

## CHAPTER 2

## CHAPTER 2

A SURVEY OF THE RELEVANT LITERATURES RELATING TO:

A) ORGANOTIN AND OTHER GR.(IVB) METAL COMPLEXES OF MONOTHIO AND DITHIO CARBOXYLATES B) ORGANOTIN (IV) COMPLEXES OF 4-PYRIDYLTHIO AND 2-PYRIMIDYLTHIO ACETIC ACID.

§ 2.1 INTRODUCTION -

§ 2.2. PREPARATORY METHODS OF DITHIOCARBOXYLIC ACIDS AND THE RELATED THIO-ACETIC ACID LIGANDS AND THEIR ORGANOTIN(IV) DERIVATIVES - A BRIEF GENERAL REVIEW.

§ 2.3. STRUCTURE AND BONDING.

§ 2.4. REFERENCES.

## § 2.1 INTRODUCTION :

An exhaustive survey of the literature was undertaken in respect of the organotin(IV) complexes of the monothio and dithio carboxylic acids and the related aryl thiocarboxylate ligands. The results of the survey are described in this chapter briefly.

The field of organotin chemistry was reviewed in details by Gilman et.al. in 1960<sup>1</sup> and then again by Neuman and Poller in 1970.<sup>2 3</sup>

Later on in the year of 1970, a multi-author work was edited by Sawyer.<sup>4</sup>

The recent progress upto 1980 had been reviewed by Davies et.al.<sup>5</sup>

B Åhrand Pawlenko on the other hand dealt particularly with the different general preparative methods while Gmelin<sup>6</sup>

covered specially the tetraorganotins.<sup>7-8</sup> Structural aspects had been reviewed in 1978<sup>9</sup> and a comprehensive study of bibliography was available from ITRI in 1981.<sup>10</sup>

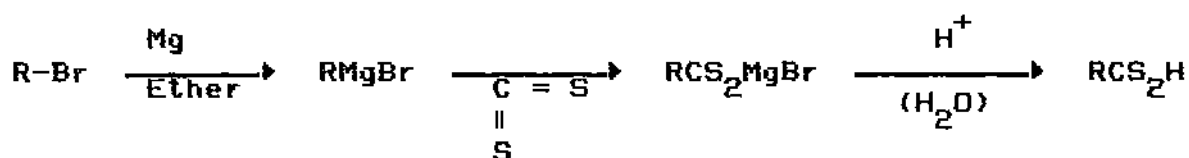
M. Pereyre and J. C. Pommier reviewed the use of organotin compounds in organic synthesis.<sup>11 12</sup>

A review of 275 references on the chemistry of metal and organometallic radicals and their reactions had been done in the recent past by R. David Tayler, in 1988. Some aspects of the chemistry of tin(IV) with oxygen and sulfur ligands had recently been discussed along with a review of 43 references by R. C. Mehrotra and his coworkers.<sup>13</sup>

§ 2.2. PREPARATORY METHODS OF DITHIOCARBOXYLIC ACIDS AND THE RELATED THIO-ACETIC ACID LIGANDS AND THEIR ORGANOTIN(IV) DERIVATIVES - A BRIEF GENERAL REVIEW :

The general method of preparation of aliphatic dithiocarboxylic acid derivatives are well known and were carried out as early as in 1902 by Houben <sup>14-16</sup> et.al., where the dithiocarboxylic acids such as  $\text{CH}_3\text{CS}_2\text{H}$ ,  $\text{C}_2\text{H}_5\text{CS}_2\text{H}$ ,  $\text{C}_6\text{H}_5\text{CS}_2\text{H}$ ,  $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CS}_2\text{H}$  were synthesised and their organotin salts were reported.

A number of aromatic dithiocarboxylic acids and their salts <sup>17-18</sup> were also synthesised and reported. In both the cases, the aliphatic as well as the aromatic dithio carboxylic acids were prepared by using Grignard reaction as shown below :



Although the synthesis of aliphatic dithio acids and their organic ester derivatives had been carried out, as early as in 1902 by Houben <sup>14-16</sup> et.al., the salts (almost entirely metal salts), which are very important as intermediate in the preparation of the derivatives of these acids, had not been synthesised till Kato et.al. <sup>19</sup> first reported the synthesis of stable crystalline amine salts of aromatic dithioacids obtainable from the reaction of corresponding aromatic dithioacids and various secondary and tertiary amines. Later on the successful preparation of some crystalline piperidinium salts of aliphatic dithioacids were also

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 reported, by the reaction of the acid with equimolecular proportion of piperidine. All the piperidinium salts except that of dithiopropionic acid were fairly stable at room temperature and did not undergo any change when left standing for more than three days but were found to be decomposable above 50°C. except the salt of dithiopropionic acid which reportedly decomposed after seven days even at 0°C from solid to oily material. In table 1, a list of amine salts of different dithioacids and their properties are given:

TABLE-1  
 PROPERTIES OF AMINE SALTS OF ALIPHATIC DITHIO ACIDS

$RCS_2^- Pip^+$ R =	m.p.	IR, KBr $\nu_{C=S}$ cm <sup>-1</sup>	$\lambda_{EtOH}(\epsilon)_{max}$ nm	Colour <sup>a</sup> (yield %)
C <sub>2</sub> H <sub>5</sub>	113-114°C	950, 925	339, 455 (17300), (31)	Y (67)
i-C <sub>3</sub> H <sub>7</sub>	133-134°C	850	339, 455 (16500), (39)	OY (82)
n-C <sub>4</sub> H <sub>9</sub>	62-63°C	970	339, 455 (17500), (30)	OY (72)
n-C <sub>5</sub> H <sub>11</sub>	92-93°C	1000	399, 455 (17300), (31)	OY (84)
n-C <sub>6</sub> H <sub>11</sub>	131-132°C	990	339, 455 (17700), (39)	OY (79)

<sup>a</sup> = Y:yellow, OY:orange yellow

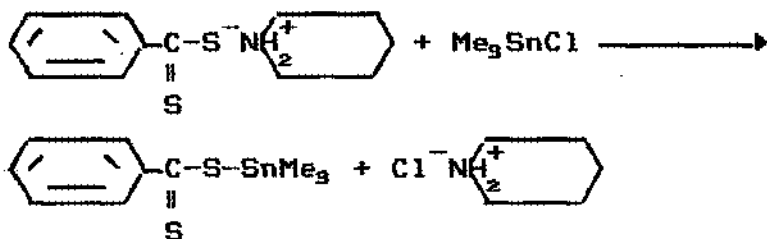
The salts were found to be slightly soluble in ether, benzene, acetonitrile, but were easily soluble in dichloromethane, chloroform, acetone and ethanol. The corresponding alkyl esters in almost quantitative yields were also prepared by the reaction with different alkyl bromides or iodides in dichloromethane. The

reactions with butyl bromide or alkyl chlorides with no electron withdrawing group on their  $\alpha$ -position did not occur, even under more severe conditions. The salts could also be isolated as anhydrous crystals from the reaction of bis(thioaroyl) disulfides with the corresponding amines<sup>19</sup> as shown below:



A number of organotin esters such as  $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{SMR}_3$ <sup>21-22</sup>,  $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OMR}_3$ <sup>23-24</sup>, etc.

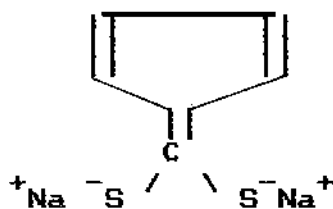
[where R = alkyl, R' = aryl and M = Group IVB metal] containing monothio carboxylate moiety had been synthesised and reported. The corresponding esters of dithio acids were unknown till the report by Kato and Mizuta<sup>25</sup> in 1973. The organotin esters of dithio acids prepared by ready reaction of piperidinium salt of dithiobenzoic acid with trimethyltin chloride at room temperature to give the desired product in quantitative yield as shown below.<sup>25-26</sup>



The structure of the organotin (IV) esters was confirmed by elemental and spectral data. The compound was, however, not examined by the X-ray diffraction. Similarly organotin esters of piperidinium dithio isobutyrate was also prepared.<sup>25</sup> The preparation of the organotin(IV) dithio carboxylates using the corresponding sodium and potassium salts of acids appear to be very difficult due to the highly hygroscopic nature of them.<sup>18, 25-28</sup> Proton magnetic resonance spectra of some 13 organotin monothio and dithio carboxylates had been reported by Coldea *et.al.*<sup>29</sup> and Kato *et.al.*<sup>30</sup>

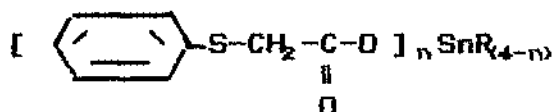
Literature survey show report of a few alkenyl dithioacetic acids and alkenyl organotin(IV) dithioacetates. Insertion of unsaturated substrate namely  $CS_2$  across the metal-allyl and metal phenyl bonds of tetraorganotin(IV) was used to prepare the triphenyl-2-propenyl ester of stannane carbodithioic acid *viz.*  $Ph_3Sn-S-C(S)-CH_2-CH=CH_2$ . Similar insertion reactions with  $PhNCX$  ( $X=O, S$ ) were also done with  $Ph_3M-CH_2-CH=CH_2$  ( $M=Pb$ )<sup>31</sup>.

Similar nucleophilic addition of triorganotin anions  $R_3SnLi$  to  $CS_2$  was used as a method of preparation of  $R_3SnCS_2R'$  ( $R, R' = Me, Et, CHMe_2, allyl, phenyl, p\text{-}tollyl, m\text{-}tollyl$ ). In this connection it is important to note the literature report of few dithioacids and their sodio salts with cyclopentadiene of the type:



formed by the reaction of 2 equivalent of sodium cyclo-  
 pentadienide to 1 equivalent of CS<sub>2</sub> in anhydrous T.H.F. at -30°C,  
 in inert atmosphere of nitrogen resulting into a bright yellow  
 solid.

The organotin(IV) thiophenoxy acetates can be prepared by the  
 azeotropic dehydration of the stoichiometric mixture of the  
 respective thiophenoxy acetic acid and organotin(IV) oxide in  
 benzene solution, the products being crystallised from  
 benzene-petroleum ether (60°C-80°C) mixture (1:1), to get the  
 compounds of the general formula as shown below:

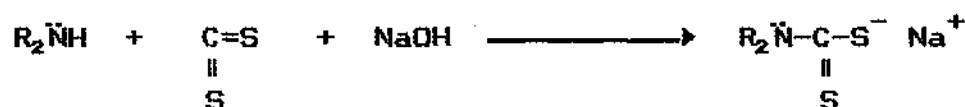


[where R = aryl groups and X = 1,2]

or by the reaction of the sodio-salt of the same thiophenoxy  
 acetic acid and organotin halides.

Another very important class of organotin(IV) compounds are  
 the organotin(IV) dithiocarbamates. The first report of clearly  
 defined aryl tin(IV) dithiocarbamate compounds came from Kupchik  
 and calabretta as early as in 1965. The work was extended and  
 various synthetic routes were developed.

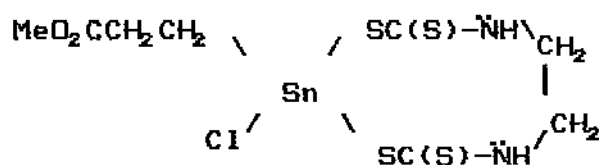
The dithiocarbamates are generally prepared by mixing acetone  
 solutions of carbon disulfide, the appropriate amine and  
 concentrated sodium hydroxide at 0°C-10°C and crystallisation of  
 the product from acetone and petroleum ether.





The first reported organotin(IV) complexes of the monothio carbamate ligand was  $[Ph_3Sn S.CD.N(CH_2)_4O]$ .

Eight tri- and di- organotin derivatives of piperazine bis(dithiocarbamic) acid  $H_2pdtc$  of formula  $(R_3Sn)_2pdtc$  (R= Me, Bu, Ph,  $\nabla C_6H_{11}$ ) and  $R_2Snpdtc$  (R= Me, Bu, Oct, Ph,) had been synthesised and studied.  $(R_3Sn)_2pdtc$  was found to contain tin in the environment of tetrahedral type distorted towards five coordinate cis- $S_2SnR_3$  each by a weakly bidentate  $CS_2$  group whereas diorganotin derivatives are polymeric with a distorted trans- $R_2SnX_4$  geometry about metal. Study of coordination chemistry of a number of cyclohexyltin(IV) dithiocarbamate complexes e.g.  $R_2SnL_2$  [R=  $\nabla Cy$ , L= N,N dimethyl dithiocarbamate], and  $(Me_3C)_2Sn(Cl)L$  [same L] were done by far IR and  $^{119}Sn$  NMR studies. X-ray structure determination of a number of dithiocarbamates of the general formula  $\nabla Cy_2Sn(S_2CNMe_2)_2$  has been established to have  $C_2$ -symmetry with dithiocarbamate ligands bonding in an anisobidentate mode and the local geometry of the hexacoordinated tin(IV) was in distorted octahedral arrangement with two  $\nabla Cy$  groups in trans position. The physical and chemical characteristics suggested polymeric and trimeric structures for  $\nabla Cy_2SnO$  and  $\nabla Cy_2SnS$  respectively.  $[\beta$ -(alkoxycarbonyl) ethyl] tin dithiocarbamates of the type:



was found to be useful as agrochemical fungicide.

### § 2.3. STRUCTURE AND BONDING:

A survey of the literature reveals that the bonding pattern and structure of organotin(IV) derivatives of monothio, dithio, thioalkoxy, thioaryloxy carboxylic acids have been elucidated mainly from IR, NMR and UV-Visible spectrophotometric analytical techniques. Very few X-Ray studies had been noticed.

In some respect tin-sulfur compounds are parallel to that of tin - oxygen compounds, the principal difference being the nature of bonding. The sulfur bonds form readily and once formed they are less reactive to water and carbon dioxide than tin-oxygen bonds.

#### IR spectra:

The most important diagnostic chromophore is the  $>C=S$  group whose stretching frequency varies with the environment. Bak <sup>43</sup> *et.al.* showed from a simplified force constant calculation that  $>C=S$  stretching frequency should be in the vicinity of  $1200\text{ cm}^{-1}$  and the C-S frequency at  $\sim 700\text{ cm}^{-1}$  in organotin(IV) esters of dithiocarboxylic acids. In a series of carboxymethyl dithio esters, the values  $\nu_{(C=S)}$  were found to lie between 1190 and 1225  $\text{cm}^{-1}$ . The observations were confirmed by Bellamy <sup>44</sup> *et.al.* But in case of dithiocarboxylates of the type  $\text{Ph}_3\text{Sn}-\text{S}-\text{C}(\text{OC}_2\text{H}_5)_2$ ,  $\nu_{(C=S)}$  appears at 1040  $\text{cm}^{-1}$  due to the variation of the environment. <sup>45</sup> In the case of esters of dithio isobutyric acid, the bands for  $>C=S$  were found at lower frequencies of 1187 and 1015  $\text{cm}^{-1}$ . The assignment was difficult because the  $\nu_{(C=S)}$  bands for amine salts of corresponding aromatic and aliphatic dithioacids were observed near 1010 and 970  $\text{cm}^{-1}$  respectively. <sup>46</sup> Hence the

intense absorption band in the 1240-1180  $\text{cm}^{-1}$  region was assigned to  $\nu_{\text{C=S}}$  in the metalloidal Gr.(IVB) esters of dithio acids. The spectral properties of some typical compounds are summarised in the table 2.

TABLE-2  
SPECTRAL PROPERTIES OF SOME TYPICAL COMPOUNDS:

Sl. NO.	Compound	IR(neat) $\nu_{\text{C=S}}$ $\text{cm}^{-1}$	NMR( $\text{CCl}_4$ ) ppm downfield to TMS		
			$\delta[\text{C}(\text{CH}_3)_3(\text{M})]$ ppm	(p- $\text{CH}_3$ )	Aromatic
1.	p- $\text{CH}_3\text{C}_6\text{H}_4\text{CS}_2\text{Sn}(\text{CH}_3)_3$	778, 1222	9.40(s)	7.68(s)	1.75-3.05(m)
2.	$\text{C}_6\text{H}_5\text{CS}_2\text{Sn}(\text{CH}_3)_3$	778, 1217	9.40(s)		1.75-2.85(m)
3.	p-Cl $\text{C}_6\text{H}_4\text{CS}_2\text{Sn}(\text{CH}_3)_3$	778, 1214	9.40(s)		1.70-2.85(m)

Kato et.al. concluded that the bonding of organotin(IV) dithioacids is similar to those of the organotin(IV) dithioacetates and coordination of thiocarbonyl sulfur to tin is small or negligible, by recording and studying IR and Raman spectra of a thioacetoxithio group,  $(-\text{S}-\overset{\text{SO}}{\text{C}})$ , with the characteristic



absorption bands of C(S)S group at 880- 860  $\text{cm}^{-1}$ . The IR spectra of thioacetoxithio derivatives of  $\text{M}(\text{CH}_3)_3$  group where M denotes a Group-IVB metals were recorded and an attempt was made to elucidate the structures by Kato et.al. in 1974, where the C(S)S groups were found to appear at 880- 860  $\text{cm}^{-1}$ . There must be some difference between the  $\nu_{\text{C-S}}$  frequency in  $-\text{C}-\text{S}-$  and  $-\text{C}-\overset{\parallel}{\text{S}}$  principally because of the change in the conjugate system in

$\text{S}-\text{C}-\text{S}-\text{M}$  resulting from the replacement of 'O' by 'S' for ordinary aliphatic esters.

Here is given below the band frequencies of carboxylic phenylthiomethyl stretching frequencies of two compounds in solid and solution phase for comparasions with those of phenoxy acetates.

TABLE-3

COMPARISONS OF STRECHING FREQUENCIES OF TWO COMPOUNDS OF CARBOXYLIC PHENYLTHIOMETHYL AND PHENOXY ACETATE TYPE IN SOLID AND SOLUTION PHASE:

Compound	solid phase		solution phase	
	$\nu_{\text{as}} \text{COO}^-$ cm $^{-1}$	$\nu_{\text{s}} \text{COO}^-$ cm $^{-1}$	$\nu_{\text{as}} \text{COO}^-$ cm $^{-1}$	$\nu_{\text{s}} \text{COO}^-$ cm $^{-1}$
$\text{C}_6\text{H}_5-\text{S}-\text{CH}_2\text{COOSn}(\text{C}_4\text{H}_9)_3$	1575(vs)	1370	1665(vs) 1655(vs)	1340(sh) 1327(vs)
$(\text{C}_6\text{H}_5-\text{S}-\text{CH}_2-\text{COO})_2\text{Sn}(\text{C}_4\text{H}_9)_2$	1592(vs)	1370(vs)	1612(vs)	1360(vs)
$\text{C}_6\text{H}_5-\text{O}-\text{CH}_2\text{COOSn}(\text{C}_4\text{H}_9)_3$	1587(vs)	1421(s)	1690(vs) 1665(vs)	1358(m) 1340(s)
$(\text{C}_6\text{H}_5-\text{O}-\text{CH}_2-\text{COO})_2\text{Sn}(\text{C}_4\text{H}_9)_2$	1615(vs)	1416(vs)	1637(vs)	1407(vs)

The thiophenoxy acetates are comparable to the organotin(IV) carboxylates in respect to the environment of tin atom and nature of bonding with the carboxylate group; The symmetric and assymmetric frequencies are expected to take important role in determining the nature of carboxylate binding to the metal atom. Similar to the case of carboxylic acids, if the difference between  $\nu_{\text{sym}}$  and  $\nu_{\text{asym}}$ ,  $\Delta\nu$ , be greater than 250  $\text{cm}^{-1}$ , it indicates the unidentate nature of carboxylic acid group.

Honda *et.al.* used IR spectroscopic methods to establish the chelating nature of the dithiocarbamates in a series of methyl

<sup>46</sup>  
compounds. Later on the chelation was found to be unsymmetrical.  
<sup>47</sup>  
Bonati and Ugo attempted to establish the physical methods to distinguish between two possible covalent bonding models for the dithiocarbamate ligand in aryltin(IV) dithiocarbamate complexes, e.g.: the unidentate [Ester type structure or the bidentate (Chelate)] structure. Since then a good deal of interest has been centred around the structural aspects of organotin(IV) dithiocarbamates.

NMR spectra : The review article, published in the year of 1965 dealt with the application of NMR to the study of organometallic compounds. Of the 10 isotopes of tin, there are three in which the nuclear spin quantum number  $I = \frac{1}{2}$ , abundance of the <sup>115</sup>Sn isotope (0.34%) is so low that NMR study with this isotope is rarely possible. There are also <sup>117</sup>Sn (7.54%) and <sup>119</sup>Sn (8.62%) of reasonable abundance. So, <sup>119</sup>Sn measurements are generally made. The most widely used method is to employ PMR measurements involving the hydrogen atoms of the organic groups attached to the tin. <sup>51</sup>  
<sup>52</sup>  
The tin, <sup>1</sup>H NMR, <sup>13</sup>C and <sup>119</sup>Sn NMR spectra of hepta co-ordinated diorganotin(IV) complexes of the type R<sub>2</sub>Sn(dib) [R= Me, Bu, Ph, Cl and dib= quinquidentate dianion from diacetyl pyridine bis(benzoyl) hydrazone had been reported. Till 1970 PMR measurements have predominantly been carried with the methylene compounds than aryl and higher alkyl tin derivatives. The proton of Ph- group attached to tin show chemical shifts of <sup>53</sup>  
<sup>54</sup>  
 $\delta \sim 7.3$  ppm.

The chemical shifts of methylene protons are more sensitive than those of the methyl protons to the changes in the extent of halogenation. A list of PMR measurements of olefinic tin compounds were first done by Leusink and his coworkers, two of which are shown below:

Compound	$\delta$ (ppm)
$  \begin{array}{ccc}  \text{H} & & \text{H} \\  \text{a} & & \text{b} \\  \backslash & & / \\  \text{C} = & \text{C} & \\  / & & \backslash \\  \text{Et}_3\text{Sn} & & \text{COOEt}  \end{array}  $	$a = 7.1$ $b = 6.71$
$  \begin{array}{ccc}  \text{H} & & \text{SnBu}_3 \\  \text{c} & & \\  \backslash & & / \\  \text{C} = & \text{C} & \\  / & & \backslash \\  \text{Me} & & \text{COOEt}  \end{array}  $	$c = 7.41$

#### Uv-visible spectra :

The organotin(IV) dithiocarboxylates have generally two characteristic maxima at 300-320( $\epsilon = 15000-25000$ ) and 520-530( $\epsilon = 70-90$ , aliphatic) respectively. The former band can be ascribed to the  $\pi-\pi^*$  and the latter to the  $n-\pi^*$  transition of the thio carbonyl group. There is a large red shift for  $n-\pi^*$  transition in comparison to that for carbonyl analogues which can be interpreted in terms of an interaction between the free electron pair of the sulfur atom lying in the  $p_y$  orbital orthogonal to the C=S  $\pi$  bond system and a sulfur d- orbital of tin atom to form M-S-C=S super chromophore.

<sup>119</sup>Sn Mössbauer and X ray crystallographic study:

Related to the organotin dithioacetates, organotin(IV) thioaryloxy acetates are also of great interest for their structural features besides their physical and chemical potent biocidal properties. Interaction of the sulfur atoms of Ar-S-CH<sub>2</sub>- i.e. thioalkyl or thioaryloxy group with the tin atom leading to intramolecular coordination is a distinct possibility in these types of compounds.

Ng. Seik Weng, J. J. Zuckerman and their coworkers have recently studied the crystal structure of dimethylphenyl tin(IV) acetate and tin atom was found to have trigonal bipyramidal structure. Tricyclohexyltin carboxylate was shown to be monomeric species in solution, irrespective of its structure in the solid state. Variable temperature <sup>119</sup>Sn Mössbauer and X-ray study of triphenyltin(IV) chloroacetate revealed the five coordinated compound to have rigid carboxylate bridged trans- C<sub>9</sub>SnO<sub>2</sub> chain structure. The compound was found to be isostructural to triphenyltin acetate. In another study dibutyl tin di-*p*-bromobenzoate was similarly shown to possess 2- fold rotation axis passing through tin atom, coordination geometry being best described by a skew-trapezoidal bipyramid, in which the carboxylate oxygen atoms comprise the trapezoidal part. Trimethyltin 2-furan carboxylate was again studied crystallographically recently in 1989 which revealed the distorted trigonal bipyramidal geometry of the tin atom. Tricyclohexyltin aryloxyacetates were recently synthesised by reaction of  $\nabla$ cy<sub>3</sub>SnOH with ROCH<sub>2</sub>COOH [R= Ph or substituted Ph] and their structure elucidated by IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and the environment around tin

atom was found to be distorted tetrahedron with four coordination.<sup>50</sup>  
Mössbauer spectral studies also confirmed the above conclusion.<sup>41</sup>

Single crystal structural study of  $\text{Ph}_3\text{Sn}[\text{CS}(\text{CS}(\text{N}(\text{CH}_2)_5)]$ <sup>62</sup> had thrown light on the details of the environment around the tin atom. OK Sang Jung,<sup>41</sup> and coworkers recently studied dithiocarbamate derivatives and characterised the structure of the dithiocarbamate  $\nabla \text{C}_6\text{H}_5\text{Sn}(\text{S}_2\text{-NMe}_2)_2$  by IR, NMR and X-ray study. The molecules had been established to have  $\text{C}_2$ - symmetry with the dithiocarbamate ligand bonding in an anisobidentate mode and the local geometry around tin metal being distorted tetrahedral with two cyclohexyl groups in trans- position.<sup>41</sup> Trimethyl-, trivinyl-, and tribenzyltin carboxylates of the type  $\text{R}_3\text{Sn}(\text{O}_2\text{CCX}_3)$  where  $\text{X} = \text{H}$  or  $\text{F}$  was found to have one dimensional polymeric geometry.<sup>60</sup> Similar one dimensional polymeric geometry was also found in  $(\text{CH}_2=\text{CH})_3\text{SnO}_2\text{CR}$  ( $\text{R} = \text{CCl}_3$ ).<sup>61</sup>



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