as the product of the reaction of the Me_2SnCl_2 and the sodium salt of the ligand acid (L^2Na).The product is most probably obtained from the hydrolysis of the dimethyltin dicarboxylate by aerial

moisture or by traces of moisture present in the solvents used [1,21,62,124] .**14** was isolated as a dicarboxylate and is a viscous liquid. The analytical data for these complexes are presented in Table 3.20.

$R_2SnCl_2 + 2\,L^2Na \longrightarrow [R_2Sn(L^2)_2]_2\,[R_2SnO]_2 + 2NaCl$ ....(24)

13 : Me

$R_2SnCl_2 + 2\,L^2Na \longrightarrow R_2Sn(L^2)_2 + 2NaCl$ .....(25)

14 : n-Bu

Table 3.20 The Physical and analytical data for **13, 14**[a,b,c]

Complex	Crystallization Solvent	Yield (%)	Melting Point(°C)	Elemental Composition[a](%)		
				C	H	Sn
13	Petroleum ether (b.p.60-80°C)	72	102-104	42.19 (42.35)	6.72 (6.73)	37.98 (38.07)
14[c]	-	65	-	57.45 (57.49)	8.82 (8.84)	21.84 (21.87)

[a]Calculated values in parentheses.

[b]Reaction time was 5-6 h.

[c] viscous liquid

3.4.4.2.2 IR spectra of diorganotin (IV) derivatives of L^2H (R= Me, n-Bu) (13,14)

The assignments of IR bands for the complexes are made by comparison with the IR spectra of the free aids, its sodium salt and similar organotin compounds [16]. The IR spectral data for **13** & **14** are presented in Table 3.21.

In **13**, the magnitude of $\Delta[\nu\,(OCO)_{asym} - \nu\,(OCO)_{sym}]$, of 310 cm^{-1} and 146 cm^{-1} indicates the presence of two types of carboxylate moieties, functioning as monodentate and bidentate, respectively. This is usually observed for dicarboxylato tetraorganodistannoxanes[125,186]. In **14**, $\Delta\nu$= 145 cm^{-1} indicates that the carboxylate ligand is functioning as a bidentate one [66,185].

Table 3.21 Characteristic IR absorption bands (cm^{-1}) for **13,14**[a]

Complex	$\nu(OCO)_{asym}$	$\nu(OCO)_{sym}$	$\Delta\nu(OCO)$	ν(Sn-C)	ν (Sn-O-Sn)
13	1561(s) 1635(m)	1415(m) 1325(m)	146 310	551(m) 453(w)	626(s)
14	1558(m)	1413(w)	145	542(m) 451(w)	-

[a]s, strong; w, weak; m, medium.

*3.4.4.2.3. NMR spectra of diorganotin (IV) derivatives of L^2H (R= Me, n-Bu) (**13,14**)*

The ^1H and ^{13}C NMR spectral data of **13** & **14** are given in Table 3.22 and 3.23 respectively. The ^1H and ^{13}C NMR spectra of **14** is presented in Fig. 3.24. For R=Me, compound, two sets of methyl resonances are observed which show different $^2J(^{119}Sn\text{-}^1H)$ values, as expected for dicarboxylato tetraorganodistannoxanes [59]. The high field methyl resonance with smaller $^2J(^{119}Sn\text{-}^1H)$ value is assigned to *exo*-cyclic Me_2Sn group and the low field resonance, with higher $^2J(^{119}Sn\text{-}^1H)$ value is assigned to *endo*-cyclic Me_2Sn moiety [124].^{13}C NMR spectra of **13** also displayed two sets of Me-Sn resonances, as expected for dicarboxylato tetraorganodistannoxanes [59, 124].

^1H and ^{13}C NMR spectral data of **14** shows only one set of Sn-Bu resonances indicating that it is a dicarboxylate [99,201].

The ^{119}Sn NMR spectra of **13** displayed two well-separated resonances(Table 3.24), as is usually observed for dicarboxylato tetraorganodistannoxanes [117,121], and supporting the presence of dimeric structure in solution. The low field and high field shifts observed for distannoxanes are attributed to *exo*-cyclic and *endo*-cyclic tin atoms, respectively [1,185]. The ^{119}Sn NMR spectra of **13** is presented in Fig. 3.25.

Diorganotin dicarboxylates having a five-coordinate tin centre show tin chemical shifts in the range of -110 to -161 ppm [202].The ^{119}Sn NMR spectra of **14** show a sharp signal at -148.63 ppm which can therefore be assigned to a five-coordinate tin atom[169]. The ^{119}Sn NMR spectra of **14** is presented in Fig. 3.26.

Table 3.22 ^{1}H NMR data(in ppm) for ***13,14*** [a,b,c]

	Ligand skeleton	Sn-R
13	(H-2) , 2.18(t, 4H); H-3, 1.49-1.41(m,4H); H-4,5 1.71-1.67 (m,10H); H-6, 1.27-1.10 (m,8H); H-7, 0.96-0.82 (m,4H)	H-α(12H) : *exo*-cyclic 0.76 [84][d] *endo*-cyclic 0.78 [90][d]
14	(H-2) , 2.36(t, 4H); H-3, 1.41-1.32(m,4H); H-4,5, 1.72-1.48 (m,10H); H-6, 1.25-1.10 (m,8H); H-7, 0.93-0.83 (m,4H)	H-α, 1.72 – 1.48(m,4H) H-β, γ, 1.41 – 1.32 (m,8H) H-δ, 0.91 (t, 6H)

[a] Spectra recorded in $CDCl_3$,downfield to TMS, multiplicity is given as t, triplet; m, multiplet.

[b] For numbering scheme of the ligands see Scheme 3.4.

[c] Numbering scheme for Sn-R skeleton as shown below:

$^{\alpha}CH_3$-Sn; $^{\delta}CH_3$-$^{\gamma}CH_2$-$^{\beta}CH_2$-$^{\alpha}CH_2$-Sn

[d] $^{2}J(^{119}Sn\text{-}H)$ in Hz.

Table 3.23 ^{13}C NMR data (in ppm) for **13,14**[a,b,c]

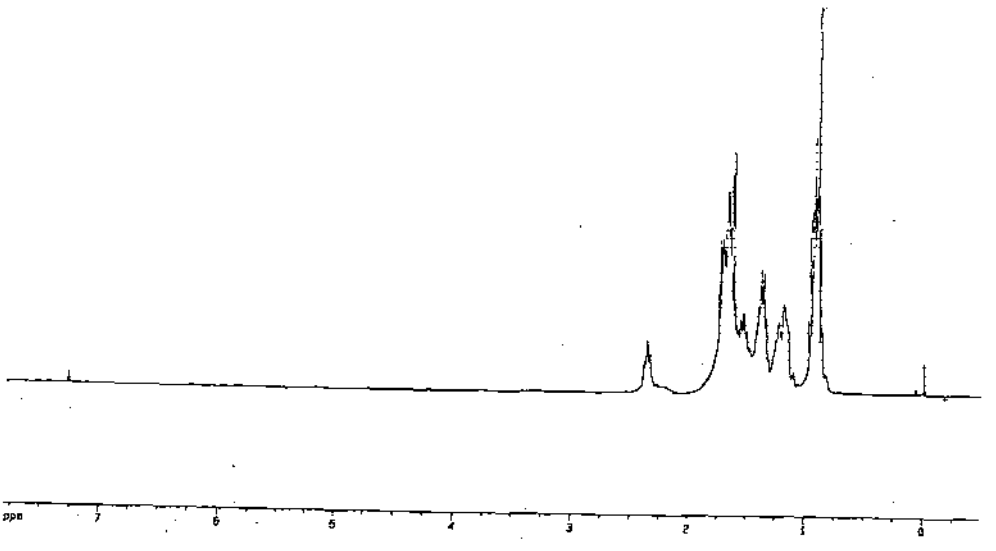
	Ligand skeleton							δ(Sn-R)
	C-1	C-2	C-3	C-4	C-5	C-6	C-7	
13	180.61	37.37	33.79	30.04	30.09	26.53	26.25	8.75[807.69][d] 6.35[750.0][d]
14	184.55	37.28	32.88	27.19	31.71	26.57	26.23	α : 24.81, β :26.45, γ : 26.16, δ : 13.45

[a] Spectra recorded in $CDCl_3$,downfield to TMS.

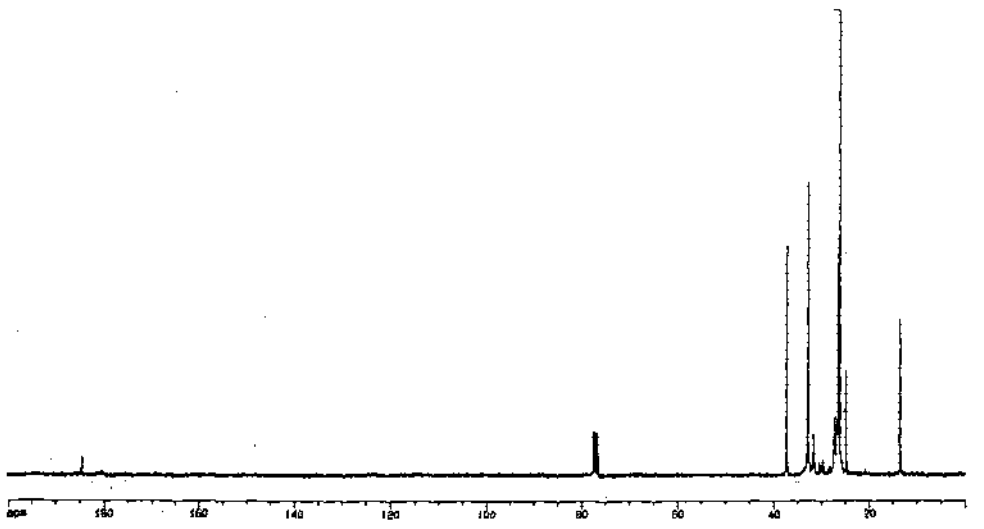
[b] For numbering scheme of the ligand see Scheme 3.4.

[c] For numbering scheme of Sn-R skeleton see footnotes of Table 3.22.

[d] $^{1}J\ (^{119/117}Sn\text{-}^{13}C)$ in Hz.



(a)



(b)

Fig. 3.24 (a) ^{1}H NMR spectrum of **14** (b) ^{13}C NMR spectrum of **14**.

Table 3.24 ^{119}Sn NMR data (in ppm) for **13** and **14**[a]

Complex	$\delta(^{119}Sn)$
13	$\delta(^{119}Sn)_{exo}$, -176.1; $\delta(^{119}Sn)_{endo}$, -186.9
14	-148.63

[a] Spectra recorded in $CDCl_3$ with Me_4Sn as an external reference.

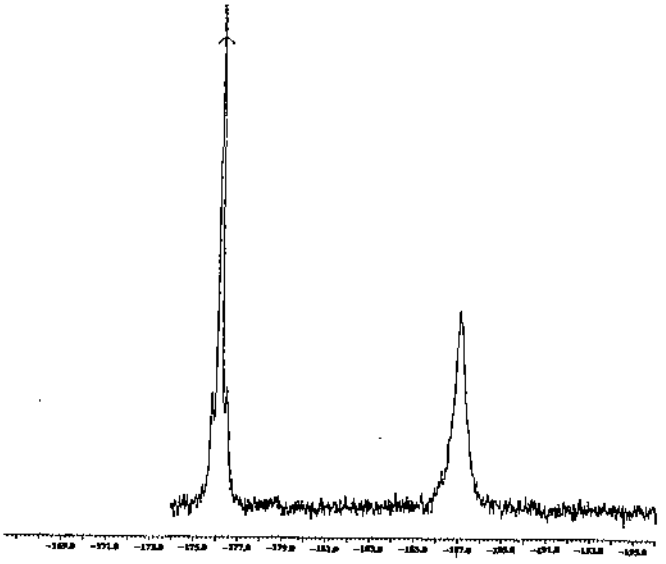


Fig. 3.25 ^{119}Sn NMR spectrum of **13**.

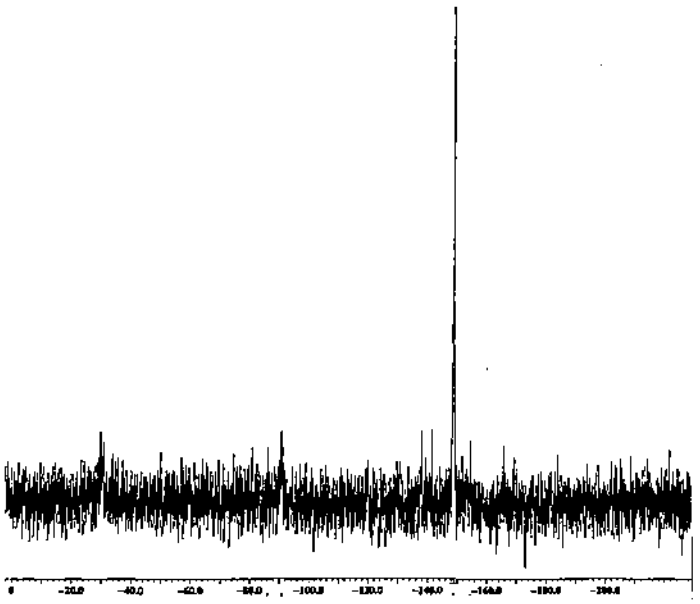
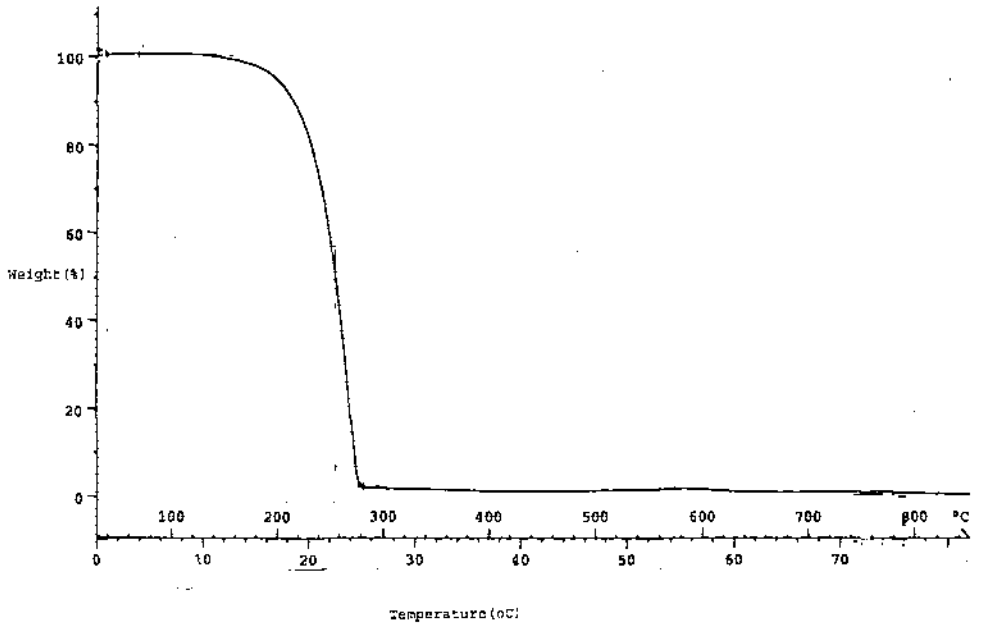


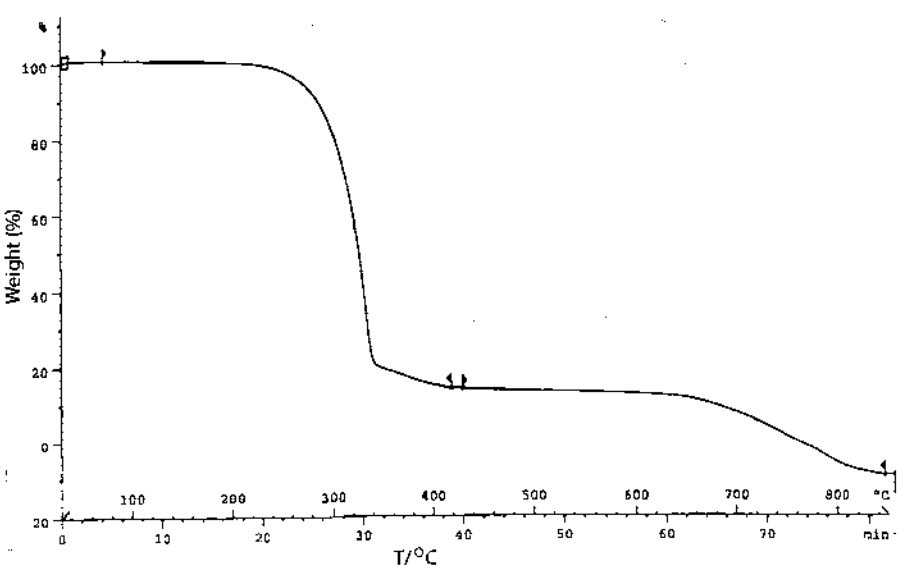
Fig. 3.26 ^{119}Sn NMR spectrum of **14**.

3.4.4.2.4 Thermogravimetric analysis of organotin(IV) carboxylates of 3-cyclohexylpropanoic acid

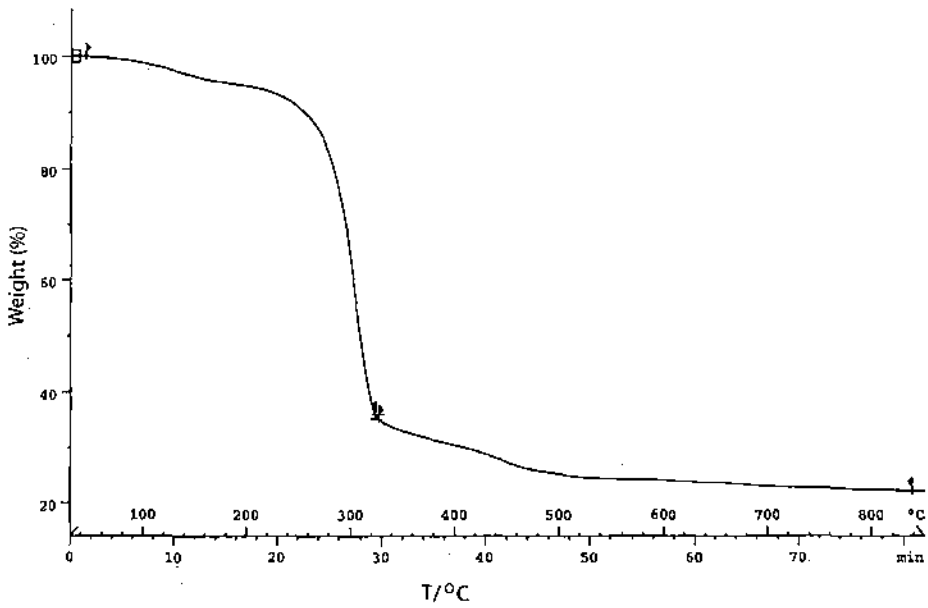
The thermogravimetric (TG) analysis of di- and tri- organotin(IV) derivatives of L^2H reveal that decomposition of the complexes occur as the temperature increases. The degradation pattern of the triorganotin complexes is different from those of the diorganotin complexes. The triorganotin complexes of L^2H (tri-c-Hex and tri-Ph) exhibit a two-step decomposition in a similar manner as that observed for the diorganotin derivatives. The tri-n-Bu derivative though, decomposed in a single step similar to that of the triorganotin derivatives of L^1H. The TG curve of triorganotin and diorganotin(IV) derivatives are presented in Fig. 3.27 and 3.28 respectively. Powder XRD analysis of the final product of **11** obtained at 800 °C show this to be a mixture of SnO_2 (JCPDS: 41-1445), SnO (JCPDS: 24-1342) and β-SnO (JCPDS: 07-0195).


Weight (%)
100
80
60
40
20
0
100
200
300
400
500
600
700
800
°C
0
10
20
30
40
50
60
70
Temperature (oC)

(a)


Weight (%)
100
80
60
40
20
0
100
200
300
400
500
600
700
800
°C
0
10
20
30
40
50
60
70
min
T/°C

(b)



(c)

Fig. 3.27 (a) TG curve of **9** (b) TG curve of **10** (c) TG curve of **11**.

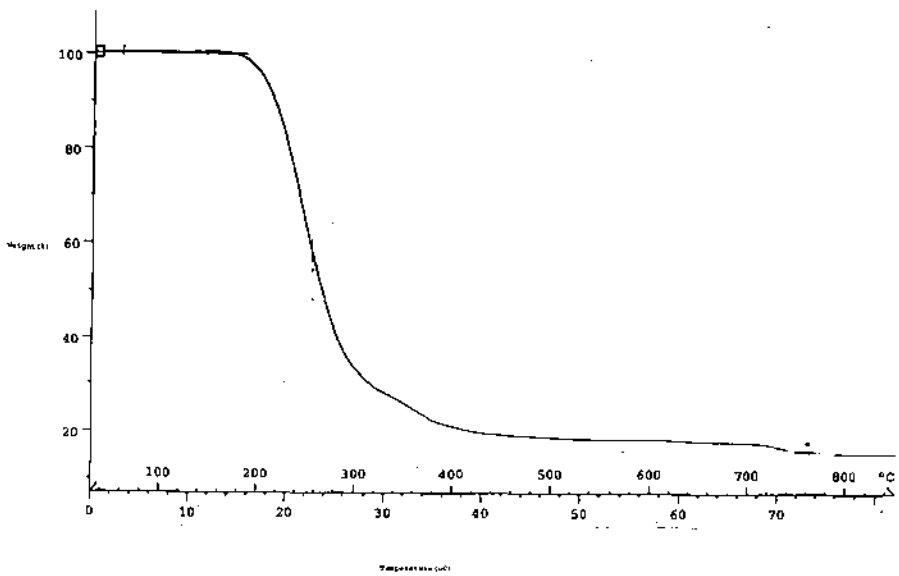


Fig. 3.28 TG curve of **13**.

3.4.5 Biocidal activity

The results of antifungal assay, antibacterial assay and phytotoxicity studies are presented in Table 3.25, 3.26 and 3.27 respectively.

3.4.5.1 Study of the antifungal activity of the organotin(IV) carboxylates

The newly synthesized tri- and diorganotin(IV) complexes of cyclopropane carboxylic acid and 3-cyclohexylpropanoic acid were tested for their antifunal activity by spore germination method as described by Rouxel *et al.* [163]. The data are given in Table 3.25.Most of the compounds showed moderate fungicidal activity. However, enhanced fungicidal activity was found to be associated with the tributyl and triphenyl tin carboxylates. It is well established that triorganotin compounds are significantly more biologically active than classes with either more or less hydrocarbons bonded to tin [158].Within the triorganotin carboxylates, the nature of the R group was found to play a pivotal role in the determination of the fungicidal activity of the complex. In this case, the tri-n-butyl carboxylates were found to be more active (over the range of fungi tested) than tri-phenyltin derivative which was found to be more active than the tri-cyclohexyltin complex [16, 158]. Apparently, the function of the ligand is to support the transfer of the active organotin moiety to the site of action where it was released by hydrolysis. The findings are in agreement with the literature reports which says that anionic groups in the organotin complexes play a secondary role in determining the degree of activity of R_3SnL compounds [6,12]. It was noticed that fairly high concentrations of diorganoin derivatives of L^1H and L^2H were required to inhibit the fungal growth when compared to the R_3SnL analogues. The dibutyltin derivative of L^1H is found to be the least effective among the compounds against the tested fungal strains.The biocidal activity of the triorganotin carboxylates relate to their structure by the fact that the species generating tetrahedral structure in solution are more active[158]. And as explained before, while discussing the NMR spectra of these complexes, all the triorganotin complexes adopted tetrahedral structure in solution.

3.4.5.2 Study of the antibacterial activity of the organotin(IV) carboxylates

The compounds were also screened for their antibacterial activity against *Pseudomonas fluorescens*, a fish-pathogenic, Gram-negative bacteria by following agar well diffusion method [164]. The inhibition zones appearing around each disc were measured and the sensitivity determined from the zone diameters appearing on the plates based on NCCLS charts. When the bacteria gave a zone with diameter less than 13 mm in the presence of an organotin, it was interpreted as resistant (R), when the zone had a diameter of 15-16 mm, the bacteria were considered to have intermediate sensitivity (I) and a clear zone with diameter of 17 mm or more indicated a high degree of sensitivity towards the compound (S).All the compound were tested at 1 mg/ml concentration level. The results are given in Table 3.26. The screening tests show that the tributyltin carboxylates **1** and **9** are the most potent candidates against *Pseudomonas fluorescens,* with decreasing activity for the other triorganotin complexes followed by the diorganotin derivatives [6,41].

3.4.5.3 Phytotoxicity Studies

Wheat seed (variety Sonalika) germination studies (Table 3.27) showed that the compounds have practically insignificant phytotoxicity at the concentrations levels tested. A comparison among the level of phytotoxicities among these compounds reveals that the tri-n-butyl compounds are more phytotoxic than the triphenyltin compounds followed by the other organotin derivatives of L^1H and L^2H. The difference may, however, be attributable to the triphenyltin moiety in **2** and tributyltin moiety in **1,** and is consistent with literature observation that triphenyltin derivatives are tolerated by plants to a greater degree compared to the tributyltin compounds [40].

Table 3.25 Effect of Organotin(IV) carboxylates on spore germination

Spore	Complex	MIC[a]
Curvularia eragrostidis	**1**	2.08
	2	22.40
	3	49.80
	6	50.00
	7	570.00
	9	3.15
	13	62.5
Alternaria porri	**1**	1.95
	2	2.24
	3	50.50
	6	60.00
	7	57.00
	9	2.95
	13	64
Dreschlerea oryzae	**1**	1.64
	2	2.29
	3	49.80
	6	56.00
	7	570.00
	9	3.00
	13	62.5
Macrophomina phaseolina	**1**	2.00
	2	2.45
	3	4.58
	6	52.00
	7	59.00
	9	3.15
	13	70.5

[a] Minimum Inhibitory Concentration in µg/ml

Table 3.26 Effect of different organotin compounds on bacterial growth[a,b]

Complex	Zone of Inhibition (in mm)
1	30
2	20
3	9
6	11
7	14
9	26
10	21
13	13

[a] The values represent mean of three experiments.

[b] Concentrations of compound used: 1 mg/ml.

Table 3.27 Effect of organotin(IV) derivatives of cyclopropane carboxylic acid and 3-cyclohexylpropionic acid on wheat seed germination

Complex	Concentration (μg/ml)	Percentage of germinated seeds[a] after treatment		
		Duration of treatment		
		1h	4 h	8h
1	100	90	90	85
	50	93	93	92
	25	95	95	94
2	100	97	97	97
	50	98	98	98
	25	99	98	98
3	100	97	96	96
	50	99	98	98
	25	99	99	99
6	100	97	97	97
	50	98	98	98
	25	98	98	98
7	100	97	97	97
	50	97	97	97
	25	98	98	98
9	100	91	91	87
	50	94	94	92
	25	95	95	94
13	100	92	92	95
	50	95	95	98
	25	96	96	98
Control	100	100	99	99
	50	99	99	99
	25	99	99	99

[a] With respect to the control.

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