STUDIES ON THE ORGANOTIN CARBOXYLATES AND RELATED COMPOUNDS :

Syntheses, Structures And Properties, Including Biocidal Properties of Organotin Derivatives of Carboxylate Ligands Containing Additional Donor Sites (e. g. N, S.)

THESIS SUBMITTED FOR THE DEGREE OF DOCTOR OF PHILOSOPHY (SCIENCE) OF THE UNIVERSITY OF NORTH BENGAL

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P R E F A C E

The present investigation carried out on Organotin Carboxylates is divided into the following five chapters:

Chapter 1 :

The first chapter of this dissertation deals with a brief overall literature survey relating to organotin compounds in general, specially highlighting the developments in the field of organotin carboxylates. Specific classes of compounds, related to the present investigation, have been reviewed in appropriate chapters.

Chapter 2 :

This chapter deals with the synthesis of first transition series metal complexes of (4-pyridyl thio) acetic acid and (2-pyrimidyl thio) acetic acid. The new complexes were synthesised to examine the binding mode of the two ligands with metals, the change in their biocidal activity upon complexation and to compare the structural aspects and biocidal properties of these transition metal complexes with the organotin (IV) complexes of the same. [The organotin (IV) (4-pyridyl thio) acetates will be discussed in third chapter .]

The complexes were synthesised by stirring a mixture of metal chloride or sulphate solution and sodium salt of the ligand acid in methanol or ethanol-water mixture and are characterised on the basis of elemental analyses, Infrared spectra and magnetic moment. The complexes are probably the examples of low spin type having bidentate carboxylate as well as $SO_4^{=}$ groups in the coordination spheres.

Chapter 3:

This chapter describes the syntheses of organotin (IV) esters of (4-pyridyl thio) acetic acid. In addition to the -COO group, the ligand contains 'N' atom as well as 'S' atom as donors. The reactions were carried out using the following route:

$$(4-n)RCOOH \xrightarrow{(4-n)NaOH} (4-n)RCOONa \xrightarrow{R_nSnCl_{(4-n)}} (RCOO)_{4-n}SnR_n$$

$$\left[R = O-\overset{O}{\overset{\|}{C}}-CH_2-S-\langle\bigcirc\rangle^{N}\right]$$

The reactions were carried out in dry methanol, in appropriate ratios of reactants as detailed in relevant sections. All the new compounds were characterised and found to be air stable.

Fungicidal activity and phytotoxicity of these compounds have been discussed in this chapter.

Chapter 4 :

This chapter deals with the synthesis, characterisation and biocidal properties of the products from the reactions of phenyl thio hydantoic acid, Ph-N = $\overset{NH_2}{\underset{|}{C}}-SCH_2COOH$, with organotin (IV) oxides or hydroxides. Phenyl thio hydantoic acid did not bind the organotin group through the expected carboxylate moiety. Instead an entirely different series of organotin compounds containing Sn-S bond were obtained. On the basis of physical methods of analysis including X-ray crystallographic studies on two of the compounds, namely $Cy_3Sn(SCH_2CONHPh)$ and $Bu_2Sn(SCH_2CONHPh)_2$ the rearrangement of the ligand during the reaction with the loss of one 'N' atom has been confirmed and the tentative reaction sequences have been proposed.

Biocidal activity patterns are presented for a selection of the new compounds.

Chapter 5 :

The last chapter describes the syntheses of new organotin (IV) hydantoates. Syntheses of the compounds were done by heating under reflux the mixture of the respective organotin (IV) oxide or hydroxide and hydantoic acid in benzene and azeotropically distilling off the water

formed. The compounds have been characterised on the basis of elemental analyses, IR, NMR and X-ray crystallographic studies. The structure of $[Ph_3SnOCOCH_2NHCONH_2]$ is polymeric owing to the presence of bridging hydantoate ligands. And the structure of $[Cy_3SnOCOCH_2NHCONH_2]$ is the isolated, distorted tetrahedral arrangement.

The results of fungitoxicity and phytotoxicity studies have been presented in this chapter.

CHAPTER 1

A brief review of Organotin Carboxylates

1.1. Introduction:

Organotin compounds are defined as those that contain at least one Sn-C bond, the carbon atom being part of an organic group. The ground state for tin is a ^3P state, derived from S^2P^2 configuration[1]. In this state, there are only two unpaired electrons and a covalence of two would be expected. But the tetra-covalent occurs much more frequently than divalent state. The four-covalent state is derived from the SP^3 ^5S state of the atom, which is not the ground state but the first excited state. While tin(II) compounds are mostly bent, pyramidal or otherwise distorted (due to the presence of an electron pair that does not participate in bonding and displays stereochemical activity), tin (IV) compounds adopt regular geometries as tetrahedra, bipyramides or octahedra, depending on the coordination number. The electronegativity of tin change with its oxidation number. Tin (II) compounds are more ionic than the corresponding tin (IV) derivatives[2]. The marked increase in stability of R_4Sn compounds over R_2Sn types demonstrates the effect of increased hybridisation. Thus, the organic chemistry of tin is essentially restricted to the +4 oxidation state[3].

The Tin-Carbon bond should be polar since Tin is electro positive with respect to carbon as represented by $C^{\delta-} - Sn^{\delta+}$. But the polarity is so low as in the tetra alkyl and aryl derivatives of tin that these are not actually hydrolysed by water. A rather unusual feature of the organotin compounds is the ionisation of some of the R_3SnX and R_2SnX_2 compounds in water[4].

A bond between M-C, where M is carbon, there is possibility of forming double bond ($P\pi - P\pi$). When M substitutes other element of Group IVA of the Periodic Table, such as silicon, germanium, tin or lead, there is enough evidence that the d orbitals of these elements are used for bonding ($d\pi - p\pi$). A simple example illustrates this phenomenon. With the four acids of the type $p\text{-}R_3M.\ C_6H_4.COOH$, where M represents carbon, silicon, germanium or tin, carbon is the most electro-negative and should enhance the acid strength to the greatest extent. Actually the carbon compound shows the lowest acid strength, indicating that $d\pi - p\pi$ bonding is operative in the other three compounds[5,6]. It seems that the tendency to use d orbitals in bonding decreases from Si to Sn, since in $(GeH_3)_2S$ and $(GeH_3)_2O$, the Ge-S-Ge and Ge-O-Ge appear to be highly bent[7] whereas in $(SiH_3)_2O$ the Si-O-Si angle is around 150°[8]. However, the possibility of $d\pi - p\pi$ bonding in tin cannot be completely ignored, at least with elements of higher atomic numbers e.g., Cl, Br, I etc. In fact, $d\pi - p\pi$ bonding

is partly responsible for higher values of Sn-Cl stretching frequency in certain tin compounds[9] and Sn-O frequency in $(Ph_3Sn)_2O$[10].

The first chemist to report the existence of "Organic bodies of tin", as they were then known, seems to have been E. Frankland[11,12]. But his work remained unknown to most of his contemporaries as well as to later authors. The work of Carl Lowing[13] in 1852 has usually been considered to represent the beginning of organotin chemistry. The search to isolate a series of dialkyltin (R_2Sn) compounds in the second half of the 19th century was destined to be unsuccessful could only be established by experiment, and in the course of experimental studies of this point, there were a number of erroneous reports[14,15]. The isolation of diethyltin and diphenyltin are now known to be polymers of tin (IV), that is, $(Et_2Sn)_2$ and $(Ph_2Sn)_2$[16].

In 1879, Frankland[17] studied the reaction between stannous chloride and diethyl zinc, hoping by analogy with results obtained by Buckton[18] simply to displace the chlorides with ethyl groups. The product, however was not Et_2Sn, but Et_4Sn. As a route to Et_4Sn, this reaction proved superior to Buckton's original method[18], which used $SnCl_4$. This new reaction remained the method of choice for preparing tetraalkyltins until the early years of the 20th century, when Pope and Peachey[19] first made use of the action of a Grignard reagent

on $SnCl_4$. The early history of organotin chemistry has been recently reviewed by N.W. Nicholson[20].

The first review of organotin compounds was achieved in 1937 by Krause and Van Grosse[21]. Ingham, Rosenberg and Gilman[22] extended the literature upto 1959. Weiss[23] compiled an exhaustive list of organotin compounds covering the literature from 1937 to 1964. Afterwords, several monographs by J.J. Zuckerman (Ed)[24], by Newmann[16] and by Poller[25], and a multi-author work edited by A.K. Sawyer[26] were published in 1970-1972 and Davies and Smith in 1980[27] and 1982[28]. Structural aspects of this class of compounds have been reviewed[29] and a comprehensive bibliography of X-ray deffraction studies is available from the International Tin Research Institute[30]. Properties, preparations and applications of the monoalkyltin compounds have been reviewed by Guo, Yushen in 1991[30a].

The basic studies in the field of organotin compounds have been developed due to the success of a large number of modern techniques applied to the organotin compounds. Investigations can be performed by the general techniques such as UV[25], IR[25,31], ^{1}H-NMR[25,32], ^{13}C-NMR[33], Mass Spectroscopy[34] and also by the specialised techniques of ^{119m}Sn Mossbauer Spectroscopy[25,28] and ^{119}Sn NMR[28,35] spectrometry. Because of diverse applications in industry and in basic research, the chemistry of organotin compounds has gained considerable importance[28,36].

1.2. Organotin Carboxylates:

In the even expanding field of Organotin Chemistry, Organotin Carboxylates comprise one of the most important class of compounds. Apart from the theoretical and structural interests, organotin carboxylates are finding tremendous importance in industry and agriculture. New applications are likely to emerge in the near future.

The compounds containing — OCOR' groups bonded to tin are defined as organotin esters which may be either monomeric or polymeric and of three general types, viz. $R_3SnOCOR'$, $R_2Sn(OCOR')_2$ and $RSn(OCOR')_3$, where R and R' may be same or different groups. Many discussions with varying degrees of details are available on these compounds[16,25,26,37] and as such only the more important aspects will be presented here.

1.2.1. Preparative Methods:

Among the preparative methods employed for the synthesis of organotin carboxylates, the oldest and the most general procedure is the reaction of organotin oxides (or hydroxides) and carboxylic acids or their anhydrides[38,39,40].

$$R_3Sn - O - SnR_3 + 2R'COOH \longrightarrow 2R_3SnOCOR' + H_2O \quad \ldots (1)$$

$$R_2SnO + 2R'COOH \longrightarrow R_2Sn(OCOR')_2 + H_2O \quad \ldots (2)$$

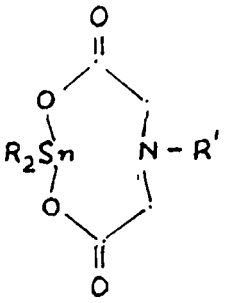
$$R_3Sn\text{-}O\text{-}SnR_3 + (R'CO)_2O \longrightarrow 2R_3SnOCOR' \quad \ldots (3)$$

A Dean-Stark apparatus is used to azeotropically distil out the water formed during the reactions (equations (1) & (2)). Alternatively, the reactants are heated in neat mixture until the evolution of water ceased, e.g.[41].

$$(Bu_3Sn)_2O + 2\text{-}O\text{-}HO\text{-}C_6H_4\text{-}COOH \xrightarrow[\text{Neat mixture}]{100\text{-}110^{\circ}C} 2\text{-}O\text{-}OH\text{-}C_6H_4COOSnBu_3 + H_2O \quad \ldots\ldots (4)$$

Diorganotin (IV) derivatives of bis(Carboxymethyl)amine and its N-Me derivative may be prepared by the condensation of R_2SnO and $R'N(CH_2COOH)_2$, where R = Bu, Octyl, CH_2Ph; R' = H, Me[42,42a].

$$R_2SnO + (HOOCCH_2)_2NR' \longrightarrow$$

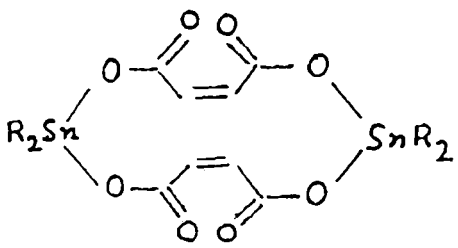


One of the convenient methods is the reaction between metal salts of carboxylic acids and organotin halides[43,44,45], or silver salts of carboxylic acids and organotin sulfides[46].

$$R_{4-n}SnX_n + xM(OCOR')_y \longrightarrow R_{4-n}Sn(OCOR')_n + xMXy$$

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

In a refluxing polar organic solvent R_2SnS (R = Bu, octyl) reacts with Cu, Hg or Pb maleate to give the following dimeric compound[47]:



The reaction of $(Bu_2SnX)_2O$ (X = Cl, Br) with Li and subsequent alkylation with RX' (R = Me, Bu; X' = Br, iodo) and Ac_2O gives $RBu_2Sn\ OAc$, an organotin carboxylate with different alkyls[48].

Tagliavini et al[49] have given a novel method of preparation of trialkyltin carboxylates by electrochemical method using the cleavage of organic groups from R_4Sn (R = Me, Et, Pr, Bu) and Hg(I) carboxylates. At room temperature tetramethyltin produces trimethyl tin acetate when treated with Hg(I) acetate in MeOH.

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

Organotin carboxylates are prepared by the cleavage of one or more organic groups of tetraorganotin compounds by carboxylic acids[50,51].

$$R_4Sn + nR'CO_2H \longrightarrow R_{4-n}Sn(OCOR')_n + nRH$$

The cleavage of organic groups depends on the acid strength, nature of the groups R and R' and also on temperature[52,53]. Vinyl groups are cleaned more readily than saturated alkyl radicals, but less readily than phenyl[22] and successive groups are lost with increasing difficulty. Tetralkyltin is more reactive than tetravinyltin[51].

Triorganostannate esters of dicarboxylic acids can be prepared by the reaction of triorganotin hydroxide with dicyclohexylammonium salt of the dicarboxylic acid[54]. Thus Ph_3SnOH reacts with dicyclohexyl ammonium oxalate (M^+ oxalate) to give $M^+ [(C_6H_5)_3SnOC(O)C(O)O]^-$.

Organotin halocarboxylate, $R_2Sn(X)OCOR'$, may conveniently be prepared by heating equimolecular mixture of the diorganotin dihalide and diorganotin dicarboxylates in an inert solvent[55].

$$Bu_2SnBr_2 + Bu_2Sn(COMe)_2 \longrightarrow 2Bu_2Sn(Br)OCOMe.$$

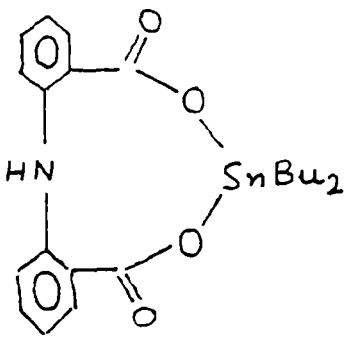
C. Deb and B. Basu have showed that alkyl or aryl esters (carboxyl group attached to primary or tertiary carbon atom) may be transesterified to triorganotin carboxylates[56].

$$R' -COOR'' + (R_3Sn)_2O \longrightarrow R'-COOSnR_3 + R''OSnR_3.$$

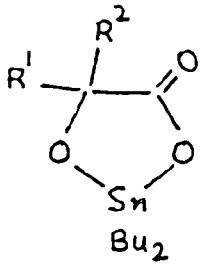
Organotin tricarboxylates, $RSn(OCOR')_3$ are usually prepared from the corresponding organotin trichloride by the action of silver salts of carboxylic acids[43].

$$RSnCl_3 + 3R'COOAg \longrightarrow RSn(OCOR')_3 + 3\ AgCl.$$

Willem et al[57] have prepared a number of compounds of the type $Bu_2Sn(O\text{-}X\text{-}Y\text{-}O)$ by the cyclocondensation of Bu_2SnO with the corresponding dihydroxyl organic compound, e.g.,



and



(R' = Me, R^2 = Me, H;
R' = H, R^2 = Ph).

Reaction between R_2SnO and tri-methyl acetic acid in 1/1 stoichiometry gives $\{[R_2Sn(O_2CCMe_3)]_2O\}_2$ (R = Me, Et, Pr, Bu), which adopt the dicarboxylatotetraorganodistannoxane structure[58].

Holmes et al[58a] prepared oxocarbxoylate tin lader clusters, $[BuSn(O)O_2CC_6H_4NO_2\text{-}2]_6 \cdot 3C_6H_6$ and $[MeSn(O)O_2CC_6H_{11}]_2MeSn(O_2CC_6H_{11})_3]_2$ were prepared from the stannoic acid and carboxylic acids.

1.2.2. Physical Properties of Organotin Carboxylates:

Many of the carboxylates have low melting points which indicates that these are covalent compounds. The carboxylates with small organic groups are more soluble in alcohol, ether etc than in water[16] because the Sn-O bond is essentially covalent. The solubility of triorganotin carboxylates is low in common organic solvents because of their polymeric associated structure.

The melting (or boiling) points of some common organotin carboxylates are listed in Table - 1[16,25,26,43,59,60].

Table - 1

Compound	M.P. (°C)	B.P. (°C/mm Hg)
1. $R_3SnOCOR'$		
$Ph_3SnOCOPh$	84-85.5	
$Ph_3SnOCOH$	202-203	
$Cy_3SnOCOMe$	62-63	
$Bu_3SnOCOMe$	85	
$Bu_3SnOCOPh$		166-168/1
$Me_3SnOCOMe$	196.5-197.5	
$Pr_3SnOCOCF_3$		88-90/1

Contd..

Table - 1 (Contd..)

Compound	M.P. (^{o}C)	B.P. (^{o}C/mm Hg)
2. $R_2Sn(OCOR')_2$		
$Ph_2Sn(OCOMe)_2$	116-117	
$Bu_2Sn(OCOCH = CHMe)_2$	34	
$Bu_2Sn(OCOMe)_2$		144.5-145.5/10
3. $R\ Sn(OCOR')_3$		
$BuSn(OCOCH_3)_3$		117-119/1
$EtSn(OCOPh)_3$		171-173/1
4. $R_2SnX(OCOR')$		
$Et_2SnCl(OCOMe)$	94	
$Bu_2SnBr(OCOMe)$	67-68.5	

1.2.3. Chemical Properties of Organotin Carboxylates:

The Sn-C bond is covalent in nature due to small electromegativity difference between Sn and C. However, Sn-C bond can readily participate in ionic reactions through polarisation, where the carbon atom acts as a nucleophile and the tin atom as an electrophilic centre. On the other hand, the bonds between tin and heteroatoms (Sn-X, where X = O, N, halogen, etc.) are thermodynamically stable but are chemically highly

labile and readily participate in substitution reactions. The large size of the tin atom (covalent radius 1.4A°), the greater polarisability of the Sn-X bond relative to that of C-X bond and the possible participation of the tin 3d orbitals spear to be the major factors responsible for the greater ease of substitution reaction at tin than at carbon[61].

Thermal decarboxylation of triorganotin esters[31] may be utilised in the preparation of unsymmetrical tetraorganotin compounds of the type $R'SnR_3$, where the R-Sn bond formation takes place. However, trialkyltin formate leads to the formation of trialkyl tin hydride[62].

$$R_3SnOCOH \xrightarrow[(R=Bu,\ Pr)]{100\text{-}170^{\circ}C} R_3SnH + CO_2$$

Trialkyltin carboxylates of unsaturated acids give trialkylalkynyltins on decarboxylation

$$Bu_3SnOCOC \equiv CPh \xrightarrow{60^{\circ}C} Bu_3SnC \equiv CPh + CO_2 \quad [62]$$

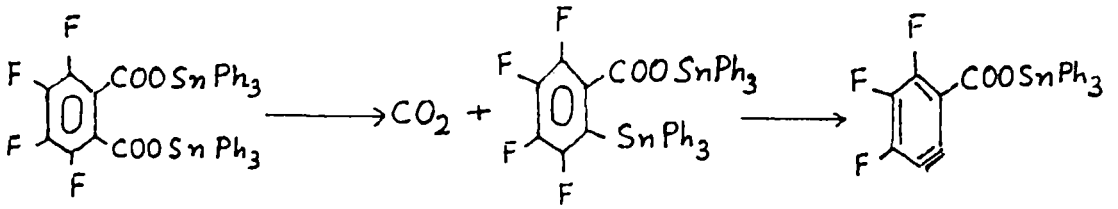
$$R_3SnOCOC \equiv COOSnR_3 \xrightarrow[(R=Bu,Pr,\ Et)]{160^{\circ}C} R_3SnC \equiv CSnR_3 + 2CO_2 \quad [63]$$

Deacon and Farquharson[64], in 1977 prepared several polyfluoro phenyl stannanes utilising this thermal decarboxylation in boiling pyridine.

$$RCOOSnPh_3 \xrightarrow[(boiling)]{Pyridine} R\text{-}SnPh_3 + CO_2$$

($R=C_6F_5$, $P\text{-}MeO.C_6F_4$, $p\text{-}EtOC_6F_4$ or $o\text{-}HC_6F_4$)

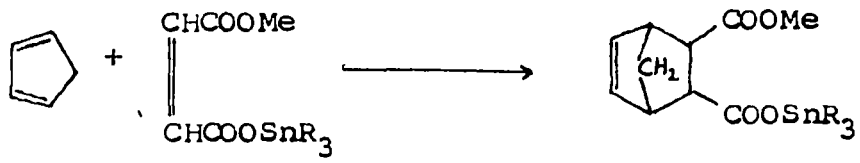
They also reported that thermal decomposition of bis(triphenyltin) tetrafluorophthalate gave a high melting solid, Ph_3SnF, identified by IR spectroscopy[65]. A possible mechanism comprising hemidecarboxylation[66] followed by elimination of the fluorine ortho to the bulky triphenyltin substituent[67], was proposed.



(X)

However the aryne (X) was not isolated or characterised.

Unsaturated organotin carboxylate also undergoes Diels-Alder type reactions with dienes[68,69].



(R = Ph, Bu)

Mixed organotin carboxylates can be formed by redistribution of organotin carboxylates with other organotin compounds[26,70,71].

$$Bu_3SnOCOC_5H_4N\text{-}2 + RSnCl_3 \xrightarrow{MeOH} RSn(OCOC_5H_4N\text{-}2)Cl_2 + Bu_3SnCl$$

(R = Ph, Bu)

$$R_2Sn(OCOR')_2 + R_2SnX_2 \longrightarrow 2R_2Sn(OCOR')X$$

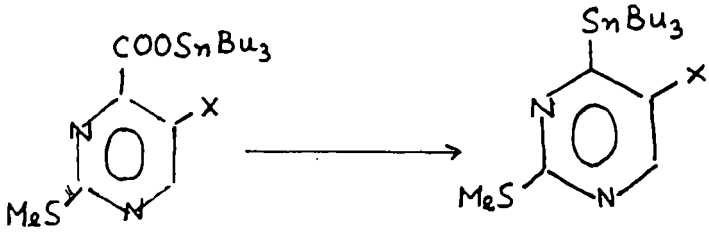
(X = hal., OR, H, etc.)

Van der Kerk and Luijten[72] prepared triphenyl cyanomethyltin by heating triphenyltin cyanoacetate under vacuum.

$$Ph_3SnOCOCH_2CN \xrightarrow{140\text{-}150^{\circ}C} Ph_3SnCH_2CN + CO_2$$

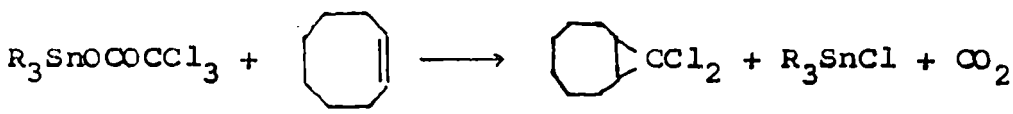
The decarboxylation can be catalysed by Pd(II) complex and then better yields are obtained[73], e.g. thermal decarboxylation of the 2-methyltio derivatives in refluxing anisole gave the 4-stannylated products in only 30-40% yield whereas use of bis(acetonitrile) and bis(triphenyl phosphine) palladium(II)

dichloride increased the yield of 4-stannylated product upto 70% after refluxing in anisole.



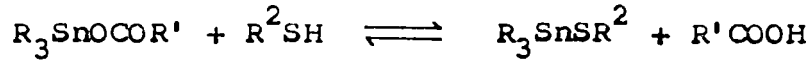
(X = Cl, Br)

Seyferth and his associates[74] found that by heating, organotin esters of trichloro acetic acid were able to transfer dichloro carbene which reacted with unsaturated substrates



(R = Me, Ph)

A state of equilibrium is established with thiols and the reaction can be carried out in forward direction by removing the organic acid from the mixture[75].



α-iodo triorganotin carboxylates react with electron-rich alkenes in the presence of radical initiator to produce γ-lactone. AIBN was found to be more effective and convenient than any other initiation procedure[76].

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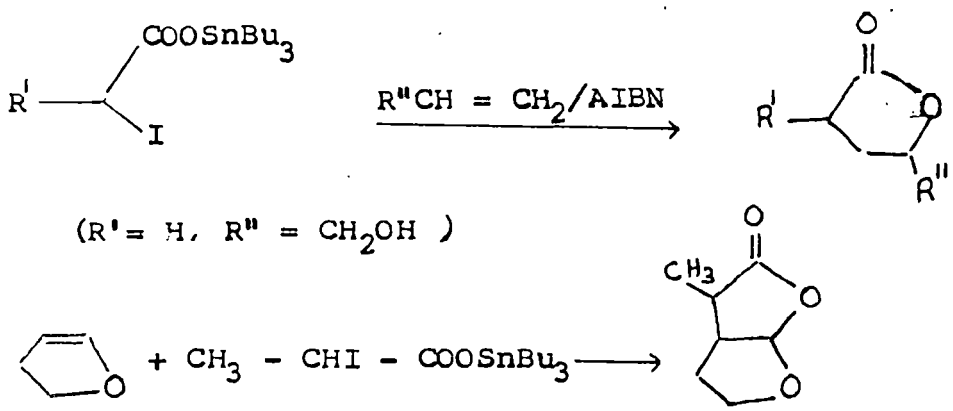


The authors proposed the generation of a radical which then added to the alken before cyclisation, with simultaneous elimination of the tributyl-stannyl radical. This reaction proved to be of high synthetic value.

Recently, the copolymerisation of functional and alkyl methacrylates with tributyl tin methacrylates have been described by Babu et al[77]. They showed that the presence of functional units in the copolymers can be utilised to selectively cross-link the polymers so that the rate of release of tin moiety can be controlled which is believed to have played a role in biocidal properties.

Complex formation by esters is less extensive than by organotin halides due to weaker acidity of organotin esters which may be related to the lower electron-withdrawing power of OCOR group compared to Cl atom[78]. The presence of electron-withdrawing groups attached to the tin and/or carboxylate moiety will favour complex formation, e.g. $Ph_3SnOCOCCl_3.MeOH$[79,79a],

$(CH_2 = CH_2)_2Sn(OCOCF_3)_2 \cdot$ bipy[80], $Me_3SnOCOC_5H_4N\text{-}2.H_2O$[81] and $Sn_4Ph_8(O_2CCCl_3)_6(OH)_2$[79a] which is a novel linear chain connected by hydroxy and acetate bridges.

$Et_2Sn(OAc)Cl$ reacts with RC ≡ CH to give RC ≡ $CSnEt_2OAc$ in 53 to 84% yields (R = Ph, Bu, Me_3Si)[84a]

$$PhC \equiv CH + Et_2Sn(OAc)Cl \longrightarrow PhC \equiv CSnEt_2OAc \ .$$

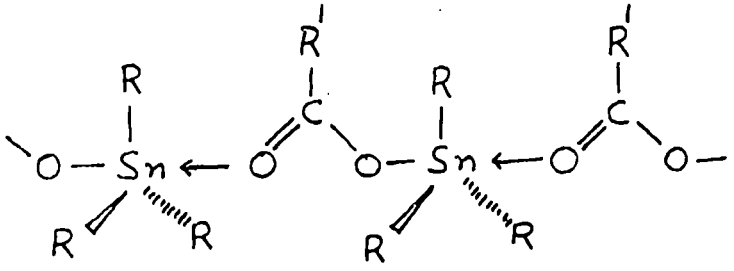
1.2.4. Structure of Organotin Carboxylates:

The structure of organotin esters are studied by IR, NMR and Mössbauer spectroscopy and by X-ray crystallography. Tin possesses, two spin of one half isotopes, ^{117}Sn and ^{119}Sn which become important in NMR studies. Tin has stable isotopes, which allow the easy identification of the tin-bearing fragments in the mass spectrometer. Mössbauer resonance from the ^{119}Sn nucleide can be easily recorded. Further tin-carbon stretching frequencies in the IR and Raman spectra can be assigned in most cases.

A vast literature on the structure of organotin carboxylates were covered in the review written by Davies et al[28] and on ^{119}Sn-NMR spectroscopy by P.J.Smith and A.P. Tupcianskas[35a] and by B. Wrackmeyer[35b]. The subject has also been discussed and reviewed by R.C. Poller[25], R. Okawara and M. Wada[26,37].

In the absence of hindered groups, organotin carboxylates

exist in polymeric associated form in the solid phase.

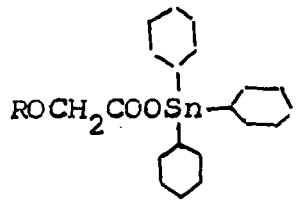


This chain polymer, involving bridging carboxylate groups and planar or near planar R_3Sn moieties, has been demonstrated crystallographically, e.g., for $Me_3SnOCOMe$[82], $MeSnOCOCF_3$[82] $(CH_2 = CH)_3SnOCOCH_3$[83] and $Bz_3SnOCOMe$[84].

V.G. Kumar Das and his coworkers[85] analysed X-ray data for a number of polymeric triorganotin carboxylates which gave a repeat distance of 5.19 $\pm$ 0.21 A^o for the carboxylate-bridged R_3SnO_2CR' unit that defines the crystal lattice. The repeat distance is sensitive to the organic substituents on either the tin or carboxylate group.

Sterically hindered groups, prevent the association. $Cy_3SnOCOMe$ is present as monomer with the Sn atom occupying a distorted tetrahedral geometry[86].

Q. Xie and J. Zheng[87] in 1991 showed by IR, ^{1}H-NMR and ^{13}C-NMR studies that compounds of the type:

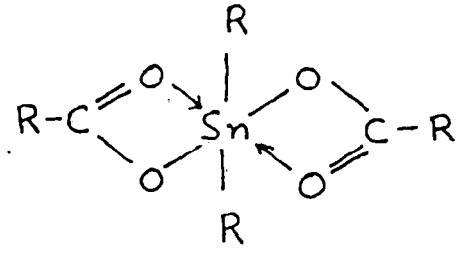


(R = Ph, substituted Ph)

adopt a distorted tetrahedron containing four coordinated Sn atom.

The structural aspects of triorganotin carboxylates in the solid state and in solution phase have been investigated by several workers[88a,88b,88c] by IR and far-IR spectroscopy. Conclusion was that upon dilution of the associated triorganotin esters in organic solvents usually produces oligomeric and finally monomeric species containing tetrahedral tin atom and free ester carbonyl functionality[88a,88b,88c,89].

Dialkyltin dicarboxylates were suggested to be monomeric with hexa coordinate tin[90].



N.W. Alcock and S.M. Roe[79a] established the structure of some phenyltin trichloroacetate complexes by X-ray crystallography. The complex $SnPh_3(O_2CCCl_3)(MeOH)$ is a five-

coordinate monomer. Two isomers of $\{[SnPh_2(O_2CCCl_3)]_2O\}_2$ are centrosymmetric dimers with all their carboxylate groups bridging and with half of them unidentate respectively. The complex $Sn_6Ph_6(O_2CCCl_3)_{10}O_4 \cdot 2C_6H_6$ is a linear hexatin compound containing three $(Sn-O)_2$ stannoxane rings. The hexatin compound $[SnPh(O_2CCCl_3)_3]_6 \cdot 3C_6H_6$ has a drum structure. The complex $Sn_4Ph_8(O_2CCCl_3)_6(OH)_2$ is a linear chain connected by hydroxy and acetate bridges.

E.R.T. Tiekink and his coworkers[58] established by X-ray crystallography, that the compounds, $\{[R_2Sn(O_2CCMe_3)]_2O\}_2$ (R = Me, Et, Pr, Bu), adopt the dicarbxoylate tetraorganodistannoxane structure.

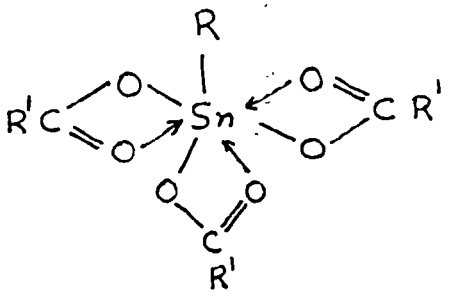
Attempts have been made to correlate tin-proton coupling constants with the structures of organotin esters and it is now generally accepted that the values of $J(^{119}Sn-C-H)$ increase with increasing percent S-character of the Sn-C bond.

^{13}C-NMR spectroscopy has certain advantages over ^{1}H-NMR in the elucidation of structure of organotin carboxylates[92]. For example (i) the differences in the coupling constant $^{1}J(C-Sn)$ are much greater than those in $^{2}J(H-Sn)$; (ii) since the carbon of the alkyl or aryl group is directly bonded to Sn, the variations in $^{1}J(C-Sn)$ more accurately reflect rehybridisation at the tin atom than do those in $^{2}J(H-Sn)$; (iii) for alkyl groups like propyl, butyl etc., it is possible to measure

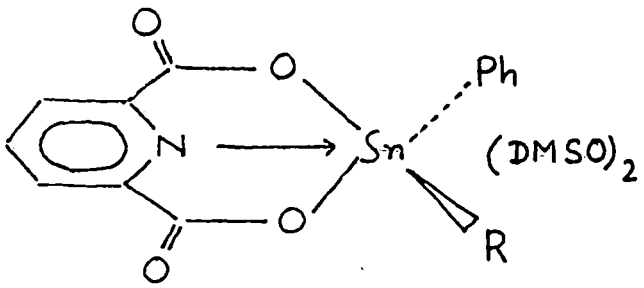
^{1}J(C-Sn) accurately where ^{2}J(H-Sn) can not be measured under normal conditions; (iv) for such long-chain alkyl groups the identity of the compound and within limits, its p.rity can be established undoubtedly.

K.C. Molloy[93] in his study of solid state ^{119}Sn-NMR of organotin carboxylates found that compounds which undergo auto-association in the solid to yield coordination polymers should be identified by an upfield chemical shift in the solid and a lower field shift in solution. Both Ph_3SnO_2CMe and Ph_3SnO_2C-$C_6H_4N_2$-2 meet these structural criteria.

The IR spectra of a number of monoorganotin tricarboxylates in CCl_4 show coordinated carbonyl stretching band, and additionally, $BuSn(OOCMe)_3$ and $BuSn(OOCEt)_3$ were found to be monomeric in camphor solution[43]. This is indicative of a 7-coordinated tin atom geometry for these compounds.



The ^{1}H-NMR spectra in the pyridine proton region of 2,6-pyridine dicarboxylato(phenyl)(organo)tin compounds of the type:



(R = Me, Pr, $CHMe_2$, Bu, CMe_3, $PhCH_2$)

in DMSO-d_6 solutions exhibit a pattern that, together with ^{13}C coupling data and ^{119}Sn chemical shifts, can be interpreted by a hepta coordinated pentagonal bipyramidal structure in which the Sn atom likely to be surrounded by two DMSO ligands in equatorial positions[94].

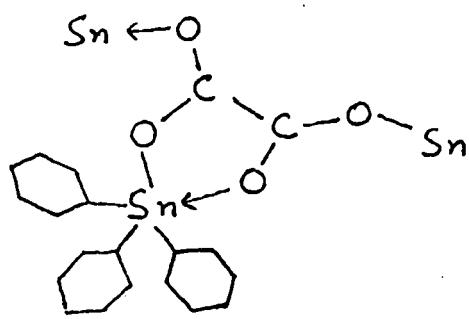
Handlir et al[95] investigated the structure of the compounds $Bu_2Sn[(O_2C)_2X]$ [X = $(CH_2)_n$ (n = 0-8), cis- and trans- CH :CH; O-, p-C_6H_4] by IR and ^{13}C-, ^{17}O-& ^{119}Sn-NMR spectroscopy and came up to the conclusion that the crystalline compounds are formed as linear or cyclic oligomers composed of the central tin atom substituted by two Bu groups and coordinated with both oxygen atoms of two anisobidentate carboxylic groups derived from different molecules of a dicarboxylic acid.

Holmes et al[58a] reported a new structural class of organotin compounds, the oxo carboxylate tin ladder clusters, e.g. (I) $[BuSn(O)O_2CC_6H_4NO_2\text{-}2]_6 \cdot 3C_6H_6$, (II) $[MeSn(O)O_2CC_6H_{11}]_2 MeSn(O_2CC_6H_{11})_3]_2$ and (III) $[BuSn(O)O_2CR]_2 BuSn(O_2CR)_3]$ (R = Ph, Me). X-ray analysis showed that II and III have unfolded drum or ladder structure and that I has a drum structure. ^{119}Sn-NMR data showed that the drum and ladder structure interconvert reversibly.

In 1990, J. Li and coworkers[96] studied the ^{13}C- and ^{119}Sn-NMR spectra of some tricyclohexyl tin (IV) carboxylates and showed that the chemical shifts ($\delta^{119}Sn$) and the coupling constants ^1J (^{13}C, ^{119}Sn) depend markedly on the coordination number of the Sn atom. The chemical shifts and coupling constants ^1J (^{13}C, ^{119}Sn) for aliphatic tricyclohexyltin (IV) carboxylates are in the range 6-11 ppm and 341-345 Hz, and for aromatic tricyclohexyltin (IV) carboxylate, the range is 10 to 40 ppm and 310-340 Hz, which provide evidence that the compounds are monomeric species in solution irrespective of their structure in the solid state.

Recently Thomas C.W. Mak and his coworkers[121] obtained μ-oxalato bis(tricyclohexyltin), μ-$(O_2CCO_2)[(C_6H_{11})_3Sn]_2$ in the attempt to prepare $[(CH_3)_4N][(C_6H_{11})_3SnO_2CCO_2]$ by the reaction of $[(CH_3)_4N]Cl$, $(C_6H_{11})_3SnCl$ and $Ag_2O_2CCO_2$ in methanol. The X-ray diffraction study of the compound revealed the presence of two symmetry-independent molecules, each of which contains a pair of tin atoms in an isomeric cis-, trans- C_3SnO_2

trigonal bipyramidal configuration arising from the quadridentate (chelating and bridging) behavior of the oxalato ligand.



1.2.5. Biological properties of organotin carboxylates:

With the possible exception of organomercurials, organotin compounds have received more attention for their biological effects than organic compounds of any other metal. The inorganic tin compounds hardly have any biological activity whereas organotin compounds exhibit high biocidal activity, probably due to their lipid solubility, which facilitates better transport to the reaction sites than the corresponding inorganic tin compounds.

Due to their high mammalian and phytotoxicities, a number of present applications of organomercurials may be partly taken over by highly effective but relatively non toxic organotin preparations in near future[97].

The systematic studies of biological activities of organotins were initiated in 1950 by the pioneering work of the TNO group[98].

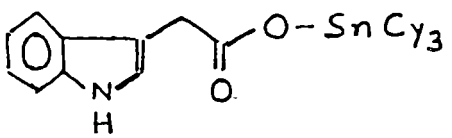
Van der Kerk and Luijten[99] in 1954 published that many organotin derivatives having the general formula of R_3SnX are powerful fungicides. Within any R_3SnX series, the activity is markedly dependent upon the nature of the organic group (R) but relatively independent of the anionic radial X[100]. For a high anti fungal activity the total number of carbon atoms in the alkyl groups of a trialkyltin compound should be about 9-12[100a]. The toxicity of tin compounds were reviewed in 1959[101] and 1964[102].

The following table[119] will show a considerable influence of the length of the alkyl groups.

Anti fungal Activity of some Triorganotin Acetates:

Compounds	Minimal concentration in mg/l causing complete inhibition of growth of the fungi		
$R_3SnOCOCH_3$ R =	Botrytis allii	Penicillium italicum	Aspergillus niger
CH_3	200	500	200
C_2H_5	1	10	2
n-C_3H_7	0.5	0.5	0.5
n-C_4H_9	0.5	0.5	1

K.C. Molloy and his coworkers[109] proposed that in order to obtain possible synergistic activity between an organotin and a ligand of complementary activity, the ligand should be C-bonded to tin, rather than through readily hydrolysable Sn-O, Sn-S or Sn-N (etc) bonds and reported the pesticidal, bactericidal and fungicidal activity of



Four coordinate tin monomers or five-coordinate tin polymers are often more active than chelated five coordinate tin species[116].

The principal advantages of the organotin agro chemicals (which mainly possess prophylactic action) are their relatively low phytotoxicity, their generally low toxicity[103,104] to non-target organism and the lack of resistance by crop pests to these chemicals. Furthermore, triorganotin compounds undergo degradation in the environment, eventually, to form harmless inorganic tin residues[105].

Inorganic tin compounds have no anti tumour activity although a number of organotin compounds with antitumour activity are known[106,107]. A possible mechanism suggested recently for

the antitumour activity of the tin compounds is that the tin, whatever its form, is biochemically converted to the anticarcinogenic entities in the thymus and thus distributed around the body as anticarcinogen through lymph fluids[106]. The possibility of generation of some active free radicals causing interaction with DNA can not be ruled out.

In general organotin carboxylates show biocidal activity[117].

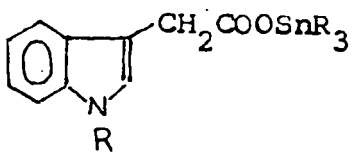
The toxicological and biological properties as manifested in the organotin carboxylates are summarised in Table-2[100,108].

Table - 2

Property	Compounds
1. Fungicidal	
a) Agricultural	$Ph_3SnOOC.CH_3$, $BuSn(OOC.CH_3)_3$
b) Horticultural	Bu_3SnOCO(Naphth)
2. Phytotoxicity	$Ph_3SnOCOCH_3$, $Ph_3SnOOC.C_6H_5$
3. Bacteriostatic	$Bu_3SnOCOCH_3$, $Ph_3SnOCOCH_3$
	$Bu_3SnOCOC_6H_5$
4. Insecticidal	$R_3SnOCOCH_3$ (R = Me, Et, Bu, Ph)
	$Me_3SnOCO.CH_2Cl$
	$Et_3SnOOC.C(Me) = CH_2$
	$Pr_3SnOOC.C(Me) = CH_2$
5. Mammalian toxicity	$R_3SnOOC.CH_3$ (R=Me,Et,Pr, Bu, Ph)

The first commercial products were introduced during the early 1960's : triphenyltin acetate (fentin acetate : Brestan) by Hoechst and triphenyltin hydroxide (fentin hydroxide : Duter) by Philips Duphar. Both compounds are effective against almost the same range of fungi as the copper fungicides, but about one-tenth the dosage[114]. A promising anti spider compound, trisneophyltin acetate, $(\langle\bigcirc\rangle\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}CH_2)_3SnOAc$, is marketed by Shell[118].

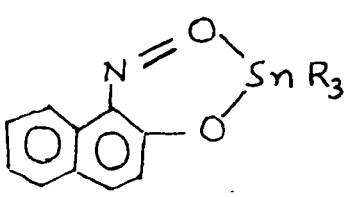
Recently, Molloy *et al*[109] showed that triorganotin indolylacetates of the type:



(R = Me, H, Cy)

possess fungicidal, bactericidal and insecticidal activity.

The compounds :

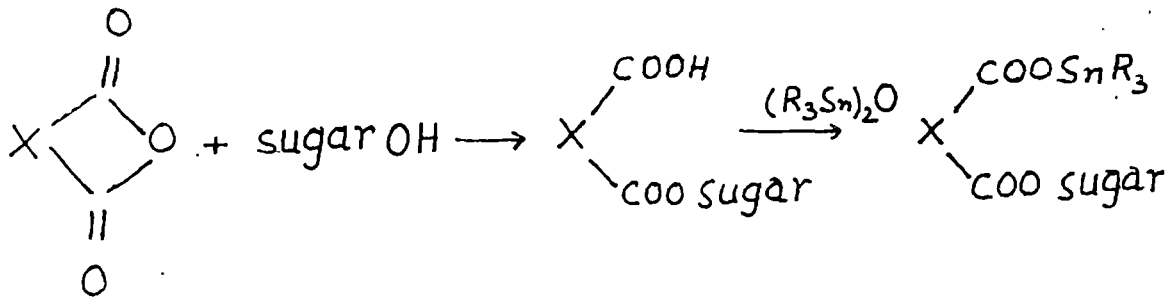


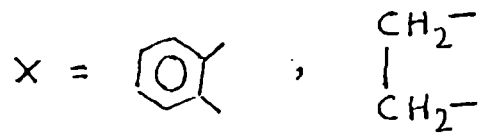
(where R = Bu, Ph, Cl) which contain Sn-O bond and a nitrogen atom in the molecule show an antibacterial activity comparable to or higher than that of streptomycin sulfates[110].

As many as thirty butyltin carboxylates were shown that they may be used as fungicides for fruit by Hu et al[111].

Organotin carboxylates having biological activity are being reported continuously[112,113]. Use of organotin compounds as fungicides have been comprehensively reviewed by Bock[115].

In a recent study, Poller et al[120] reported that direct phthalation and succinylation of sugars gave mono esters which were converted to stannyl sugar esters having enhanced biocidal properties:





The organotin compounds show a unique combination of chemical, physical and biological properties, and our understanding of their fundamental chemistry is now well advanced. The applications of these compounds, however, have still been relatively little explored and even less exploited. This is a field which would repay further study, and novel applications can confidently be expected.

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Chapter - 2

Synthesis and Characterisation of Cr(III), Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) Complexes of 4-pyridyl thio acetic acid and 2-pyrimidyl thio acetic acid.

2.1. Introduction:

In the regulation of life processes metal ions play an unique role by regulating the osmotic phenomenon within cells and tissues and also function as constituent of oxygen carriers. They also act as biocatalysts such as enzymes and co-enzymes. Metals like iron, copper, vanadium are present in the oxygen carrying system in the blood of vertebrates, many invertibrates and tunicates respectively. The role of magnesium in chlorophyll, zinc in the enzyme and cobalt in Vitamin $-B_{12}$ are well established. On the other hand many metal ions are more or less toxic towards living organisms.

While many metals are essential for different life processes in small amounts, introduction of such metals in larger quantities may destroy those living species. For example, fungi requires iron, copper and zinc and few other metals for proper growth and development. But when zinc or

specially copper ions are supplied in more than optimal amounts, they behave as fungicides. Certain other metals like nickel, mercury and lead which have no known physiological activity can act as fungicides[1]. Chromium is toxic to both animals and plants and is known to interfere with many biochemical processes of the plants, besides causing retarded growth[2]. Keeping in view of these facts it is of much interest to probe the role of metal complexes as biocides.

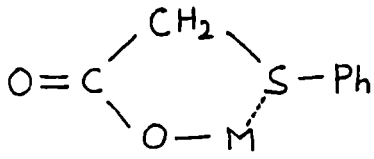
Transition metal complexes (e.g. of Cu, Ni, Cr, Fe etc) are associated with a broad spectrum from biological activity, to numerous commercial applications[3-9].

Several cupric carboxylates are dimeric either in the crystalline state, in solution, or both[10]. Considerable controversy has been caused over the mode of bonding in the dimeric copper (II) acetate monohydrate[11]. The main cause of the problem may arise from the method of preparation of the complexes. Frequently, they are initially isolated as hydrates or solvates followed by dehydration by heating under vacuum. This application of heat may cause slight decarboxylation of the compounds affording anhydrous materials contaminated with small amounts of copper oxide in insufficient quantities to effect the elemental analyses[12].

This contamination of the complex would significantly effect the magnetic properties[11].

Biocidal properties of phenyl thio acetic acid and its derivatives are sufficiently known[13].

A characteristic structural feature usually found in phenylthio acetates of metals (transition metals in particular) is a five-membered chelate cycle:



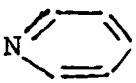
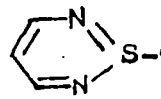
(M = metal atom)

in which an important part is played by the donor-acceptor intramolecular connection of the S atom and the central metal atom M[14]. But this feature was reported to be absent in tri and dibutyltin phenylthio acetates by A.K. Kumar and his co-workers[15].

2.2. Scope and Objective :

Copper fungicides are potentially comparable to organotin compounds, such as Triphenyltin acetate and Triphenyltin hydroxide[16].

The most desirable compounds are those where biocidal properties are due not only to the metal ion or the ligand but to both, because in these cases the effects are mutually combined and complemented.

Thio aryloxy acetates may be analogous to the aryloxy acetates in physical, chemical and structural characteristics. Specially the probable interaction of the nitrogen and sulfur atoms with the central metal atom, their nature of intermolecular interactions through coordination are of immense interest. Apart from theoretical and structural interests, the positive biocidal activities can also be expected due to the presence of S[17,18] as well as N atom in (4-pyridylthio) acetic acid  -S-CH_2COOH and (2-pyrimidylthio) acetic acid,  S-CH_2COOH[13,15] and in general thio aryloxy acetates are worth studying in the wide spectrum of agriculture to industry[19]. Many thioaryloxy acetates have been found to have fungicidal and biocidal properties[20,21].

The main objective of this work was to examine the binding mode of the two ligands with metals, the change in their biocidal activity upon complexation and to compare the structural aspects and biocidal properties of the transition metal complexes of the two thio aryloxy acetates with the Organotin (IV) complexes of the same. It should be

mentioned here that the Organotin (IV) (4-pyridyl thio) acetates will be discussed in the next chapter.

2.3. Experimental and Characterisation:

The ligands, (4-pyridylthio) acetic acid and (2-pyrimidyl thio) acetic acid were Aldrich products. The solvents were purified and dried before use by standard methods[22].

The IR spectra were recorded using PY-UNICAM-SP 3-300S Infrared Spectrophotometer (Philips) with CsI optics and nujol as mulling agent. The UV spectral data were recorded in SHIMADZU, UV-240 Spectrophotometer using 'UVASOL' (Merck) methanol.

Micro analyses (C, H, N) were performed at R.S.I.C, Punjab University, India. Metals were estimated by standard methods[23]. Magnetic moments were determined following Gouy powder technique[24] at room temperature (27°) using $Hg[Co(NCS)_4]$ as standard.

2.3.1. Preparation of Starting Materials:

2.3.1.1. Preparation of the Sodium Salt of (4-pyridyl thio) acetic acid.

(4-pyridyl thio) acetic acid (2 gm, 11.834 mmol) was taken in 100 ml of dry methanol and was titrated in

hot condition by 0.5(N) methanolic solution of sodium hydroxide using an indicator. The neutral solution was concentrated on water bath, crystals of the salt appeared which were filtered out and recrystallised from methanol (m.p. $>275^{o}C$).

Elemental analysis : Found (Calcd):

C	H	N	S
43.98	3.14	7.32	16.74
(43.96)	(3.10)	(7.29)	(16.75)

Relevant spectral data:

I.R. (cm^{-1}) : (Prominant absorptions are given below) Vide Table 1 & 2, (Chapter-3)

2900, 1590, 1495, 1460, 1420, 1374, 1230, 1170, 1120, 1110, 1080, 1000, 940, 915, 820, 800, 730, 720.

I.R. Data (of the parent acid for comparison):

2900, 2840, 1710, 1620, 1500, 1470, 1425, 1390, 1240, 1180, 1120, 1060, 1000, 950, 920, 900, 880, 830.

2.3.1.2 Preparation of sodium salt of (2-pyrimidyl thio) acetic acid:

The sodium salt of the ligand, (2-pyrimidyl thio) acetic acid was prepared by titrating the methanolic solution of the acid by 0.5(N) methanolic solution of sodium hydroxide using an indicator, while the sodium salt formed a heavy white fine needle shaped crystals on cooling. The solid was filtered off and recrystallised from methanol, m.p. 240°C.

Elemental analysis : Found (Calcd.) :

C	H	N	S
14.01 (14.06)	2.60 (2.58)	14.55 (14.58)	16.61 (16.66)

Relevant I.R. data (cm^{-1}) : 3000, 1590, 1570, 1430, 1390, 1410, 1374, 1235, 1195, 1120, 1080, 1000, 940, 915, 820, 800.

2.3.2.1. Synthesis of Sodium dichloro bis-(4-pyridyl thio) acetato diaquo chromate (III),

Na $\left[Cr(OCOCH_2\text{-}S\text{-}\langle O \rangle N)_2Cl_2(H_2O)_2\right]$

Sodium salt of (4-pyridyl thio) acetic acid (0.8 gm, 2.09 mmol) was dissolved in 100 ml methanol and the solution was taken in a 250 ml round bottomed flask fitted with a

pressure equalising dropping funnel and magnetic stirrer. The hydrated metal (III) chloride (0.56 gm, 1.05 mmol) dissolved in methanol (40 ml) was placed in the dropping funnel. The solution of hydrated metal (III) chloride was added drop-wise to the solution of the sodium salt of (4-pyridyl thio) acetic acid with constant stirring. The addition was completed within 30 minutes. An ash coloured precipitate was obtained. Stirring was continued for further 30 minutes. The product obtained was filtered out, washed with hot methanol and dried over fused $CaCl_2$, m.p. $>270^{o}C$, yield, 0.43 gm, 40%.

Elemental analysis : Found (Calcd.)

C%	H%	N%
34.70	3.20	5.73
(32.43)	(3.08)	(5.40)

2.3.2.2 Synthesis of bis-(4-pyridyl thio) acetato diaquo manganese (II), $\left[Mn\ (OCOCH_2\text{-}S\text{-}\langle O \rangle N)_2 (H_2O)_2 \right]$

1 gm, 5.25 mmol of the sodium salt of (4-pyridyl thio) acetic acid was placed in a 250 ml round bottomed flask containing 100 ml methanol, fitted with a pressure equalising dropping funnel and magnetic stirrer. The sodium salt was dissolved by stirring. Hydrated metal (II) chloride

(0.52 gm, 2.6 mmol) dissolved in 40 ml methanol was taken in the dropping funnel and was added dropwise to the sodium salt of the acid with constant stirring. The precipitated colourless product was filtered out, washed with methanol and dried over anhydrous calcium chloride, m.p. $>270^{o}C$, yield, 0.51 gm, 46%.

Elemental analysis : Found (Calcd.)

C	H	N	Mn
41.61 (39.35)	2.34 (3.74)	6.73 (6.55)	12.30 (12.86)

2.3.2.3. Synthesis of (4-pyridyl thio) acetato Sulphato monoaquo Iron (III), $[Fe(OCOCH_2\text{-}S\text{-}\langle O \rangle N)(SO_4)(H_2O)]$

To a solution of the sodium salt of (4-pyridyl thio) acetic acid (0.8 gm, 4.19 mmol) in 100 ml methanol, was added dropwise a solution of ferrous sulphate hepta hydrate (0.58 gm, 2.09 mmol) in methanol (50 ml) with constant stirring. Addition was completed within 30 minutes. Stirring was continued overnight. Next day the precipitated brown coloured product was filtered out, washed with hot methanol and dried over fused $CaCl_2$, m.p. $> 270^{o}C$, yield, 0.49 gm, 70%.

Elemental analysis : Found (Calcd.)

C	H	N	Fe
25.86 (24.86)	2.16 (2.36)	4.08 (4.14)	15.08 (16.53)

2.3.2.4 Synthesis of Cobalt di(4-pyridyl thio) acetate, $[Co(OCOCH_2\text{-}S\text{-}\langle O \rangle N)_2]$

Sodium salt of (4-pyridyl thio) acetic acid (0.8 gm, 4.19 mmol) dissolved in 90 ml methanol was placed in a 250 ml round bottomed flask. The hydrated Cobalt (II) chloride (0.49 gm, 2.08 mmol) dissolved in 50 ml methanol was added dropwise to the sodium salt of the acid from a dropping funnel with constant stirring. Addition was completed within 15 minutes. Stirring was continued for further 30 minutes. A rose red coloured precipitate was obtained. The product was filtered out, washed with methanol and dried over fused calcium chloride, m.p. $> 270^{\circ}C$, yield 0.52 gm, 63%.

Elemental analysis : Found (Calcd.)

C	H	N	Co
41.95 (42.54)	3.32 (3.04)	8.16 (7.09)	14.45 (14.90)

2.3.2.5 Synthesis of Sodium dichloro bis-(4-pyridyl thio) acetato diaquo Nickelate (II),

$Na_2[Ni(OCOCH_2\text{-}S\text{-}\langle O \rangle N)_2Cl_2(H_2O)_2]$

A 250 ml round bottomed flask fitted with a dropping funnel was placed upon a magnetic stirrer. Sodium salt of (4-pyridyl thio) acetic acid (1 gm, 5.23 mmol) dissolved in 100 ml methanol was taken in the round bottomed flask and the hydrated Nickel (II) chloride (0.62 gm, 2.6 mmol) dissolved in 50 ml of methanol was taken in the dropping funnel. Hydrated metal (II) chloride solution was added dropwise to the sodium salt of the acid with constant stirring. After the addition was over the solution was stirred for overnight. A light blue solid product was obtained, filtered out, washed with hot methanol and dried over fused calcium chloride, m.p. $>270^{\circ}C$, yield, 0.97 gm, 68%.

Elemental analysis : Found (Calcd.)

C	H	N	Ni
30.99 (30.67)	3.20 (2.92)	5.03 (5.11)	10.52 (10.71)

2.3.2.6. Synthesis of Sodium bis-(4-pyridyl thio) acetato sulphato cupprate (II), $Na_2[Cu(OCOCH_2-S\langle O \rangle N)_2SO_4]$

Solution of copper (II) sulphate penta hydrate (0.6 gm, 2.40 mmol in 40 ml methanol) was added dropwise to a solution of sodium salt of (4-pyridyl thio) acetic acid (0.92 gm, 4.79 mmol in 100 ml methanol) with constant stirring. A blue coloured product was obtained. Filtered, washed with hot methanol and dried over anhydrous $CaCl_2$, m.p., decomposes at 210°C, yield 0.92 gm, 71%.

Elemental analysis : Found (Calc.)

C	H	N	Cu
33.57 (31.01)	2.94 (2.22)	5.50 (5.17)	10.98 (11.73)

2.3.2.7 Synthesis of tris-(2-pyrimidyl thio) acetato triaquo chromium (III), $[Cr(OCOCH_2-S-\langle N, O, N \rangle)_3(H_2O)_3]$

A solution of hydrated chromium (III) chloride (0.46 gm, 1.73 mmol) in water-ethanol mixture, 30 ml/70 ml (40 ml), was added dropwise to the solution of sodium salt of (2-pyrimidyl thio) acetic acid (1 gm, 5.2 mmol) in water ethanol mixture (100 ml) with constant stirring. A green

coloured product was obtained, filtered out, washed with ethanol and dried over fused $CaCl_2$, m.p. >270, yield, 0.45 gm, 42%.

Elemental analysis : Found (Calcd.)

C	H	N
35.15 (35.23)	3.12 (3.42)	13.26 (13.70)

2.3.2.8. Synthesis of bis-(2-pyrimidyl thio) acetato diaquo manganese (II),

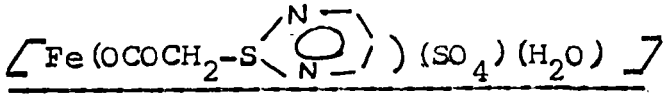
$[Mn(OCOCH_2-S-\langle{}^{N}_{N}\rangle)_2\ (H_2O)_2]$

1.2 gm, 6.24 mmol of the sodium salt of (2-pyrimidyl thio) acetic acid was placed in a 250 ml round bottomed flask containing ethanol (100 ml), fitted with a dropping funnel and magnetic stirrer. The salt was dissolved by stirring. Hydrated metal (II) chloride (0.61 gm, 3.10 mmol) dissolved in 40 ml ethanol was taken in the dropping funnel and was added dropwise to the sodium salt solution with constant stirring for 3 hours. The solution was kept overnight. Next day a white solid product was found and filtered out. The product was washed with ethanol and dried over fused $CaCl_2$, decomposes at 200°C, yield, 0.61 gm, 46%.

Elemental analysis : Found (Calcd.)

C	H	N	Mn
35.31	3.49	10.62	12.13
(33.54)	(3.26)	(13.04)	(12.79)

2.3.2.9. Synthesis of (2-pyrimidyl thio) acetato sulphato monoquo Iron (III),



Sodium salt of (2-pyrimidyl thio) acetic acid (1 gm, 5.20 mmol) dissolved in 90 ml methanol was placed in a 250 ml round bottomed flask which was fitted with a dropping funnel. The ferrous sulphate hepta hydrate (0.72 gm, 2.60 mmol) dissolved in 50 ml methanol was placed in the dropping funnel and was added dropwise to the sodium salt solution with constant stirring. Stirring continued for 3 hours. The solution was kept overnight. A brown precipitate was found, filtered out. The product was washed with methanol water mixture and dried over anhydrous calcium chloride. The product decomposes at 170°C, yield 0.56 gm, 64%.

Elemental analysis : Found (Calcd.)

C	H	N	Fe
23.23	2.28	8.70	15.91
(21.25)	(2.06)	(8.26)	(16.47)

2.3.2.10. Synthesis of bis-(2-pyrimidyl thio) acetato tetraaquo nickel (II) di hydrate,

$[Ni(OCOCH_2-S\langle{}^{N}_{N}\rangle)_2(H_2O)_4]\cdot 2H_2O$

A solution of Nickel (II) chloride hexahydrate (0.618 gm, 2.60 mmol) in methanol (40 ml) was added dropwise to a solution of sodium salt of (2-pyrimidyl thio) acetic acid (1 gm, 5.20 mmol) in 90 ml methanol with constant stirring. After the addition was over, the mixture was stirred for 2 hours and kept for overnight. A green coloured solid product was found, filtered and washed with methanol. The product was dried over fused $CaCl_2$. m.p. 185°C, yield 0.72 gm, 55%.

Elemental analysis : Found (Calcd.)

C	H	N	Ni
28.17 (28.50)	4.39 (4.35)	8.83 (11.00)	11.23 (11.65)

2.3.2.11. Synthesis of sodium bis-(2-pyrimidyl thio) acetato sulphato cupprate (II) dihydrate,

$Na_2[Cu(OCOCH_2-S\langle{}^{N}_{N}\rangle)_2(SO_4)]\cdot 2H_2O$

To a solution of sodium salt of (2-pyrimidyl thio) acetic acid (1 gm, 5.20 mmol) in 100 ml methanol, was added dropwise a solution of copper sulphate penta hydrate (0.65 gm,

2.60 mmol) in 40 ml methanol with constant stirring. Stirring was continued for further 4 hours. A green coloured solid product was found, filtered out. The product was washed with hot methanol and dried over fused calcium chloride. The product decomposes at 150°C, yield, 1.19 gm, 79%.

Elemental analysis : Found (Calcd.)

C	H	N	Cu
25.89 (24.83)	2.34 (2.41)	9.58 (9.65)	10.36 (10.95)

2.4.

Results and discussion:

Table 1, 2 and 3 contain the relevant pysical data of the new compounds.

The complexes produced are both of neutral chelated and anionic types. These are air stable solids having very poor solubility in water and organic solvents. The analytical data corresponds to the composition of the complexes.

Infrared spectral data in solid clearly indicate the presence of coordinated H_2O molecule (3350-3290 cm^{-1})[25,26,29], COO group (carboxylate group) (1630-1540 cm^{-1})[25,29] metal-halogen stretching bands (340 cm^{-1})[27] and coordinated SO_4 group (sulphate group) (in the region 1145, 1110 cm^{-1} and 640-595 cm^{-1})[25,26,28,29] in the new compounds.

The distinction between the water molecules which are present in the first sphere of attraction as strongly coordinated and the water molecules which are loosely bound outside the coordination sphere (e.g., $[MnR_2(H_2O)_2]$ (2) and $Na_2[CuR'_2SO_4].2H_2O$ (11) were made on the basis of change in the IR spectra of the compound (11) on prolonged heating at 80°C (24 hours) under vacuum. The stretching band due to H_2O molecule slowly disappears in this case whereas no change is observed when compound (2) is subjected to the same treatment. This indicate different binding modes of H_2O molecules to the metals in these compounds.

The carboxylate stretching frequency indicate it to be a unidentate group (Fig I) rather than a bidentate type (Fig. II). In all the compounds the $\nu(COO^-)$ appears around 1600 cm^{-1}, in most cases below it. The $\nu_s(COO^-)$ appears around 1370 cm^{-1}, the difference between $\nu_{as} - \nu_s = \Delta\nu$ is an indication of the unidentate nature of the ligand[25].

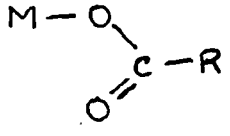


Fig I

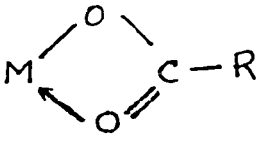


Fig II

In case of organotin derivative of (2-pyrimidyl thio) acetic acid, the crystallographic analysis shows the unidentate nature of the carboxylate group in respect to metal coordination[30].

The SO_4^{2-} group in the coordination sphere shows its characteristic absorptions between 1145-1110 cm^{-1} and 640-595 cm^{-1} as suggested by L.J. Bellamy[29].

The metal chlorine stretching frequencies are rather weak and are tentatively assigned[28] at 340 cm^{-1}.

The magnetic moment data (Table 3) correspond satisfactorily to the required values for 1, 2, 3 or 5 unpaired electrons in the compounds for an octahedral, square planar, tetrahedral disposition around the central metal ion[24].

Thus, the complexes are probably the examples of low spin type having unidentate carboxylate as well as SO_4^{2-} groups and H_2O in the coordination spheres as suggested in their composition.

Table - 1 Physical data

Sl. No.	Compound	m.p. (°C)	Colour	Solubility	Yield	[a]U.V., λ_{max} (nm)
1.	$Na[CrR_2Cl_2(H_2O)_2]$	>270	Ash	Very low in H_2O & organic solvents	40%	260
2.	$[MnR_2(H_2O)_2]$	>270	White	"	46%	265
3.	$[FeR(SO_4)(H_2O)]$	>270	Brown	"	70%	262
4.	CoR_2	>270	Rose red	"	63%	265
5.	$Na_2[NiR_2Cl_2(H_2O)_2]$	>270	Light blue	"	68%	265
6.	$Na_2[CuR_2SO_4]$	decomposes at 210°C	blue	"	71%	268
7.	$[Cr\ R'_3(H_2O)_3]$	>270	Green	"	42%	245
8.	$[MnR'_2(H_2O)_2]$	decomposes at 200°C	White	"	46%	248
9.	$[FeR'(SO_4)(H_2O)]$	decomposes at 170°C	Brown	"	64%	248
10.	$[NiR'_2(H_2O)_4].2H_2O$	185	Green	"	55%	250
11.	$Na_2[CuR'_2SO_4]2H_2O$	decomposes at 150°	Green	"	79%	249

[a]Spectra recorded in MeOH R = $-OOCCH_2-S-$ R' = $-OOCCH_2-S-$

Table 2 IR Spectral data[a]

Compound	$\nu(H_2O)$	$\nu_{as}(COO^-)$	ν M-Cl	$\nu(SO_4^{2-})$	
$Na[CrR_2Cl_2(H_2O)_2]$	3340 (mb)	1595 (s)	340 (w)		
$[MnR_2(H_2O)_2]$	3350 (mb)	1585 (vs)			
$[FeR(SO_4)(H_2O)]$	3320 (mb)	1610 (s)		1140 (sb)	610 (s)
		1570 (vs)			
$Na_2[CoR_2NiR_2Cl_2(H_2O)_2]$	3290 (mb)	1595 (vs)	340 (w)		
$Na_2[CuR_2SO_4]$		1575 (vs)		1110 (mb)	595 (w)
$[CrR'_3(H_2O)_3]$	3320 (sb)	1540 (vs)	1590 (sh)		
$[MnR'_2(H_2O)_2]$	3240 (sb)	1560 (vs)			
$[FeR'(SO_4)(H_2O)]$	3305 (sb)	1600 (s)	1535 (vs)	1135 (vs,b)	600 (s)
$[NiR'_2(H_2O)_4].2H_2O$	3350 (sb)	1590 (sh	1543 (vs)		
$Na_2[CuR'_2SO_4].2H_2O$	3345 (sb)	1630 (vs)		1145 (sb)	640 (m)

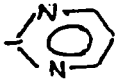
[a] nujol mull on CsI optics, s = strong, m = medium, w = weak, v = very, b = broad, sh = shoulder

R = $-OCOCH_2-S-$

R' = $-OCOCH_2-S-$

Table 3 - Magnetic moment data[a]

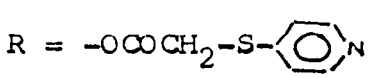
Compound	Magnetic moment (B.M.)	No. of unpaired spins	Hybridisation	Stereochemistry
$Na[CrR_2Cl_2(H_2O)_2]$	3.71	3	d^2sp^3	Octahedral
$[MnR_2(H_2O)_2]$	5.86	5	sp^3	tetrahedral
$[FeR(SO_4)(H_2O)]$	5.80	5	sp^3	tetrahedral
CoR_2	4.60	3	-	-
$Na_2[NiR_2Cl_2(H_2O)_2]$	2.89	2	sp^3d^2	octahedral
$Na_2[CuR_2(SO_4)]$	1.80	1	dsp^2	square planar
$[CrR'_3(H_2O)_3]$	3.85	3	d^2sp^3	octahedral
$[MnR'_2(H_2O)_2]$	5.75	5	sp^3	tetrahedral
$[FeR'(SO_4)(H_2O)]$	5.83	5	sp^3	tetrahedral
$[NiR'_2(H_2O)_4].2H_2O$	2.76	2	sp^3d^2	octahedral
$Na_2[CuR'_2(SO_4)].2H_2O$	1.82	1	dsp^2	square planar

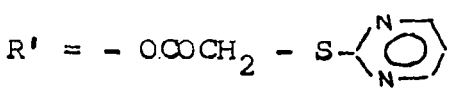
[a] $Hg[Co(NCS)_4]$ as standard R = $-OCOCH_2-S-$ R' = $-OCOCH_2-S-$ 

U.V. Spectra

U.V. spectra, recorded in methanol.
The data are presented in the following table

Compound	λ_{max} (nm)
$Na[CrR_2Cl_2(H_2O)_2]$	261
$[MnR_2(H_2O)_2]$	264
$[FeR(SO_4)(H_2O)]$	262
CoR_2	261
$Na_2[NiR_2Cl_2(H_2O)_2]$	261
$Na_2[CuR_2SO_4]$	268
$[CrR'_3(H_2O)_3]$	248
$[MnR'_2(H_2O)_2]$	249
$[FeR'(SO_4)(H_2O)]$	249
$[NiR'_2(H_2O)_4].2H_2O$	250
$Na_2[CuR'_2(SO_4)].2H_2O$	249

R = 

R' = 

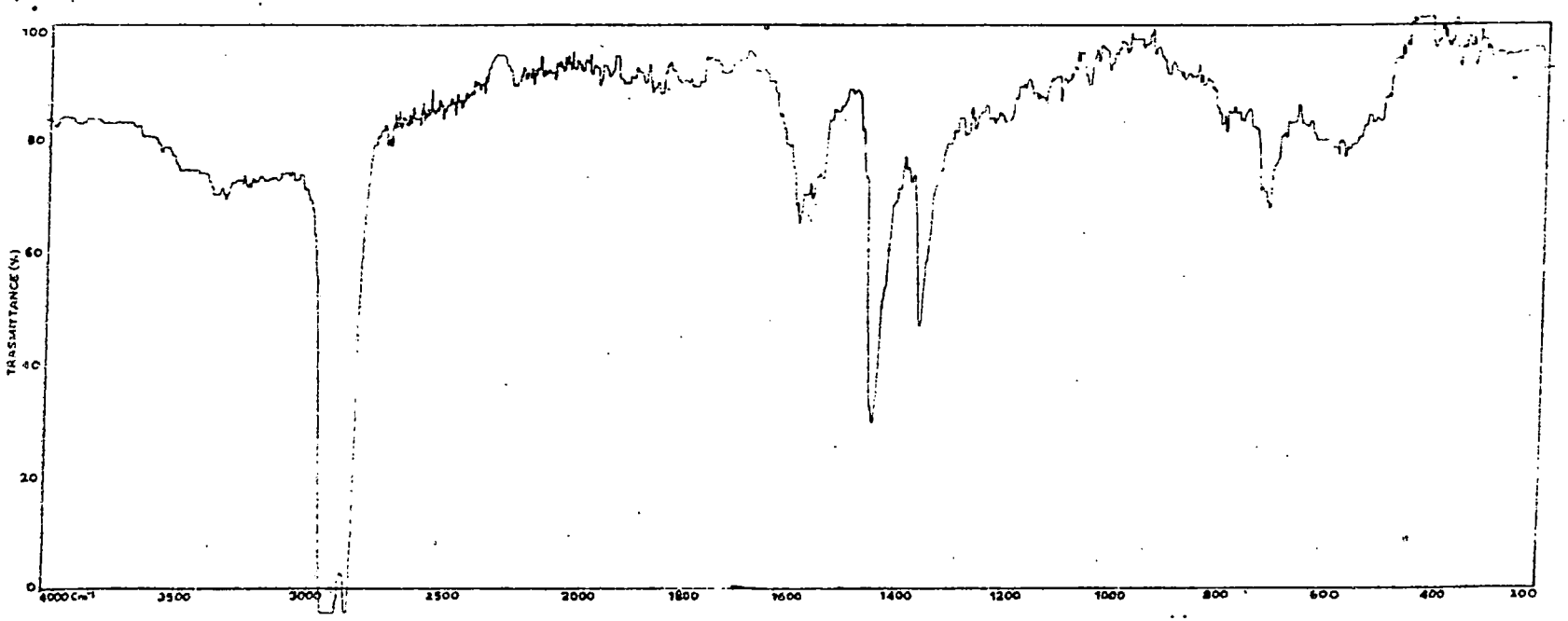


Fig.1. IR spectrum of sodium dichloro bis (4-pyridyl thio) acetato diaquo chromate(III)

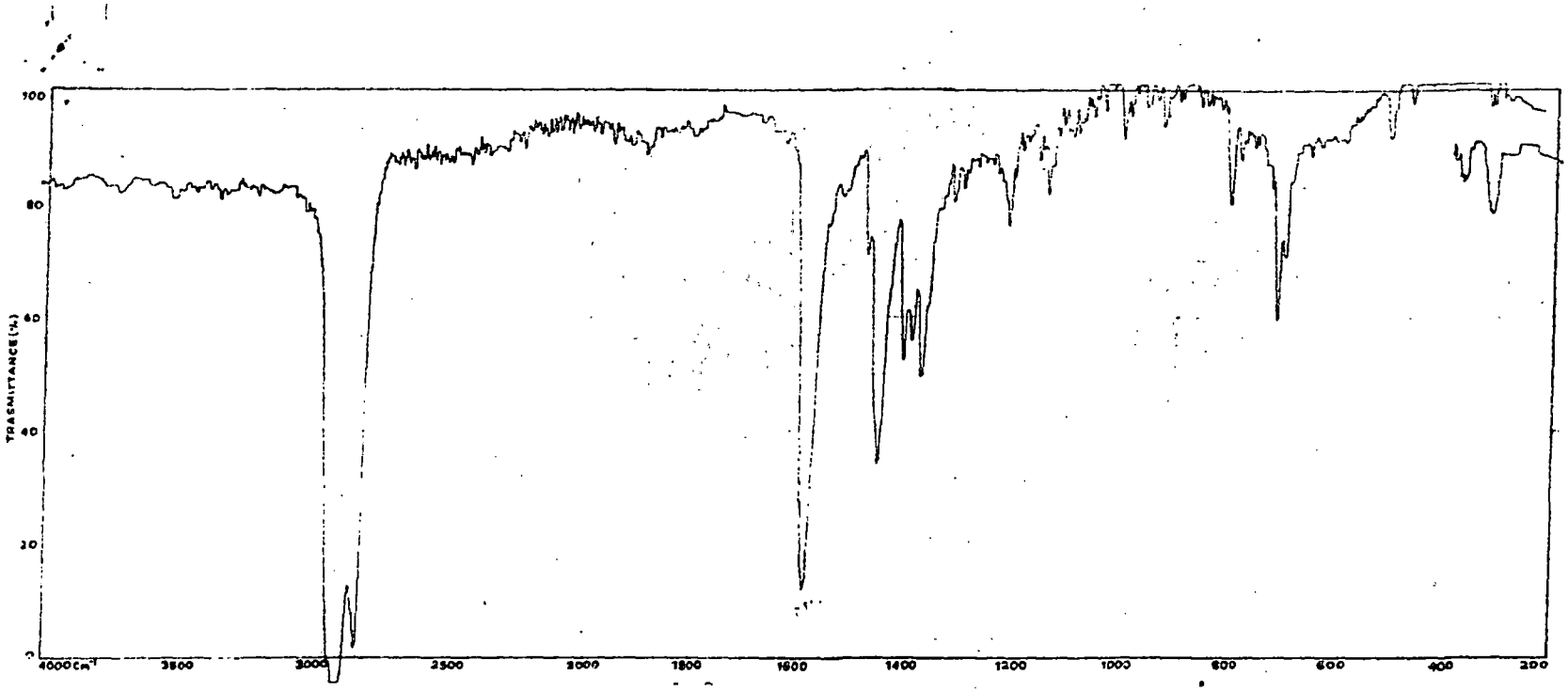


Fig. 2 IR spectrum of bis (4-pyridyl thio) acetato diaquo manganese (II)

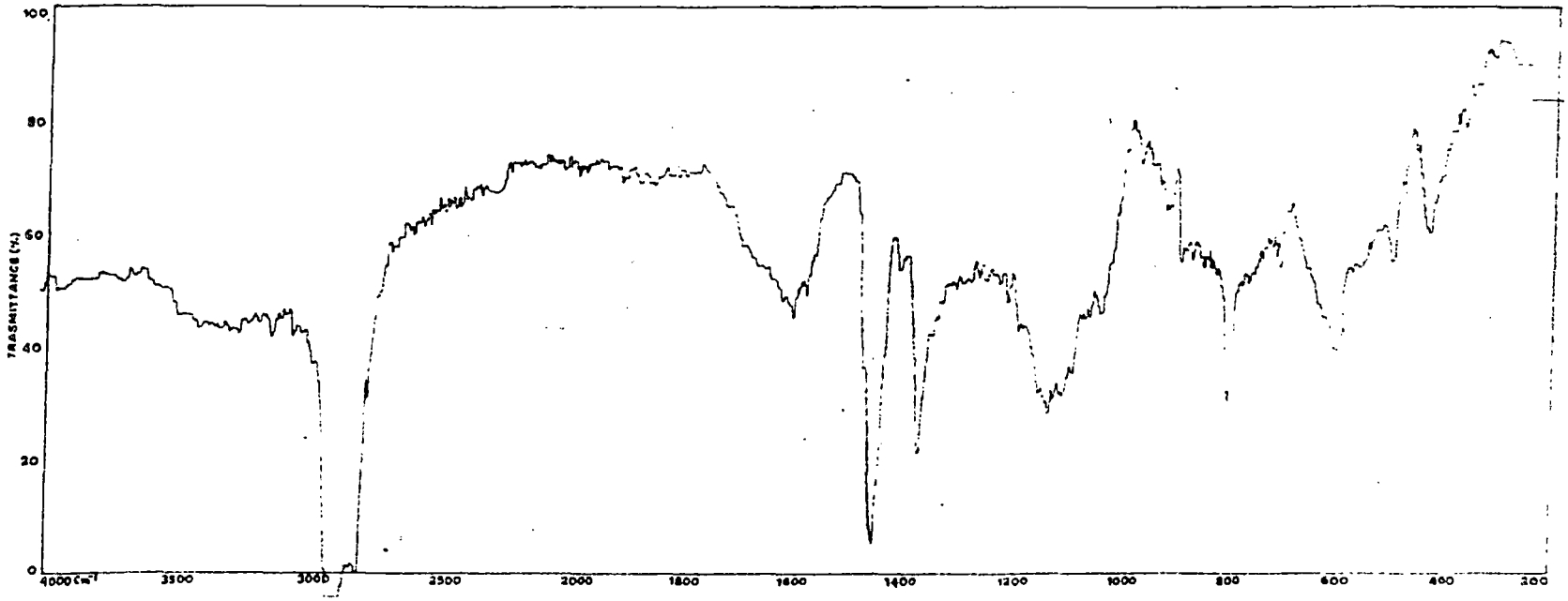


Fig.3 IR spectrum of (4-pyridyl thio) acetato sulphato monoaquo Iron (III)

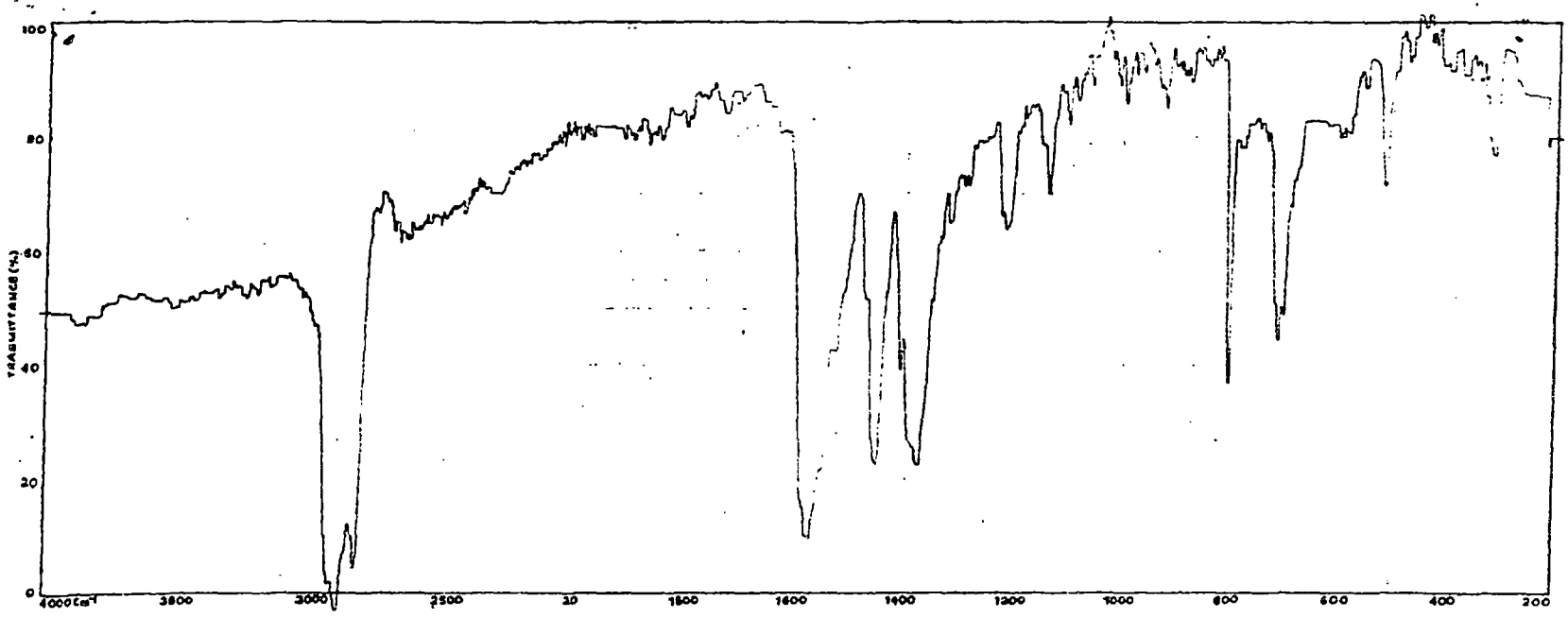


Fig. 4 IR spectrum of Cobalt di (4-pyridyl thio) acetate

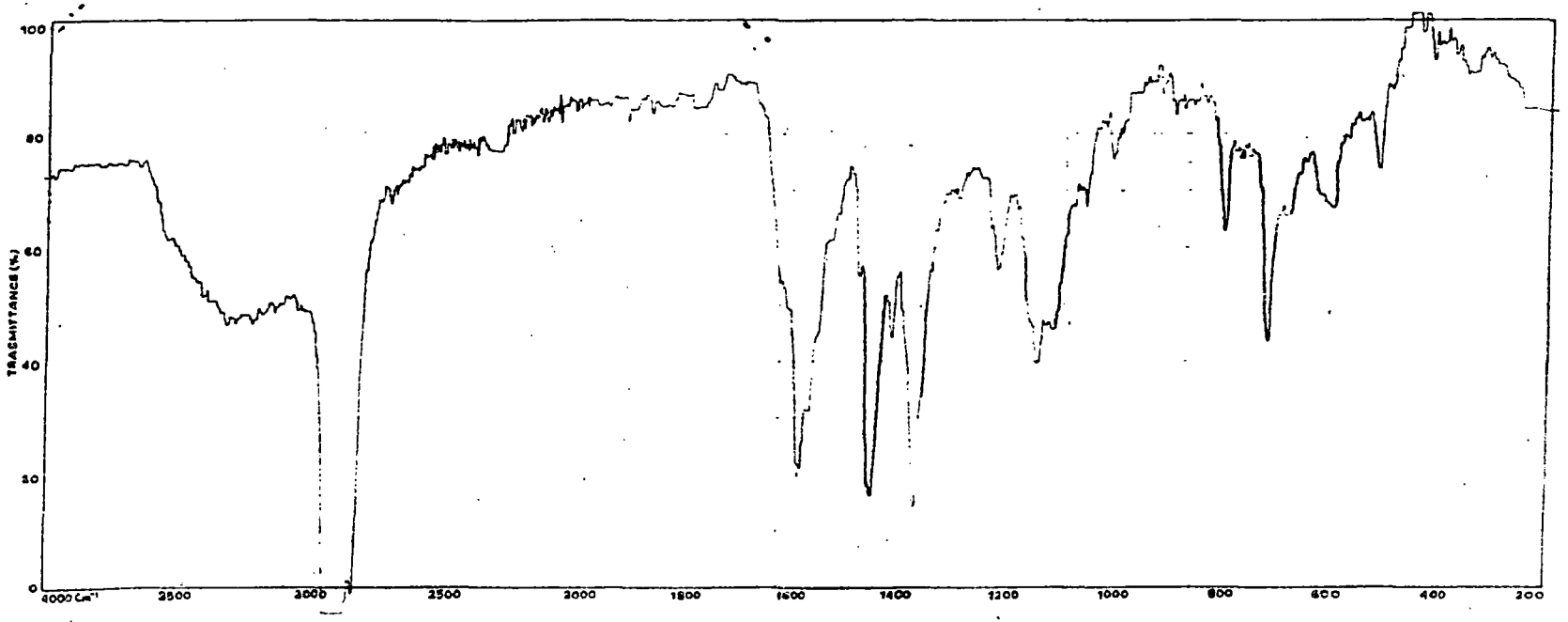


Fig. 5 IR spectrum of sodium dichloro bis (4-pyridyl thio) acetato diaquo Nickelate (II)

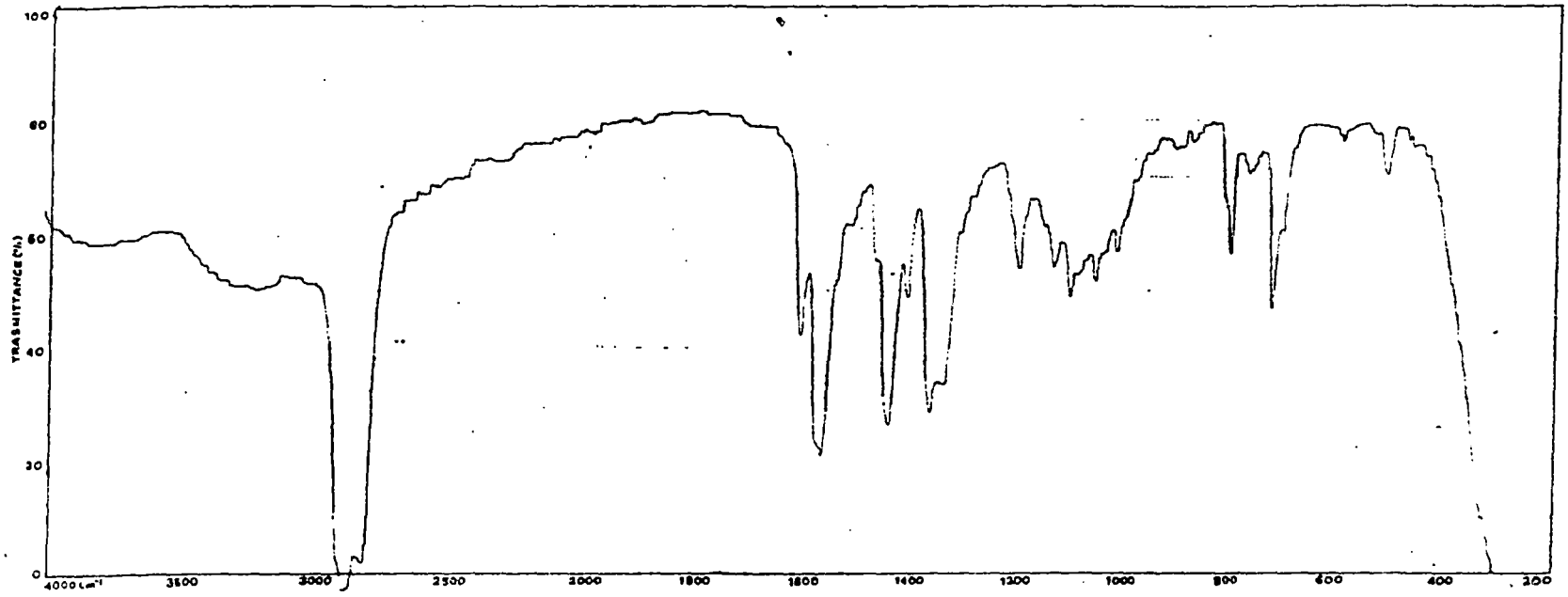


Fig.6 IR spectrum of sodium bis (4-pyridyl thio) acetato sulphato cupprate (II)

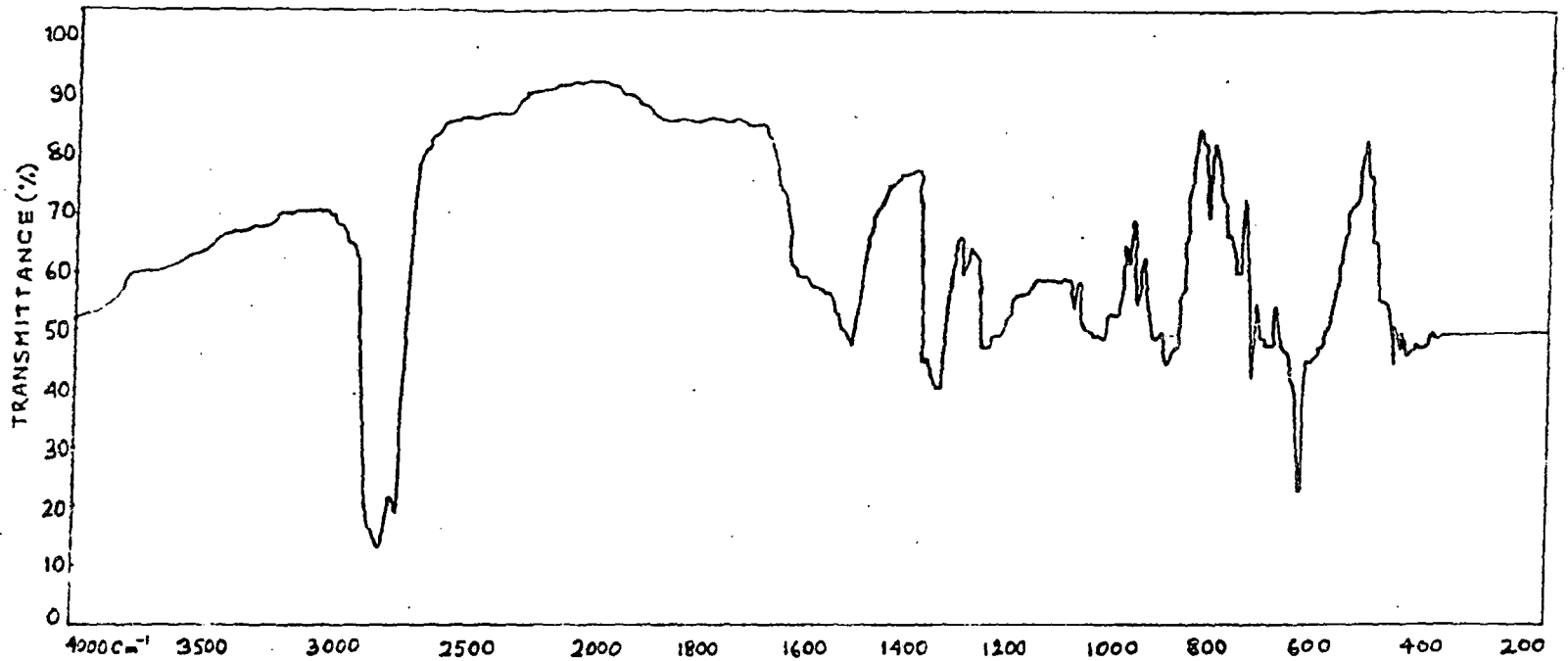


Fig. 7 IR spectrum of (4- pyridyl thio) acetic acid

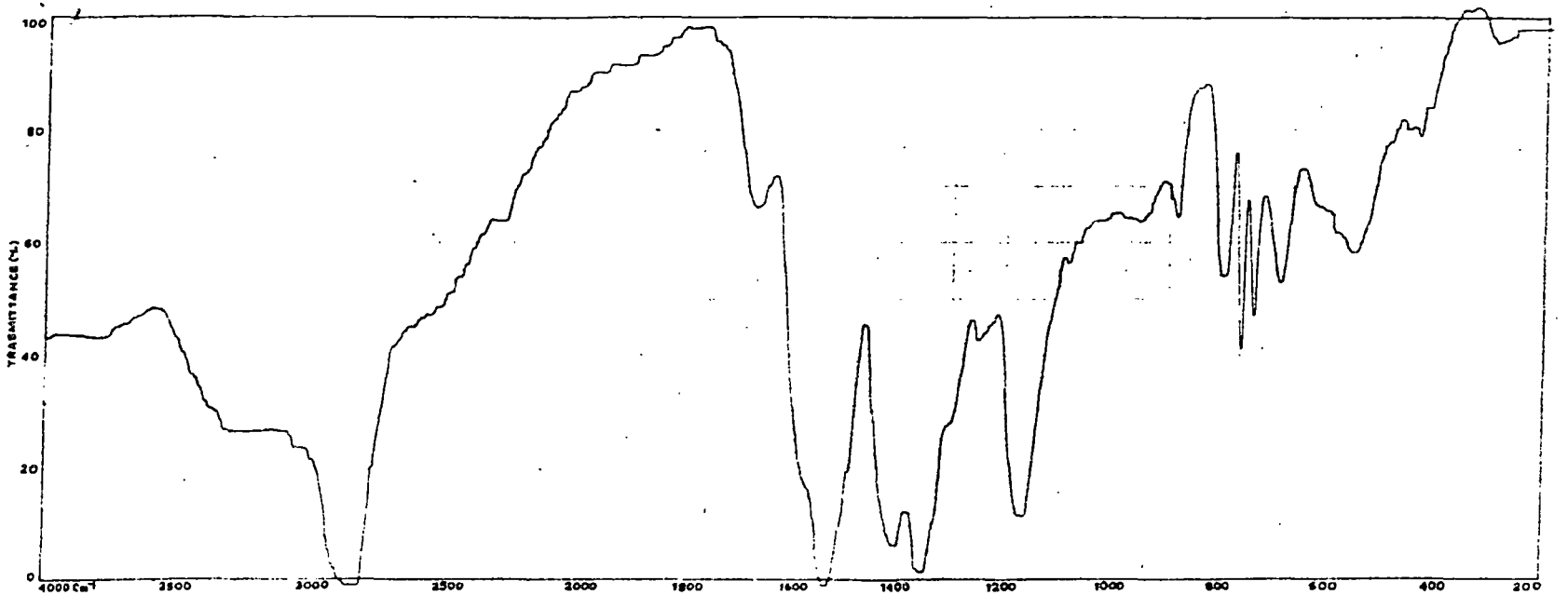


Fig. 8 IR spectrum of tris (2- pyrimidyl thio) acetato triaquo chromium (III)

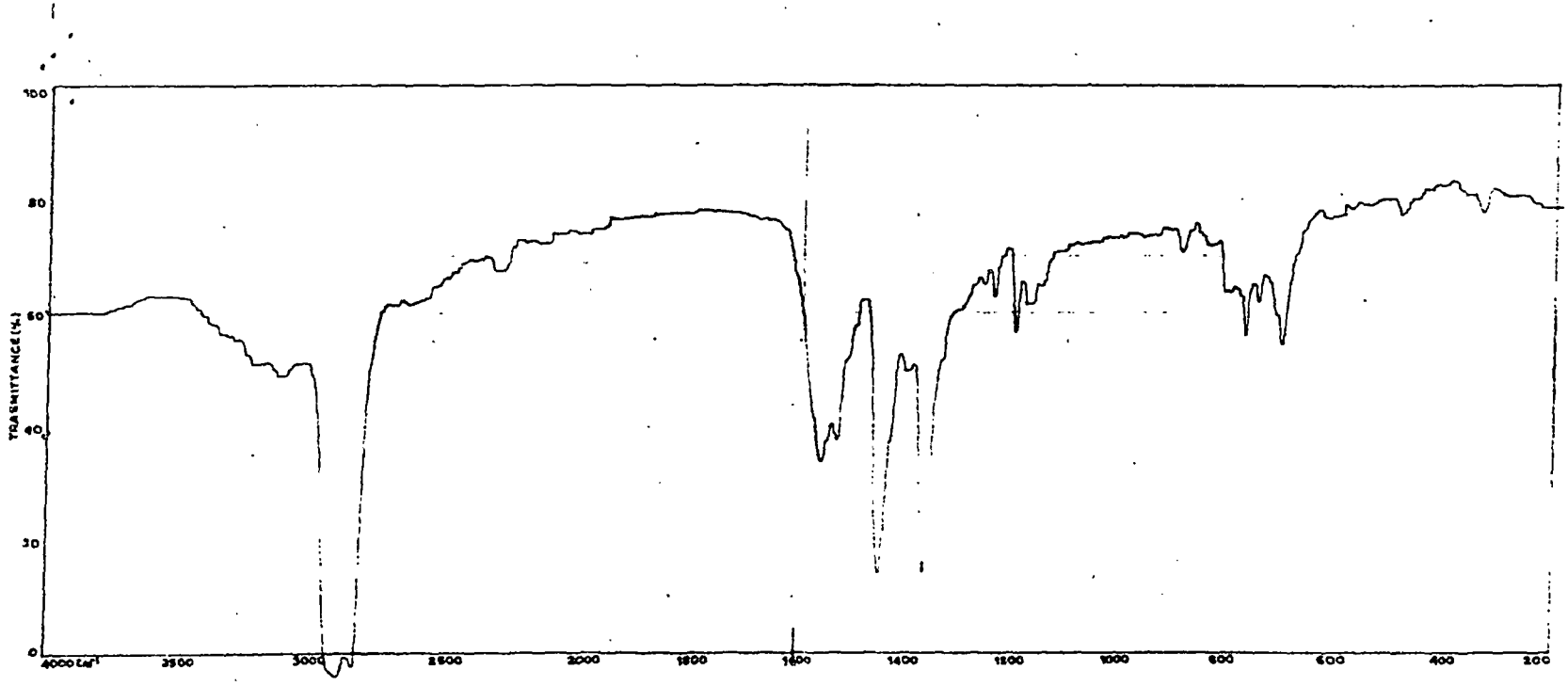


Fig. 9 IR spectrum of bis (2-pyrimidyl thio) acetato diaquo manganese (II)

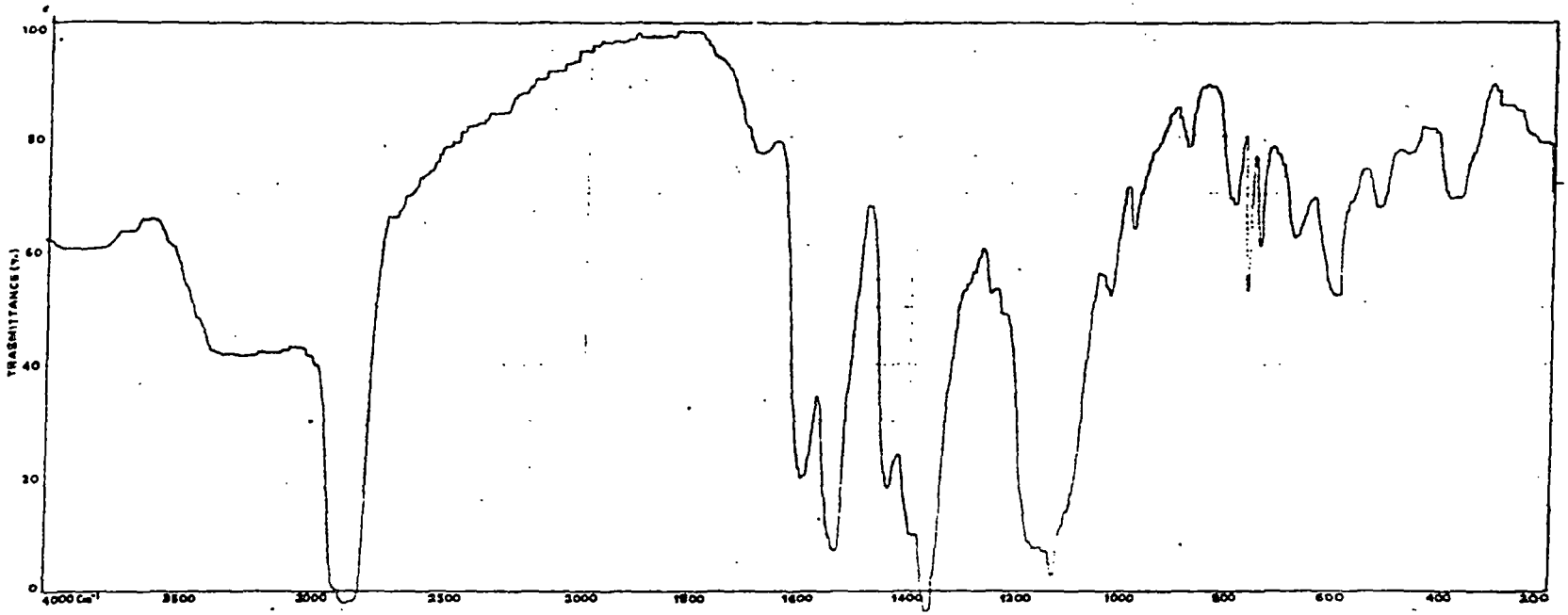


Fig.10 IR spectrum of (2- pyrimidyl thio) acetato sulphato monoaquo Iron (III)

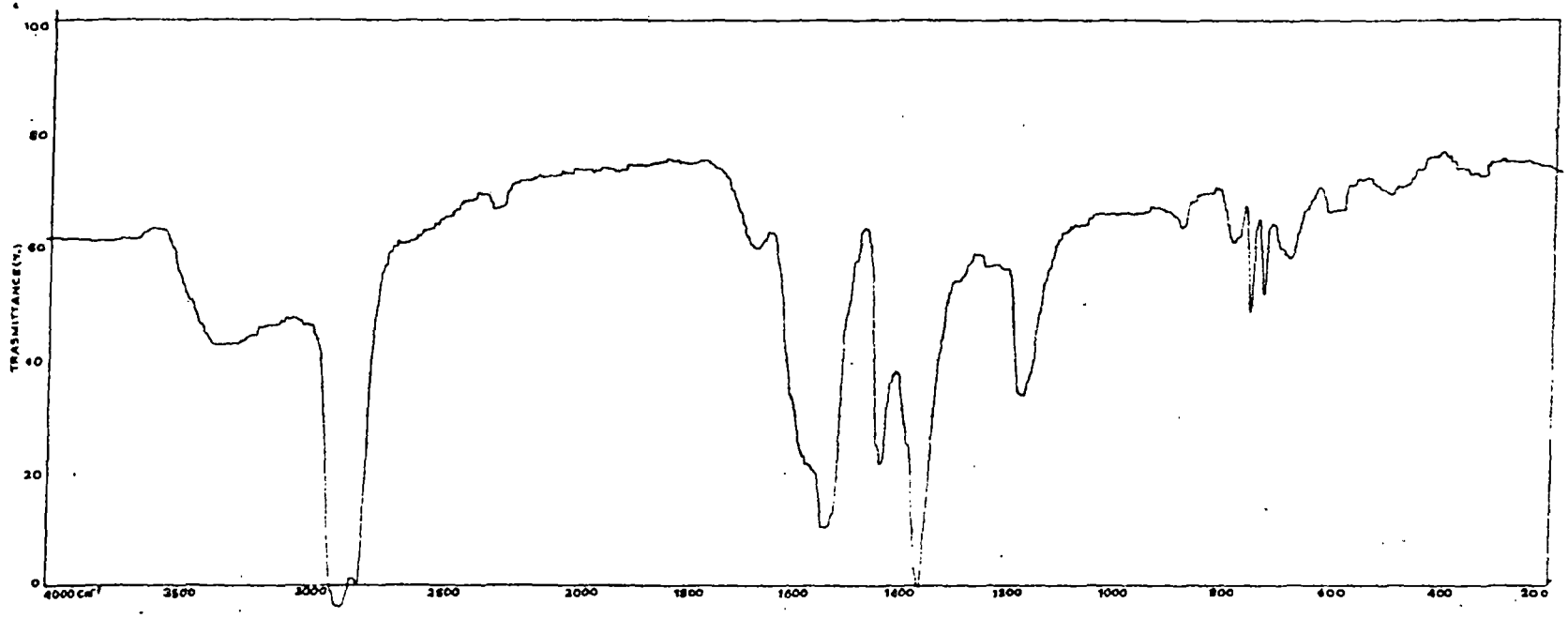


Fig. 11 IR spectrum of bis (2- pyrimidyl thio) acetato tetraaquo nickel (II) dihydrate

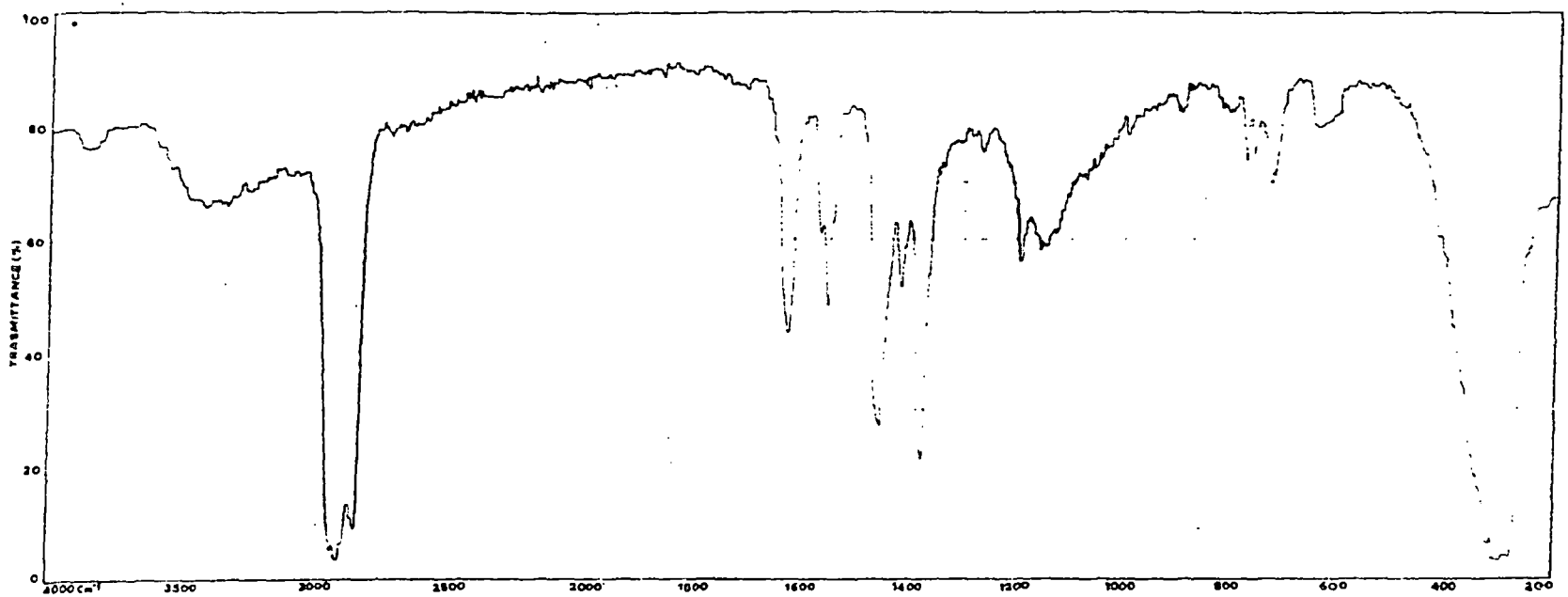


Fig.12 IR spectrum of sodium bis (2-pyrimidyl thio) acetato sulphato cupprate (II) dihydrate

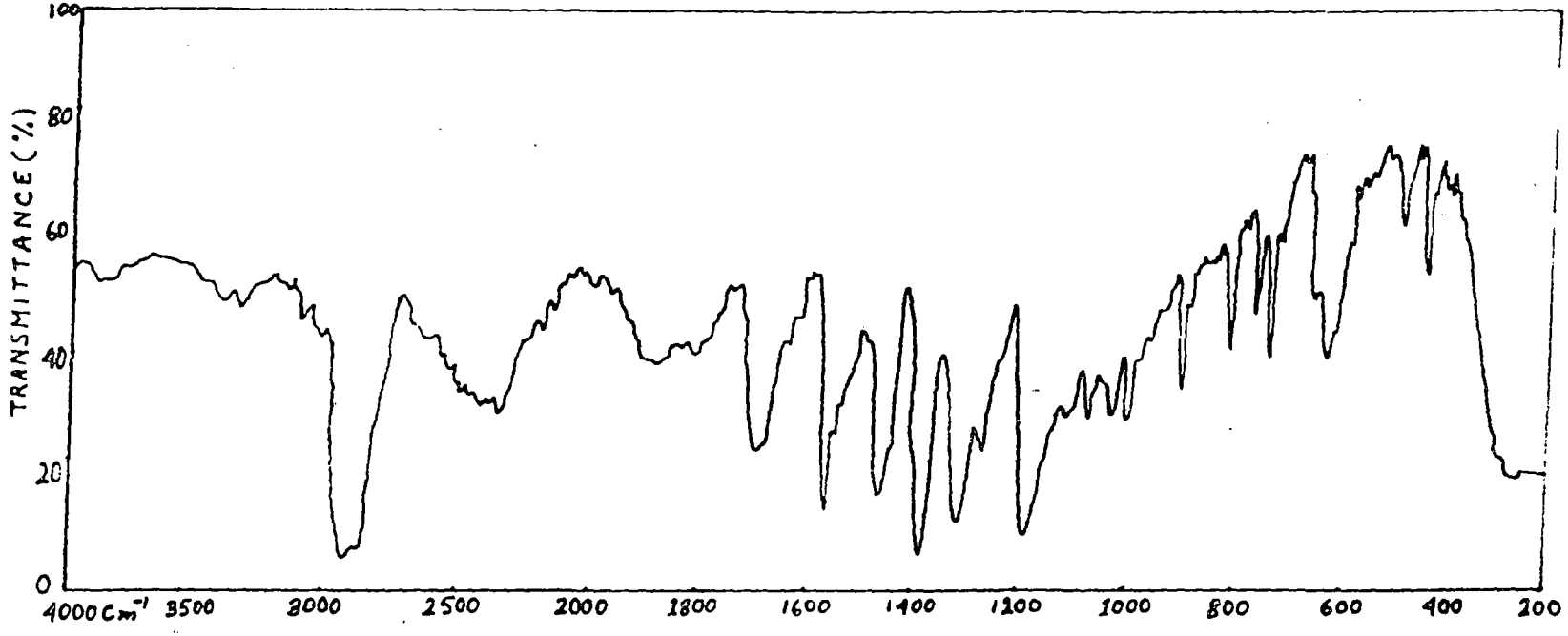


Fig. 13 IR spectrum of (2-pyrimidyl thio) acetic acid

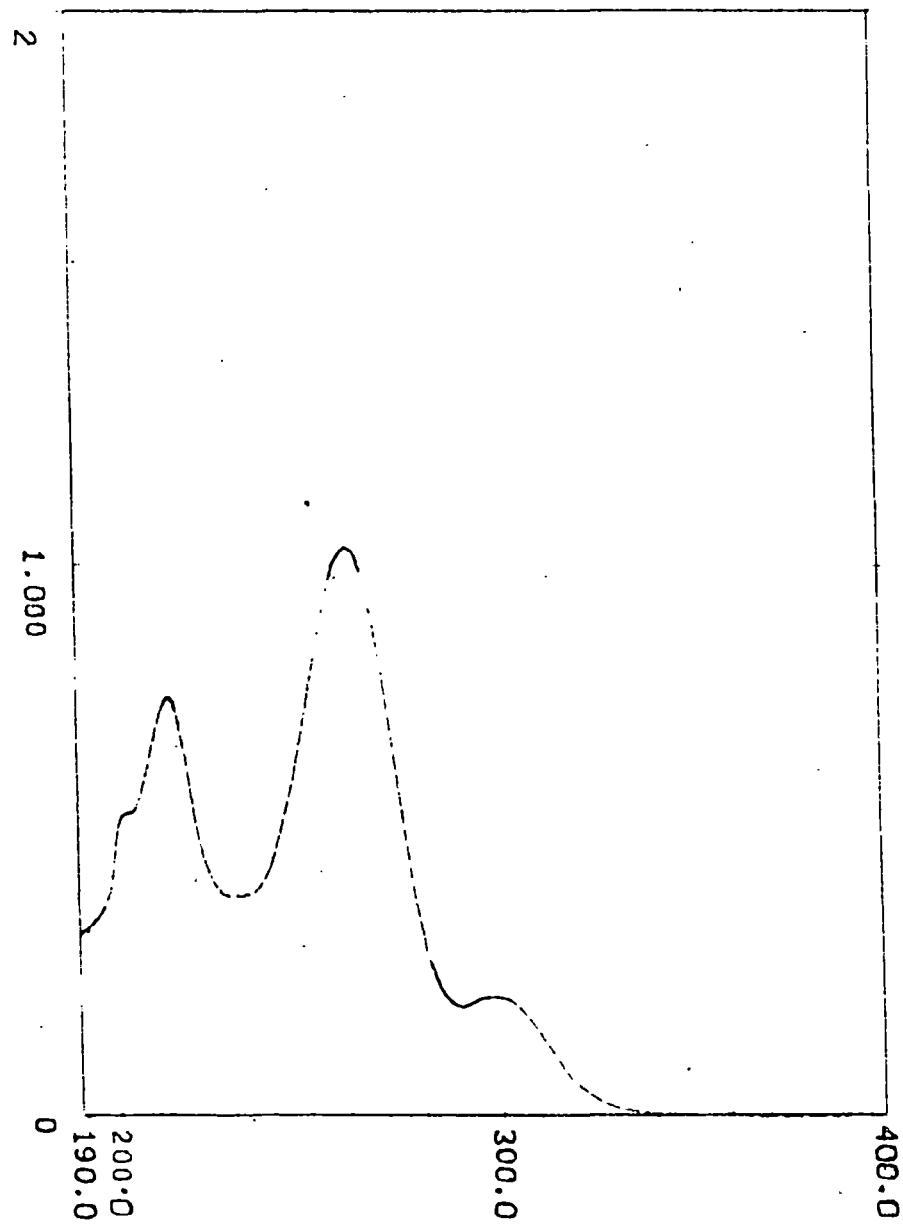


Fig. 14 UV spectrum of sodium dichloro bis (4-pyridyl thio) acetato diaquo chromate (III)

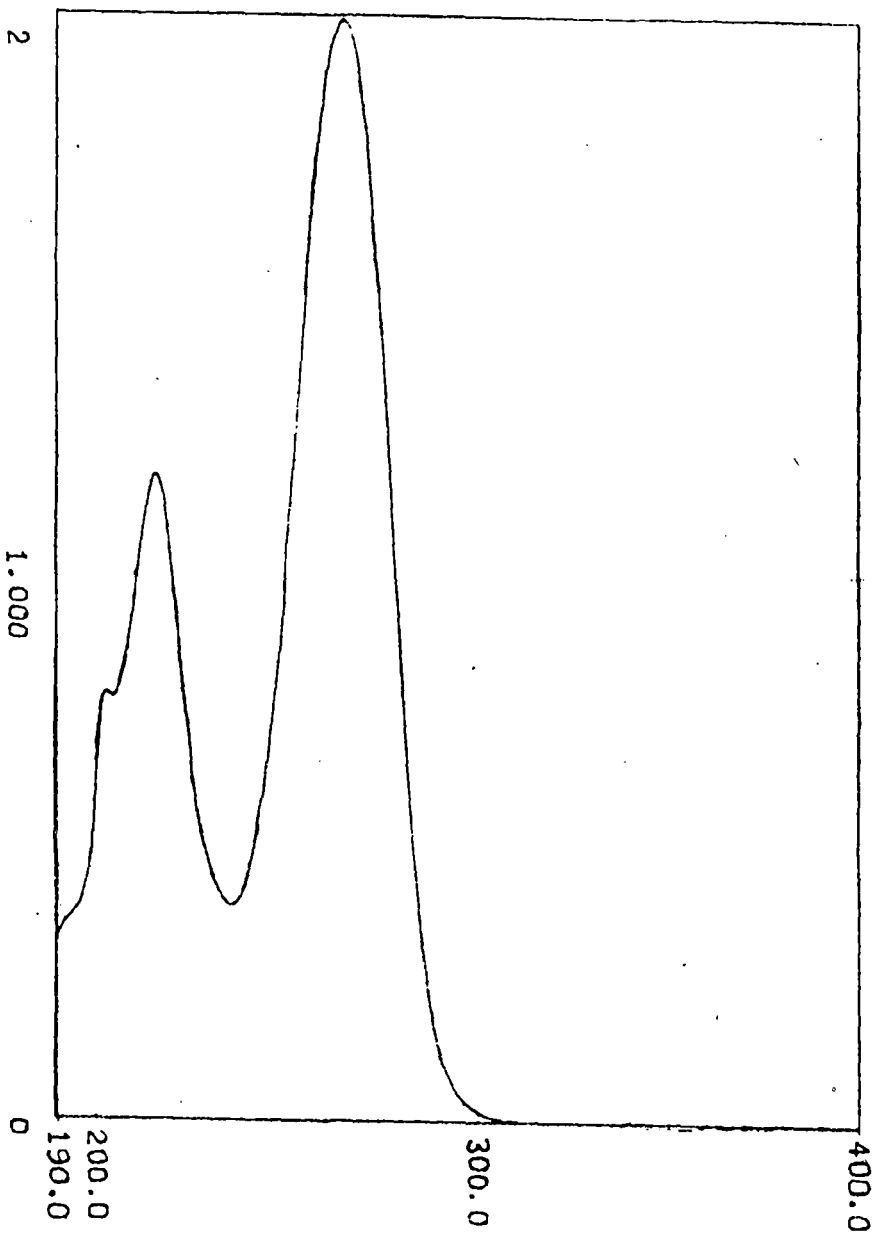


Fig. 15 UV spectrum of bis (4- pyridyl thio) acetato diaquo manganese (II)

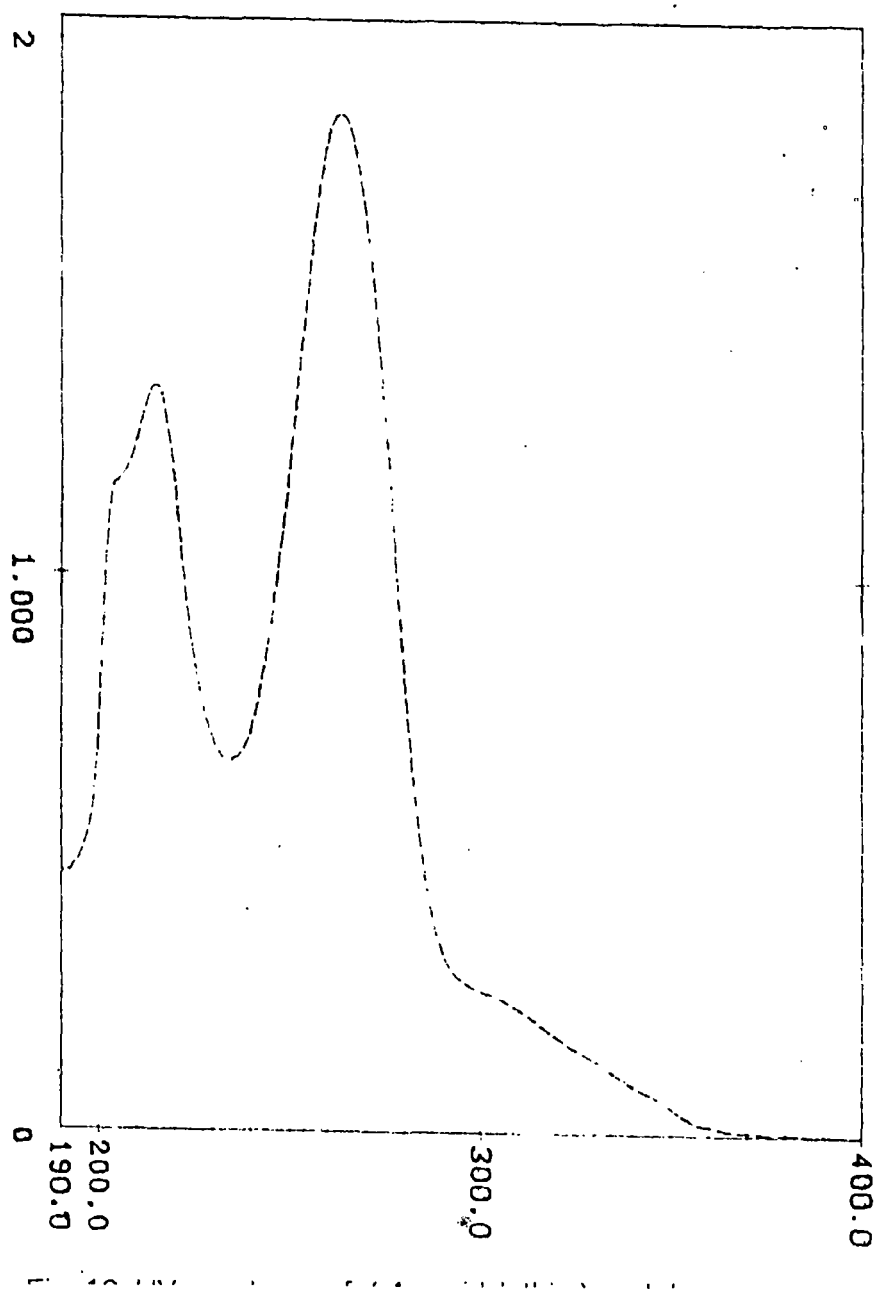


Fig. 16 UV spectrum of (4- pyridyl thio) acetato sulphato monoaquo Iron (III)

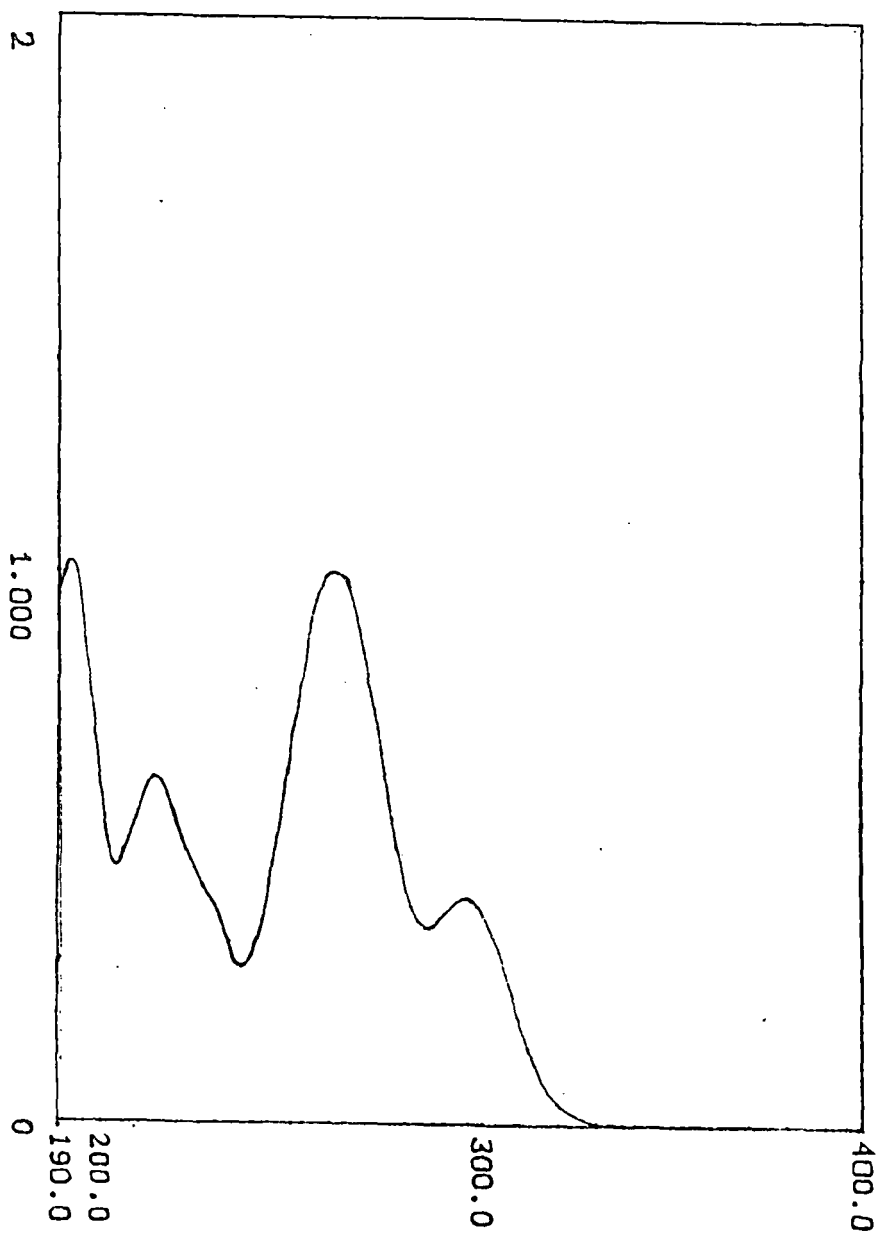


Fig. 17 UV spectrum of Cobalt di (4- pyridyl thio) acetate

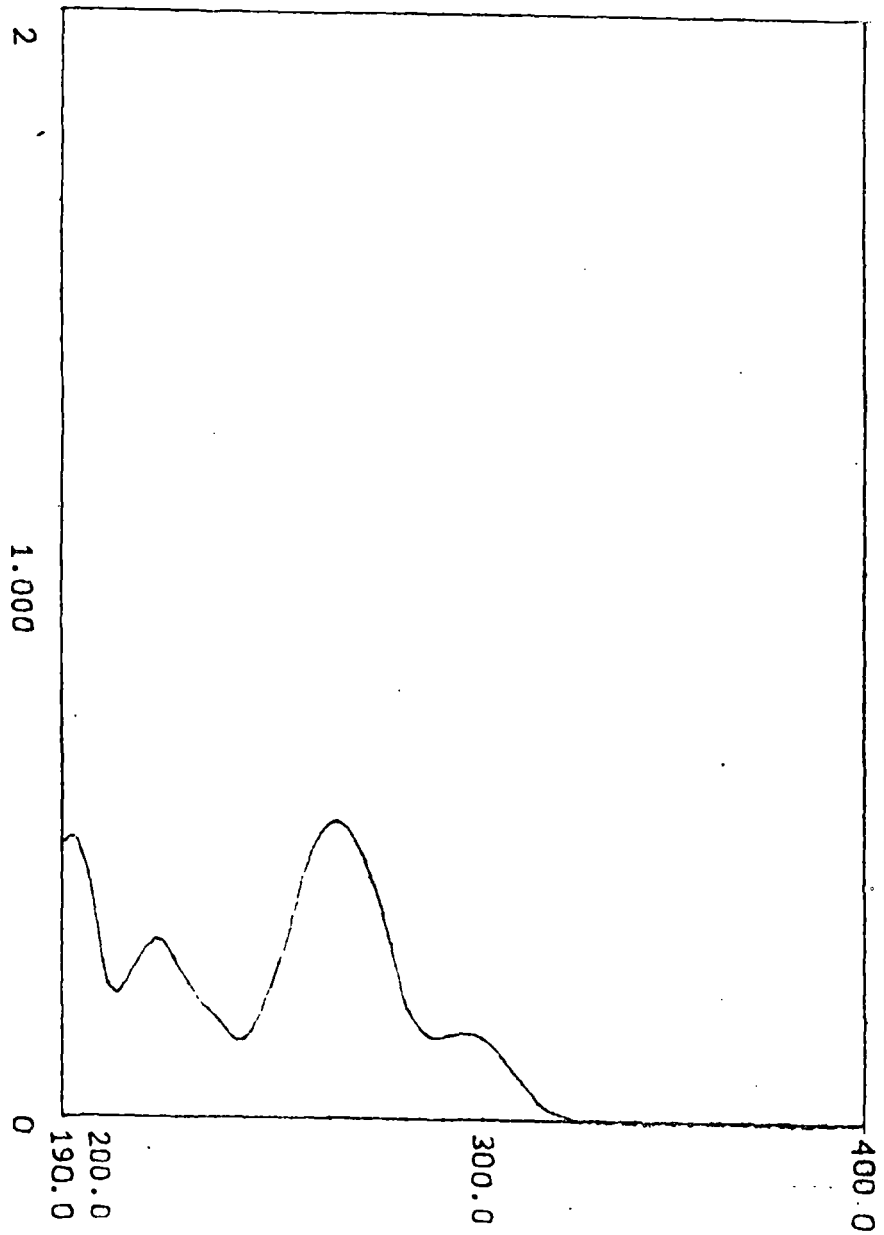


Fig. 18 UV spectrum of sodium dichloro bis (4-pyridyl thio) acetato diaquo Nickelate (II)

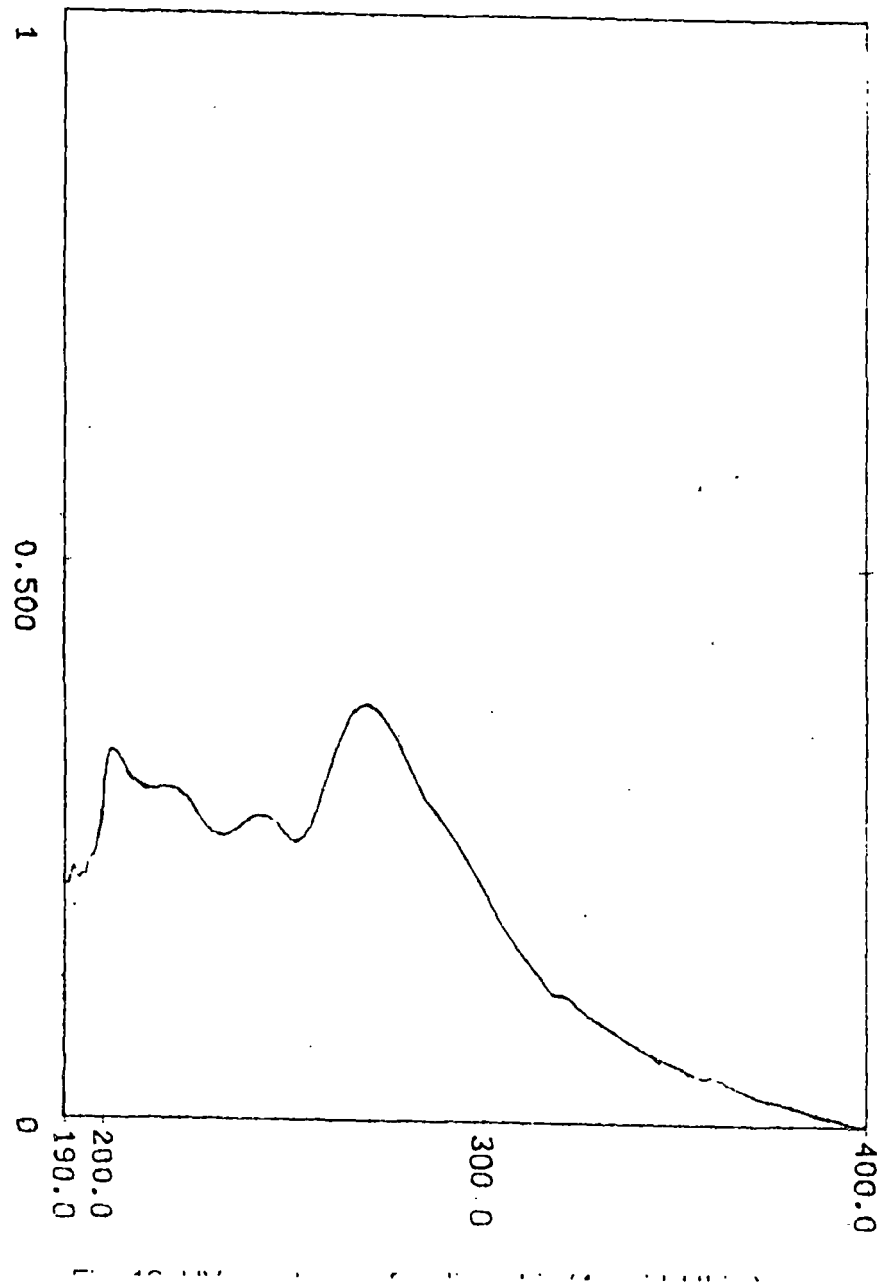


Fig. 19 UV spectrum of sodium bis (4-pyridyl thio) acetato sulphato cupprate (II)

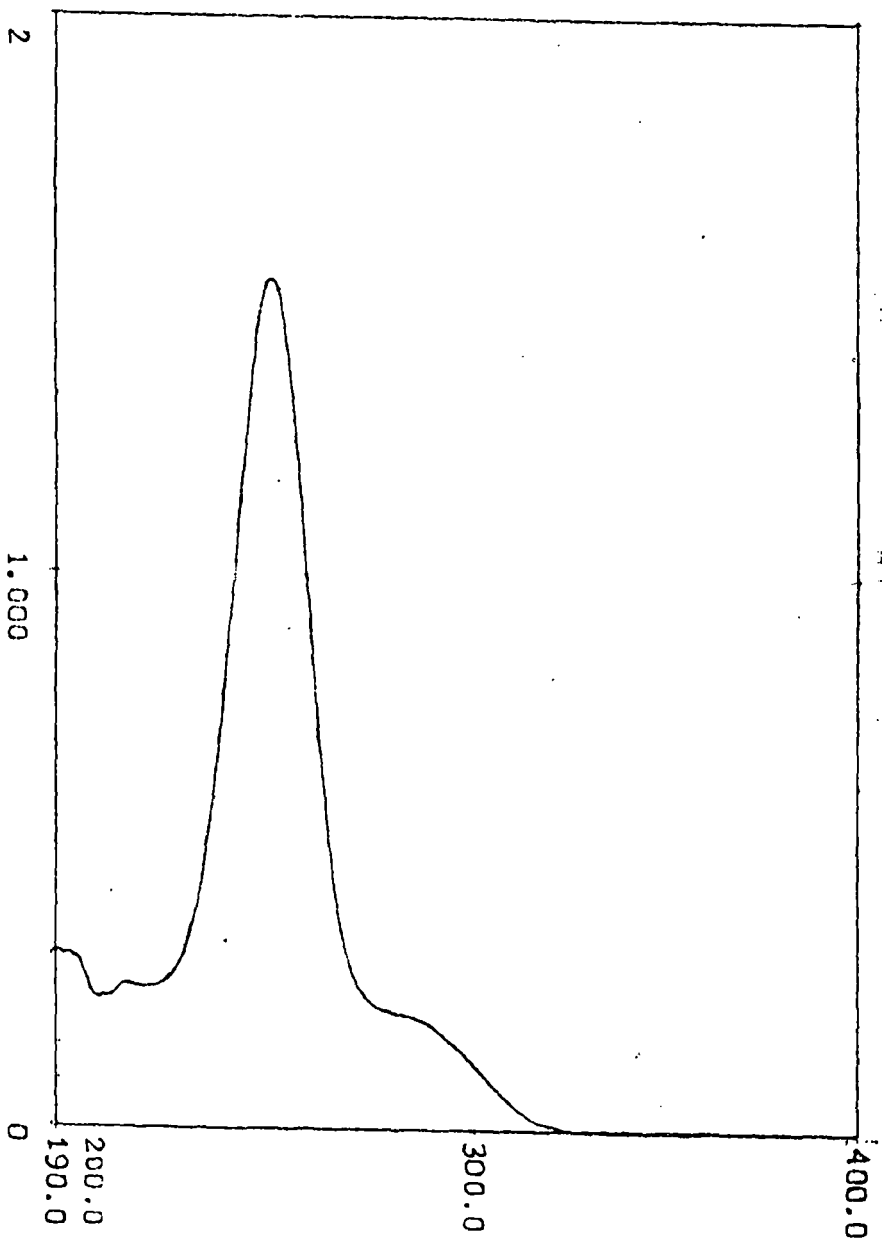


Fig 20 UV spectrum of tris (2-pyrimidyl thio) acetato triaquo chromium (III)

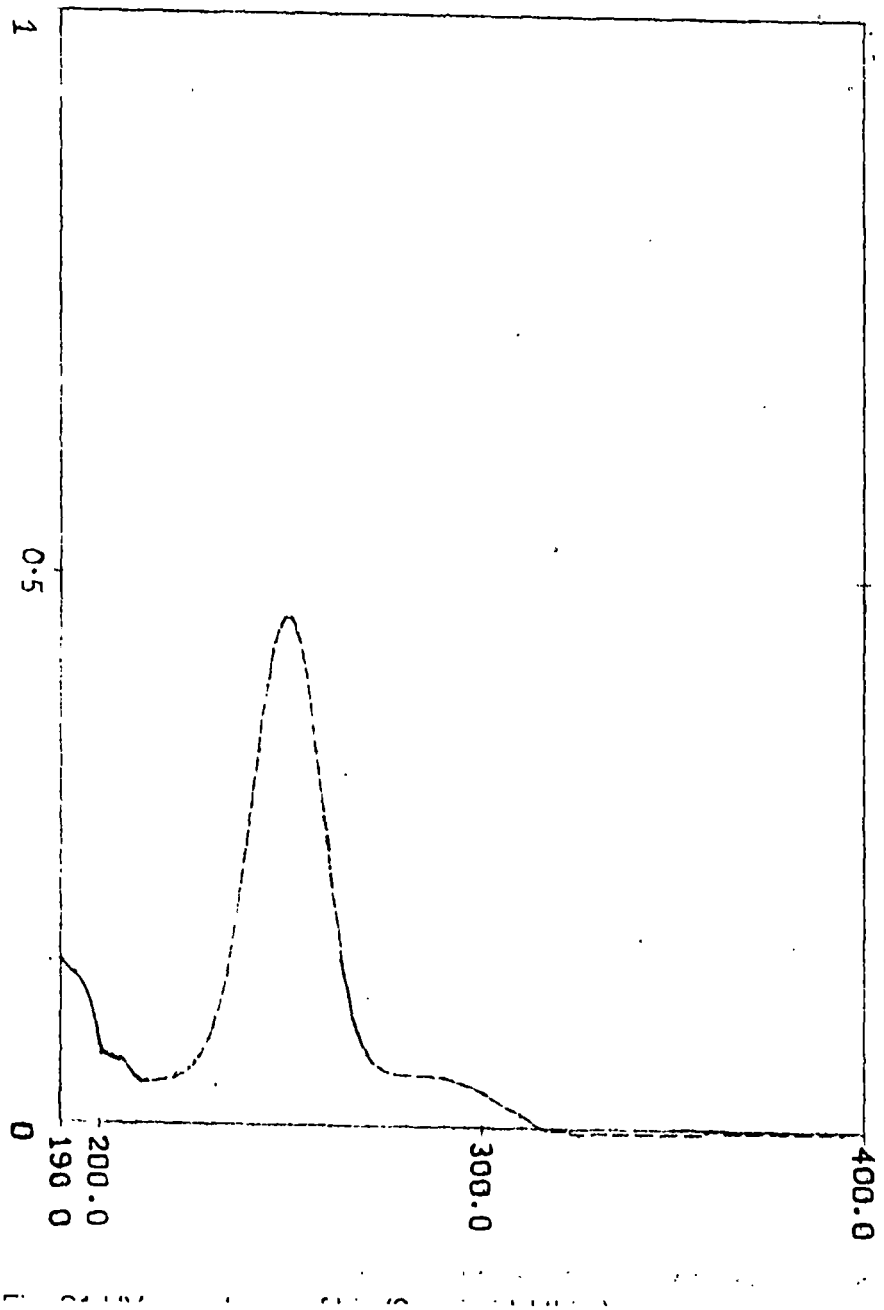


Fig. 21 UV spectrum of bis (2-pyrimidyl thio) acetato diaquo manganese (II)

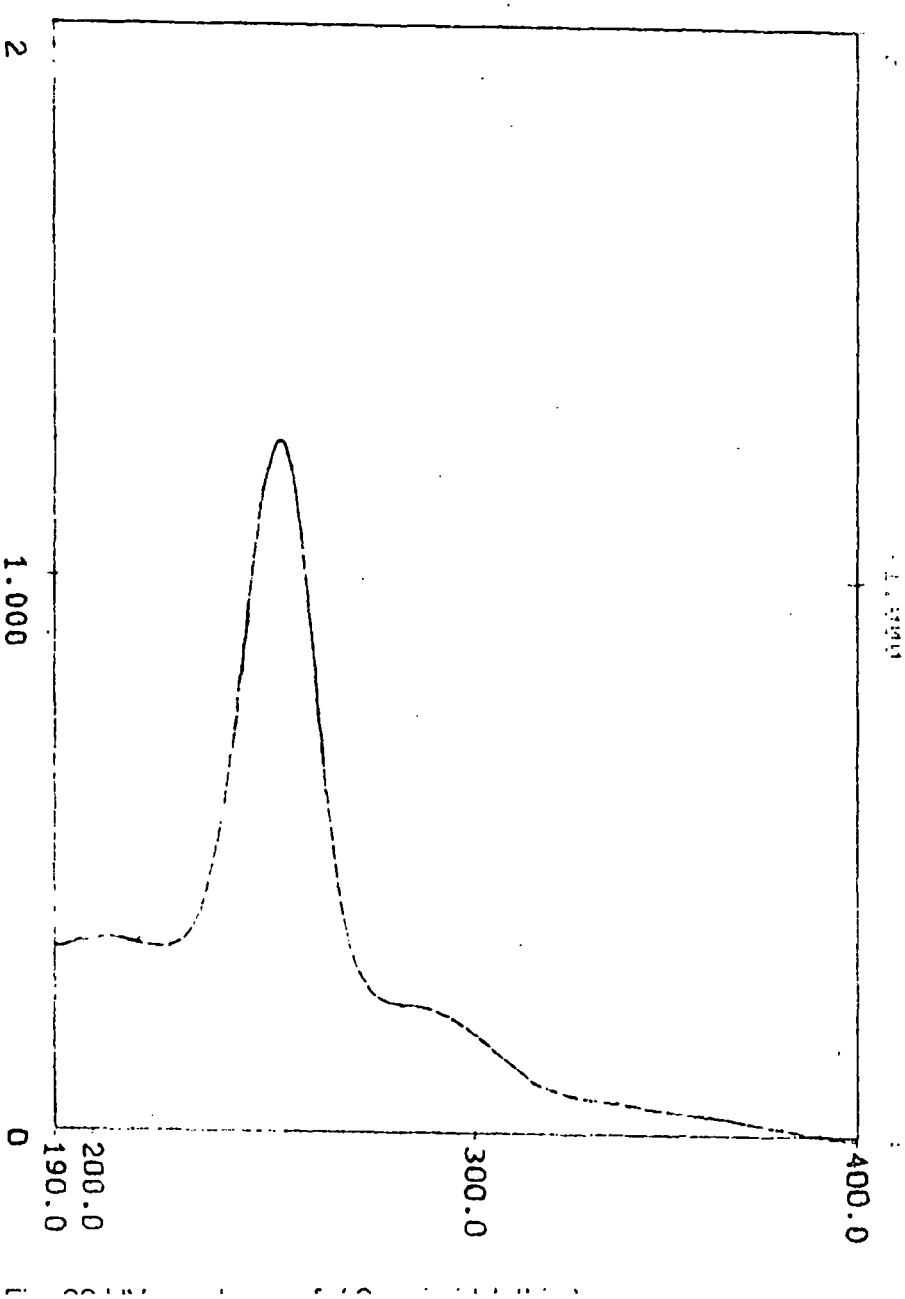


Fig. 22 UV spectrum of (2-pyrimidyl thio)acetato sulphato monoaquo Iron (III)

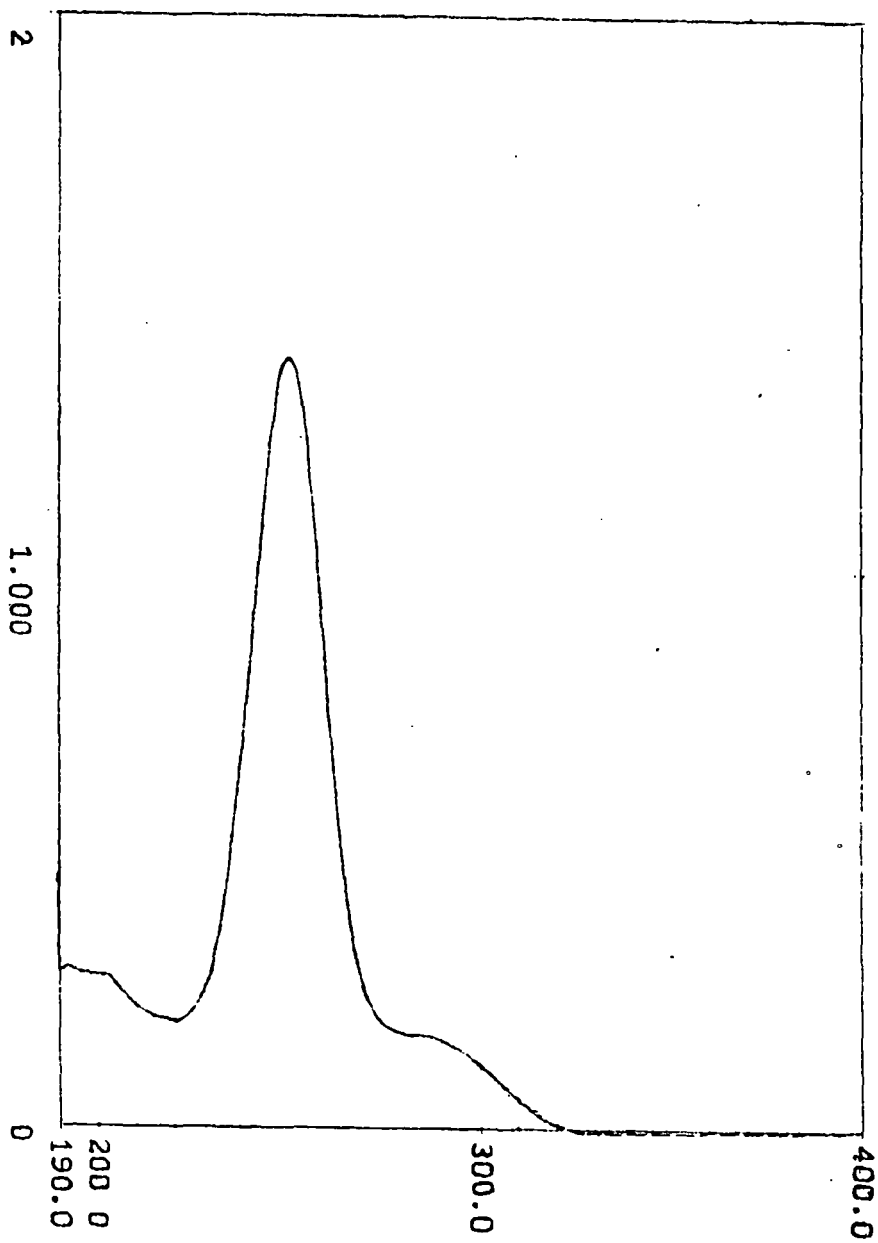


Fig. 23 UV spectrum of bis(2-pyrimidyl thio) acetato tetraaquo Nickel (II) dihydrate

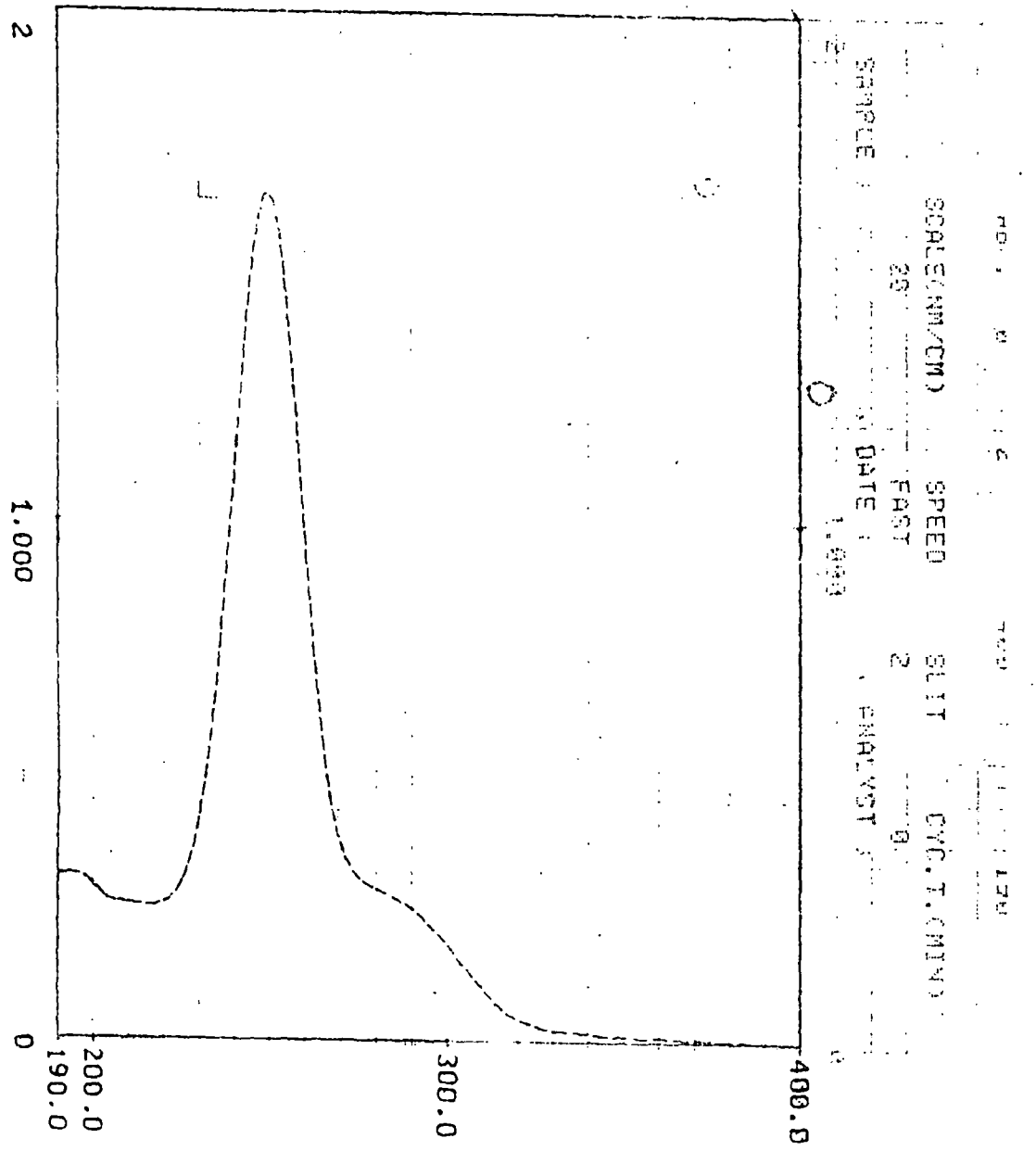


Fig. 24 UV spectrum of sodium bis (2-pyrimidyl thio) acetato sulphato cupprate (II) dihydrate

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Chapter - 3

Synthesis, Characterisation and biocidal properties of Organotin (IV) (4-pyridyl thio) acetate compounds:

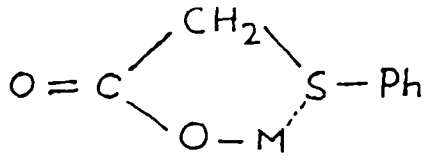
3.1. Introduction

Biocidal properties of organotin compounds and the consequent application to the pest control, ecology problems, human medicine and veterinary medicine, etc. have lead to the observed increase in production of organotin compounds during the past few years. Compounds of the type, R_nSnX_{4-n} where R is an organic substituent and X means a polar group (anion of an acid) are biologically active. The most desirable compounds are those where biocidal properties are due not only to the R_nSn group but also to the X group, because in these cases the effects are mutually combined and complemented. The organotin (IV) compounds of this type in which the X group is formed by phosphate or its organo-analogues and sulfur analogues were studied in more detail both from physical and from chemical point of view[29-32].

The industrial importance of organotin compounds is well documented but questions of their mode of action still remain[33,34]. The incorporation of sulfur into the R group of carboxylic acids generates a series of compounds with useful properties such as thermal stabilization of

PVC[34,35]. Biocidal properties of phenylthioacetic acid and its derivatives are sufficiently known[1]. They were also reexamined in combination with the organotin (IV) component[36]. The biocidal properties and/or ways of their practical application are significantly dependent upon the structure of these compounds[37].

A characteristic structural feature usually found in phenylthioaceates of metals (transition metals in particular) is a five-membered chelate cycle



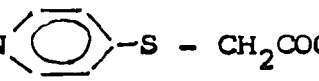
(M = metal atom)

in which an important part is played by the donor-acceptor intramolecular connection of the S atom and the central metal atom M[38]. But this feature was reported to be absent in tri- and dibutyltin phenylthioacetates by A.K. Kumar and his coworkers[2].

As a general rule, when the additional donor atom is a 'N' atom, as in 2-pyridinecarboxylate for example, the 'N' atom invariably participates in formal coordination to the Sn atom and consequently has a direct influence

on the structure ultimately adopted by the compound. In contrast, when the additional donor atom is 'O' or a 'S' atom, such interactions are generally not observed with some exceptions found in the structures containing di-negative, mixed carboxylate/thiolate ligands, as in the compounds $[Bu_2Sn(O_2CCH_2CH_2S)]_6$[35] and $[Ph_3SnO_2CC_6H_4S)SnPh_3]$ in which significant Sn-S interactions are present[39]. Recently E.R.T. Tiekink and his coworkers reported the compound, $[Bu_2Sn(O_2CCH_2SPh)_2]$ in which the 'S' atoms were found not to interact with the Sn atom[40].

3.2. Scope and Objective

Thio aryloxy acetates may be analogous to the aryloxy acetates in physical, chemical and structural characteristics. Specially the probable interaction of the nitrogen and sulfur atoms with the central tin atom, their nature of inter-molecular interactions through coordination are of immense interest. Apart from theoretical and structural interests, the positive biocidal activities can also be expected due to the presence of 'S'[5,6] as well as 'N' atom in (4-pyridyl thio) acetic acid,  [1,2] and in general thio aryloxy acetates are worth studying in the wide spectrum of agriculture to industry[8]. Many thio aryloxy acetates have been found to have fungicidal and biocidal properties[3,4]. These may also be used in polymer industries

as stabilisers[7].

The main objective of our work was to synthesise the compounds, to study the bonding interactions including that between sulfur and tin atom, and to test their fungicidal activity. We were also interested in the possible donor properties of the heteronitrogen atom.

Here, it may be mentioned that tri-n-butyltin p-chlorophenoxy acetate was found to be more active to fungus than TBTO as reported by V.G. Kumar Das and his coworkers[9].

3.3. Experimental and Characterisation:

The solvents were purified and dried before use by standard methods[9a]. The organotin reagents were of commercial origin. The ligand (4-pyridyl thio) acetic acid was an Aldrich product. The synthesised compounds were analysed and characterised by elemental analysis, various spectroscopic methods and two of these newly synthesised compounds were studied by Mössbauer spectral study.

The IR spectra in the range between 4000-300 cm^{-1} were recorded using PYE-UNICAM-SP3-300S Infrared Spectrophotometer (PHILIPS) with CsI optics and nujol as mulling

agent. Solution spectra were recorded in the range between 2000-1400 cm^{-1} with Perkin-Elmer 1720X FT-IR spectrophotometer.

The abbreviations used to express the intensity of the IR bands : vs = very strong, s = strong, m = medium, w = weak and b = broad.

The UV spectral data were recorded in SHIMADZU, UV-240 spectrophotometer using "UVASOL" (Merck) solvents. ^1H NMR spectra were recorded by VA-EM 390 (90 MHz) machine at RSIC, NEHU, Shillong, using $CDCl_3$ as solvent. TMS was used as the internal standard. 'Sn' was estimated gravimetrically as SnO_2.

All the manipulations involving benzene as solvent were carried out with due precautions and care.

All the melting points reported here are uncorrected.

3.3.1. Preparation of Starting Materials:

3.3.1.1 Preparation of the Sodium Salt of (4-pyridyl thio) acetic acid.

(4-pyridyl thio) acetic acid (2 gm, 11.834 mmol) was taken in 100 ml of dry methanol and was titrated in hot condition by 0.5(N) methanolic solution of sodium hydroxide using an indicator. The neutral solution was

concentrated on water bath. Crystals of the salt appeared which were filtered out and recrystalised from methanol (m.p. $> 275^{o}C$)

Elemental Analysis : Found (Calcd.):

C(%)	H(%)	N(%)	S(%)
43.98	3.14	7.32	16.74
(43.96)	(3.10)	(7.29)	(16.75)

Relevant Spectral Data:

I.R. spectral data : (Vide Table 1 & 2) Prominent absorptions are given below:

2900, 1590, 1495, 1460, 1420, 1374, 1230, 1170, 1120, 1110, 1080, 1000, 940, 915, 820, 800, 730, 720.

I.R. Spectral Data : (of the parent acid for comparison):

2900, 2840, 1710, 1620, 1500, 1470, 1425, 1390, 1240, 1180, 1120, 1060, 1000, 950, 920, 900, 880, 830.

3.3.1.2. Synthesis of Triphenyltin (4-pyridyl thio) acetate:

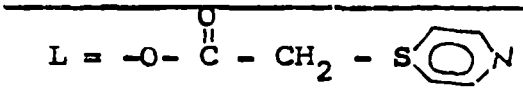
1 gm (2.594 mmol) triphenyltin chloride dissolved in 75 ml dry methanol was taken in a 250 ml three necked round bottomed flask fitted with a double surface reflux condenser, nitrogen gas inlet, and a pressure equalising dropping funnel in which 0.5 gm (2.617 mmol) of the Na-salt

of (4-pyridyl thio) acetic acid dissolved in 40 ml dry methanol was placed. The Na-Salt solution was added in drops from the pressure equalising dropping funnel with constant

Table - 1[a]

Relevant I.R. data

Compound	Solid			Solution		
	ν_{as}(OCO) (cm^{-1})	ν_{s}(OCO) (cm^{-1})	$\Delta\nu$ (cm^{-1})	ν_{as}(OCO) (cm^{-1})	ν_{s}(OCO) (cm^{-1})	$\Delta\nu$ (cm^{-1})
Ligand(HL)	1620(s) 1720(vs)					
Na-Salt of L	1590(vs)	1420(s)	170			
Ph_3SnL	1625(m)	1320(s)	305	1640(m)	1320	320
Ph_2SnL_2	1670(s)	1350(m)	320	1675(m)	1345(m)	330
Cy_3SnL	1615(s)	1355(s)	260	1640(s)	1315(m)	325
Bu_3SnL	1615(s)	1335(m)	280	1645(s)	1320(s)	325
$BuSnL_3$	1690(bm) 1625(s)	1475(m)	215			
Bu_3SnBrL	1590(s) 1565(s)	1330(m)	260			
Bz_3SnL	1628(s)	1355(s)	273	1650(m)	1320(m)	330
Me_2SnL_2	1640(bs)	1340(m)	300	1660(m)	1340(m)	320

L = 

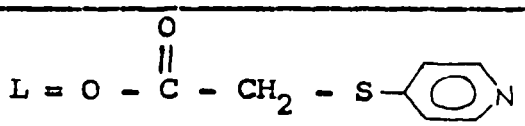
[a]Spectra were recorded on CsI optics using nujol mull or in CCl_4 solution. vs = very strong, s = strong, m = medium, b = broad.

$$\Delta\nu = \left[\nu_{assym}(OCO) - \nu_{sym}(OCO)\right]$$

Table - 2[a]

Relevant IR data

Compounds	Solid	Solid	Solution	
	ν_{CH_2-S-C} (cm^{-1})	ν_{Sn-C} (cm^{-1})	$\nu_{as}Sn-C$ (cm^{-1})	$\nu_{s}Sn-C$ (cm^{-1})
Na-Salt of L	1230(s)			
Ph_3SnL	1220(m)	515	550(m)	490(m)
Ph_2SnL_2	1200(s)	510(m) 440(s)	515(m)	420(m)
Cy_3SnL	1230(m)	515(m)	545(m)	500(m)
Bu_3SnL	1210(m)	515(m)	545(m)	490(m)
$BuSnL_3$	1200(s)	520(m)		
$Bu_2Sn(Br)L$	1230(m)	515(m)		
Bz_3SnL	1215(s)	520(m)	545(m)	490(m)
Me_2SnL_2	1190(m)	515(m) 430(m)	510(m)	420(m)



s = strong, m = medium, w = weak.

[a]Spectra were recorded on CsI optics using nujol mull or in CCl_4 solution.

... stirring under the inert atmosphere of nitrogen. After the addition was over the reaction mixture was refluxed for about 1½ hours. The solvent was then distilled off and the residue was washed repeatedly with petroleum ether (60°-80°C) to remove any unreacted triphenyltin chloride and then extracted with benzene. The benzene extract on concentration afforded a solid product which was recrystalised from acetonitrile (yield 90%, m.p. 160°C).

Elemental Analysis : Found (Calcd.):

C	H	N	S	Sn
56.19 (57.92)	3.59 (4.05)	2.58 (2.70)	6.19 (6.18)	23.48 (22.96)

Relevant spectral data:

IR : 1625(b,m), 1585(m), 1430(m), 1320(m), 580(m), (Vide Table 1&2)560(m) .

^{1}H NMR : (1) δ Sn-Ph or ligand ring protons, 7.52(m, 19H), (δ ppm) 8.01(d); (ii) δ CH_2 of ligand, 3.2 (S, 2H).

3.3.1.3 Synthesis of Diphenyltin bis(4-pyridyl thio) acetate:

Diphenyltin dichloride (0.45 gm, 1.30 mmol) was dissolved in 50 ml dry methanol taken in a 250 ml three

necked round bottomed flask provided with a magnetic stirrer, a reflux condenser, nitrogen gas inlet and a pressure equalising dropping funnel. 0.5 gm (2.617 mmol) of the Na-Salt of (4-pyridyl thio) acetic acid dissolved in 50 ml dry methanol was taken in the pressure equalising dropping funnel and was added dropwise to the diphenyltin dichloride solution with constant stirring under inert condition of nitrogen. The addition was completed within 35 minutes. A heavy white ppt was found to appear. Stirring was continued for further 4 hours. Then the reaction mixture was refluxed for about 1 hour. The volatiles were distilled off and the residue was washed repeatedly with petroleum ether. The solid was then extracted with ethyl alcohol, which left a residue (0.35 gm), insoluble in common organic solvents having melting point $>300^{o}C$. This indicated a probable polymeric nature of the residue. Concentration of the alcohol soluble part afforded a white precipitate (crystalline) which was established to be diphenyltin bis (4-pyridyl thio) acetate (m.p. 237-240°C, with decomposition to a brown liquid, yield 30%).

Elemental analysis:

C	H	N	S	Sn
51.22 (57.90)	3.58 (3.60)	4.41 (4.54)	10.32 (10.51)	19.40 (19.52)

Relevant spectral Data

IR : 1670(s), 1350(m), 1200(s), 510(m), 440(s). (Vide Table 1&2)

^{1}H NMR (δ ppm) : δ Sn-Ph or ligand ring protons, 7.53 (m, 14H) 8.52(d); δ CH_2 of ligand, 3.55 (s, 4H).

3.3.1.4. Synthesis of Tricyclohexyltin (4-pyridyl thio) acetate:

0.5 gm (2.617 mmol) of Na-Salt of the acid was dissolved in 40 ml of dry methanol and transferred to a pressure equalising dropping funnel. Tricyclohexyltin chloride (1.05 gm, 2.59 mmol) was similarly dissolved in 50 ml dry methanol, taken in a 250 ml round bottomed flask fitted with a double surface reflux condenser, nitrogen gas inlet, and the pressure equalising dropping funnel. Sodium-salt solution of the acid was added in drops from the pressure equalising dropping funnel with constant stirring under inert condition of nitrogen. After the addition was over the reaction mixture was refluxed for about 1½ hours. The solvent was removed and the residue was washed repeatedly with petroleum ether. The solid was then extracted with benzene, which left a residue insoluble in common organic solvents having melting point $>300^{\circ}C$. This indicated a polymeric nature of the residue. The benzene soluble part on concentration afforded the white crystalline product (m.p. $200^{\circ}C$, yield 40%).

Elemental analysis:

C	H	N	S	Sn
55.55 (56.60)	6.00 (6.23)	2.52 (2.64)	5.91 (6.04)	20.87 (22.40)

Relevant spectral data:

IR data : (Vide Table - 1&2) 1615(m), 1355(m), 1230(m), 515(m)

^{1}H NMR (δ ppm) : δ ligand ring protons, 7.44 (d, 4H), 8.55(d); δ CH_2 of ligand, 3.55 (s, 2H); δ Cy protons, 1.53 (bm, 33H).

3.3.1.5 Synthesis of Dimethyltin bis (4-pyridyl thio) acetate :

0.4 gm (1.82 mmol) of dimethyltin dichloride dissolved in 50 ml dry methanol was taken in a 250 ml three necked round bottomed flask provided with a magnetic stirrer, a reflux condenser, nitrogen gas inlet and a pressure equalising dropping funnel in which 0.695 gm (3.64 mmol) of the sodium-salt of the acid dissolved in 50 ml of dry methanol was taken. Sodium-salt solution of the acid was added dropwise from the pressure equalising funnel to the dimethyl tin dichloride solution with constant stirring within 30 minutes. After the addition was over the reaction mixture was refluxed for 1.5 hours. The

reaction mixture gradually became turbid. The solvent was removed under vacuum and the residue was washed with petroleum ether (60-80°C) to remove any unreacted dimethyltin dichloride and then extracted with benzene. The benzene extract afforded a solid product which was recrystalised from acetonitrile (m.p. 265°C; yield, 80%).

Elemental Analysis : Found (Calcd.):

C	H	N	S	Sn
39.50 (39.59)	3.55 (3.71)	5.45 (5.77)	13.08 (13.19)	19.69 (24.52)

Relevant spectral data :

IR : (Vide Table-1 & 2) 1640(s), 1340(m), 1565 (s), 1430(m), 1190(m), 570(m), 515(m), 430(m).

^{1}H NMR (δ ppm) : δ ligand ring protons, 7.54(d,8H), 8.46(d); δ CH_2 of ligand, 3.12 (s, 4H); methyl protons, 0.55 (s, 6H).

3.3.1.6 Synthesis of Dibutyltin bromo (4-pyridyl thio) acetate :

0.23 ml (1.04 mmol) dibutyltin dibromide in 50 ml of dry methanol was placed in a 250 ml three necked flask fitted with a double surface reflux condenser, nitrogen gas inlet and a pressure equalising dropping funnel in which 0.4 gm (2.09 mmol) of sodium-salt of (4-pyridyl thio) acetic acid dissolved in 50 ml of dry methanol was

taken. The acid salt solution was added in drops from the pressure equalising funnel with constant stirring under inert atmosphere of nitrogen. After the addition was over the rreaction mixture was refluxed for about 2 hours. The volatiles were distilled off and the residue was washed repeatedly with petroleum ether (60-80°). The solid was extracted with ethyl alcohol which afforded a white solid on concentration which was further recrystallised from ethanol (m.p. 248°C; yield 82%).

Elemental Analysis : Found (Calcd.) :

C	H	N	S	Sn
37.37 (37.43)	4.82 (4.99)	2.79 (2.91)	6.31 (6.65)	30.23 (24.72)

Relevant spectral data :

I.R (Vide Table - 1&2 : 1590(s), 1570(m), 1565(s), 1430(m), 1330(m), 1230(m), 515(m).

3.3.1.7. Synthesis of Butyltin tris (4-pyridyl thio) acetate :

0.81 gm (4.24 mmol) of the sodium-salt of (4-pyridyl thio) acetic acid dissolved in 40 ml of dry methanol was placed into a pressure equalising dropping funnel which was fitted to a 250 ml three necked flask provided with a reflux condenser, nitrogen gas inlet and a magnetic stirrer.

0.23 ml (1.41 mmol) butyltin trichloride in 50 ml dry methanol was placed in the three necked flask. The salt solution was added dropwise from the pressure equalising funnel to butyltin trichloride solution, with constant stirring under nitrogen atmosphere. After the addition was over the reaction mixture was refluxed for about 2.5 hours. The reaction mixture gradually became turbid due to the formation of a precipitate. After the reaction was over the precipitate formed was filtered off to get 0.32 gm solid product which was washed with petroleum ether and methanol successively (m.p. 248-250°C; yield 60%). The filtrate was found to contain unreacted sodium-salt and butyltin trichloride.

Elemental analysis : Found (Calcd.):

C	H	N	S	Sn
43.79	4.32	6.08	13.97	17.64
(43.93)	(4.39)	(6.15)	(14.45)	(17.40)

Relevant spectral data:

IR (Vide Table - 1) : 1690(b,m), 1625(s), 1575(m), 1475(m), 1200(s), 575(m), 520(w).

3.3.1.8. Synthesis of Tributyltin (4-pyridyl thio) acetate :

0.7 gm (2.15 mmol) of tributyltin chloride in 50 ml dry methanol was placed in a 250 ml three necked flask fitted with a double surface reflux condenser, nitrogen gas inlet and a pressure equalising dropping funnel in which 0.4 gm (2.094 mmol) sodium-salt of the acid dissolved in 50 ml dry methanol was taken. The salt solution was added in dropwise manner to the tributyltin chloride solution with constant stirring, under nitrogen atmosphere, within 30 minutes. After the addition was over the reaction mixture was refluxed for about 1.5 hours. The solvent was removed and the solid obtained was extracted with benzene. The residue was soluble in water having m.p. $>275^{o}C$, indicating to be the unreacted salt. Solvent from the benzene extract was removed by distillation and the solid thus obtained was washed repeatedly with petroleum ether ($60-80^{o}C$) to wash off any unreacted tributyltin chloride. The residue was then recrystallised from benzene-petroleum ether mixture (1:1) which gave the desired product (m.p. $85-86^{o}C$, yield 24%).

Elemental Analysis : Found (Calcd.):

C	H	N	S	Sn
49.71 (49.68)	7.49 (7.41)	3.06 (3.05)	6.77 (6.97)	25.39 (25.93)

Relevant spectral data:

IR (Vide Table -1 & 2) : 1615(s), 1335(s), 1210(s), 515(m).

^{1}H NMR (δppm) : ligand ring protons, 7.56(d,4H), 8.52(d); δCH_2 of ligand 3.54(s, 2H).

3.3.1.9. Synthesis of Tribenzyltin (4-pyridyl thio) acetate :

1.1 gm (2.57 mmol) tribenzyltin chloride dissolved in 60 ml dry methanol was taken in a 250 ml three necked round bottomed flask provided with a magnetic stirrer, a double surface reflux condenser, nitrogen gas inlet and a pressure equalising dropping funnel. 0.5 gm (2.617 mmol) of sodium-salt of (4-pyridyl thio) acetic acid dissolved in 50 ml dry methanol was placed in the pressure equalising funnel and was added in drops to the tribenzyltin chloride solution with constant stirring under nitrogen atmosphere. The reaction mixture was then refluxed, 2 hours. Then solvent was distilled off and the residue was washed

repeatedly with petroleum ether (60-80°C) to remove any unreacted tribenzyltin chloride and then extracted with benzene. The benzene extract on concentration afforded a solid product which was recrystallised from acetonitrile (m.p. 154°C; yield 92%).

Elemental Analysis : Found (Calcd.):

C	H	N	S	Sn
59.22 (60.02)	4.16 (4.85)	2.34 (2.50)	5.40 (5.70)	20.65 (21.23)

Relevant spectral data:

IR (Vide Table - 1&2 : 1620(s), 1570(m), 1355(s), 1215(s), 520(m), 485(m).

^{1}H NMR (δ ppm) : benzyl ring/ligand ring protons, 7.33(m,19H), 8.43(d); δ CH_2 of ligand, 3.66 (2H); δ CH_2 of benzyl group, 2.61 (6H).

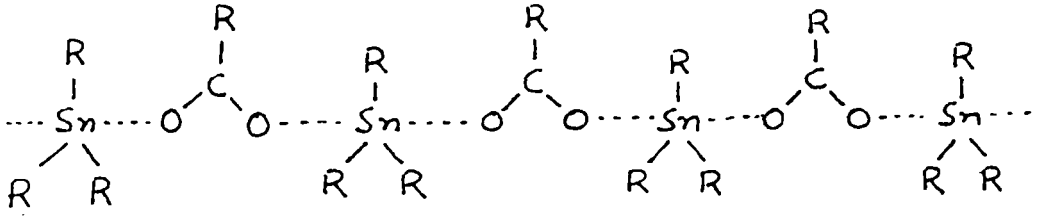
3.4. Results and Discussion:

3.4.1. Infrared spectra :

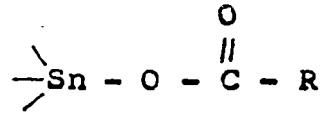
The tentative assignments for ν_{OCO-}, ν_{CH_2-S-C}[10] and ν_{Sn-C}[11] are presented in Table -1 and Table -2 after careful comparisons of the spectra[12-18]. The bridging or free ester type character of the carboxylate group have been interpreted by using $\Delta\nu$ values, the

difference between $\nu_{as}(OCO)$ and $\nu_{s}(OCO)$. The $\Delta\nu$ values of 170 cm^{-1} in the solid state indicates an intermolecularly bridging polymeric carboxylate structure[6,19,20] which in solution breaks down to a monomer raising the $\Delta\nu$ values to about 300 cm^{-1}.

All the triorganotin (4-pyridyl thio) acetates have $\Delta\nu$ between 260-305 cm^{-1}. The difference are further raised slightly in CCl_4 solutions to 320-330 cm^{-1}. These larger values both in the solid state and in solution probably indicate a very weak bridging of carboxylate groups in solid polymeric chain (tin being in the trigonal bipyramidal environment) which completely breaks down to ester like monomers in dilute solutions as follows:



(I) (in solid phase)

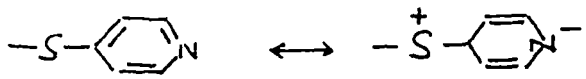


(II) (in solution phase)

[where R = alkyl, aryl etc.]

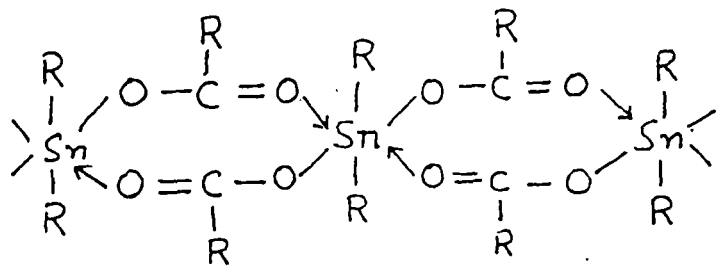
The planarity of the R_3Sn moiety may be concluded from the absence of ν_s(Sn-C) absorption in the solid state. In solution, however, both ν_{as}(Sn-C) and ν_s(Sn-C) are distinctly indicating further breakdown of structure I to structure II in solution.

The very weak carboxylate coordination in these compounds in the solid state may be due among other factors (e.g. steric factors), to the contributing resonating structures in (4-pyridyl thio) acetate such as:



which renders the lone pair on the carbonyl oxygen of the acyloxy group less available for coordination.

Appearance of both ν_{as} and ν_s(Sn-C) in the solid state probably indicates that the diorganotin dicarboxylates are hexa-coordinated carboxylate bridge polymer with <u>trans</u> nonlinear organic groups, tin being in an octahedral arrangement[21,22] as in the following figure:



A few spectra are presented in figures 3.1 to 3.7

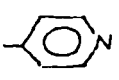
3.4.2. UV Spectra:

The UV spectra of the new carboxylates are presented in Table - 3. The spectra are largely dominated by the high energy 215 nm - 275 nm $\pi - \pi^*$ absorptions of the ligand heteroaromatic ring. Very weak absorptions at low energy region (~300 nm) for few compounds are also observed corresponding to the $n-\sigma^*$ transition of the nitrogen atom in the heteroaromatic ring. The phenyl group vibrations are

Table - 3[a]

UV spectral data

Compounds	λ_{max} (nm)	Other absorptions (nm)	ϵ_{max}
Ph_3SnL	214	265	3.33×10^4
Ph_2SnL_2	275	215	3.02×10^4
Cy_3SnL	217	263, 305	9.16×10^4
Bu_3SnL	264	215	1.07×10^4
Bz_3SnL	209	245	1.006×10^4
Me_2SnL_2	255	216, 301	1.23×10^4
Bu_2SnL_2	260	215, 304	1.86×10^4

L = O - C(=O) - CH_2 - S- 

[a]Spectra were recorded in MeOH solution.

obscured by the presence of ligand vibrations in the same regions. Therefore the UV spectra are the additional evidences.

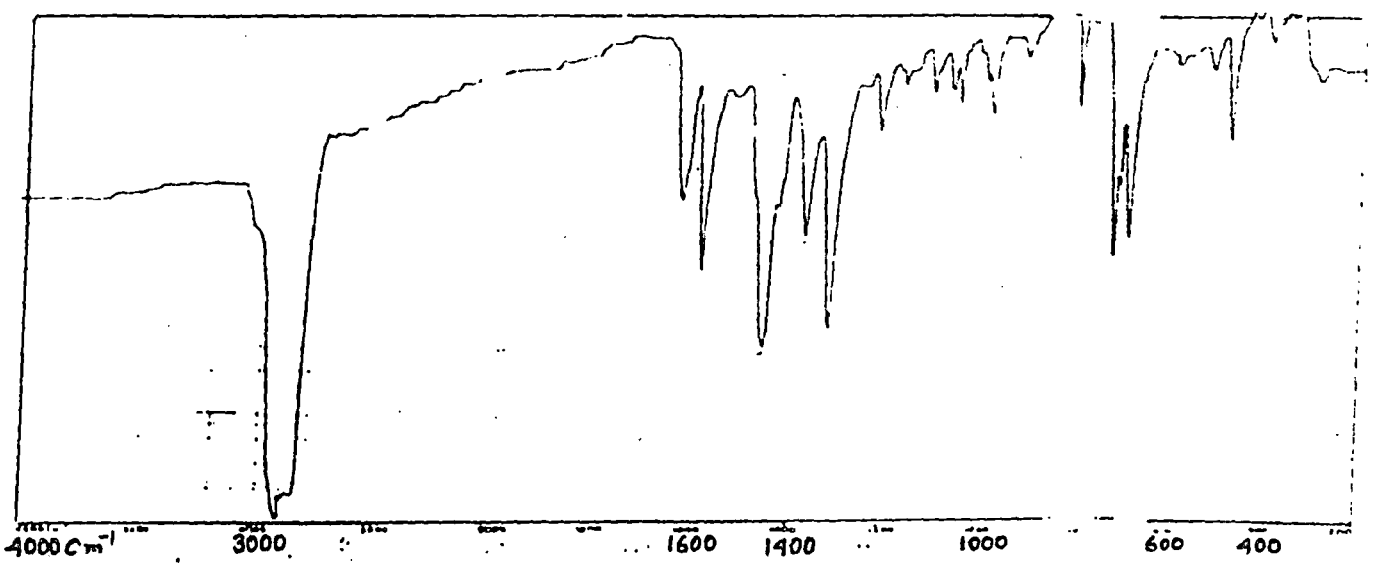
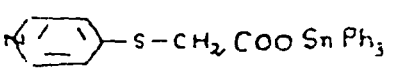


Fig. 3.1. Ir spectrum of 

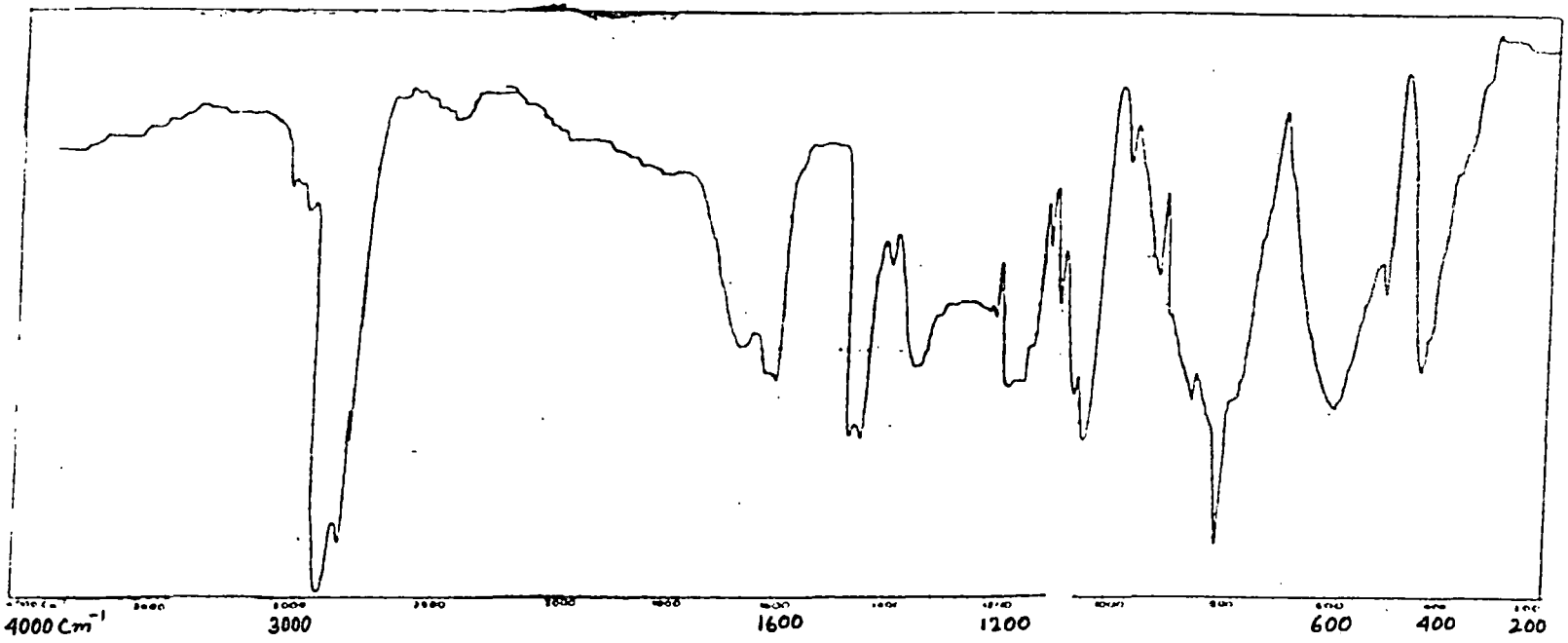
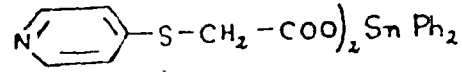


Fig.3.2 Ir spectrum of 

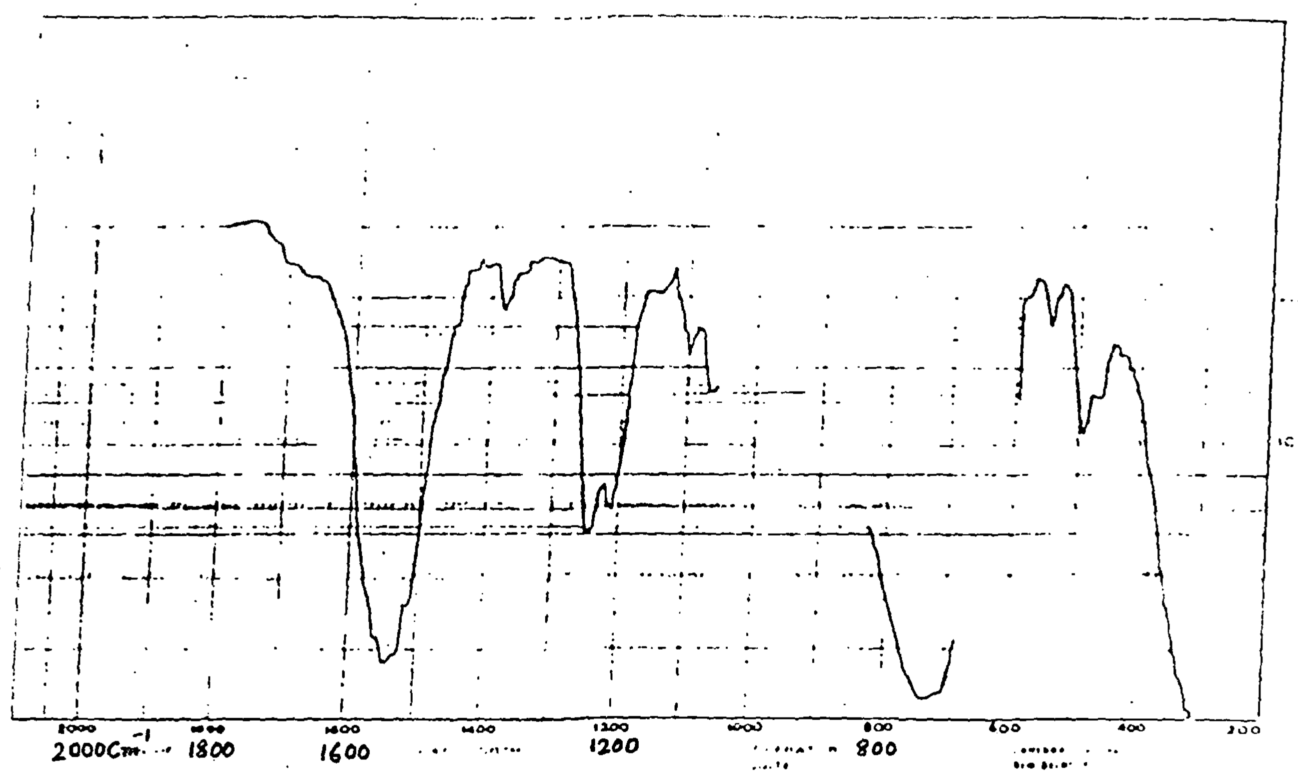


Fig.3.3. Ir spectrum of $(C_5H_4N\text{-}S\text{-}CH_2COO)_2SnPh_2$ in CCl_4

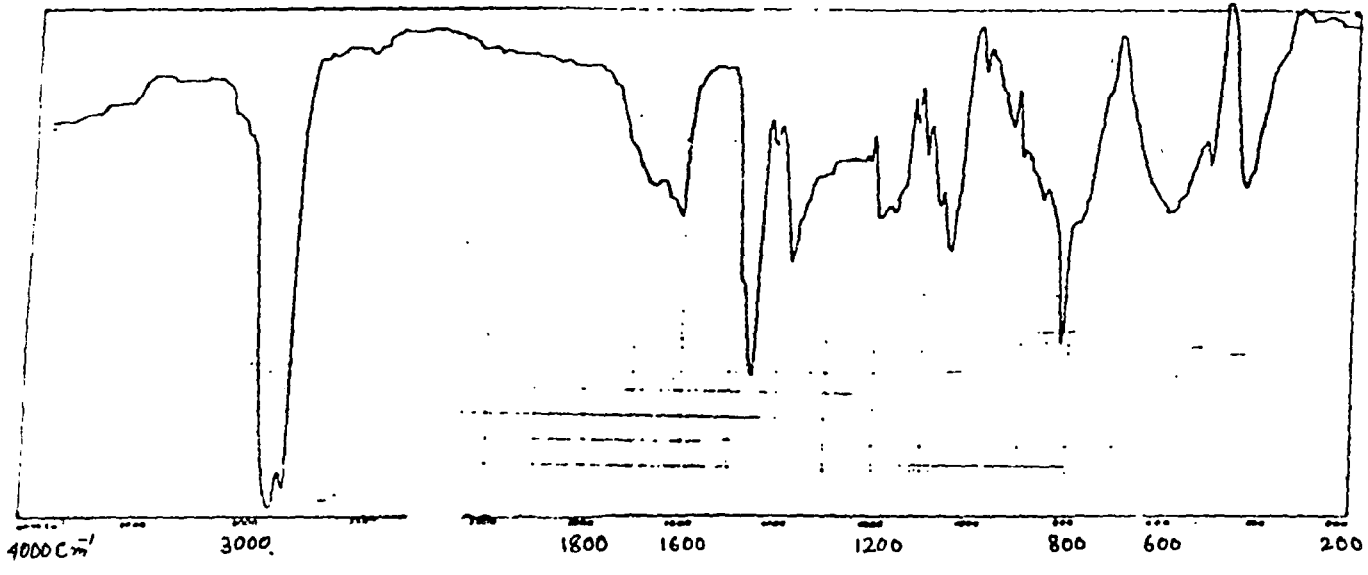


Fig.3.4 Ir spectrum of $(C_4H_9)Sn(-O-\overset{\overset{O}{\|}}{C}-CH_2-S-C_4H_3N)_3$

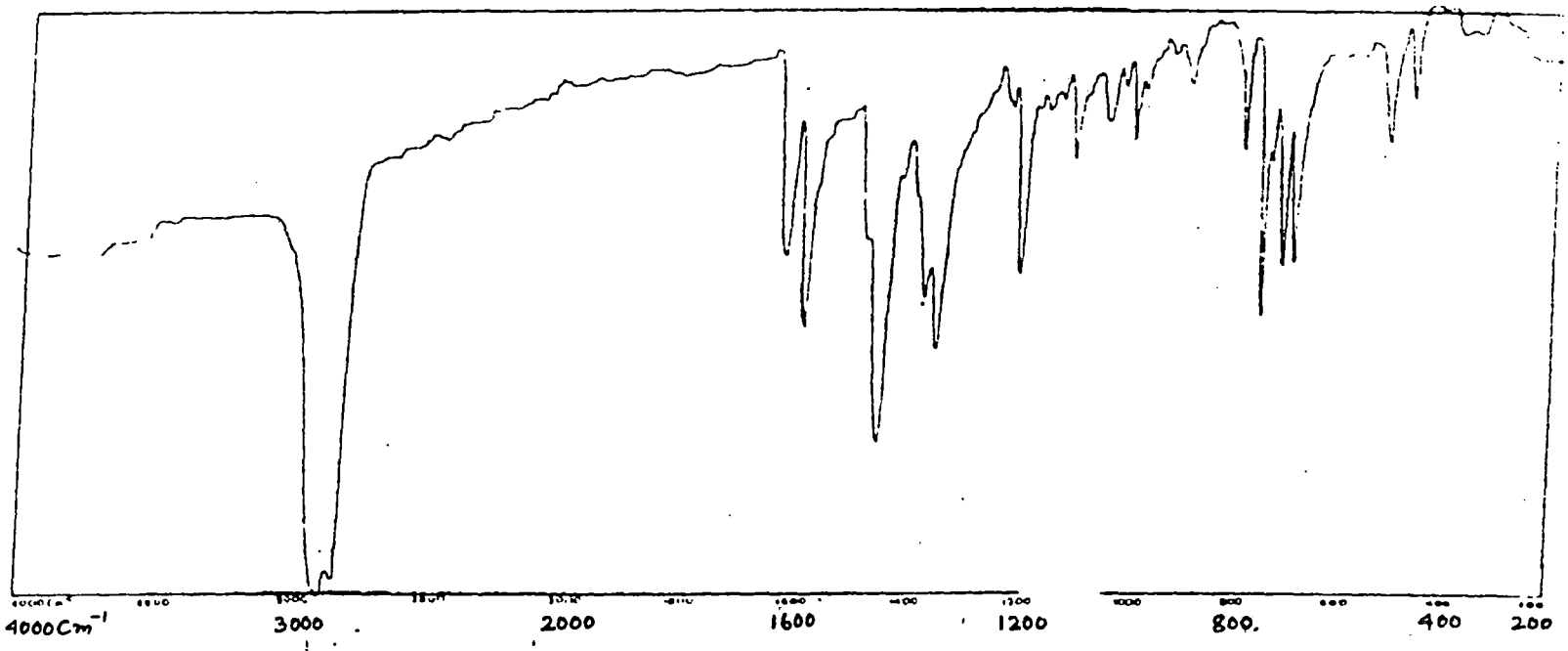
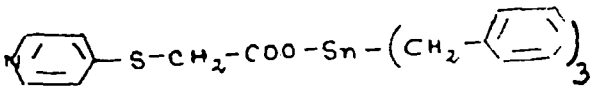


Fig.3.5 Ir spectrum of 

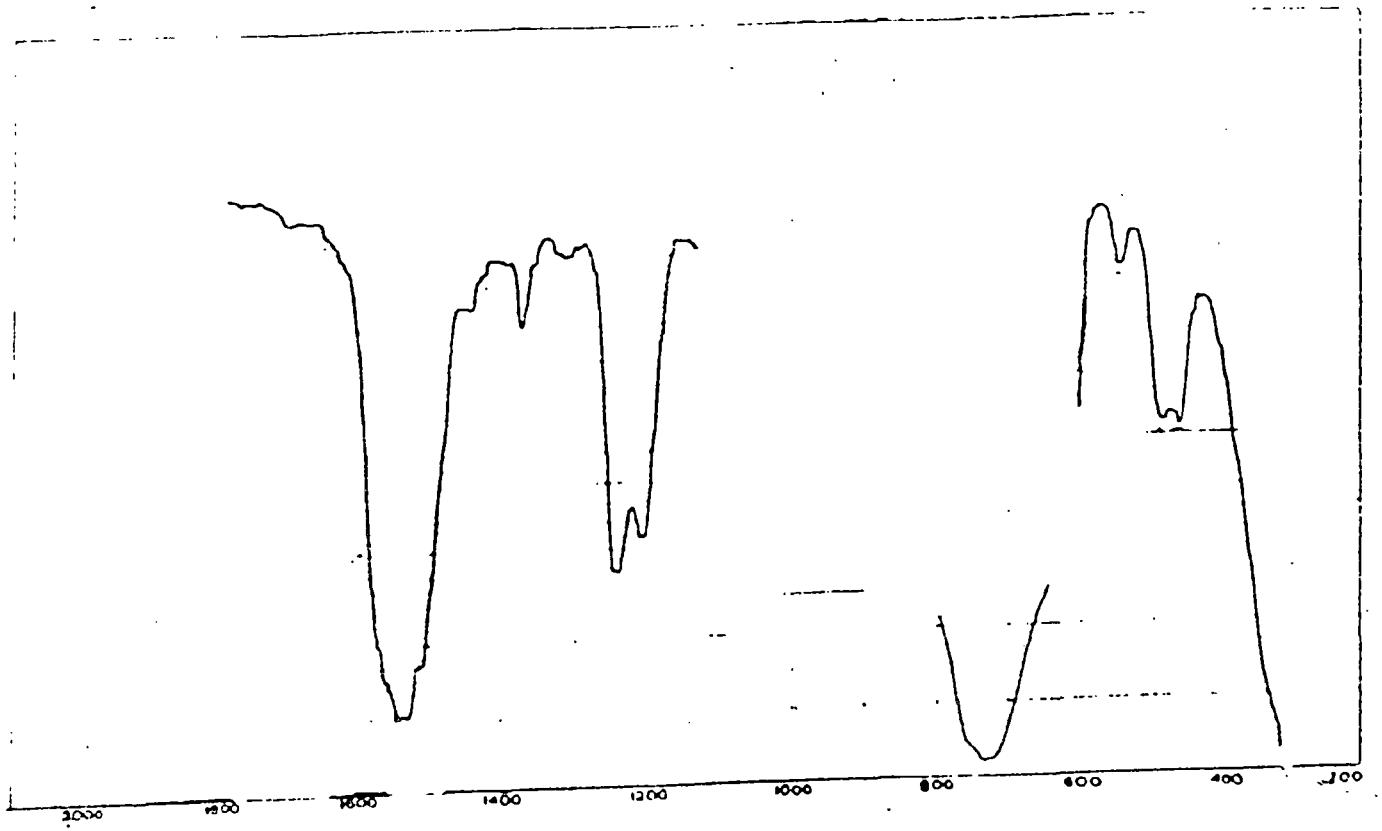
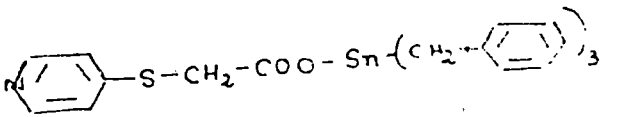


Fig.3.6 Ir spectrum of  in CCl_4

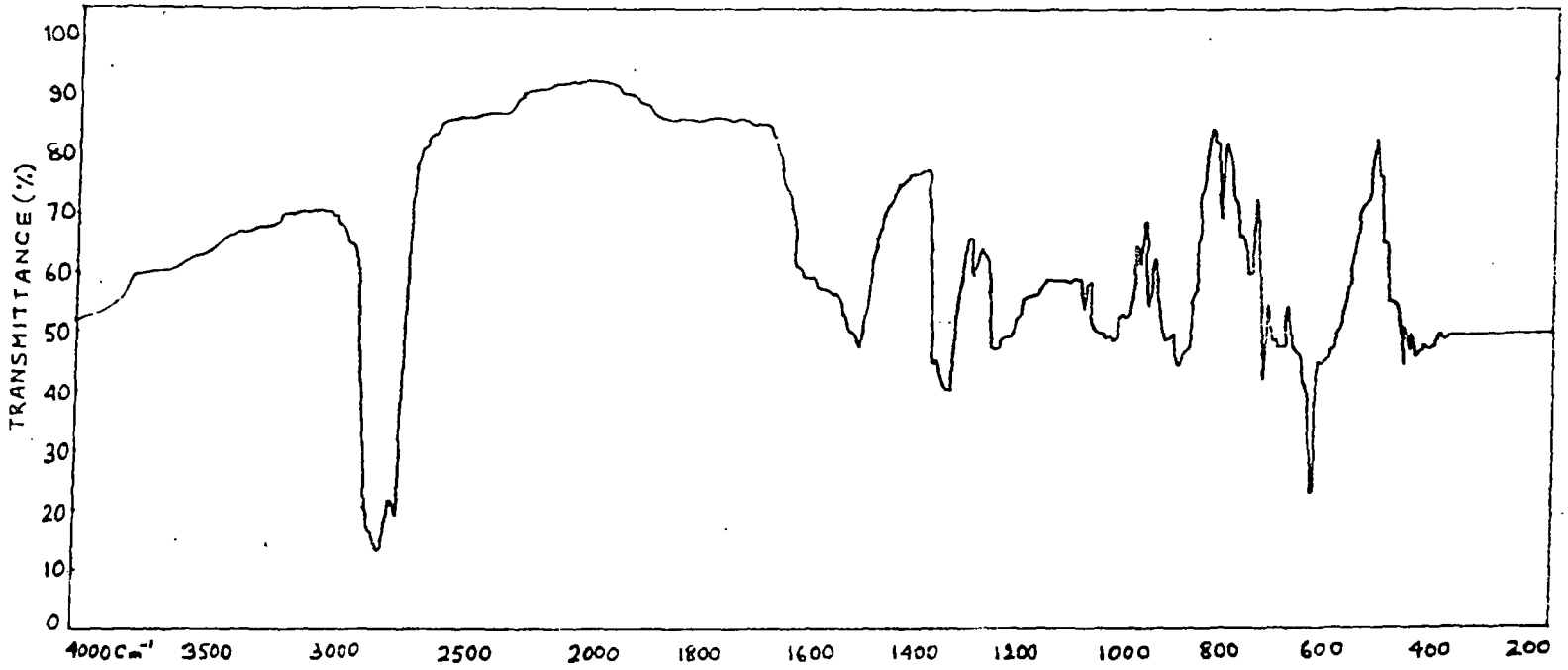


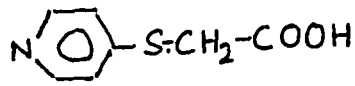
Fig. 3.7 IR spectrum of 

Fig.3.8 UV spectrum of

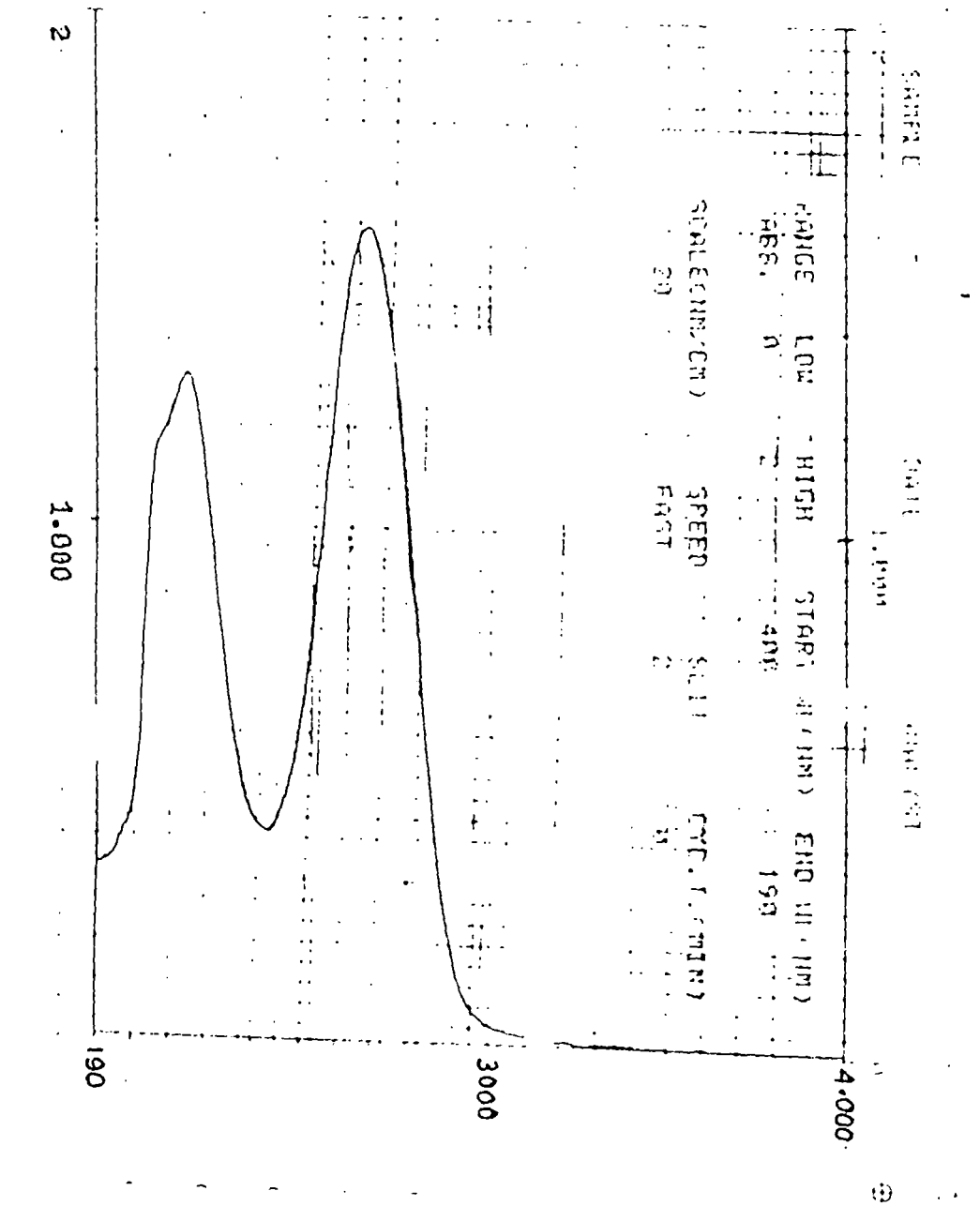


Fig.3.9 UV spectrum of $(C_6H_5-S-CH_2-COO)_2Sn(Ph)_2$

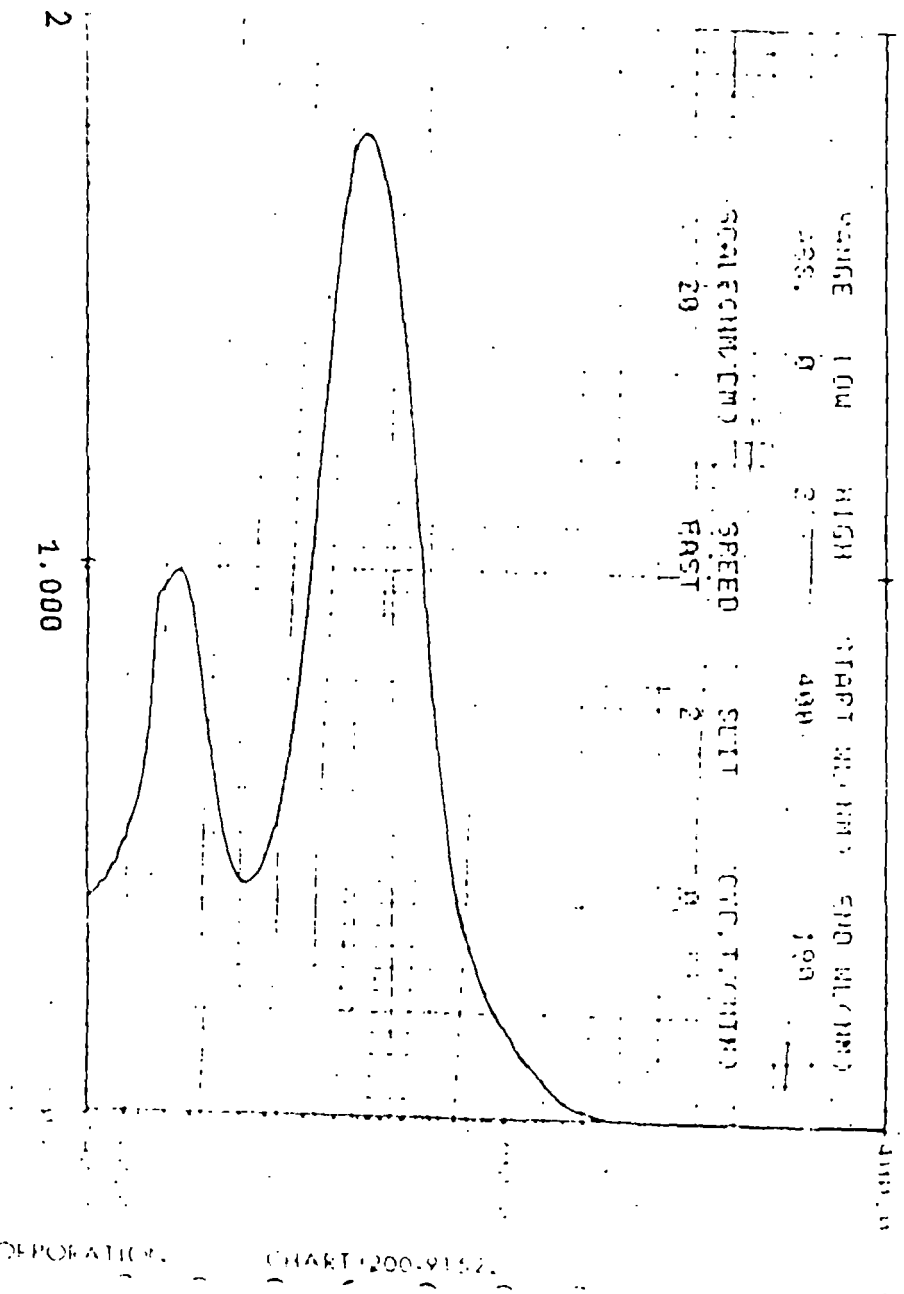
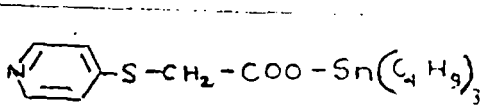


Fig.3.10 UV spectrum of 

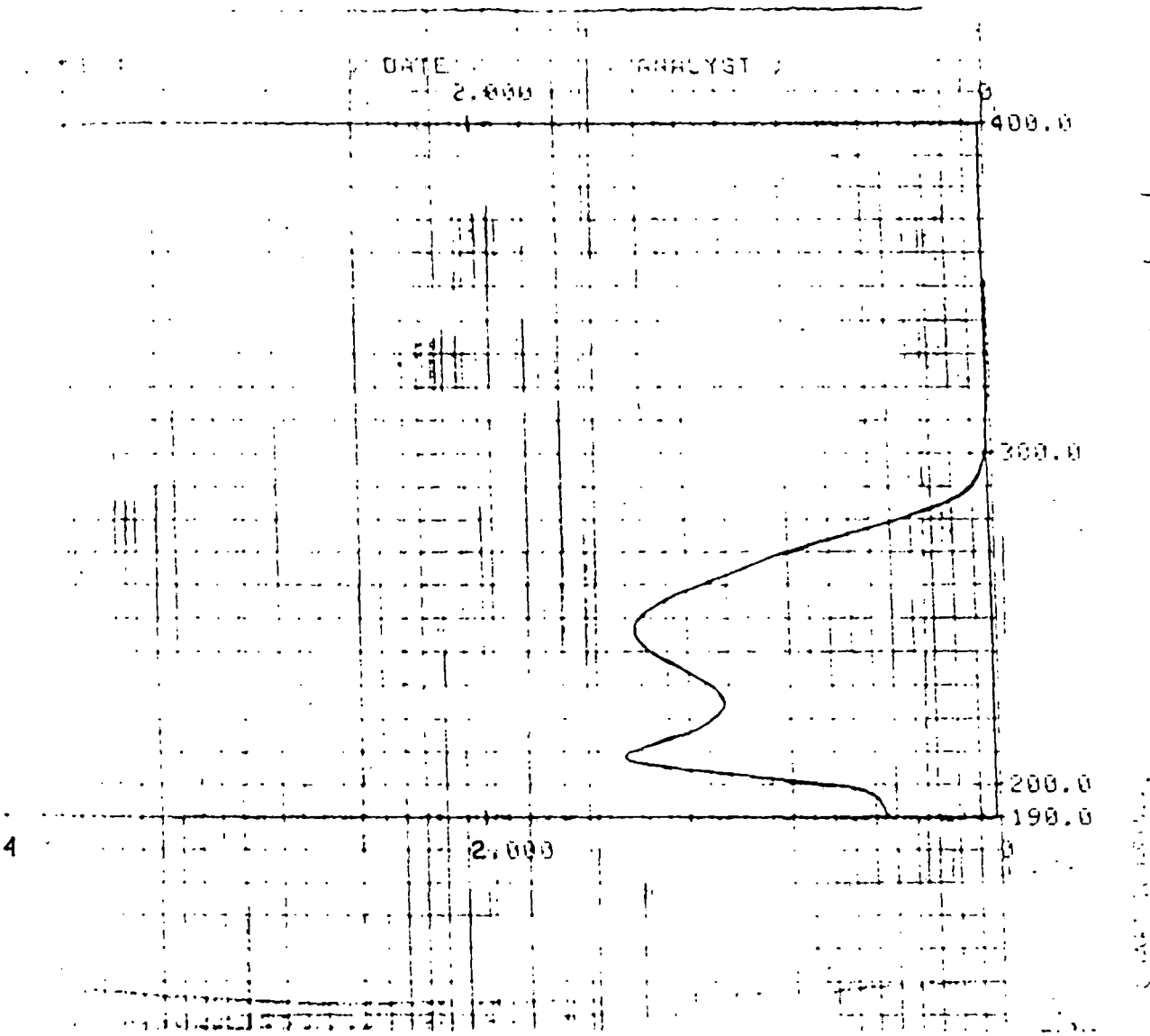


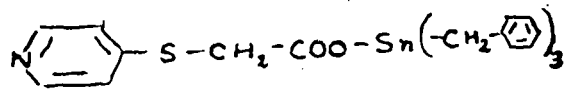
Fig.3.11 UV spectrum of 

Table - 4[a]

Relevant ^1H NMR data (ppm)

Compounds	δSn-aromatic/ligand heteroaromatic ring protons	δCH_2 of ligand	δCH_2 of benzyl group	δalkyl/cyclohexyl protons
Ph_3SnL	8.01(d), 7.52(m,19H)	3.2χ(s,2H)		
Ph_2SnL_2	8.52(d), 7.53(m,14H)	3.55(s,4H)		
Bz_3SnL	8.43(d), 7.33(m,19H)	3.66(2H)	2.61(6H)	
Bu_3SnL	8.52(d), 7.56(d,4H)	3.54(s,2H)		
Bu_2SnL_2	8.65(d), 7.54(d,8H)	3.56(s,4H)		1.42(bm,18H)
Cy_3SnL	8.55(d), 7.44(d,4H)	3.55(s,2H)		1.53(bm,33H)
Me_2SnL_2	8.46(d), 7.54(d,8H)	3.12(s,4H)		0.55(s,6H)

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

b = broad, s = singlet, d = doublet, m = complex multiplet

$$L = O - \overset{O}{\overset{\|}{C}} - CH_2 - S -$$

3.4.3. ^{1}H NMR spectroscopy:

Proton NMR spectral data for the synthesised compounds are presented in Table - 4. All the expected signals are present in the spectra with satisfactory proton integrations. Individual signal assignments were not attempted when they appeared as complex multiplets. The δSn-aromatics appeared around 7.5 as complex multiplet obscuring the heteroaromatic protons of the ligands, which also appeared almost in the same region (8.65 to 7.3 ppm)[11,23,24].

The δSn-CH_2 of the tin-benzyl group appeared at 2.61 as singlet. The tin-butyl and tin-cyclohexyl protons appeared as broad complex multiplet around δ 1.42 and 1.53 respectively, whereas tin-methyl signal appeared as a singlet at δ 0.55. In some cases $^{2}J(^{117}Sn/^{119}Sn\text{-}CH)$ could be observed as very weak signals. The CH_2 of the ligand appeared around 3.5 ppm.

3.4.4. Mössbauer Spectra:

The two Mössbauer parameters of primary interest are the isomer shift, δ (mm/sec) and the quadrupole splitting ΔE_Q (mm/sec). The isomer shift values are dependent upon the S-electron density at the ^{119}Sn nucleus, and, for most organotin (IV) compounds, fall

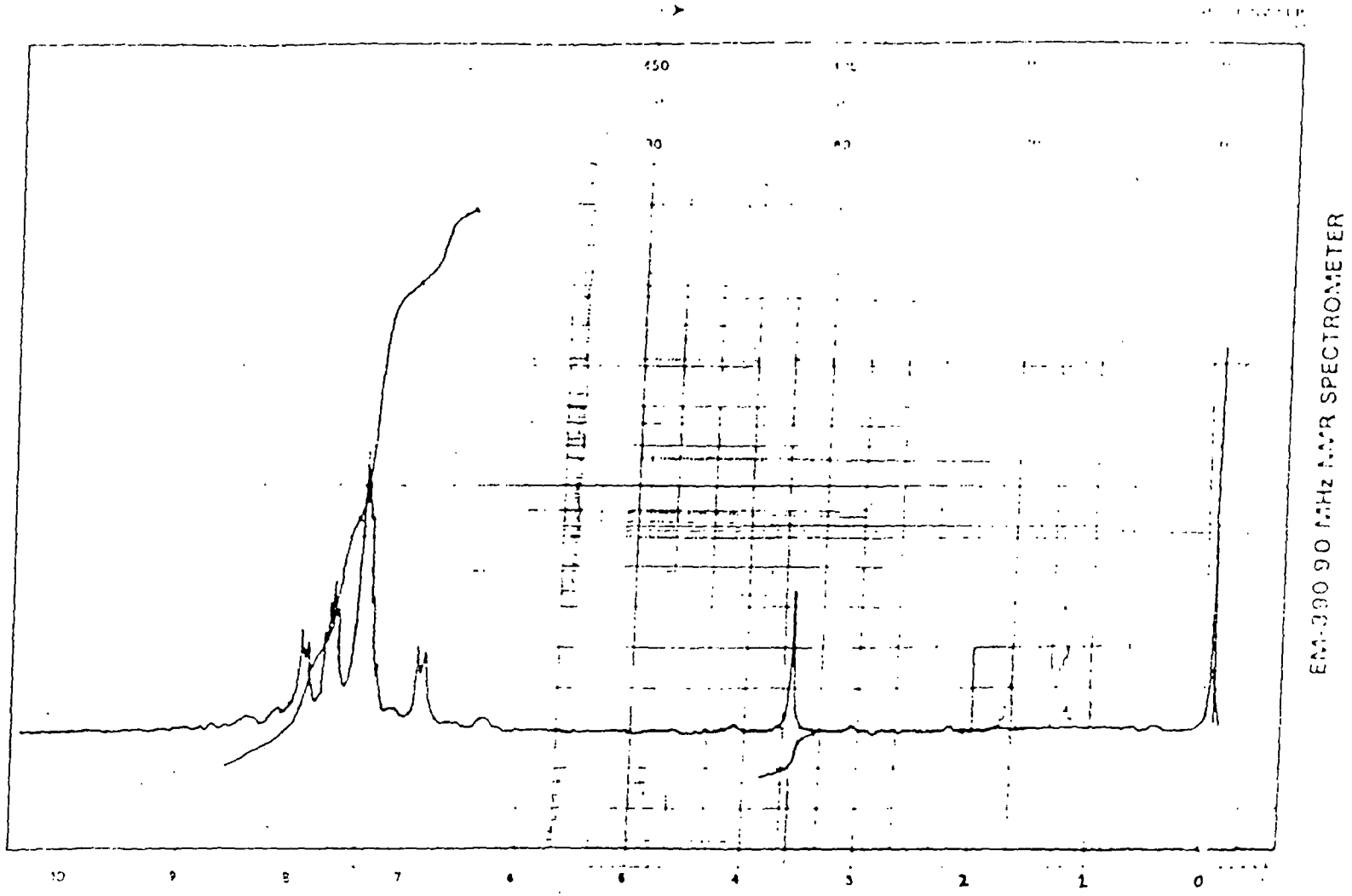
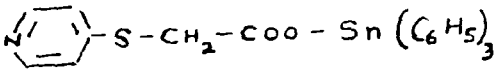


Fig.3.12 NMR spectrum of 

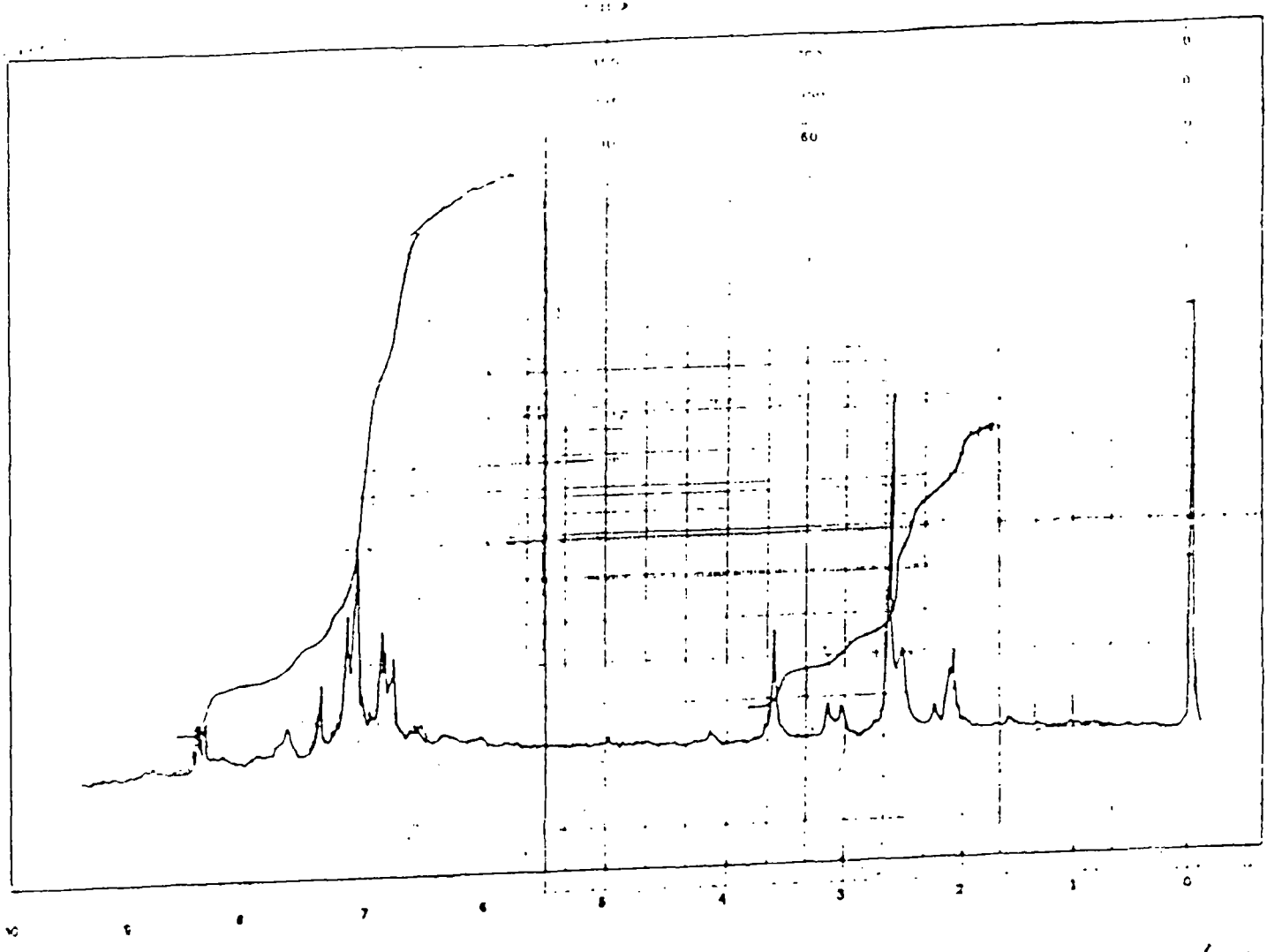
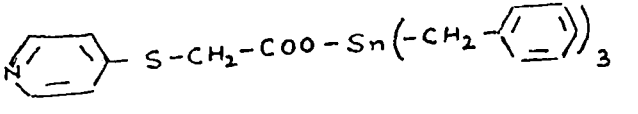


Fig.3.13 NMR spectrum of 

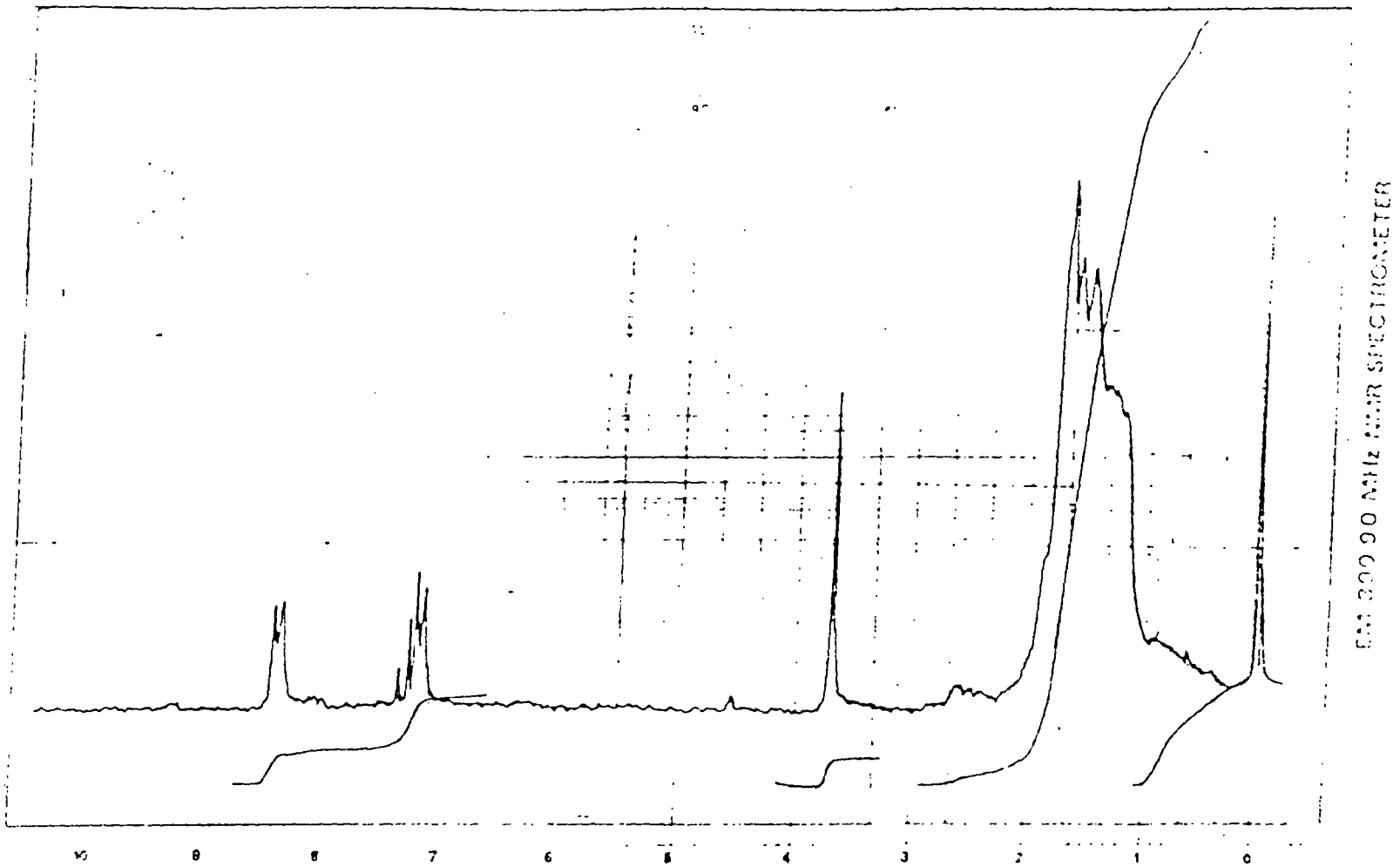
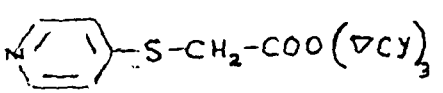
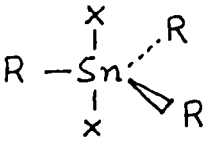


Fig. 3.14 NMR spectrum of 

in the range -0.5 mm/sec to +2.70 mm/sec with a positive δ corresponding to an increase in nuclear s-electron density at the tin atom. δ should vary with the polarity of the tin-ligand bonds[41]. Isomer shift values of the phenyl tin derivatives are usually lower than their alkyltin counterparts due to the strongly electron withdrawing nature of the phenyl group (Table - 6). If the coordination number of the tin increases from four to five or six or seven, the increased use of the metals 5d-orbitals for bonding results in a reduction in the 5s-electron density at the tin nucleus and a drop in δ, e.g., Ph_2SnI_2 : δ = 1.51 mm/sec, Ph_2SnI_2 bipy: δ = 1.41 mm/sec. Cis-complexes have lower than the trans-complexes due to the higher percentage of s-character of the Sn-C bonds in the trans isomer[41].

Only a single line is observed in the ^{119m}Sn Mössbauer spectra when the tin atom has perfectly spherical symmetry (Me_4Sn, for example). Any deviation of the ^{119}Sn nuclear charge from spherical symmetry results in a two-line quadrupole-spolitting in the spectrum and ΔE_Q is the separation between the two peaks in mm/sec. For regular tetrahedral R_3SnX and R_2SnX_2 compounds ΔE_Q falls within the range 1.00-2.40 mm/sec.

Five coordinate triorganotin compounds may have various ΔE_Q values depending on the stereochemistry.

For the trans-structure  , if

both axial Sn-X bond lengths are equal, as in Me_2SnOH which consists of chains of planar Me_3Sn groups linked symmetrically by bridging X radicals, ΔE_Q is close to 3.00 mm/sec. However, an increasing difference between the two axial Sn-X bond lengths causes a movement of ΔE_Q towards 4.00 mm/sec[41]. The cis-isomers of R_2SnX_2 give ΔE_Q values in the range 1.70-2.40 mm/sec while the trans-isomer is expected to have values in the range 3.50-4.10[41] mm/sec.

For convenience in spectral analysis, here is given a table on ranges of quadrupole splittings for compounds with different structure (Table - 5)[42-45].

Table - 5

Structure	Range of quadrupole splittings
Tetrahedral, R_nSn_{4-n} (n=1-3)	0.00-2.31 (mm/sec)
Octahedral, $RSnX_5$	1.92
Octahedral, cis-R_2SnX_4	1.63-2.34
Trigonal bipyramidal, R_3SnX_2 (X-axial)	2.76-3.86
Octahedral	3.37-4.32

Herber et al[46] have argued that so long as the range of bond ionicities in a series of compounds is not too large, the ratio of quadrupole splitting to isomer shift ($\rho = E_Q/\delta$) can be used to distinguish between compounds in which the tin atom is pentacoordinate and those in which it is tetra-coordinate. They suggest that (with δ relative to SnO_2), a value of $\rho > 2.1$ is evidence of penta-coordination about the tin atom, whereas if $\rho < 1.8$, the tin atom is tetra-coordinate. The Mössbauer parameters of some organotin carboxylates are presented in the following table-6[11,17,18,26,47,48].

Table - 6

Compound	δ (mm/sec)	ΔE_Q (mm/sec)	Structure in solid state
$Bu_2Sn(OCOMe)_2$	1.40	3.45	Polymer
$Bu_2Sn(OCO.C_7H_{15})_2$	1.45	3.50	"
$Bu_2Sn(OCO.CCl_3)_2$	1.65	3.80	"
$Me_3SnOCOCH_3$	1.35	3.68	"
$Bu_3SnOCOCH_3$	1.46	3.64	"
$Ph_3SnOCOMe$	1.27	3.40	"
$Ph_3SnOCOEt$	1.33	3.42	"
$Ph_3SnOCO.CMe_3$	1.21	2.40	Monomer
$Ph_3SnOCO.CCl_3$	1.30	2.97	"

The Mössbauer data of triphenyltin acetate are (in mm/sec): δ 1.28, E_Q 3.48, Γ_1 1.05, Γ_2 1.12 for 80K $\leqslant$ T $\leqslant$ 130K and that for triphenyltin chloroacetate are : δ 1.31, ΔE_Q 3.70, Γ_1 1.11, Γ_2 1.15 for 80K $\leqslant$ T $\leqslant$ 130K[49].

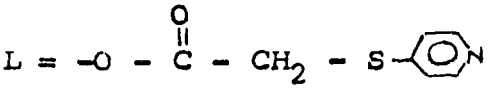
The isomer shifts of the triphenyl and tribenzyl tin compounds are typical of triorganotin compounds[26].

The Mössbauer data at 80K for two representative compounds were obtained and presented below in the Table 7.

Table - 7

Mössbauer data for organotin derivatives of heteroaromatic thio acetic acids

Sl. No.	Compound	δ (mm/sec)	ΔE_Q (mm/sec)	Γ	%
(1)	Ph_3SnL	1.20	2.91	0.91, 0.91	
(2)	Bz_3SnL	1.37	2.76	0.92, 0.93	100

L = 

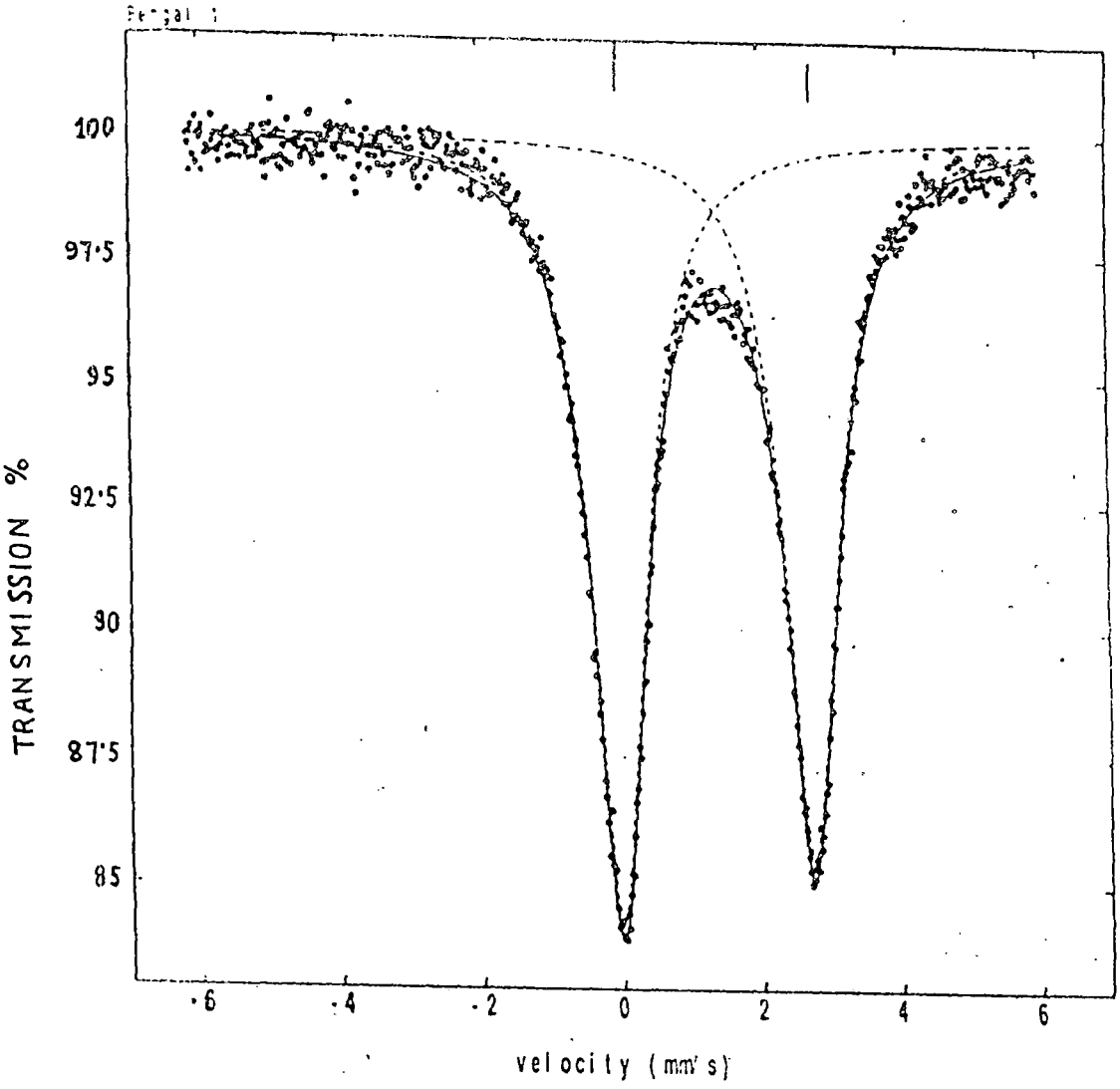
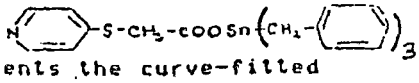


Fig 15. Tin-119 Mössbauer spectrum of  at 80K. (The solid line represents the curve-fitted Lorentzian line shapes)

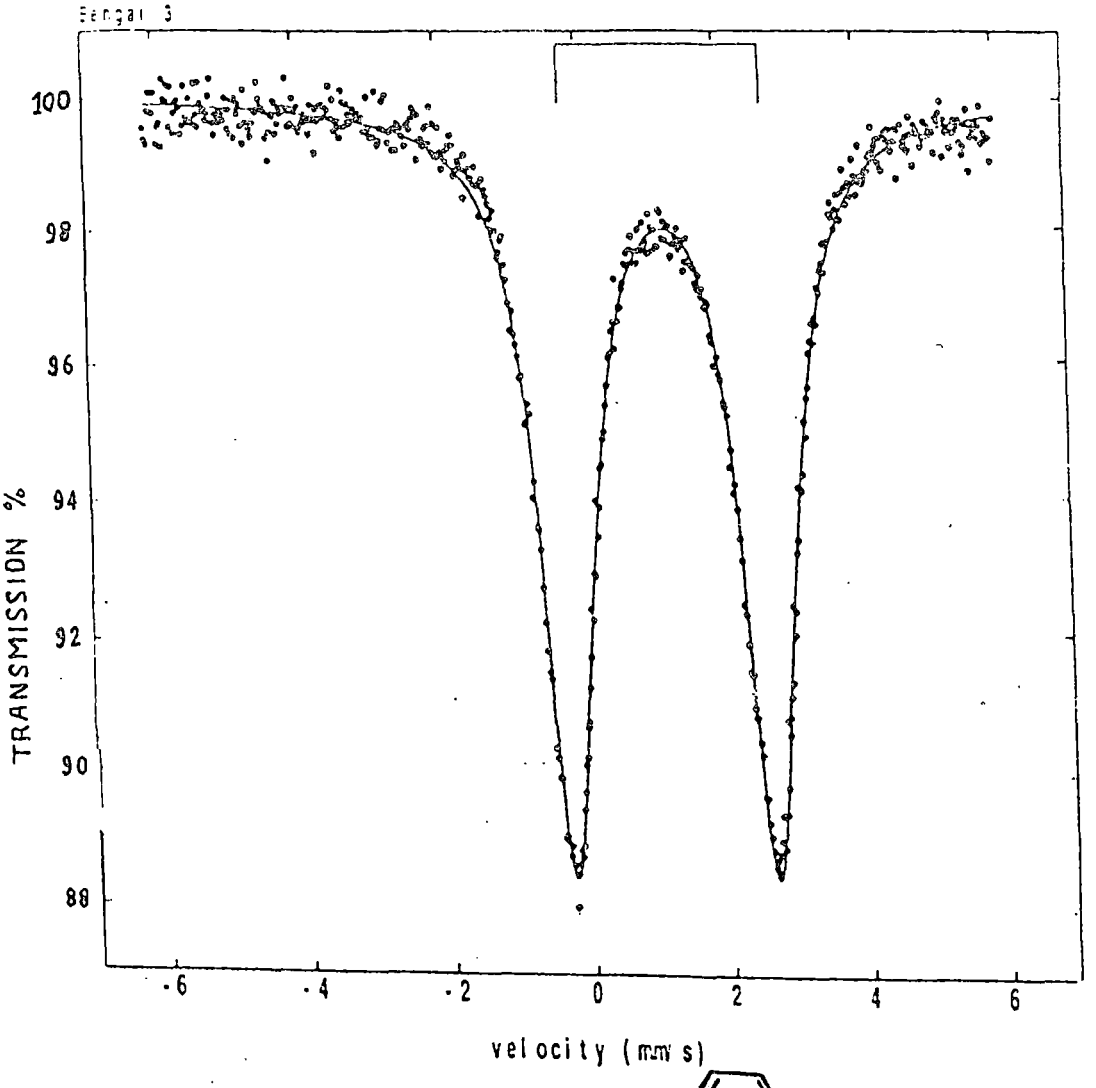


Fig 16 Tin-119 Mössbauer spectrum of

at 80K. (The solid line represents the curve-fitted Lorentzian line shapes)

The increase in the isomer shift for compound 2 compared to 1 is probably due to less electron withdrawing power of benzyl group than phenyl group. The ΔE_Q values are consistent with weakly bridged chain structure with trans C_3 trigonal bipyramidal environment around tin atom[27].

Here ρ values, i.e., the ratio of quadrupole splitting to isomer shift, are (1) 2.42 and (2) 2.02, which are also the evidences for penta-coordination around the Sn atom[46].

These δ and ΔE_Q values are well in agreement with the reported values [18,25] (Table - 6).

3.5. Study of fungicidal activity and phytotoxicity:

3.5.1. Introduction to fungicidal activity:

The purpose of the present study is to evaluate anti fungal activity of the organotin thio aryloxy acetates on plant pathogens and to compare their fungitoxicity with parent acids, in order to elucidate structure activity relationships. All the experiments were done *in vitro*. The main advantages of organotin fungicides are their relatively low phytotoxicity, low toxicity[50,51] to non target organisms and lack of resistance to crop pests to these chemicals, besides degradation

in environmental condition to harmless inorganic tin residue[52]. The first investigation in the field of antifungal activity study dates back to as early as 1954[53].

Fungicidal activity is reportedly strictly dependent upon the extent of alkylation of the tin atom, being at maximum with three tin-carbon bonds.

Maximum toxicity is associated with a total number 9 to 12 carbon atoms in the alkyl group[54]. Influence of the nature of organic toxophoric groups upon the activity can be seen from the following table in which the activity of a number of R_3SnCl compounds against Penicilium funiculosum are illustrated by the minimum inhibitory concentrations, in ppm required[11].

Compounds	Concentration (ppm)
Pr_3SnCl	1
Bu_3SnCl	4
Ph_3SnCl	8
Et_3SnCl	16
$(C_5H_{11})_3SnCl$	250
$(C_8H_{17})_3SnCl$	>125
Me_3SnCl	>500

Trialkyltin compounds find restricted application as agricultural fungicides due to high phytotoxicity, to some extent due to their mamalian toxicity and also because of less reactivity in the field than in the laboratory trials[55]. In contrast, triphenyltin compounds were found to be less phytotoxic hence greater acceptability as fungicide in agriculture. Srivastava reported Ph_2SnCl_2 also to be highly active[56].

Considerable work directed at obtaining organotin fungicides with low phytotoxicity[57-59] level were found to have other disadvantages e.g. low range[60] of activity when a number of fungi were considered.

3.5.2. Experimental

Materials and Method : The fungi used were:

Species	Code	Host of origin	Source of isolate
H. maydis	ITCC[a]-2675	Zea mays	Plant pathology laboratory, Centre for Life Sciences, N.B.U.
H. oryzae	ITCC-2537	Oryzae-sativa	
H. sativum	ITCC-2684	"	

[a]ITCC = Indian Type Culture Collection

Preparation of the culture media : 20 gms of malt extract agar (DIFCO) was boiled in water till dissolved. 20 gms agar-agar (KOBA; Japan) was added to it and boiled until agar-agar was dissolved. 0.05 gm of chloramphenicol, suspended in 5 ml of 95% alcohol was added to the medium as antibacterial agent. Now slants for culture of fungi, were prepared with this media by pouring about 2 ml of this molten media in each test tubes to remain in slanting condition till the media solidified. Then the media was impregnated with spore and kept in incubator. Average age of the spores used here was 15 days.

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.

Study of the inhibitory effects : This was done by the method of spore germination in vitro[61]. The acetone solution of the compound of a particular concentration was placed on two spots, two drops on each, in a glass slide and the solvent was allowed to evaporate. Then a drop of spore suspension was added to these treated spots. In the same way, sets for other concentrations were prepared. The glass slides were left for 24 hours at

25 ± 1°C under humid condition. Finally, one drop of cotton blue-lactophenol mixture was added to each spot to fix the germinated spores. The spots were then covered with cover slips. The number of germinated spores compared to control were calculated considering an average of 500 spores per treatment. The germination inhibition of spores were evaluated using the Vincent equation[62]:

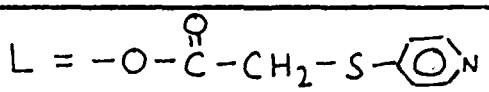
$$\% \text{ inhibition} = \frac{C-T}{C} \times 100$$

where C and T are germination of spores under control and treated spore suspension respectively. The % of spores inhibited from germinating were determined at different concentration. The ED_{50} (effective dose for 50% inhibition) values (in ppm) were obtained from the plot of % inhibition against concentration and presented in Table - 8.

Table - 8

ED_{50} values in vitro in µg/ml i.e. ppm for growth inhibition of a number of fungi of Helminthosporium group.

Compounds	Name of fungi		
	H. maydis	H. sativum	H. oryzae
Ph_3SnL	3.41	12.25	47.12
Ph_2SnL_2	39.31	65.10	116.35
Bu_3SnL	13.23	16.43	11.80



3.5.3. Discussion :

The results of thio aryloxy acetates of 4-pyridyl thio acetic acid ligand containing both nitrogen and sulphur atoms, can be compared with different tri-organotin phenoxy acetates[63] where fungitoxicity depended upon the nature of X groups. Moreover, selectivity towards one or the other of the test fungi were also observed, which is also consistent with observations made elsewhere[56,64]. Here it should be pointed out that the ligand 4-Pyridylthio acetic acid was found to be biologically inactive.

3.5.4. Phytotoxicity:

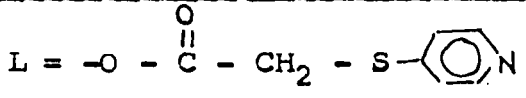
The compounds possessing fungicidal activity as determined by the tests mentioned earlier, were tested for their phytotoxicity on rice seeds also. This was only to screen out the compounds which were highly phytotoxic since any compound with fungicidal activity and also with high level of phytotoxicity will be of no use as fungicide in the practical field of applications.

Materials and Method : Healthy rice seeds of PUSA 2-21 variety, collected from Cinsurah Rice Research Farm, Hooghly, W.B., were used in the present investigation.

The rice seeds were dipped in three different sets of concentration of compound in water suspension (viz., 100, 50, 25 ppm) for 1 hr, 4 hrs. and 8 hrs. respectively. As the compounds were insoluble in water, few drops of acetone were added to make the suspension. Aceton controls for each treatment and one set of water control were also arranged. The treated seeds were then sowed over a mat of moist filtre papers arranged in covered petriplates incubated at 30 $\pm$ 1°C. 100 seeds were treated for each set. After seven days, the germinated seeds were counted against control. Seeds producing a root or coleoptile were considered as germinated. The percentage of germinated seed at different concentrations

and times with respect to control are presented in the following Table - 9.

Compound	Concentration (ppm)	% of germinated seeds with respect to control treated for		
		1 hr.	4 hrs.	8 hrs.
Ph_3SnL	100	100	100	96
	50	100	100	100
	25	100	100	100
Ph_2SnL_2	100	100	100	96
	50	100	100	100
	25	100	100	100
Bu_3SnL	100	100	100	95
	50	100	100	100
	25	100	100	100

L = 

The results show the compounds to have almost no phytotoxicity which is encouraging from the point of view of its potentiality as fungicide in practical field.

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Chapter - 4

Synthesis, Characterisation and Biocidal properties of the products from the reaction of Phenyl thiodydantoic acid with Organotin (IV) Oxides or hydroxides

4.1. Synthesis of new Organotin Carboxylates were carried out by using the biologically important ligand[1], phenyl thiodydantoic acid, $Ph-N=\overset{NH_2}{\overset{|}{C}}-SCH_2COOH$ which contains several donor atoms.

Interestingly, during the course of studies it was found that the phenyl thiohydantoic acid did not bind the organotin group through the expected carboxylate (-OCO) moiety present in it. Instead, the ligand underwent a not so unexpected transformation to produce an entirely different series of organotin compounds containing Sn-S bond.

Organotin sulfides are in general, more stable than the corresponding oxygen derivatives[2], a fact which is explained by the decreased difference in size between tin and the group VI atom and thus by an increased overlapping of the bonding orbitals. Even at low temperatures, however, the tin-sulfur bond is cleaved by mineral acids.

4.2. Scope and Objective:

The objectives of this work was to synthesise the phenyl thiohydantoic acid derivative of organotins, to study the bonding interactions between tin atom and the donor atoms of the ligand, e.g. N, S, O and to test their biological activities. In recent years organotin biocides constitute a major field of studies. The ligand contains O, N, S atoms which should lead to potential organotin biocides[13-15,31]. It is generally expected that the incorporation of biologically active metal or ligand moiety in a compound will produce potential biocides. Besides it is well known that sulfur fungicides emit sufficient vapour to prevent the growth of fungus spores at a distance of several mm from deposites on leaves[3]. The vapour phase actively ensures protection of gaps on leaf surfaces resulting from weathering or expansion of leaf areas. Apart from the biocidal properties the ligand, phenyl thio hydantoic acid (H-PTHA), containing several donor atoms, as pointed out earlier, in the molecules was expected to result interesting structural features for the new compounds.

Interestingly, by reacting the acid with corresponding organotin oxides or hydroxides, the organotin mercaptides were obtained instead of organotin carboxylates.

As expected, organotin sulfides exhibit many similarities from their oxygen analogues[2].

The tin-sulfur compounds find application as stabilisers for poly(vinyl chloride), PVC[4,17]. Probably two-thirds to three-quarters of the total annual world consumption of organotin compounds went into PVC stabilization[5]. In this respect the synthesis of organotin sulfides is important. It is expected that organotin sulfides may come out as potential biocides in near future.

In addition to the stabilisation of vinyl polymers, tin-fulsur compounds have been claimed as stabilizers of polythene[44,45], and as rubber curing agents[46,47]. Other uses are as lubricant additives[48], acaricides[49], grain and plant fungicides[50,51].

4.3. A Short review on Organotin Sulfides:

During 1950s, this area of **organo**metallic chemistry become a center of interest which led to an enormous increase in the relevant technical and patent literature. Several monographs and review articles appeared in response to the rapidly growing need for the systematic consideration of synthesis, and properties of these organotin compounds[6-12,16]. An eminently readable account of the development of these compounds has been compiled by Verity-Smith[43].

Recently Mehrotra *et al*[15], discussed the nature of Sn-S bonding, made a comparison of Sn-O and Sn-S bonded derivatives and described the Sn-S compounds as biocides.

Matschiner et al[17] showed that compounds of the type $RSn[S(CH_2)_mCO_2R']_3$ and $R_2Sn[S(CH_2)_mCO_2R']_2$ (where R = C_{1-8} alkyl; R' = long-chain alkyl; m = 1,2) are useful as stabilizers for halogenated polymers.

The synthetic and structural aspects of metal complexes derived from sulphur ligands have lately attracted much attention[53-55] in view of their biological activity[56-58] and numerous commercial applications[59,60].

4.3.1. Preparations:

Organotin halides are the most important starting materials in the preparation of many types of organotin sulfur compounds. They react with many compounds bearing an SH-function, e.g., with H_2S, mercaptans, mercaptoesters, dithiols etc in organic solvents to give the corresponding organotin sulfides with the removal of hydrogen halide:

$$R_{(4-n)}SnX_n + nRSH \longrightarrow R_{(4-n)}Sn(SR)_n + nHX$$

$$Bu_3SnCl + HSCH_2C(O)OC_4H_9 \longrightarrow Bu_3SnSCH_2C(O)OBu + HCl.$$

Or when alkali thiolates are used, alkali halides are eliminated:

$$R_{(4-n)}SnX_n + nRSNa \longrightarrow R_{(4-n)}Sn(SR)_n + nNaX$$

Organotin oxides form bis(triorganotin) sulfides by reaction with thio urea derivatives:

$$R_3SnOSnR_3 + (R_2N)_2C = S \longrightarrow (R_3Sn)_2S + (R_2N)_2C = O$$

These may also be obtained by the reaction of tetra-organotin compounds with mercaptans, thio acids or hydrogen sulfide:

$$R_4Sn + R'SH \longrightarrow R_3SnSR' + RH.$$

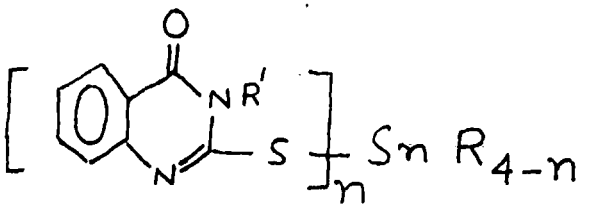
Organotin hydrides add to polar double bonds such as those in isothiocyanates, thiourea or carbon disulfide.

$$R_3SnH + C_6H_5NCS \longrightarrow R_3SnSCH = NC_6H_5$$

Alkyl tin thio alkyl carboxylates e.g., $RSn\left[S(CH_2)_mCO_2R'\right]_3$ and $R_2Sn\left[S(CH_2)_mCO_2R'\right]_2$ (R = C_{1-8} alkyl; R' = long-chain alkyl, m = 1,2), may be prepared by the reaction of mono alkyl stannoic acids, dialkyl tin oxides and/or dialkyl tin dichlorides with $NaO_3S_2(CH_2)_mCOOR'$[17].

Thus, when Bu_2SnO and 30% HCl are added after 2 hours to a mixture of isooctyl chloropropionate and $Na_2S_2O_3$ in DMF/H_2O at 70° and resulting mixture is stirred 1 hour and refluxed, isooctyl dibutyl tin dithio propionate is obtained.

Recently, R.J. Rao and his co-workers[18] synthesised compounds of the type



(where, R = Ph, Bu, Me, R' = Ph, p-ClC_6H_4; n = 1,2) by the reaction of the Na-Salt of the ligand, 3-substituted-2-mercaptoquinazol-4-one, with the corresponding organotin (IV) chlorides in non-aqueous media.

Compounds of the type Bu_3SnSR may also be prepared by the reaction of RSH with $(Bu_3Sn)_2O$ in refluxing PhMe[20].

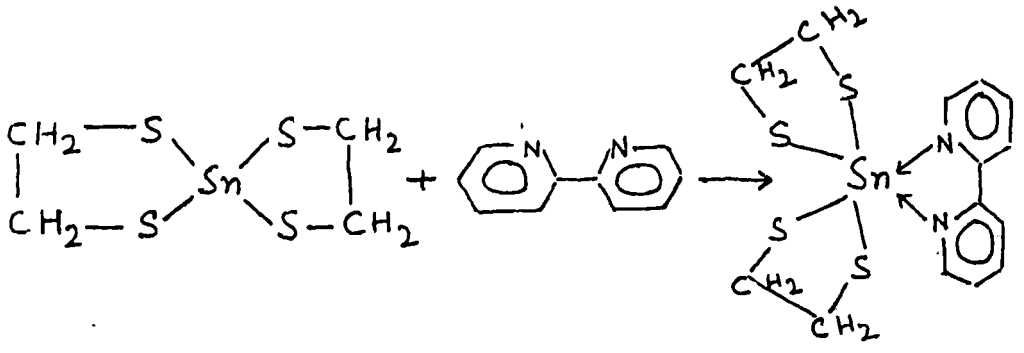
4.3.2. Chemical Properties:

Covalent halogen compounds effect cleavage of the tin-sulfur bond in organotin sulfides. The reaction with alkyl halides proceeds with the breaking of the tin-sulfur bond and formation of organotin halides and alkyl sulfonium halides.

The Sn-S bond is also attacked by transition metals. Displacement reactions take place between organotin sulfides and silver halides, silver cyanide, cyanate, and isothiocyanate. Mercuric chloride and organotin mercaptides undergo an exchange to organotin chlorides and mercuric mercaptides. Hexameric

nickel dimercaptide can be isolated as the product of the reaction between diorganotin dimercaptides and nickel chloride.

The coordination number of four, for tin in covalent organotin sulfides can be increased to five or six by complex formation with various bases particularly those containing nitrogen.



In 1987, Yu. T. Struchkov and his coworkers[19] reported that reaction between trimeric dimethyltin sulfide and CH_2BrCH_2Br at 140°C gave a complex of dimethyl tin dibromide with 1,4-dithiane formulated as :

$Me_2SnBr_2.SC_2H_4C_2H_4S.\ Me_2SnBr_2$ ($SC_2H_4C_2H_4S$ = 1,4-dithiane).

4.3.3. Physical properties:

All organotin sulfides are, under normal conditions, liquid or crystalline, which usually dissolve easily or moderately in organic solvents without decomposition. Since very little is known about the bonding in organotin sulfides,

it is to be expected that investigations in this area will increase significantly in the coming years. The most reliable information concerning the structure and bonding properties would come from X-ray structure analysis. It may be mentioned that till now complete X-ray structural analysis reports are also rare.

The Sn-S IR stretching vibration is found in the region 300-400 cm^{-1}.

The ^{1}H NMR spectra of compounds of the type $(CH_3)_3Sn-S-Sn(CH_3)_3$ showed that there is scarcely any inclusion of the free sulfur electron pairs into the tin-sulfur bonds.

Borsdorf et al[20] reported the ^{13}C and ^{119}Sn NMR chemical shifts for sixteen Bu_3SnSR compounds. The ^{119}Sn NMR signals are shifted upfield linearly (-0.06 ppm/k) with increasing temperature from 253K to 323K. Increasing concentration decreases the ^{119}Sn chemical shifts.

Thomas C.W. Mark and his coworkers[21] gave the crystal structure of tribenzyl (2-thiolatopyridine N-oxide) tin (IV). The coordination geometry about the central atom is square pyramidal, with one benzyl C atom in the apical position and the basal plane containing the other two benzyl C atoms along with the O and S atoms of the chelating ligand; the Sn atoms is displaced out of the basal plane in the direction of the apical C atom by 0.64(1)A^{o}. This is the 1st example of polytopal

dominance of square pyramidal geometry in organotin penta coordination.

Recently, White et al have shown X-ray crystallographically that both $Ph_3SnS(CH_2)_2NH_2$ and $Ph_3SnSC_5H_4NO$ possess five-coordinate cis-chelate structures with Sn-S bonds[52].

4.4. Experimental with Characterisation:

Phenyl thiohydantoic acid was prepared by literature method[22]. All the solvents were purified and dried by standard methods[23] before use. The organotin reagents were Aldrich/ Fluka products. Infrared spectra were recorded by using PYE UNICAM SP3-300S Infrared Spectrophotometer (Philips). ^1H NMR spectra were recorded by VA-EM 390(90 MHz) machine MHz machine. Tin was estimated by standard conventional procedure as SnO_2 in our laboratory and the micro analyses were done at RSIC, Punjab University.

All the manipulations involving benzene as solvent was carried out under closed condition with due precautions and care. ^1H and ^{13}C NMR were also recorded on Varian XL-300 Spectrometer.

4.4.1. Preparation of the starting materials:

4.4.1.1. Preparation of Phenyl thio hydantoic acid:

Monochloro acetic acid (18.9 gm, 0.2 mole) and ammonium thiocyanate (15.2 gm, 0.2 mole) were mixed together. Amiline

(18.6 gm, 0.2 mole) and ethyl alcohol (93 ml) were added to the above mixture. The whole mixture was heated under reflux on a water bath for 6 hours. Then it was allowed to stand until the undissolved material settled. The clear brownish liquid was poured into a large evaporating dish and allowed to cool. The yellow crystals which formed, were filtered and washed with water. The product was purified by recrystallisation from alcohol, m.p. 157°C [lit(22) m.p. 156-157°C].

Elemental analysis : Found (Calcd.) :

C	H	N
51.40 (51.43)	4.72 (4.76)	13.29 (13.33)

IR (cm^{-1}) : ν CO$_2$ - 1650; $\nu_{asy,sym}$ NH$_2$ 3280, 3390

^{1}H NMR (δ ppm): 9.72, 3.22, 3.58, 7.41

4.4.1.2. Preparation of Bis(triphenyl tin) oxide:

Bis (triphenyltin) oxide was prepared by the reaction of triphenyltin chloride with 50% excess of sodium hydroxide solution as described by Van Rij[24]. The crude product was dried in air and finally in vacuum at room temperature, which on repeated crystallisation from a mixture of petroleum ether and benzene gave crystals of melting point 122°C [lit(25) m.p. 123-124°C]. It was dried in vacuum (Found : C = 60.81%;

H = 4.47%; Calcd. for $C_{36}H_{30}Sn_2O$: C = 60.41%, H = 4.42%).

4.4.1.3. Preparation of tribenzyl tin chloride:

Tribenzyltin chloride was prepared from the reaction of benzyl chloride and tin powder, according to the method of Sisido, Takeda and Kimgawa[26]. White crystalline solid was further purified from acetone, m.p. 142°C [lit (26) m.p. 142-144°C].

4.4.1.4. Preparation of bis (tribenzyltin) oxide:

Bis (tribenzyltin) oxide was prepared[27] by shaking an etheral solution o tribenzyltin chloride with 30% aqueous solution of potassium hydroxide. The product was recovered from ether layer and finally recrystallised from acetone, m.p. 118-121°C [lit (27) m.p. 120°C]. (Found : C = 62.95%, H = 5.15%; Calcd. for $C_{42}H_{42}Sn_2O$: C = 63.05%; H = 5.28%).

4.4.1.5. Preparation of Diphenyltin oxide:

Polymeric diphenyl tin oxide was prepared by the reaction of diphenyl tin dichloride with 50% excess of sodium hydroxide solution as described by Elegbede and Mclean[28]. This was dried in air and finally in vacuum at room temperature for 12 hours. (Analysis Found : C = 49.80%, H = 3.43%; and Calcd. for $C_{12}H_{10}SnO$: C = 49.88%, H = 3.46%).

4.4.1.6. Preparation of Tricyclohexyltin hydroxide:

Tricyclohexyltin hydroxide was prepared[39] by treating $SnCl_4$ with CyMgCl in a mol ratio 1:3, hydrolysing unreacted CyMgCl, dehydrating the organic portion, then adding additional CyMgCl, in an overall ratio of 3.5-3.9:1 to initial $SnCl_4$, to convert intermediate Cy_2SnCl_2 to Cy_3SnCl, then hydrolysing the Cy_3SnCl. m.p. 219°C. [lit (40) m.p. 220-221°C].

(Analysis found : C = 56.32%, H = 8.80%; and Calcd. for $C_{18}H_{34}SnO$: C = 56.15%, H = 8.84%).

Dibutyltin oxide and dimethyltin oxide were from Alfa products.

4.4.2. Synthesis of the new organotin (IV) derivatives.

4.4.2.1. Synthesis of Triphenyltin N-phenyl amido methyl mercaptide, $Ph_3SnSCH_2CONHPh$:

Bis (triphenyltin) oxide (1.47 gm, 2.045 mmol), phenylthio hydantoic acid (0.86 gm, 4.09 mmol) and 150 ml of dry benzene were taken in a 250 ml round bottomed flask. The flask was fitted with a Dean-Stark apparatus and a water-cooled condenser. Nitrogen was used to flush the whole assemblage. The reaction was started by heating to reflux the mixture and the water formed during the reaction was azeotropically

distilled out by the Dean-Stark apparatus. Refluxation was continued for 48 hours. The solution was brought to room temperature and filtered to give a clear solution. Solvent was removed from the solution. The residue was washed with hot petroleum ether (60°-80°C). Petroleum ether washings gave a small amount of liquid product. Repeated crystallisation (from methanol) of the residue after petroleum ether washing gave pure crystals, having m.p. 120°C, yield 2.58 gm, 70%.

Elemental Analysis : Found (Calcd)

C	H	N	Sn
60.21 (60.50)	4.45 (4.45)	2.81 (2.71)	22.85 (23.01)

Relevant spectral data:

I.R (Cm^{-1}) : 3240(m), 1625(s), 510(w), 460(w).

^{1}H NMR (δ ppm) : 8.52(S,1H), 7.05(m, 20H), 3.36 (S, 2H).

4.4.2.2. Synthesis of Tribenzyltin N-Phenyl amido methyl mercaptide, $Bz_3SnSCH_2CONHPh$:

Nitrogen gas was used to flush the whole apparatus consisting of a round bottomed, 250 ml flask, a Dean-Stark apparatus and a double surface reflux consenser. To a benzene (dry, 70 ml) suspension of phenyl thio hydantoic acid (0.51 gm, 2.44 mmol) taken in the reaction flask was added bis (tribenzyl-

tin) oxide (1 gm, 1.25 mmol) in benzene (dry, 70 ml). The mixture was refluxed for 20 hours. The water formed was removed during the reaction, azeotropically with the Dean and Stark assembly. The clear solution thus obtained was stripped off in vacuo. Carbon tetra chloride-petroleum ether (60-80°C) mixture was added and kept in freezer. After one day crystals separated and filtered. It was purified by recrystallisation from carbon tetra chloride-petroleum ether mixture and dried in vacuum, m.p. 75°C, yield, 0.56 gm, 41%.

The filtrate was freed from solvent. Extracted with cold petroleum ether. The petroleum ether part was found to contain a liquid product. And the residue gave a small amount of the product having m.p. 75°C, on repeated dissolution and crystallisation.

Elemental Analysis : Found (Calcd.):

C	H	N	Sn
61.62 (62.39)	4.84 (5.19)	2.82 (2.51)	20.01 (21.28)

Relevant spectral Data:

IR (Cm^{-1}): 3275(w,b), 1650(s), 565(w), 515(m)

^1H NMR (δ ppm): 8.20(S, 1H), 7.26(m, 20H), 3.23(S, 2H), 2.63(S, 6H).

4.4.2.3. Synthesis of Diphenyltin bis(N-phenyl amido methyl mercaptide), $Ph_2Sn(SCH_2CONHPh)_2$:

The reaction was done under nitrogen atmosphere. 1 gm (4.76 mmol) of phenyl thio hydantoic acid, diphenyltin oxide (0.686 gm, 2.38 mmol) and 150 ml of dry benzene were taken in a 250 ml round bottomed flask-fitted with a Dean-Stark apparatus and a reflux condenser. The reaction was started by heating the reaction mixture on a heating mantle to reflux. The water produced during the reaction course was azeotropically distilled out. After 24 hours of refluxation the solution was brought to room temperature. Benzene was almost removed from the solution. Washed with hot petroleum ether (60-80°C). The petroleum ether washings afforded a liquid product. The residue was washed with carbon tetrachloride and recrystallised from dichloromethane to give the pure product, m.p. 145°C, yield, 0.57 gm, 40%.

Elemental Analysis, Found (Calcd.):

C	H	N	Sn
54.17 (55.56)	3.80 (4.29)	5.55 (4.63)	19.62 (18.19)

Relevant spectral Data:

IR (Cm^{-1}): 3260(w,b), 1610(s), 1600(sh), 510(m), 460(w).

^1H NMR (δ ppm): 10.33(S,2H), 7.52(m, 20H), 3.51(S, 4H).

4.4.2.4. Synthesis of Tricyclohexyltin N-phenyl amido methyl mercaptide, $Cy_3SnSCH_2CONHPh$:

Moisture was excluded from the glass apparatus consisting of a round bottomed flask (250 ml), a Dean-Stark apparatus and a double surface water cooled condenser, by flushing nitrogen. Cy_3SnOH (0.9 gm, 2.34 mmol), phenylthio hydantoic acid (0.49 gm, 2.34 mmol) and 150 ml of dry benzene were taken in the 250 ml round bottomed flask and were reacted together by heating under reflux. The water formed during the reaction was azeotropically distilled out. After 20 hours of refluxation, the reaction mixture was concentrated and kept for overnight. Next day some solid was found and filtered. The solid (40 mg) was the unreacted phenylthio hydantoic acid as confirmed by mixed melting point determination. The filtrate was freed from solvent and washed with cold petroleum ether (60°-80°C). The petroleum ether washing was found to contain a small amount of liquid product. The residue contained the desired product which was extracted out in CCl_4. The CCl_4 extract was concentrated and added petroleum ether to it and kept in the freezer for 24 hours. Crystallisation of tricyclohexyl tin N-phenyl amido methyl mercaptide was attained. Filtered out the product and washed with cold petroleum ether, dried at the pump. m.p. 101°C; yield, 0.76 gm, 62%.

Elemental Analysis, Found (Calcd.):

C	H	N	Sn
57.73	7.49	2.90	22.01
(58.45)	(7.68)	(2.62)	(22.24)

IR (cm^{-1}) : 3260(m), 1650(s), 535(w), 510(m)

^{1}H NMR (ppm) : 9.01(s,1H), 1.26-1.93(m,33H), 7.09-7.59(m,5H), 3.45(s,2H)

4.4.2.5. Synthesis of Dibutyltin Bis (N-phenyl amido methyl mercaptide):

Entire reaction was done under nitrogen atmosphere. Dibutyltin oxide (0.8 gm, 3.22 mmol) and phenyl thio hydantoic acid (1.35 gm, 6.43 mmol) taken in a 250 ml round bottomed flask were reacted together in dry benzene (150 ml) by heating on a heating mantle. The water formed during the reaction process was azeotropically distilled out by using a Dean-Stark apparatus and a reflux condenser. The mixture was refluxed for 24 hours. The solution was brought to room temperature and left for over night. A very small amount (50 mg) of unreacted phenyl thio hydantoic acid was filtered off which was identified by mixed melting point determination. It was separated by filtration. The filtrate was freed from benzene and washed with petroleum ether. The petroleum ether part contained a liquid product. The residue was taken in carbon tetrachloride and petroleum ether was added to that, kept in the freezer for one day. Next day crystals of Dibutyl tin Bis(N-phenyl amido methyl mercaptide) were obtained, filtered and washed with petroleum ether. It was dried at the pump, m.p. 122°C, yield 1.03 gm, 57%.

Elemental Analysis, Found (Calcd.):

C	H	N	Sn
50.54	5.75	4.83	21.00
(50.00)	(6.00)	(4.95)	(21.02)

Relevant spectral Data:

IR (Cm^{-1}) : 3260(m,b), 1640(s), 1625(sh), 515(m), 505(w)

^1H NMR (δ ppm): 9.75 (S, 2H), 7.55(m, 10H), 3.54 (S, 4H), 1.71 (m, 18H).

4.4.2.6. Synthesis of Dimethyl tin Bis (N-phenyl amido methyl mercaptide):

The reaction was carried out under nitrogen atmosphere. Dimethyltin oxide (0.8 gm, 4.86 mmol), phenyl thio hydantoic acid (2.04 gm, 9.72 mmol) and 150 ml of dry benzene were taken in a 250 ml round bottomed flask. The flask was placed on a heating mantle and fitted with a Dean-Stark apparatus and a Double surface reflux condenser. Reaction started by heating the mixture to reflux and the water formed during the reaction was azeotropically distilled out. The mixture was refluxed for 20 hours, concentrated and kept for over night. Some solid (40 mg) was found which was established to be unreacted phenyl thio hydantoic acid by mixed melting point determination. The solid was filtered out. The filtrate was freed from benzene, washed with petroleum ether. The

petroleum ether washings gave a liquid product which was found to be a -C≡N group containing material. The residue was extracted with hot carbon tetrachloride. It was concentrated and kept in freezer. After 48 hours a white solid, $Me_2Sn(SCH_2CONHPh)_2$ was separated, filtered and dried in a vacuum dessicator. m.p. 139°C, yield 1 gm, 43%.

Elemental Analysis, Found (Calcd.):

C	H	N	Sn
44.40 (44.93)	4.26 (4.57)	5.64 (5.82)	24.12 (24.69)

Relevant spectral Data:

IR (Cm^{-1}): 3255(m,b), 1650(s), 1630(sh), 560(w), 520(m).

^1H NMR (δ ppm): 9·69(S,2H), 7.57(m,10H), 3.57(S,4H)
0.88 (S,6H).

4.4.3. Results and Discussion:

4.4.3.1. Synthesis:

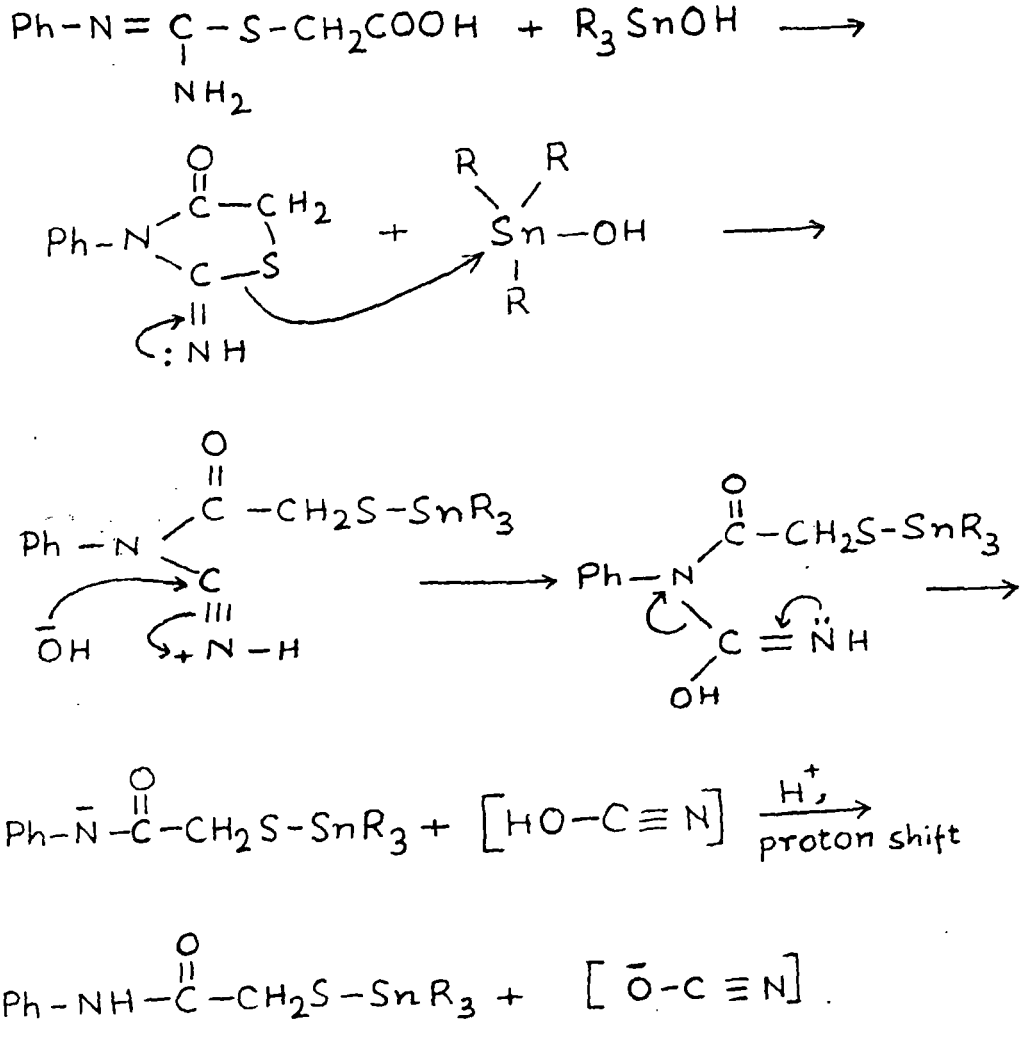
The physical data including elemental analysis (C, H, N, Sn) are presented in Table 1. The most important feature of the above reactions is the formation of the N-phenyl thiol acetamide (S-CH_2CONHPh), derivatives of tri- and diorganotin (IV) instead of the expected carboxylate derivatives of phenyl thio hydantoic acid [-OOC.CH_2S(NH_2)CNPh-]. The physical methods

of analysis and ultimately the X-ray diffraction studies on two of the synthesised compounds, namely, $Cy_3Sn(SCH_2CONHPh)$, (Cy = CyClo-C_6H_{11}) and $Bu_2Sn(SCH_2CONHPh)_2$ (discussed latter) have confirmed the transformation of the ligand, $PhNC(NH_2)SCH_2COO^-$ to $PhNHCOCH_2S^-$. Therefore, the products of these reactions are of the types : $R_3Sn(SCH_2CONHPh)$ and $R_2Sn(SCH_2CONHPh)_2$ depending on the starting tri- or diorganotin oxide or hydroxide used.

The major products containing tin from the reactions between the triorganotin oxides or hydroxides and phenyl thio hydantoic acid, on elemental analyses were found to bear 1:1 atomic ratio between 'Sn' and 'N' rather than the expected 1:2 if the ligand was $C_6H_5NC(NH_2)SCH_2COO^-$. Similarly, the tin containing major products from the reactions between the diorganotin oxides or hydroxides and phenyl thio hydantoic acid were the compounds having 1:2 atomic ratios of tin to nitrogen rather than the expected 1:4. It is, therefore, obvious from the chemical analyses that one of the two 'N' atoms of each ligand molecule was lost during the reaction process.

In each of the reactions, after isolation of the major tin containing product, a minor sticky impure organic liquid product was left which, showed a very strong infrared absorption band at 2190 cm^{-1} indicating the formation of $-C\equiv N$, group containing product in small amounts during the refluxation. However, these products could not be isolated in pure conditions yet for proper identification.

On the basis of these observations and X-ray crystallographic studies on one of the compounds, namely, $Cy_3Sn(SCH_2CONHPh)_2$ and $Bu_2Sn(SCH_2CONHPh)_2$, the rearrangement of the ligand with the loss of one 'N' atom has been confirmed and the following tentative reaction sequences may be proposed:



$$Ph-\bar{N}-\overset{O}{\overset{\|}{C}}-CH_2S-SnR_3 + [HO-C\equiv N] \xrightarrow[\text{proton shift}]{H^+}$$

$$Ph-NH-\overset{O}{\overset{\|}{C}}-CH_2S-SnR_3 + [\bar{O}-C\equiv N]$$

Hence the ligand after transformation is converted into N-phenyl thiol acetamide, which contains a 'S' atom in the molecule as the binding site. The new compounds produced, therefore, are formulated as $R_3SnSCH_2CONHPh$ and $R_2Sn(SCH_2CONHPh)_2$ types, consistent with the elemental and spectral (discussed below) analyses.

4.4.3.2. Infrared Spectra : (Fig. 4.19 - 4.25)

The special feature of the infrared spectra of these compounds are the absence of the two (ν_{asym} and ν_{sym}) stretching frequencies due to $NH_2/^+NH_2$ as would be expected for the ligand (phenyl thio hydantoic acid), $PhNC(NH_2)SCH_2COOH$. It should be pointed out that these two characteristic frequencies are present in the ligand used (Table 2). The spectra also do not contain bands attributable to ν_{asym} (OCO) and ν_{sym}(OCO) frequencies which should appear if the -COOH group of the ligand was involved in complex formation leading to the organotin carboxylates[29].

In all the compounds, ν(N-H) absorptions occur near 3250 cm^{-1} in the solid state. The bands are not sharp indicating presumably the presence of H-bonding in the molecule.

The amide bands (carbonyl absorptions) on these compounds appear at 1610-1650 cm^{-1}. The $R_3SnSCH_2CONHPh$ compounds show only a strong single absorption, whereas, the $R_2Sn(SCH_2CONHPh)_2$ compounds, in addition to the strong absorption show 'shoulders'

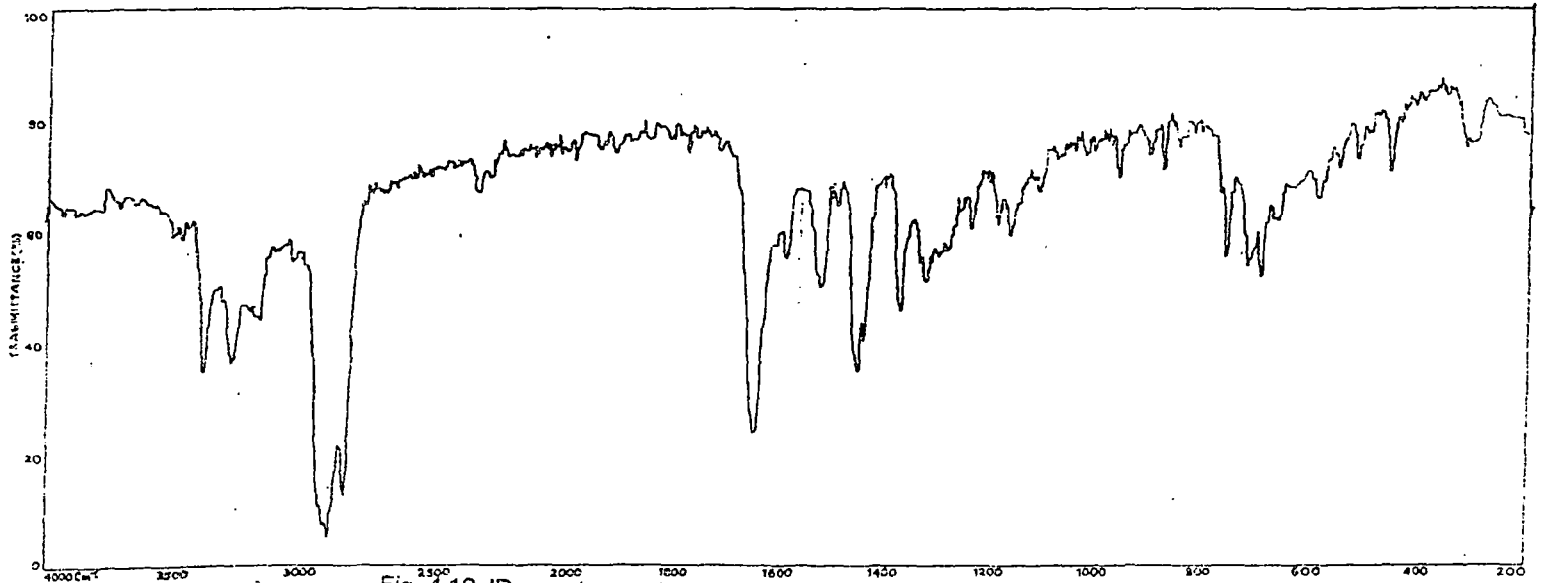


Fig. 4.19 IR spectrum of phenyl thio hydantoic acid

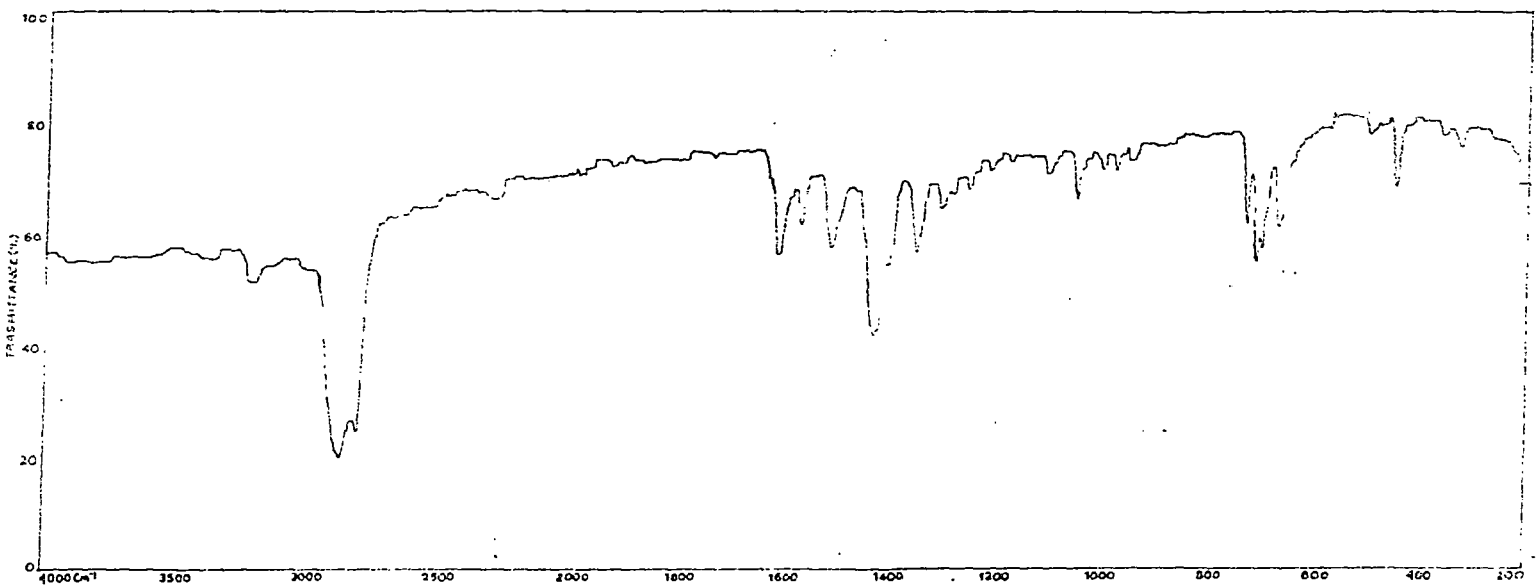


Fig. 4.20 IR spectrum of triphenyl tin (N-phenyl amido methyl mercaptide)

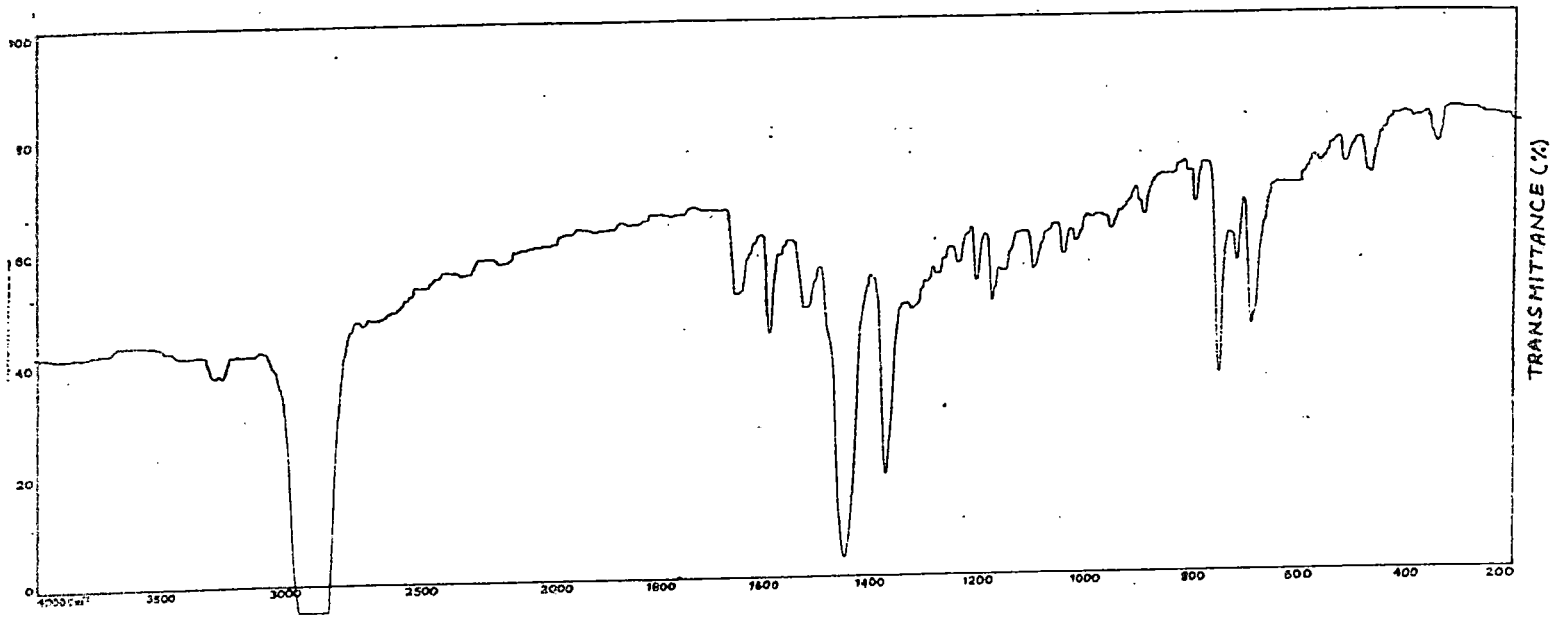


Fig. 4.21 IR spectrum of tribenzyl tin (N-phenyl amido methyl mercaptide)

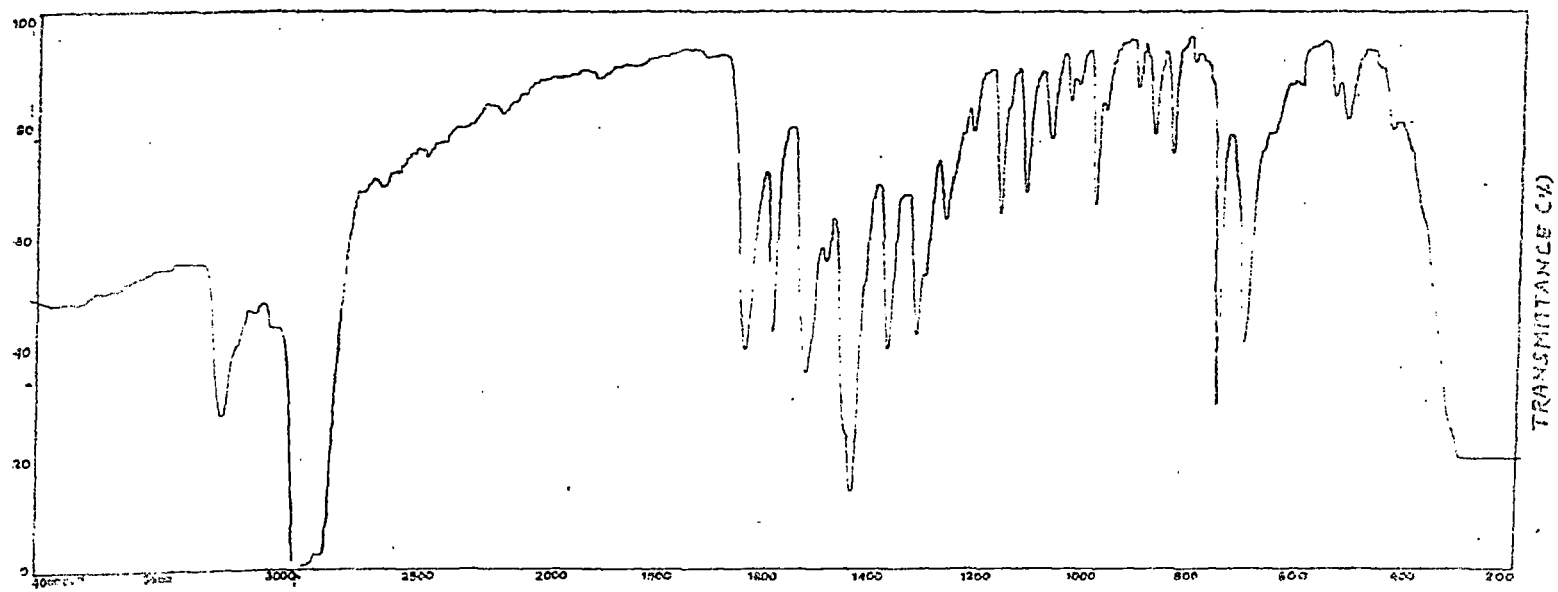


Fig. 4.22 IR spectrum of tricyclohexyl tin (N-phenyl amido methyl mercaptide)

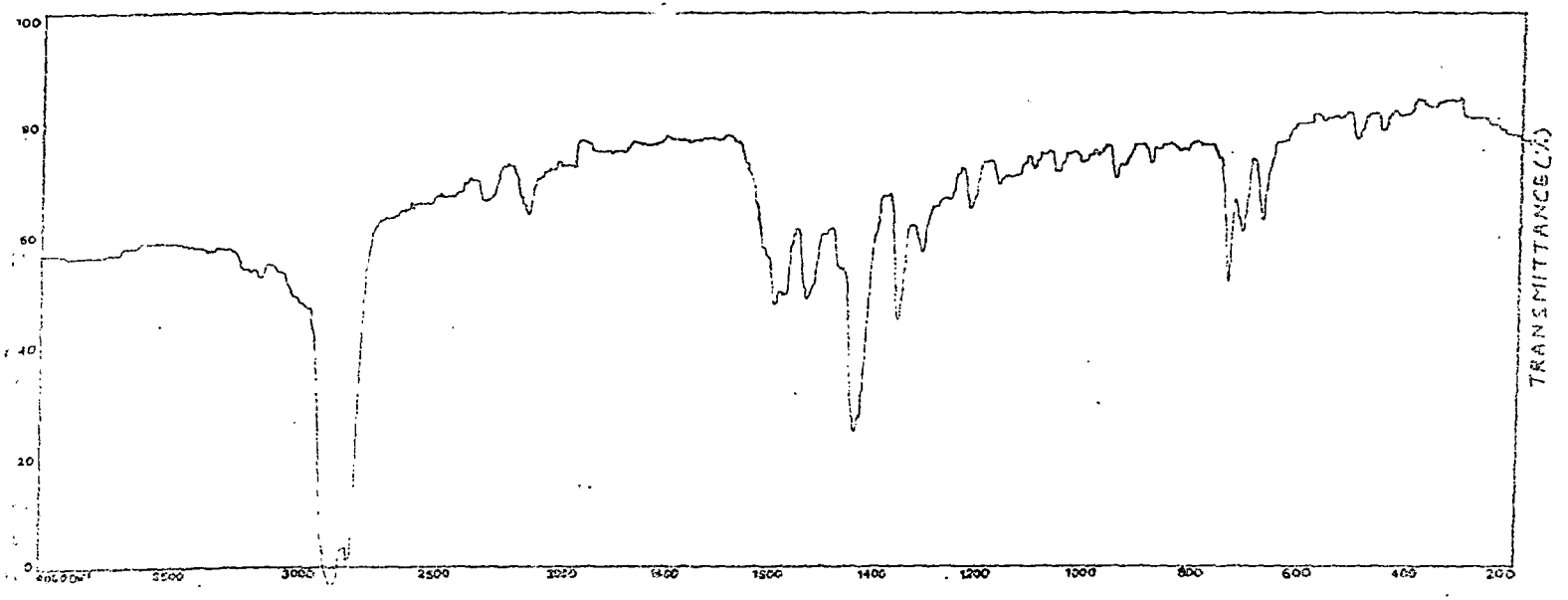


Fig. 4.23 IR spectrum of diphenyl tin bis (N-phenyl amido methyl mercaptide)

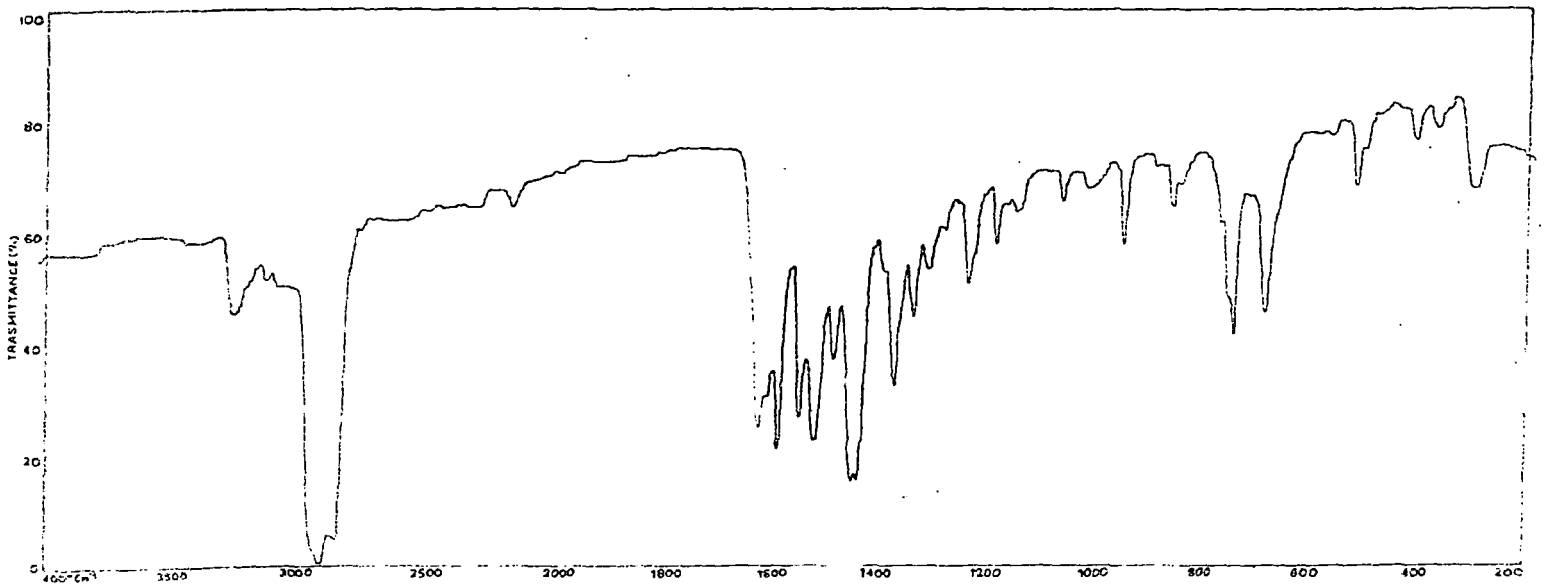


Fig. 4.24 IR spectrum of dibutyl tin bis (N- phenyl amido methyl mercaptide)

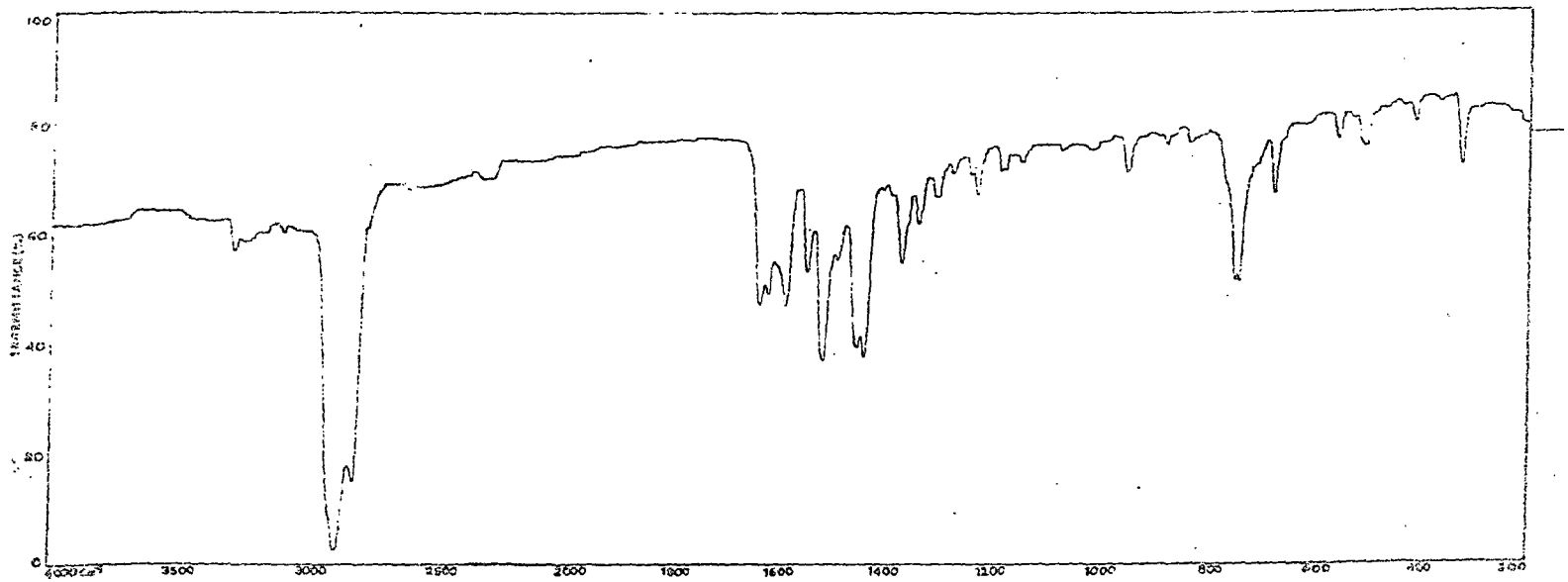


Fig. 4.25 IR spectrum of dimethyl tin bis (N-phenyl amido methyl mercaptide)

very close to the strong absorptions (Table-2). The appearance of these 'shoulders' in diorganotin derivatives may owe their origin to the presence of two types of N-phenyl thiol acetamide ligands in the compounds, one free of further coordination, the other is involved in weak intramolecular coordination through the carbonyl oxygen as evidenced by the X-ray studies on $Bu_2Sn(SCH_2CONHPh)_2$.

The ν(Sn-C) appears at ~500-600 cm^{-1} in organotin compounds[30]. The presence of ligand vibrations in these regions have obscured the identification of ν(Sn-C) bands in the compounds. However, tentative assignments have been made for these vibrations for all the new compounds (Table 2).

4.4.3.3. ^{1}H NMR Spectroscopic Studies (90 MHz and 300 MHz)

Relevant ^{1}H NMR data for the compounds are presented in Table - 3 and Table - 7.

In the ligand (PTHA), $PhNC(NH_2)SCH_2COOH$, the NH_2 proton signal appears as a broad singlet at 9.72, the OH signal as a broad singlet centered at 3.22 ppm, the CH_2 protons appear at 3.58 as a singlet whereas the aromatic protons appear as a complex multiplet centered at 7.41.

In all the synthesised compounds, the δ NH_2 and δ OH are absent. In addition, a new signal attributable to δ NH, consistent with the composition, appears between δ8.20 - δ10.3.

The δC_6H_5-Sn, δC_6H_5-CH_2-Sn, δC_4H_9-Sn and δC_6H_{11}-Sn appear as complex multiplet, the CH_2 protons of Sn-$CH_2C_6H_5$ group appear as a singlet at δ2.63. Spectra for all the compounds gave appropriate proton integrations.

^{1}H NMR Spectroscopic Studies (300 MHz):

The ^{1}H NMR of a selected number of compounds containing the ligand, N-phenyl thiol acetamide (-$SCH_2CONHPh$) were recorded at 300 MHz. All the spectra showed the expected proton peaks with satisfactory proton integrations as shown in figures 4.1-4.4 (Table 7).

The CH_2 for both Me_2- and Bu_2 - compounds show a slightly downfield shift (3.57 and 3.54 ppm respectively) compared to the corresponding Ph_3- and Cy_3- derivatives (3.36 and 3.45 ppm respectively). The X-ray crystallographic structure determinations show that in $Bu_2Sn(SCH_2CONHPh)_2$, one of the CO group is involved in coordination (intramolecular) to the tin atom whereas in $Cy_3Sn(SCH_2CONHPh)$ such coordination is absent. The downfield shift of δCH_2 in the diorgano-compounds may therefore be attributable to the deshielding effect produced aue to the coordination of CO group adjacent to the CH_2 group. Similar deshiedling effect is also observed for δNH in both dibutyl and dimethyl for δNH in both dibutyl and dimethyl-compounds compared to tricyclohexyl and triphenyl compounds (Table 7).

4.4.3.4. ^{13}C NMR Spectra:

The ^{13}C NMR spectra of a selected synthesised compounds containing the ligand, $-SCH_2CONHPh$ were recorded and presented in Table 8, Figs 4.5-4.8 . The proton decoupled carbon signals for each of the compounds were consistent with the composition and structure. It is interesting to note that the δC_6 of the CO group of the ligand for both the dibutyl and dimethyl show slightly downfield shift (See Table 8) compared to the triphenyl and tricyclohexyl derivatives. This probably suggests the involvement of CO group in coordination for the former two diorganotin compounds. Such effect is also observed for CH_2 group (C_5) adjacent to CO group (C_6) of the ligand.

4.4.3.5. UV Spectra:

UV spectra (Fig. 4.9-4.15) were recorded in Methanol. For all the compounds two peaks were found, one at around 208 nm wave length and the other at about 242 nm. The Data are presented in the table 4.

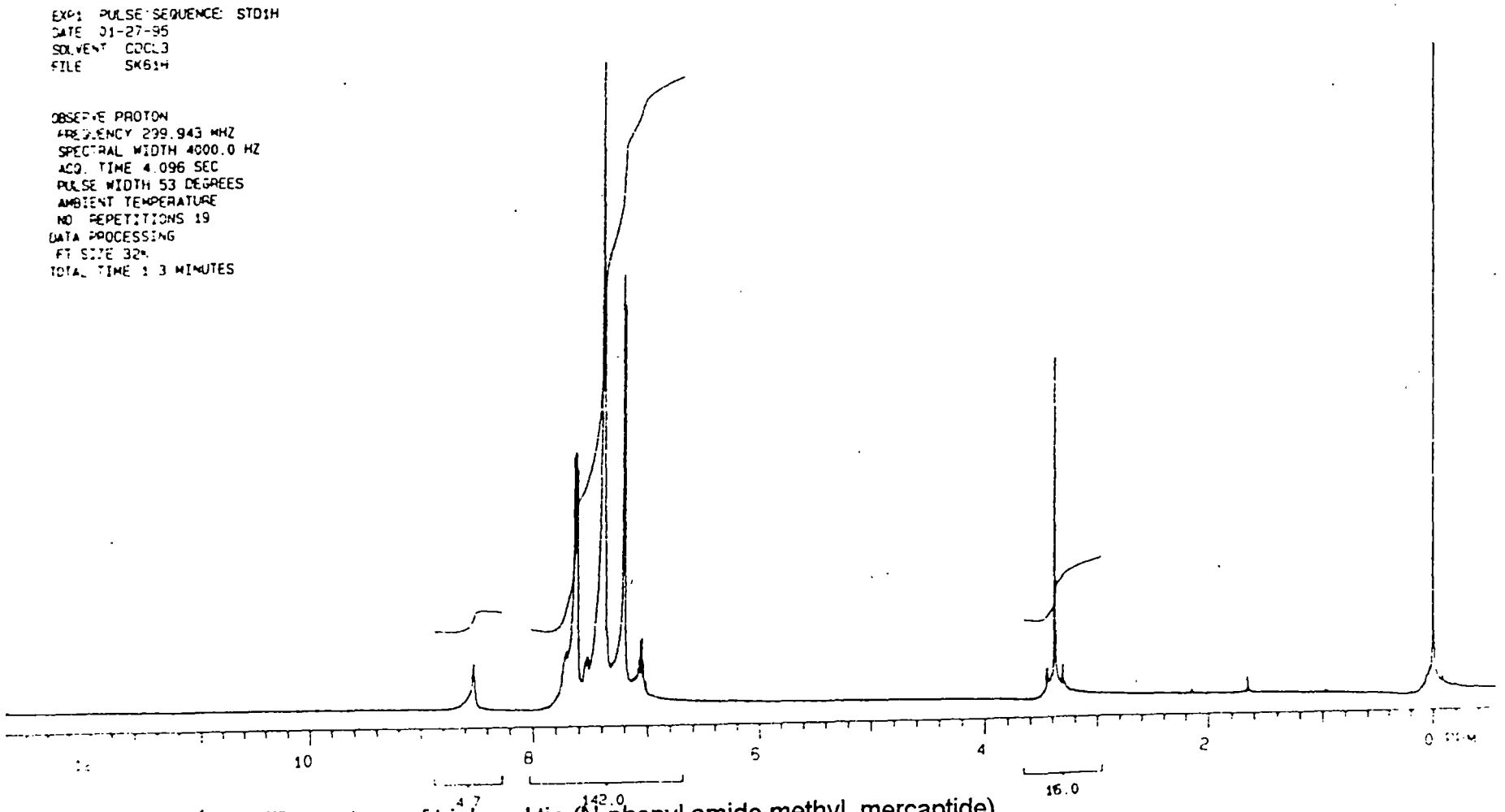


Fig. 4.1 ^{1}H NMR spectrum of triphenyl tin (N-phenyl amido methyl mercaptide)

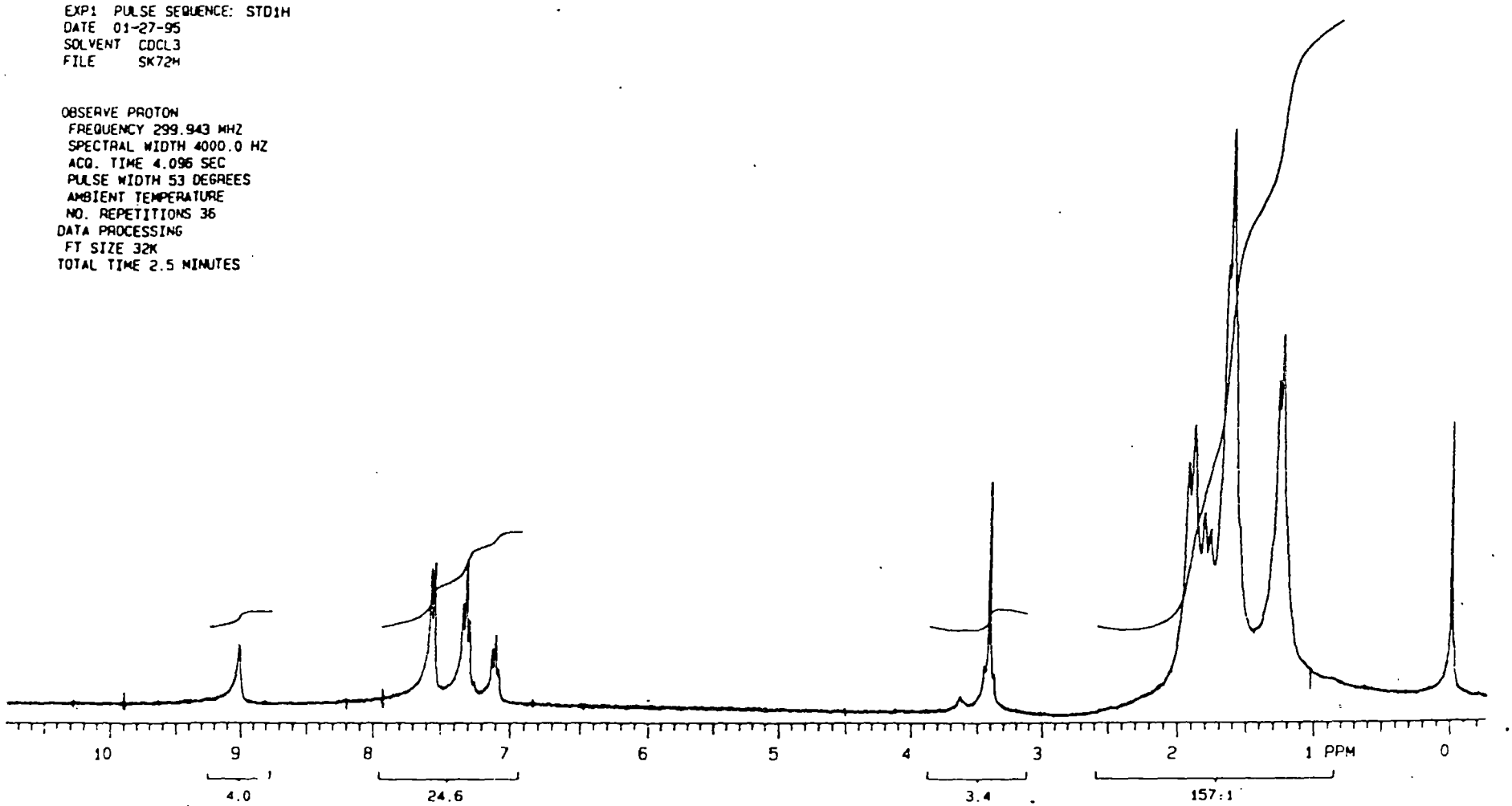


Fig. 4.2 ^{1}H NMR spectrum of tricyclohexyl tin (N-phenyl amido methyl mercaptide)

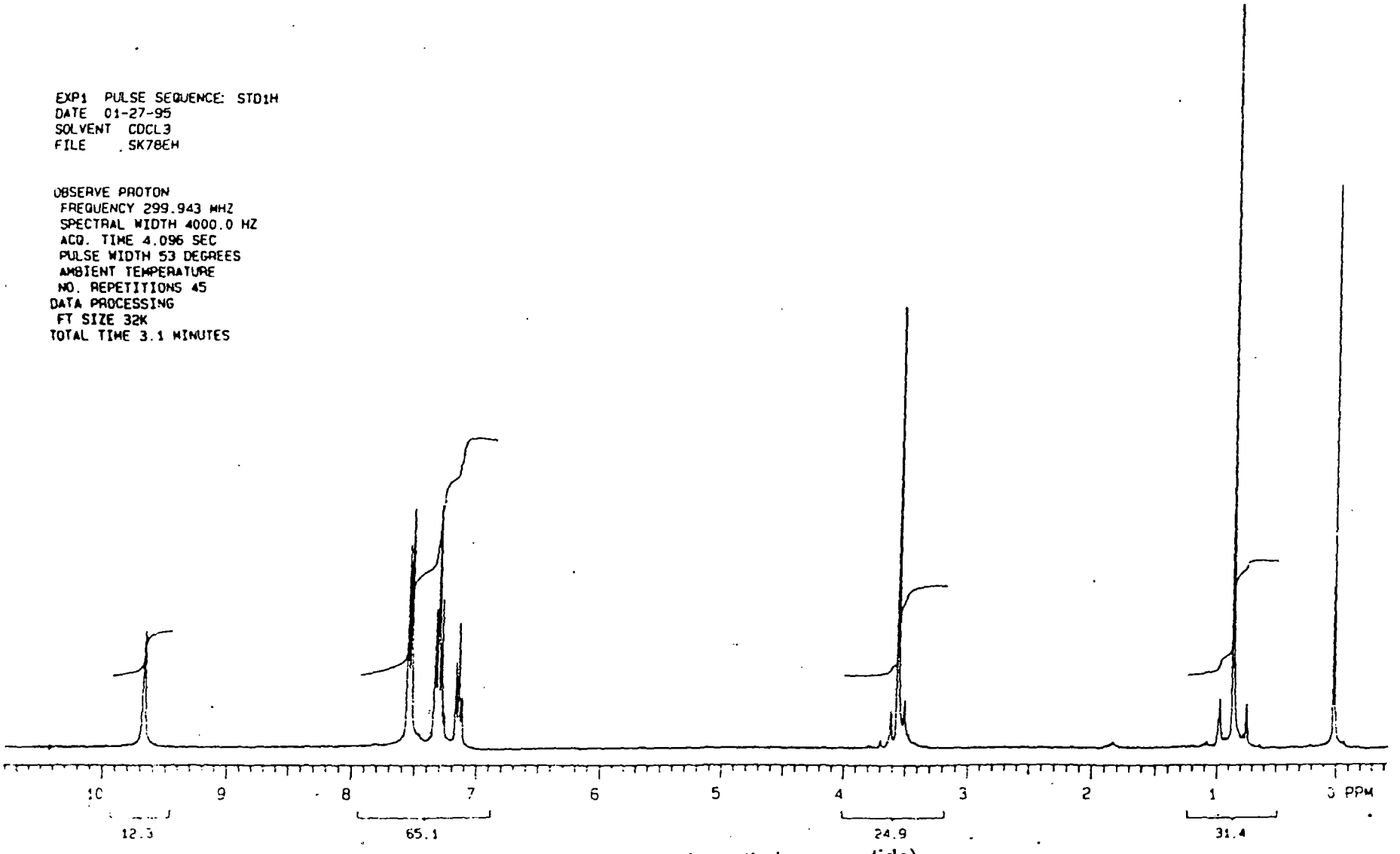


Fig. 4.3 ^{1}H NMR spectrum of dimethyl tin bis(N-phenyl amido methyl mercaptide)

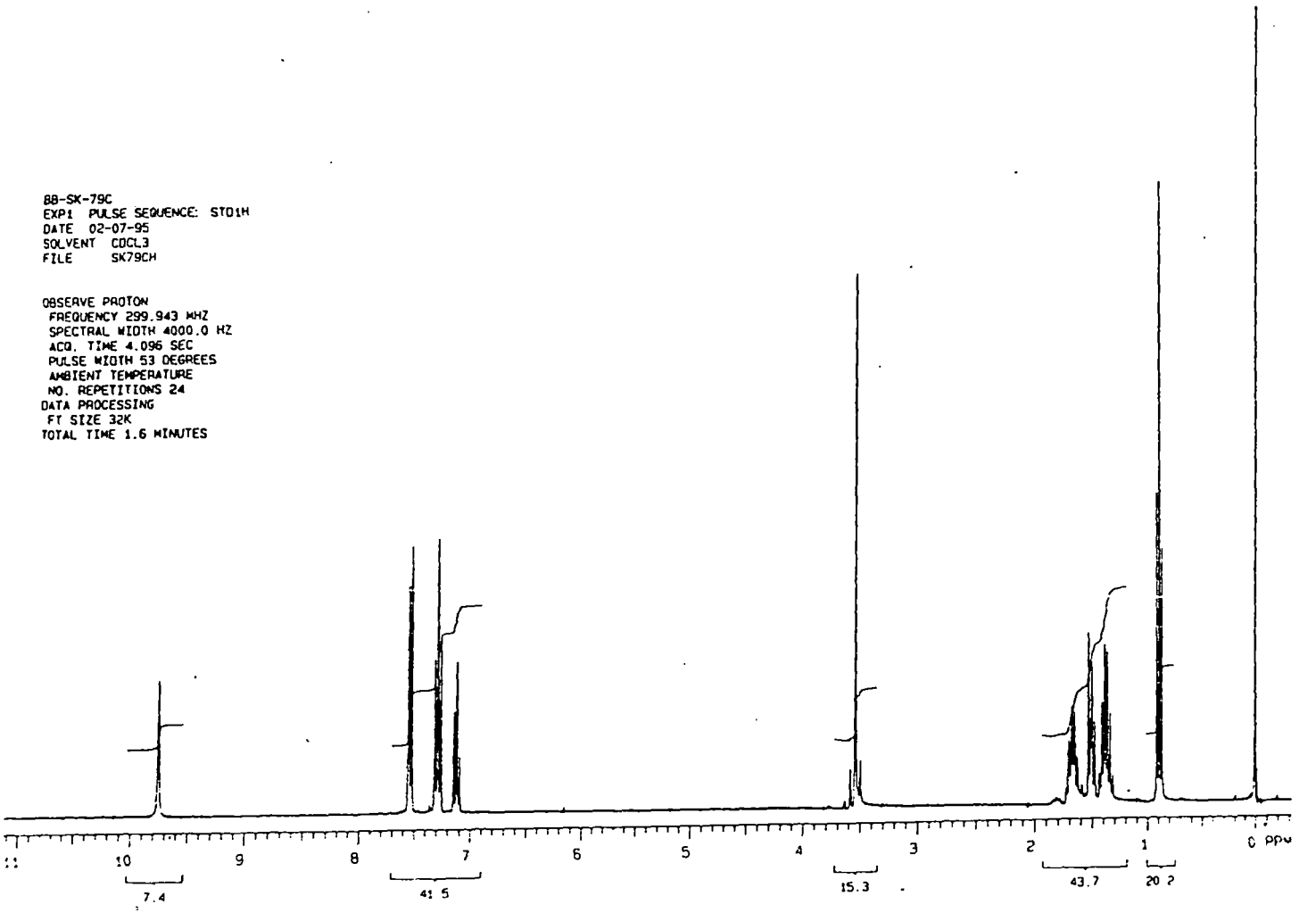


Fig. 4.4 ^{1}H NMR spectrum of dibutyl tin bis(N-phenyl amido methyl mercaptide)

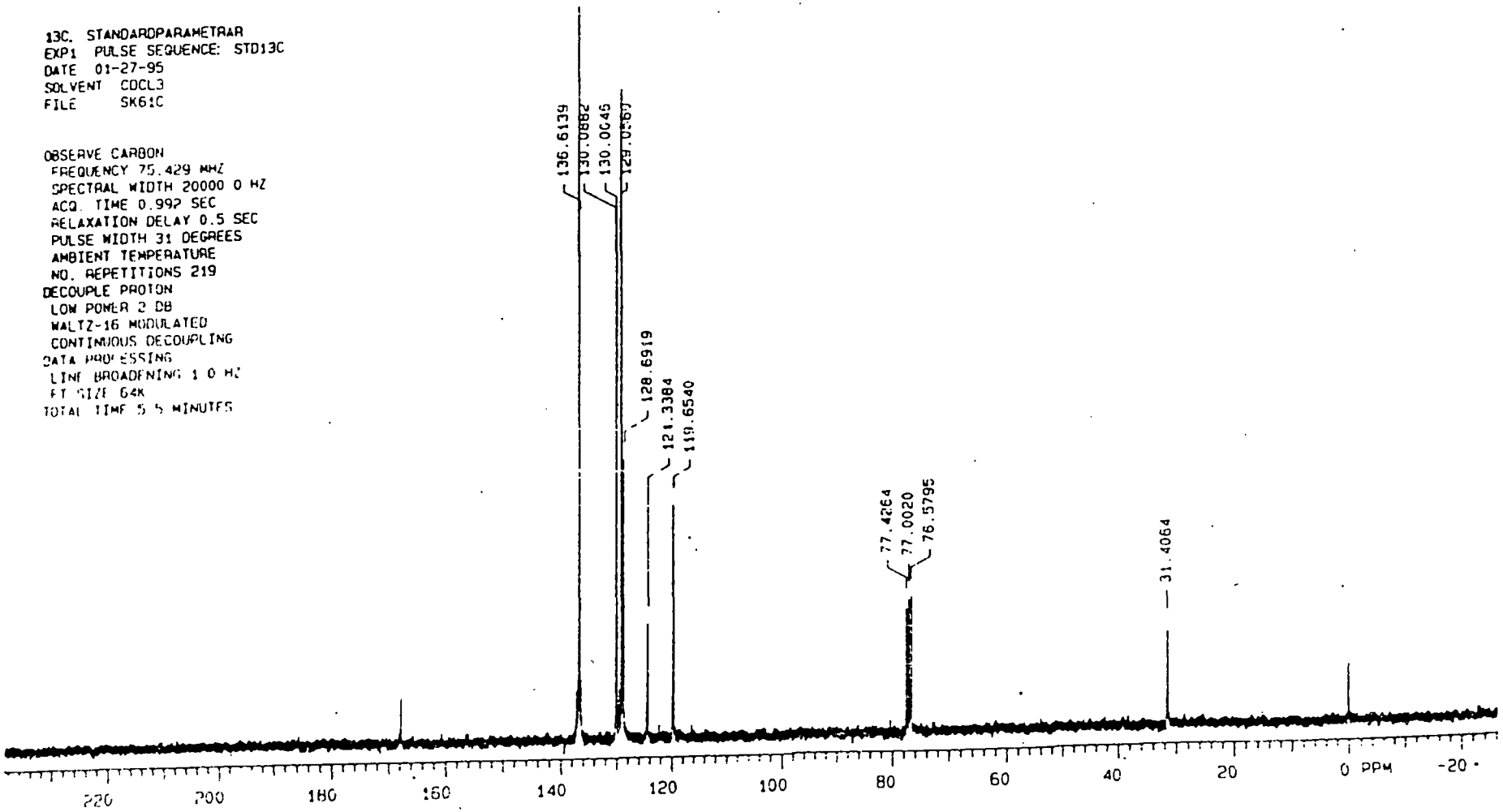


Fig. 4.5 ^{13}C NMR spectrum of triphenyl tin (N-phenyl amido methyl mercaptide)

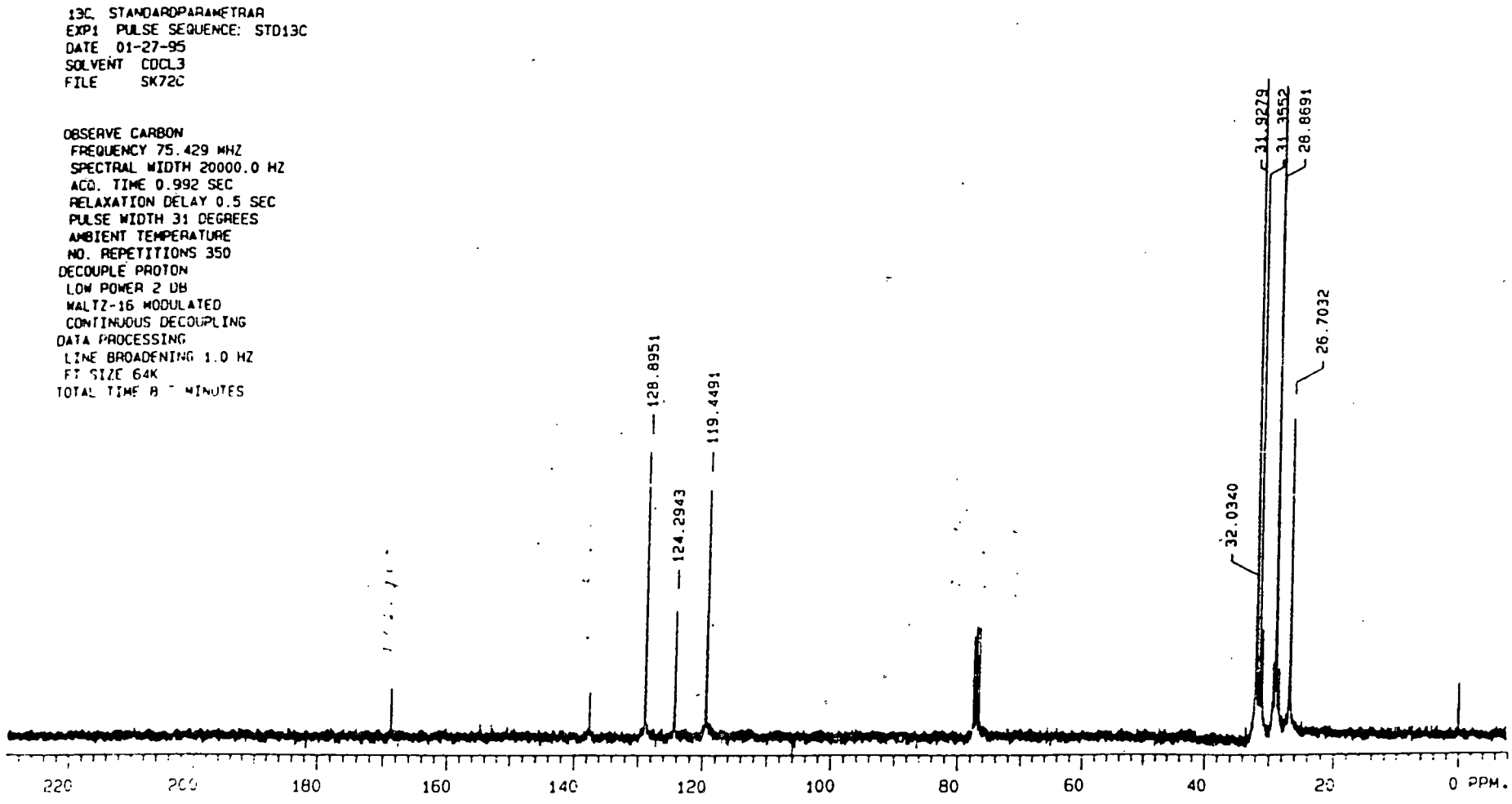


Fig. 4.6 ^{13}C NMR spectrum of tricyclohexyl tin (N-phenyl amido methyl mercaptide)

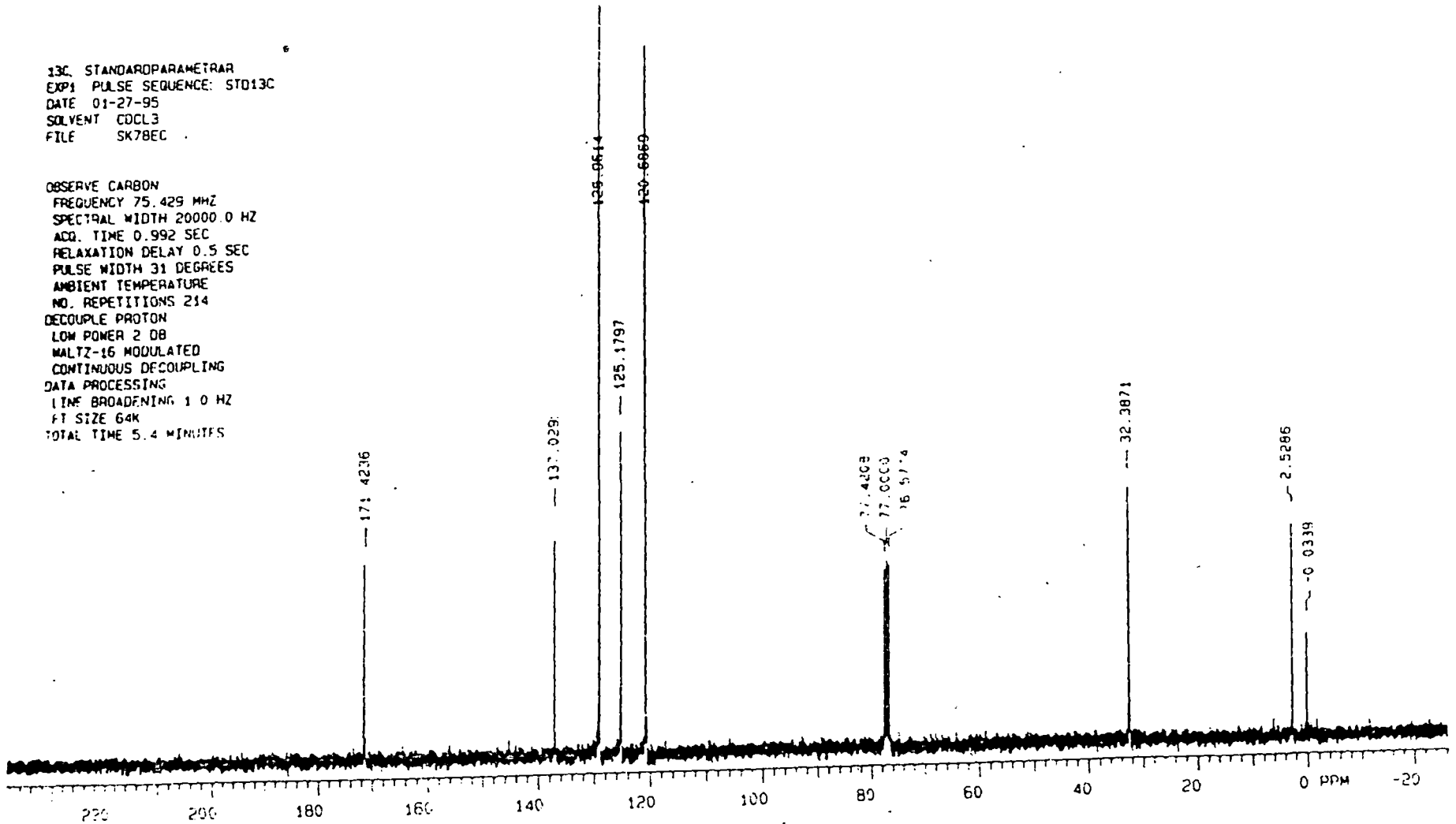


Fig. 4.7 ^{13}C NMR spectrum of dimethyl tin bis (N-phenyl amido methyl mercaptide)

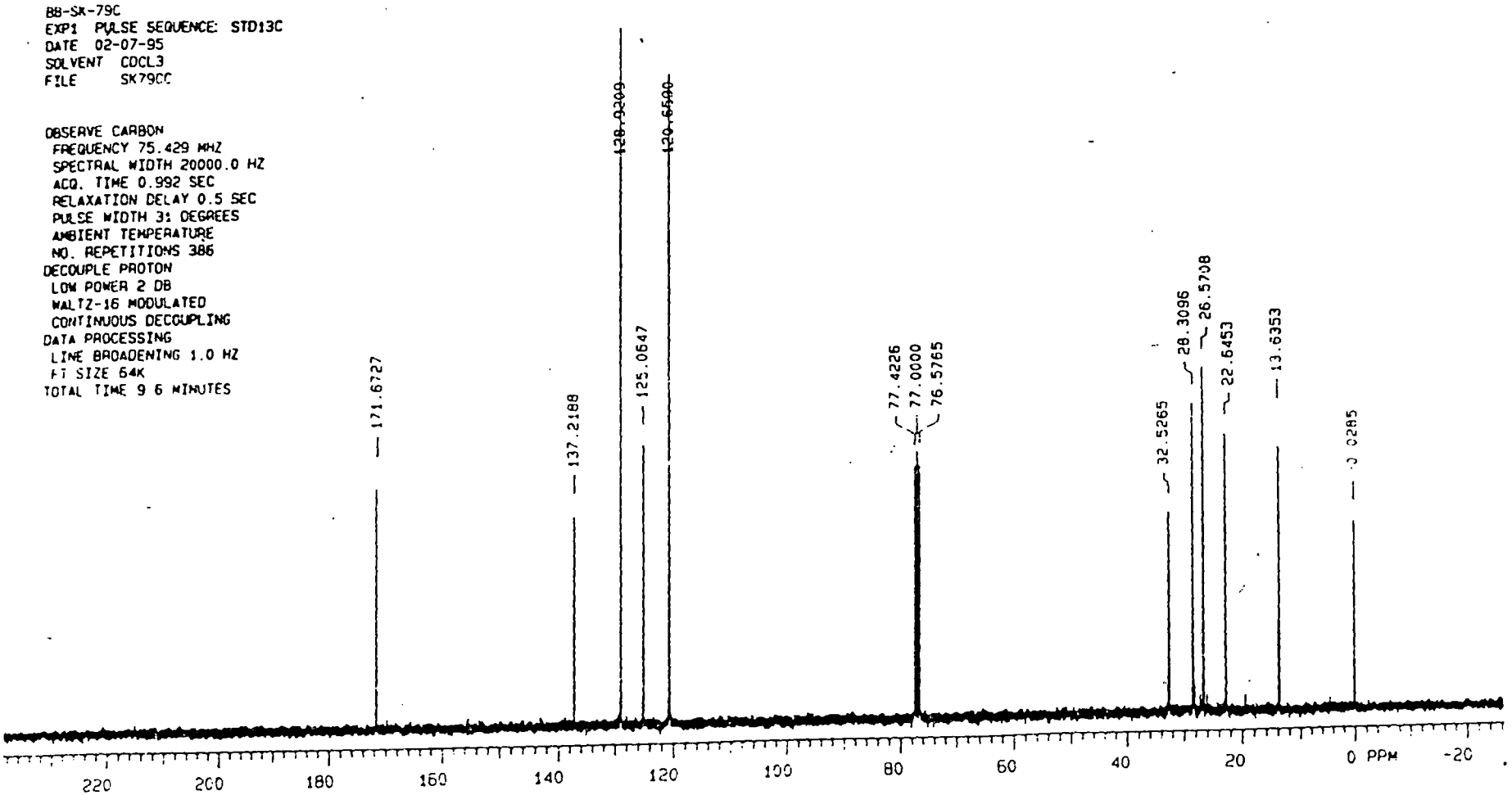


Fig. 4.8 ^{13}C NMR spectrum of dibutyl tin bis (N-phenyl amido methyl mercaptide)

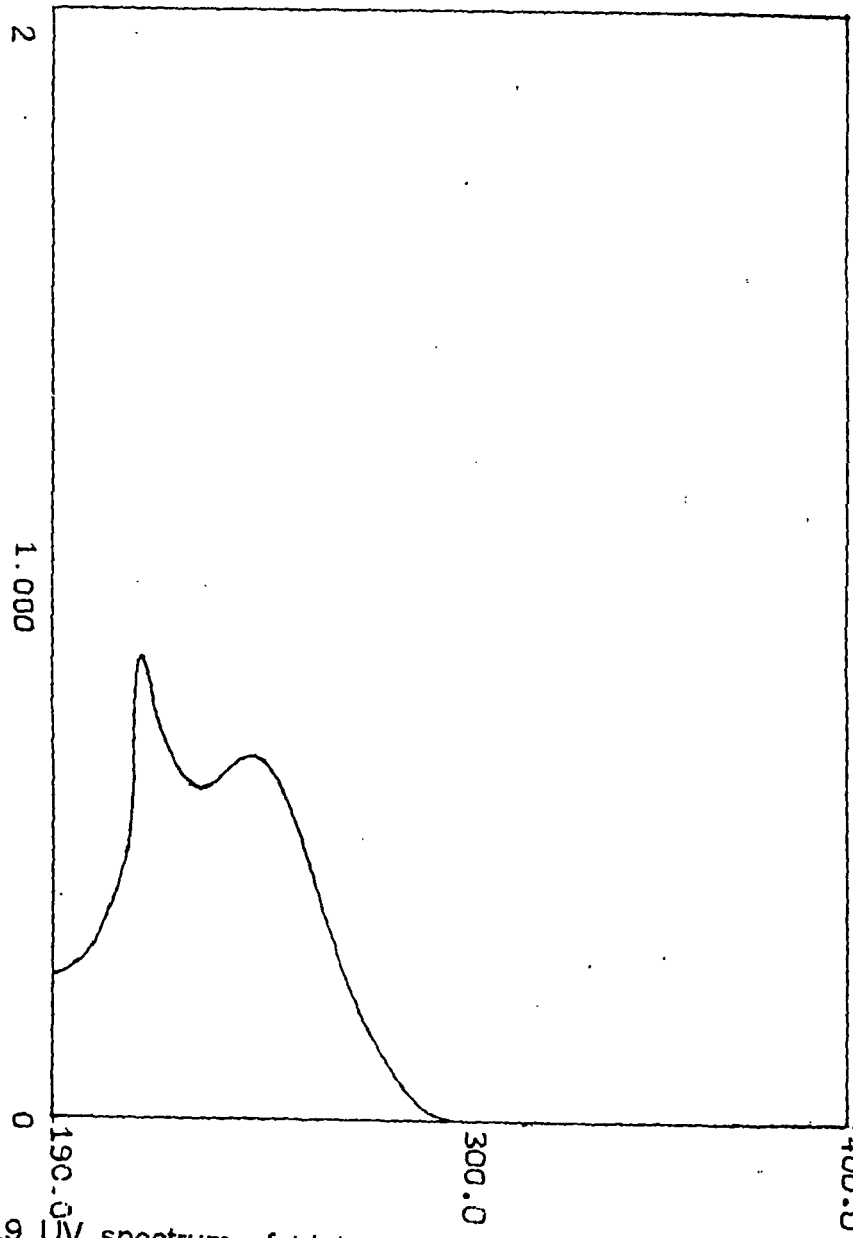


Fig.4.9 UV spectrum of triphenyl tin (N- phenyl amido methyl mercaptide)

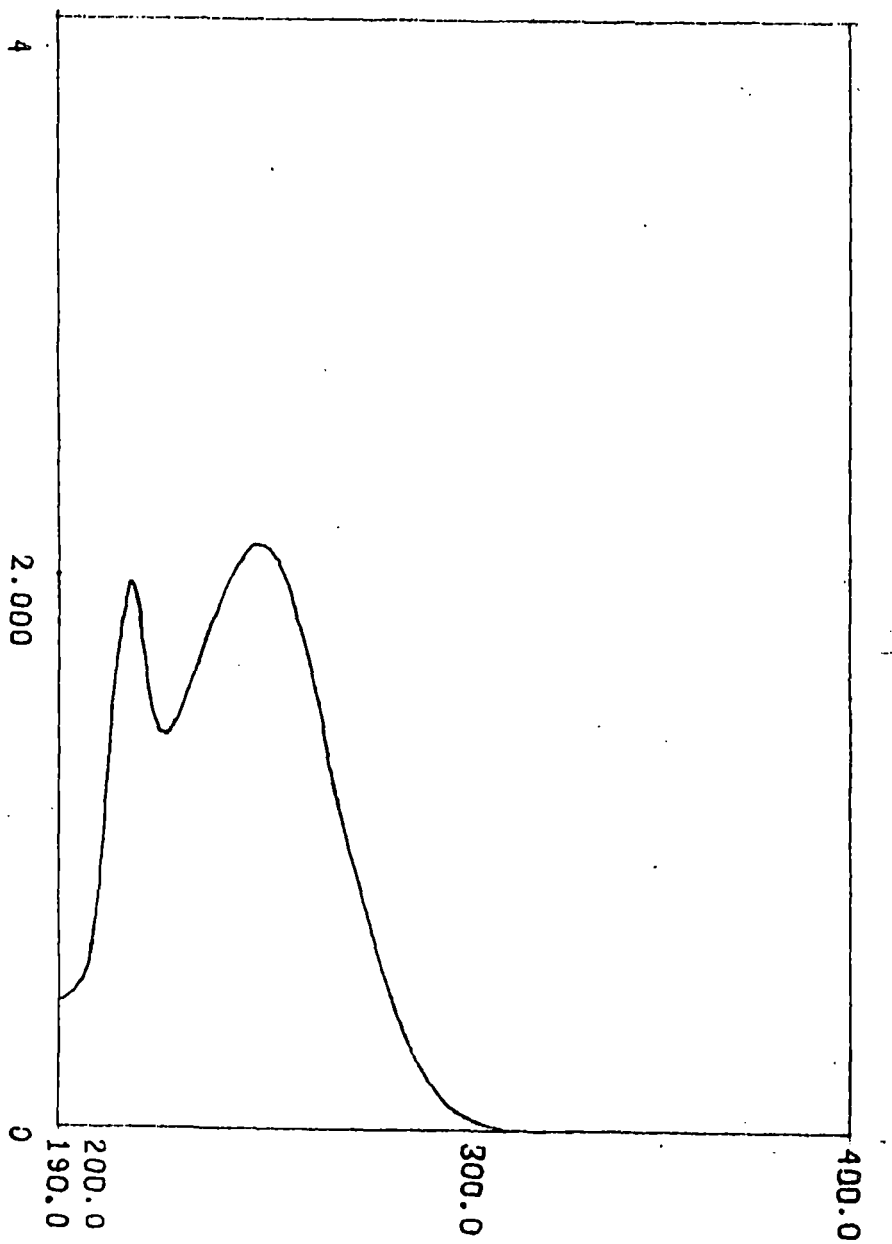


Fig.4.10 UV spectrum of tribenzyl tin (N- phenyl amido methyl mercaptide)

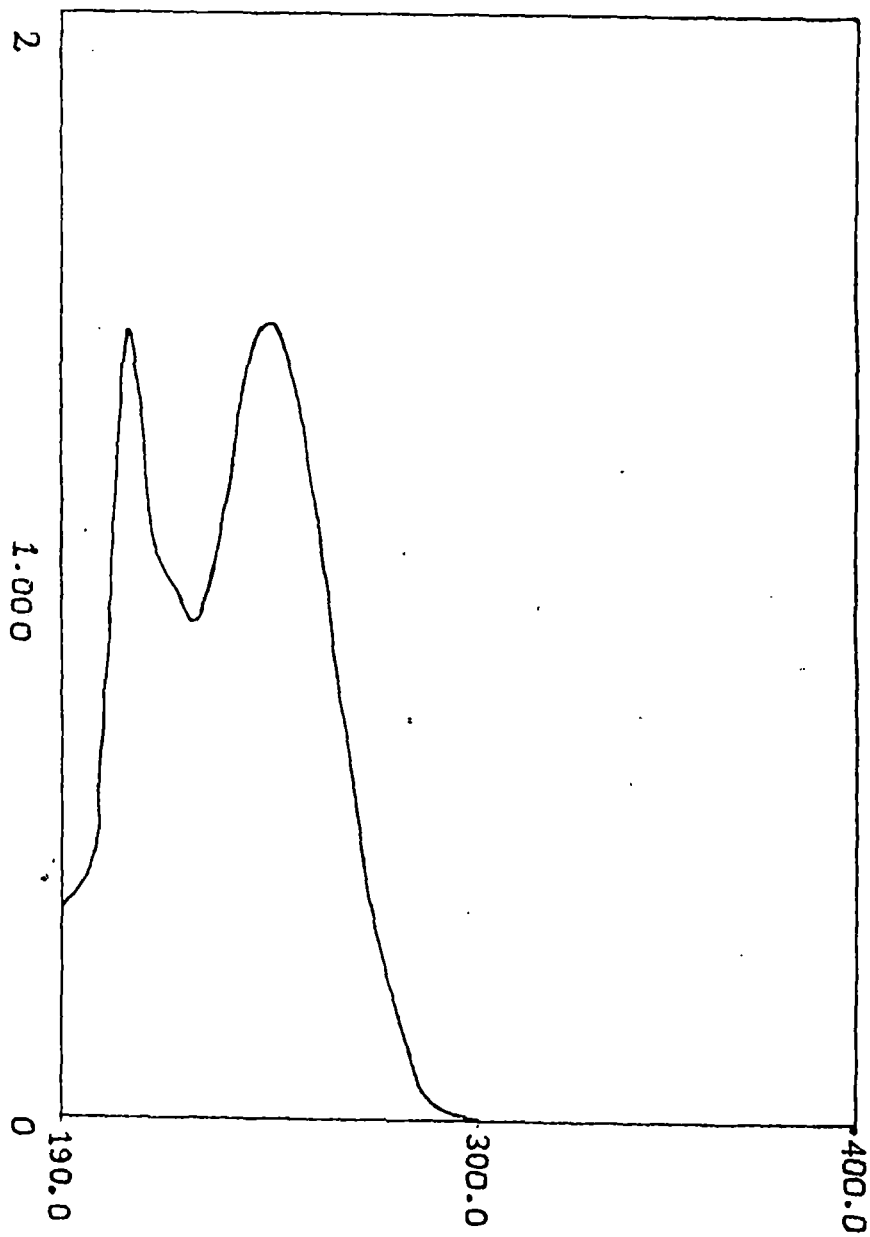


Fig.4.11 UV spectrum of diphenyl tin bis (N- phenyl amido methyl mercaptide)

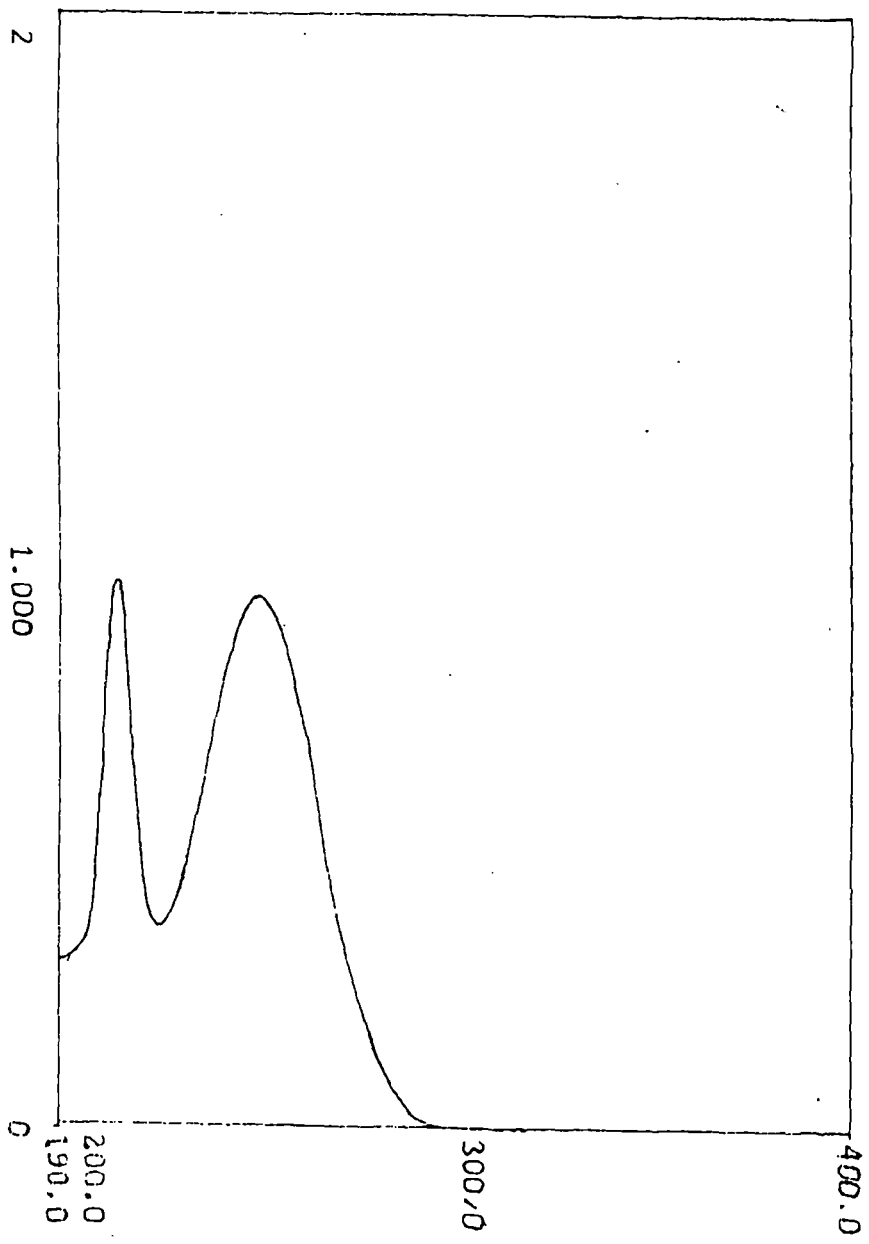


Fig.4.12 UV spectrum of dibutyl tin bis (N- phenyl amido methyl mercaptide)

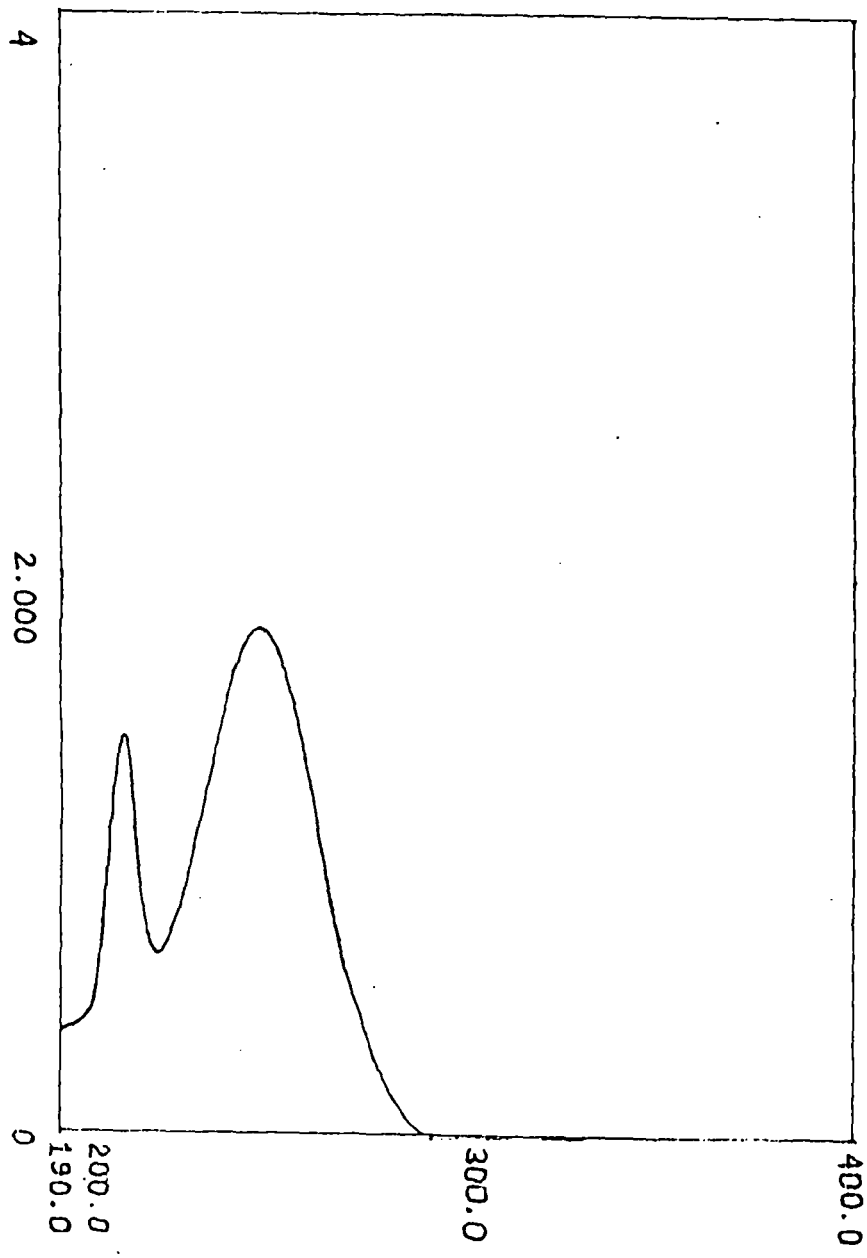


Fig 4.13 UV spectrum of dimethyl tin bis (N-phenyl amido methyl mercaptide)

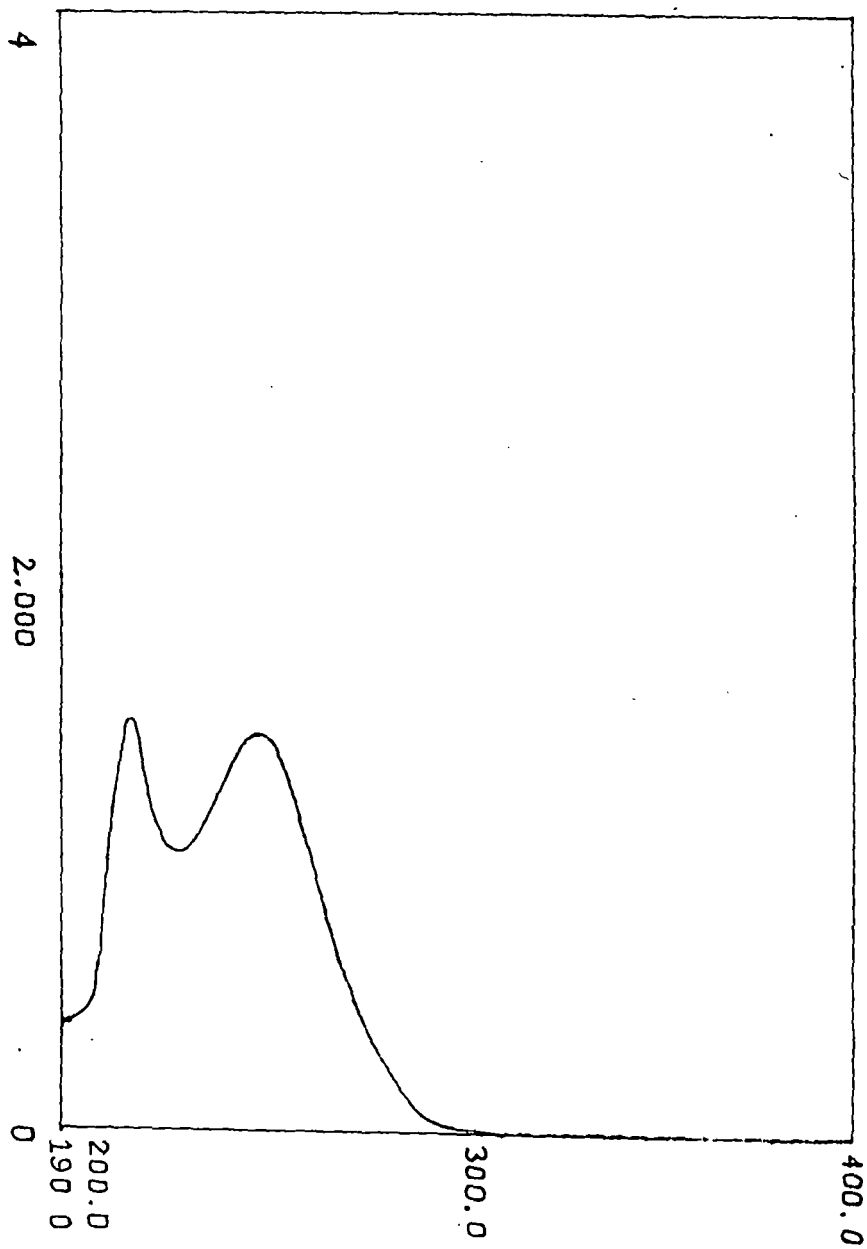


Fig. 4.14 UV spectrum of tricyclohexyl tin (N-phenyl amido methyl mercaptide)

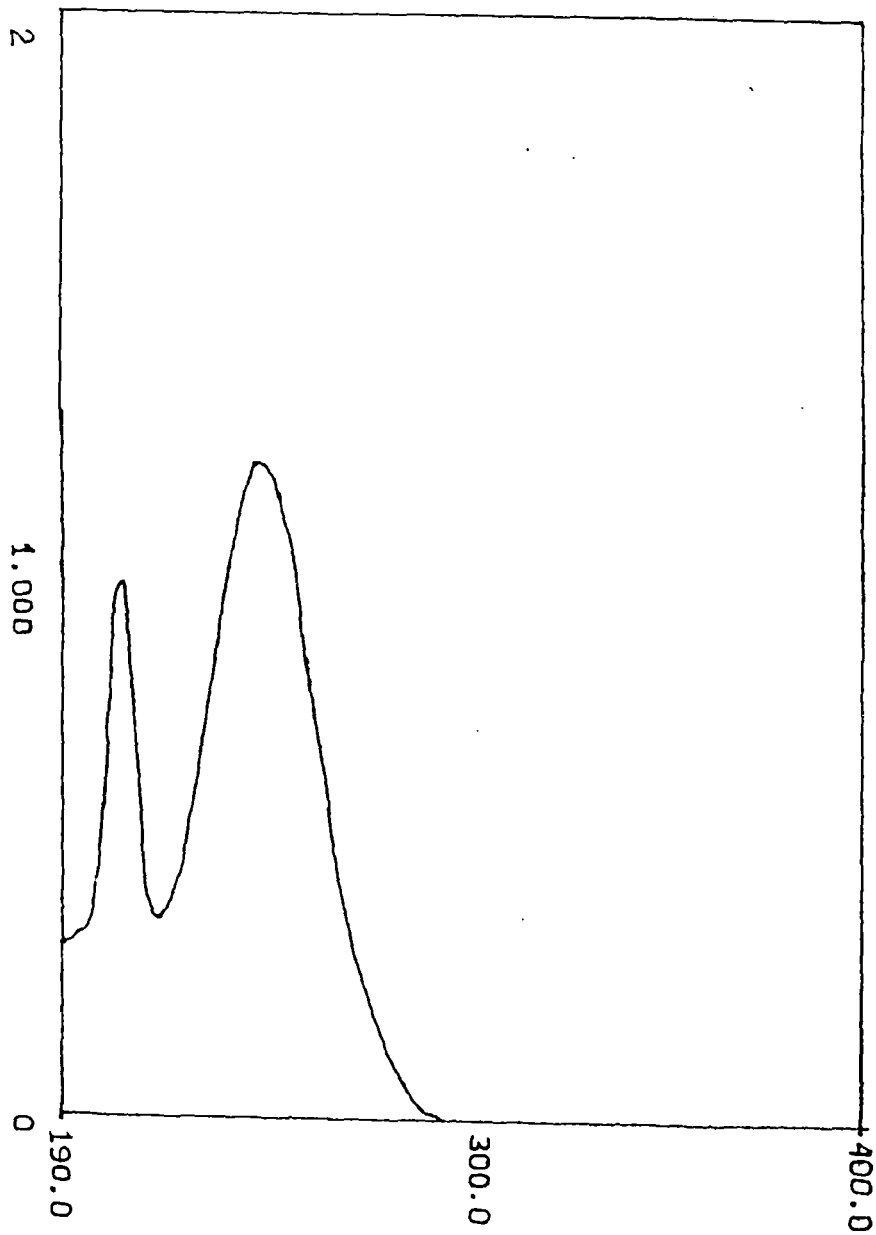


Fig. 4.15 UV spectrum of phenyl thio hydantoic acid

Table - 1 Physical Data[a]

Compound	m.p.	Yield (%)	C (%)	H (%)	N (%)	Sn (%)
Ph_3SnL	120	70	60.21 (60.50)	4.45 (4.45)	2.81 (2.71)	22.85 (23.01)
Bz_3SnL	75	41	61.62 (62.39)	4.84 (5.19)	2.82 (2.51)	20.01 (21.28)
Cy_3SnL	101	62	57.73 (58.45)	7.49 (7.68)	2.90 (2.62)	22.01 (22.24)
Ph_2SnL_2	145	40	54.17 (55.56)	3.80 (4.29)	5.55 (4.63)	19.62 (18.19)
Bu_2SnL_2	122	57	50.54 (50.00)	5.75 (6.00)	4.83 (4.95)	21.00 (21.02)
Me_2SnL_2	139	43	44.40 (44.93)	4.26 (4.57)	5.64 (5.82)	24.12 (24.69)

[a]Calculated values in parantheses (%)

L = - S-CH_2CONHPh

Table - 2. Infrared Spectral data (cm^{-1})[a]

Compound	$\nu_{asym,sym}$ (NH_2)	ν(CO_2)	ν(NH)	ν(C=O)	ν (Sn-C) asym, sym
PTHA	3390m, 3280m	1650s			
Ph_3SnL			3240m	1625s	510w, 460w
Bz_3SnL			3275w,b	1650s	565w, 515m
Cy_3SnL			3260m	1650s	535w, 510m
Ph_2SnL_2			3260w,b	1610s, 1600sh	510m, 460w
Bu_2SnL_2			3260m,b	1640s, 1625sh	515m, 505w
Me_2SnL_2			3255m,b	1650s, 1630sh	560w, 520m

[a] All spectra were recorded as KBr pellets in the range 4000-600 cm^{-1} and as Nujol mulls on CsI windows in the range 600-200 cm^{-1}.

S = Strong, m = medium, w = weak, sh = shoulder, b = broad.

PTHA = $PhNC(NH_2)SCH_2COOH$

L = $-SCH_2CONHPh$

Table - 3. ^{1}H NMR Spectroscopic data[c] (90 MHz)

Compound	Protons of organic groups on tin		Ligand protons	
	δPh of ligand/ $SnPh/SnCH_2Ph$	δ CH_2 of $SnCH_2Ph$	δ NH	δ CH_2
Bz_3SnL[a]	7.26m(20)	2.63s(6) $^{2}J(^{117}Sn-^{1}H)$-57 Hz $^{2}J(^{119}Sn-^{1}H)$-63 Hz	8.20,s(1)	3.23s(2)
Ph_2SnL_2[b]	7.52m(20)		10.33s(2)	3.51s(4)

[a] Spectra recorded in saturated solution of $CDCl_3$

[b] Spectra recorded in saturated solution of d_6-DMSO

[c] ppm relative to Me_4Si, s = singlet, m = complex multiplet. Data in paranthesis indicate number of protons.

L = $-S-CH_2CONHPh$

Table - 7. ^{1}H NMR Spectroscopic data[a] (300 MHz)

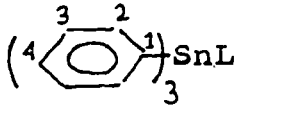
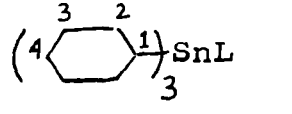
Compound	δ NH	δSn-Bu/Cy/Me	δSn-Ph/N-Ph	δ CH_2	
Ph_3SnL	8.526(1),S		7.05-7.736(20),m	3.368(2),S	47.1 Hz
Cy_3SnL	9.01(1),S	1.26-1.93(33),m	7.09-7.59(5),m	3.45(2),s	27.27 Hz
Me_2SnL_2	9.69(2),S	0.882(6),S $^{2}JSn-Ch$ 78.94 Hz	7.11-7.57(10),m	3.57(4),S	40.90 Hz
Bu_2SnL_2	9.75(2),S	0.865-1.712(18),m	7.10-7.55(10),m	3.54(4),S	27.27 Hz

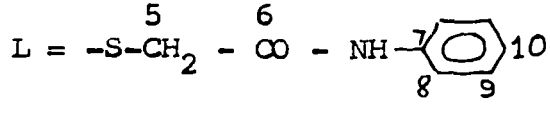
L = $-SCH_2CONHPh$

a = Spectra recorded in $CDCl_3$, chemical shift in ppm downfield relative to Me_4Si as internal standard.

S = Singlet, m = multiplet.

Table - 8. ^{13}C NMR Spectroscopic data (δppm)[a]

Compound	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}
	136.61	130.08	130.00	129.05	31.40	168.00	136.75	128.69	119.65	124.33
	31.92	31.35	28.86	26.70	32.03	168.75	137.51	128.89	119.44	124.29
$(\overset{1}{C}H_3)_2SnL_2$	2.52				32.38	171.42	137.02	128.96	120.68	125.17
$(\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}H_2)_2SnL_2$	28.30	26.57	22.64	13.63	32.52	171.67	137.21	128.92	125.06	120.65

L = 

a = Spectra recorded in $CDCl_3$

Table 4

Compound	λ_{max} (nm)	ϵ_{max}	Other absorption (nm)
Ph_3SnL	212	1.80×10^4	241
Bz_3SnL	242	3.75×10^4	209
Ph_2SnL_2	244	3.95×10^4	208
Bu_2SnL_2	205	6.16×10^4	242
Me_2SnL_2	245	0.78×10^4	206
Cy_3SnL	208	2.15×10^4	242
$PhNC(NH_2)SCH_2COOH$, (ligand)	243	3.33×10^4	210

L = $-S-CH_2-CONHPh$

4.4.3.6. ^{119}Sn Mössbauer Spectroscopy:

A selection of compounds of the tri- and di-series were examined by tin-119 Mössbauer Spectroscopy. The data are summarised in Table 9. The small increase in the Isomer Shift (IS) value for $Cy_3SnSCH_2CONHPh$ compared with $Ph_3SnSCH_2CONHPh$ and for $Me_2Sn(SCH_2CONHPh)_2$, $Bu_2Sn(SCH_2CONHPh)_2$ compared with $Ph_2Sn(SCH_2CONHPh)_2$ are due to reduced electron withdrawing ability of the cyclohexyl, methyl and butyl group substituents compared with phenyl group.

Both $Ph_3SnSCH_2CONHPh$ (1.49 mms^{-1}) and $Cy_3SnSCH_2CONHPh$ (1.85 mms^{-1}) show quadrupole splitting (QS) typical of regular tetrahedral triorganotin compounds (1.00-2.40 mms^{-1})[61]. $Cy_3SnSCH_2CONHPh$ has a tetrahedral structure (please see the crystal structure description later). Similarly the QS data suggests $Ph_3SnSCH_2CONHPh$ to have a tetrahedral structure like the tricyclohexyl derivative.

Five coordinate Cis and trans R_3SnX show QS values in the range of 1.70-2.40 mms^{-1} and 3.00-4.00 mms^{-1} respectively. The octahedral R_2SnX_4 may also show two types of QS parameters corresponding to Cis ($\sim$ 2.00 mms^{-1}) and trans ($\sim$4.00 mms^{-1}). The compound $Bu_2Sn(SCH_2CONHPh)_2$ has QS value of 2.35 mms^{-1} and possesses a tetrahedral structure distorted towards five coordinate Cis structure with Cis C_2SSnSO coordination sphere[62] as evident from X-ray crystal structure determinations (a brief description is presented later).

The similarity of QS value for $Ph_2Sn(SCH_2CONHPh)_2$ of 2.53 mms^{-1} suggests a similar structural core of C_2SSnSO in $Ph_2Sn(SCH_2CONHPh)_2$.

The QS value for $Me_2Sn(SCH_2CONHPh)_2$ is 3.12, slightly higher than the corresponding Bu_2- and Ph_2- compounds. The less bulky Me groups around the tin atom might allow further expansion of the coordination sphere leading to six coordination through the CO group of the second ligand (QS values for trans

Table - 9. ^{119}Sn Mössbauer (mms^{-1}) data for selected compounds[a]

Compound	IS	QS	Γ
Ph_3SnL	1.29	1.49	0.84, 0.83
Cy_3SnL	1.50	1.85	0.89, 0.89
Bu_2SnL_2	1.38	2.35	0.91, 0.88
Ph_2SnL_2	1.19	2.53	1.02, 0.95
Me_2SnL_2	1.30	3.02	0.92, 0.91

a = Data recorded at 78K; relative to $CaSnO_3$.

L = $-SCH_2CONHPh$

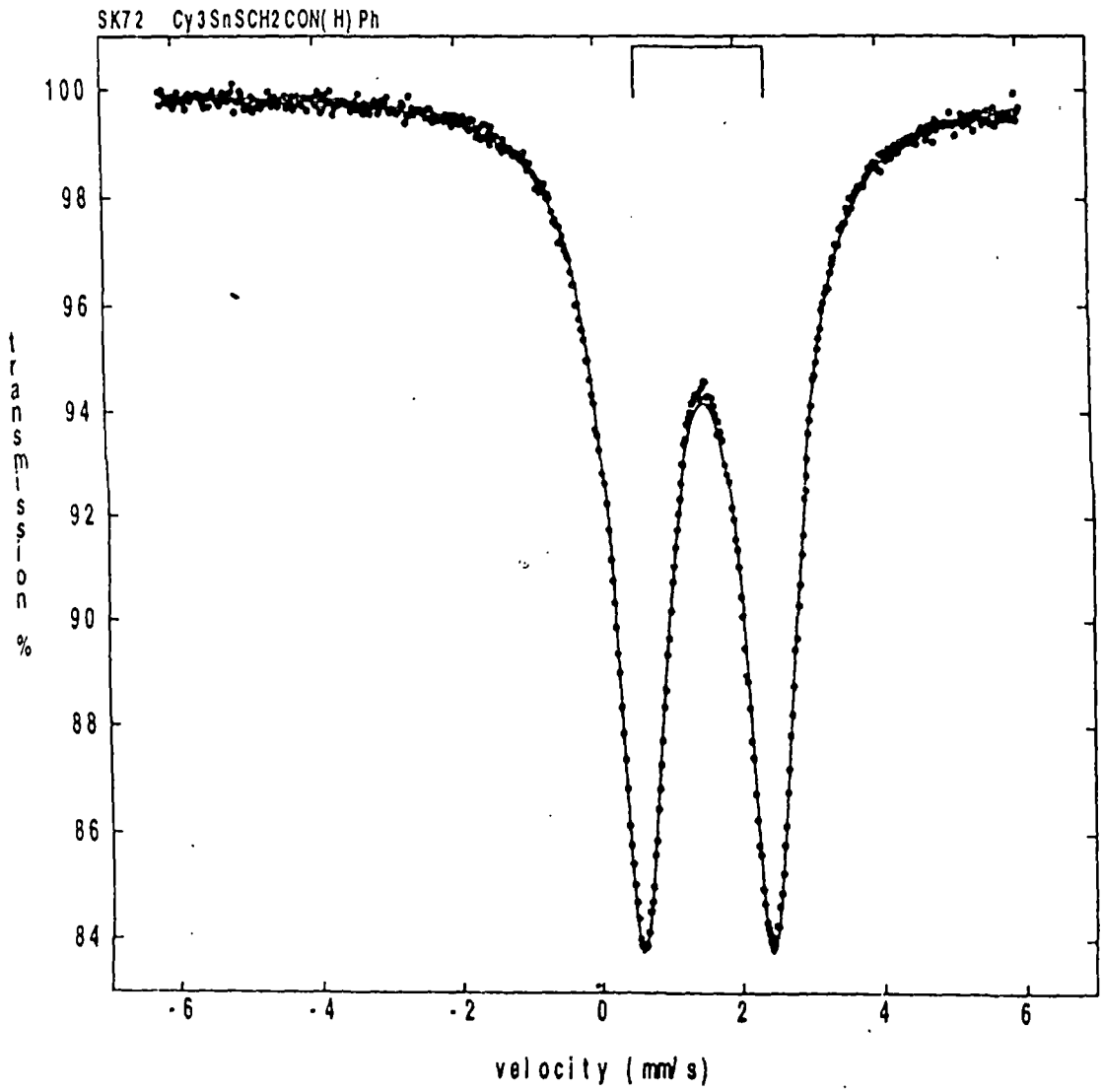


Fig. 4.18 ^{119}Sn Mossbauer spectrum of tricyclohexyl tin (N-phenyl amido methyl mercaptide)

$R_2SnX_4 \approx 4.00$ mms^{-1} and Cis $R_2SnX_4 \approx 2.00$ mms^{-1})[61]. However, it is also likely for the $Me_2Sn(SCH_2CONHPh)_2$ to be isostructural with $Bu_2Sn(SCH_2CONHPh)_2$, the exact geometry, can not be ascertained at present without the X-ray crystallographic data.

Mossbauer spectra of $Cy_3SnSCH_2CONHPh$ is given in Fig. 4.18.

4.4.3.7. Crystal Structure:

The study of the structural chemistry of organotin compounds has received considerable attention owing to the various structural types that are adopted in the solid state. These may be monomeric or polymeric species. Organotin compounds, therefore, are always interesting to study structurally. In the present study we have investigated two compounds as representative of tricyclohexyland dibutyl series containing the thio ligand, namely, $-S-CH_2-CONHC_6H_5$. The crystallographic works were carried out in collaboration with Dr. C.J. Cardin at the chemistry laboratory, Reading University, U.K. A brief description of the two structures are presented below:

EXPERIMENTAL SECTION FOR $Cy_3SnSCH_2CONHPh$

Crystal data:

$C_{26}H_{41}NOSSn$, MW.= 534.36 Triclinic. a = 9.565(6), b = 13.763(6), c = 21.701(6) A, α = 100.69°(6), β = 99.70°(6), γ = 107.88°(6), U = 2592.9A^3, Dc = 1.320 $gr.cm^{-3}$, Z = 4 , F(000) = 1036., λ = 0.71069 A, μ(Mo-K_α) = 10.81 cm^{-1}.

Data collection and reduction:

A crystal approximate size 0.1 x 0.2 x 0.2 mm^3, was mounted on an Mar Research image plate scanner, and graphite monochromated Mo-K_α radiation was used to measure 95 2° frames with an exposure time of 120 sec per frame the data were corrected using the XDS package to give 7234 unique reflections (R_{sigma} = 0.0307).

Structure solution and refinement:

The structure was solved by the direct method SHELX 86 and refined using SHELXL (courtesy of Prof. G.M. Sheldrick, University of Gottingen), by full-matrix least squares of 557 variables, to a final R-factor of 0.0718 for 5670 reflections with $[Fo] > 4_\alpha(F)$. All atoms (including hydrogens) were revealed by difference Fourier maps. Non-hydrogens atoms were refined anisotropically, Hydrogen atoms were placed geometrically and refined with a fixed temperature factor of 0.05. The final difference Fourier map had a largest peak of 1.280A^{-3}.

Crystal Structure of $Cy_3SnSCH_2CONHPh$:

The structure of $[Cy_3Sn(SCH_2CONHPh)]$ is shown in Fig. 4.16, and selected inter atomic parameters are listed in Table 10. It should be pointed out here that as mentioned in Section 4.4.3.1, the ligand $PhNC(NH_2)SCH_2COO^-$ has undergone rearrangement to $\bar{S}SCH_2CONHPh$ during the reaction which is being also indicated by the crystallographic data e.g., the angle O(1)-C(2)-N(1) is 123.4(8)°, the bond lengths, N(1)-C(2) is 1.339(11)A°, O(1)-C(2) is 1.230(11)A° and S(1)-C(1) is 1.808(9)A°. The ligand, $\bar{S}CH_2CONHPh$ coordinates the tin atom via the sulpher atom forming a Sn-S(1) interaction of 2.425(2)A°. There is no significant interaction between Sn(1)-O(1) or Sn(1)-N(1) atoms. The absence of other significant inter- or intra- molecular interactions involving the tin atom confirms the monodentate mode of coordination of the ligand. The angles, C(10)-Sn(1)-C(30) of 112.9(4)°, C(10)-Sn(1)-C(20) of 110.0(4)°, C(30)-Sn(1)-C(20) of 107.7(4)°, C(10)-Sn(1)-S(1) of 116.7(2)° and C(30)-Sn(1)-S(1) of 107.0(3)° indicates that the tin atom environment is slightly distorted tetrahedral. The maximum distortion from the ideal tetrahedral geometry being manifested in the C(10)-Sn(1)-S(1) angle of 116.7(2)° which may be traced to the proximity of the non-coordinating O(1) atom. The non-coordinating nature of the atom O(1) is indicated by the bond length O(1)-C(2) of 1.230(11)A°. The angle C(1)-S(1)-Sn(1) of 108.5(3)° is indicative of tetrahedral environment around the atom S(1).

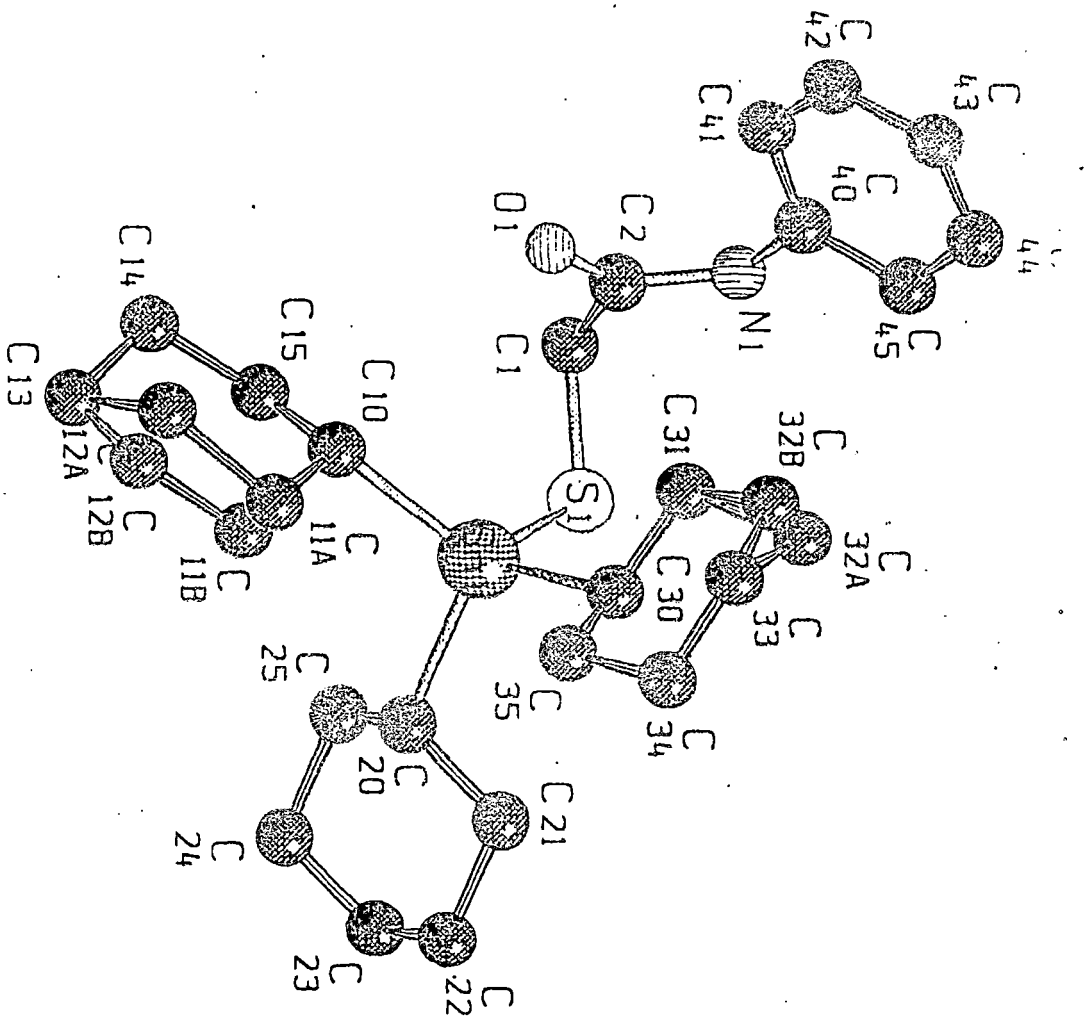


Fig. 4.16 The molecular structure and crystallographic numbering scheme for tricyclohexyl tin (N-phenyl amido methyl mercaptide)

Crystal Structure of $Bu_2Sn(SCH_2CONHC_6H_5)_2$:

The molecular structure of $Bu_2Sn(SCH_2CONHC_6H_5)_2$ is shown in Fig. 4.17 and selected inter atomic parameters are given in Table 15. It may be seen from Fig. 4.17 that the structure adopted an intermediate between tetrahedral and cis-trigonal bipyramidal structural type[63]. The Sn atom exists in a distorted trigonal bipyramidal geometry with trigonal plane formed by two Sn(1)-C(11,21) and one Sn(1)-S(1) bonds. The axial sites are occupied by the O(1) atom, Sn(1)-O(1) 2.472(4)A^o, and the S(2) at 2.460(2)A^o, distorted S(2)Sn(1)O(1) angle is 166.89(13)^o. The $-SCH_2CONHC_6H_5$ ligand spans equatorial and axial sites. The Sn(1)-S(2) bond in the second axial site trans to the co-ordinate Sn ..... O(1) bond is marginally longer [2.472(4)A^o] compared to Sn(1)-S(1) bond [2.395(2)A^o], whilst the sum of the equatorial angles at tin is 353.1^o. The axial-equatorial angles C(11)Sn(1)S(2) and C(11)Sn(1)S(1) are 96.6(2)^o and 120.4(2)^o respectively. The close proximity of the O(1) atom influences the coordination geometry about the Sn atom by opening up both the C(11)Sn(1)S(1) = 120.4(2)^o and C(11)Sn(1)C(21) = 119.9(3)^o respectively compared to the S(1)Sn(1)C(21) angle = 112.8(2)^o. Notable in the structure is the non-involvement of the O(2) oxygen in inter or intramolecular coordination. The compound is monomeric, in which the S(1)Sn(1)O(1) bite angle is 75.71(11)^o.

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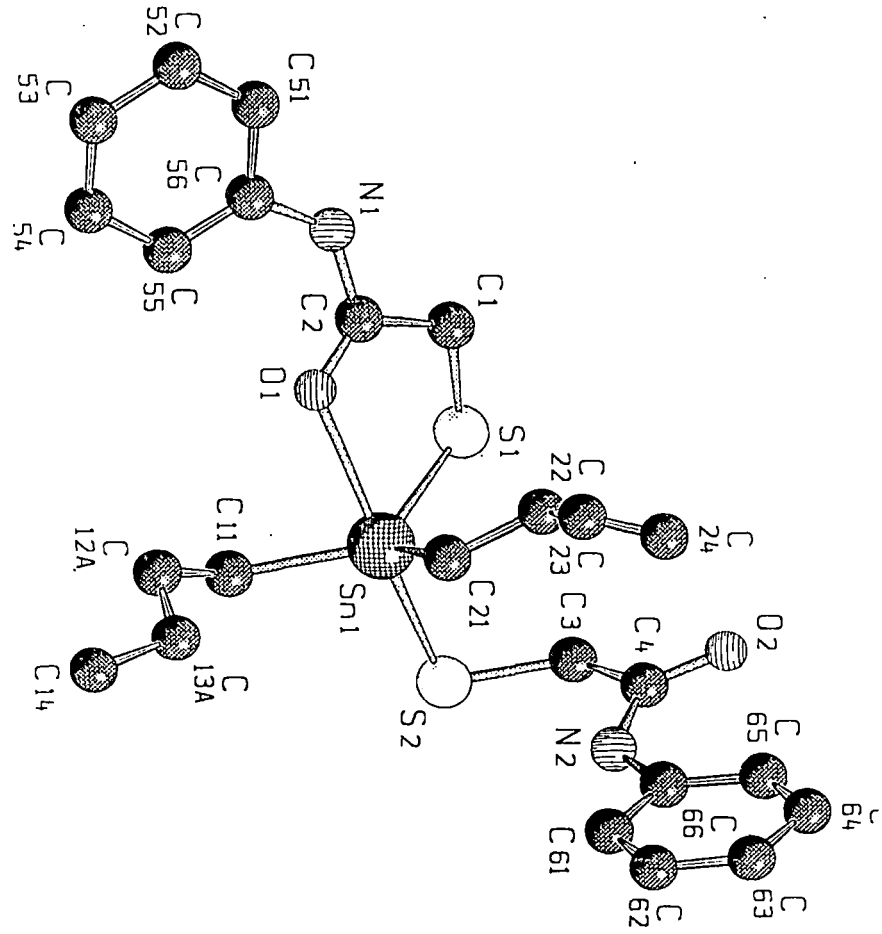

Fig. 4.17 The molecular structure and crystallographic numbering scheme for dibutyl tin bis (N-phenyl amido methyl mercaptide)

Table 10 Selected bond lengths (A) and angles (deg.) for $Cy_3SnSCH_2CONHPh$

Sn(1)-C(10)	2.114(10
Sn(1)-C(30)	2.160(9)
Sn(1)-C(20)	2.162(9)
Sn(1)-S(1)	2.425(2)
Sn(2)-C(70B)	2.11(3)
Sn(2)-C(50)	2.137(11)
Sn(2)-C(60)	2.171(13)
Sn(2)-C(70A)	2.22(2)
Sn(2)-S(2)	2.423(3)
S(1)-C(1)	1.808(9)
S(2)-C(3)	1.816(10)
O(1)-C(2)	1.230(11)
O(2)-C(4)	1.219(11)
N(1)-C(2)	1.339(11)
N(1)-C(40)	1.411(11)
N(2)-C(4)	1.338(11)
N(2)-C(80)	1.405(11)
C(10)-Sn((1)-C(30)	112.9(4)
C(10)-Sn(1)-C(20)	110.0(4)
C(30)-Sn(1)-C(20)	107.7(4)
C(10)-Sn(1)-S(1)	116.7(2)
C(30)-Sn(1)-S(1)	107.0(3)
C(20)-Sn(1)-S(1)	101.7(3)
C(70B)-Sn(2)-C(50)	117.6(8)
C(70B)-Sn(2)-C(60)	102.6(9)
C(50)-Sn(2)-C(60)	115.9(5)
C(70B)-Sn(2)-C(70A)	16.4(8)
C(50)-Sn(2)-C(70A)	113.6(5)
C(60)-Sn(2)-C(70A)	116.5(6)
C(70B)-Sn(2)-S(2)	103.9(8)
C(5)-Sn(2)-S(2)	107.9(3)
C(60)-Sn(2)-S(2)	108.1(4)
C(70A)-Sn(2)-S(2)	91.0(5)
C(1)-S(1)-Sn(1)	108.5(3)

Contd..

Table 10 (Contd..)

C(3)-S(2)-Sn(2)	106.4(3)
C(2)-N(1)-C(40)	124.5(7)
C(4)-N(2)-C(80)	124.9(7)
C(2)-C(1)-S(1)	114.2(6)
O(1)-C(2)-N(1)	123.4(8)
O(1)-C(2)-C(1)	120.7(8)
N(1)-C(2)-C(1)	115.8(8)
C(4)-C(3)-S(2)	113.5(6)
O(2)-C(4)-N(2)	123.2(9)
O(2)-C(4)-C(3)	122.2(9)
N(2)-C(4)-C(3)	114.6(8)

Symmetry transformations used to generate equivalent atoms.

Table 11. Crystal data and structure refinement for $Cy_3SnSCH_2CONHPh$

Empirical formula	C26 H41 N O S Sn
formula weight	534.362
Temperature	293(2) K
Wavelength	0.71070 A
Crystal system	Triclinic
Space group	P 1
Unit cell dimensions	a = 9.565 A alpha = 100.69 deg. b = 13.763 A beta = 99.70 deg. c = 21.701 A gamma = 107.88 deg.
Volume	2592.9 A^3
Z	4
Density (calculated)	1.320 Mg/m^3
Absorption coefficient	1.081 mm^-1
F(000)	1036
Crystal size	0.1 x 0.2 x 0.2 mm
Theta range for data collection	1.66 to 24.82 deg.
Index ranges	0<=h<=11, -16<=k<=15, -25<=l<=24
Reflections collected	7234
Independent reflections	7234 [R(int) = 0.0000]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7226 / 0 / 557
Goodness-of-fit on F^2	1.062
Final R indices [I>2sigma(I)]	R1 = 0.0718, wR2 = 0.1932
R indices (all data)	R1 = 0.0987, wR2 = 0.2219
Extinction coefficient	0.0082(9)
Largest diff. peak and hole	1.280 and -1.365 e.A^-3

Table 12. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

$Cy_3SnSCH_2CONHPh$

	x	y	z	U(eq)
Sn(1)	1238(1)	188(1)	3588(1)	51(1)
Sn(2)	6166(1)	2614(1)	480(1)	68(1)
S(1)	2721(3)	75(2)	2792(1)	65(1)
S(2)	7727(3)	1654(2)	864(1)	66(1)
O(1)	493(8)	1533(6)	2317(4)	79(2)
O(2)	5410(7)	1726(6)	1978(3)	74(2)
N(1)	2933(8)	2274(5)	2283(4)	55(2)
N(2)	7831(8)	1979(6)	2432(3)	54(2)
C(1)	1859(11)	400(7)	2088(4)	57(2)
C(2)	1688(11)	1447(7)	2224(4)	55(2)
C(3)	6742(11)	901(7)	1364(5)	63(2)
C(4)	6584(10)	1567(7)	1947(4)	53(2)
C(10)	-1081(11)	-79(7)	3231(4)	59(2)
C(11A)	-1854(32)	-111(24)	3755(13)	87(8)
C(11B)	-1936(25)	-562(20)	3748(10)	66(5)
C(12A)	-3655(39)	-266(28)	3462(16)	112(10)
C(12B)	-3620(23)	-720(17)	3579(10)	61(5)
C(13)	-4312(12)	-1446(10)	2944(6)	86(3)
C(14)	-3563(14)	-1159(12)	2422(6)	102(4)
C(15)	-1857(14)	-903(11)	2613(6)	94(4)
C(20)	1480(12)	-1038(8)	4047(5)	68(2)
C(21)	2985(15)	-745(9)	4472(6)	92(4)
C(22)	3111(18)	-1618(11)	4802(7)	115(5)
C(23)	2698(19)	-2649(10)	4310(7)	107(4)
C(24)	1243(20)	-2942(10)	3885(8)	126(7)
C(25)	1123(17)	-2079(8)	3547(6)	99(5)
C(30)	2411(13)	1686(7)	4289(4)	68(3)
C(31)	2554(20)	2597(9)	4007(6)	110(5)
C(32A)	3748(30)	3640(18)	4576(11)	72(6)
C(32B)	3147(28)	3658(17)	4479(10)	64(6)
C(33)	2780(20)	3705(10)	5104(7)	112(5)
C(34)	2688(19)	2815(11)	5386(6)	109(5)
C(35)	1818(15)	1746(9)	4877(5)	89(4)
C(40)	3044(12)	3338(7)	2468(5)	63(2)
C(41)	1952(14)	3682(8)	2207(6)	79(3)
C(42)	2115(19)	4727(11)	2395(8)	101(5)
C(43)	3396(23)	5419(11)	2817(8)	111(5)
C(44)	4540(21)	5083(10)	3069(6)	108(5)
C(45)	4358(15)	4029(9)	2903(6)	86(3)
C(50)	6391(15)	3885(9)	1269(6)	81(3)
C(51)	5907(20)	4752(11)	1048(7)	113(5)
C(52)	6088(23)	5625(13)	1612(8)	135(7)
C(53)	7570(21)	6047(11)	2058(8)	129(6)
C(54)	8130(18)	5218(10)	2274(7)	109(5)
C(55)	7973(15)	4359(9)	1676(6)	92(4)
C(60)	3886(13)	1497(13)	51(5)	95(4)
C(61A)	3068(30)	1670(23)	613(13)	82(6)
C(61B)	2781(27)	1115(20)	468(11)	71(5)
C(62A)	1400(37)	974(25)	296(15)	111(9)
C(62B)	2138(35)	2012(23)	627(14)	102(8)
C(63A)	698(29)	1515(21)	-208(12)	86(6)
C(63B)	1311(27)	2242(19)	27(11)	78(6)
C(64A)	1652(35)	1567(24)	-723(15)	106(8)
C(64B)	2505(31)	2508(21)	-396(13)	93(7)

C(65A)	3303(31)	2072(23)	-484(13)	85(7)
C(65B)	2936(27)	1488(20)	-595(11)	72(6)
C(70A)	7596(21)	3099(13)	-194(8)	43(4)
C(70B)	6918(36)	3002(22)	-333(14)	89(8)
C(71)	7087(15)	2110(8)	-787(5)	83(3)
C(72A)	8445(38)	2555(24)	-1201(15)	93(9)
C(72B)	7788(33)	2313(20)	-1354(12)	76(7)
C(73)	7944(25)	3323(14)	-1480(8)	139(7)
C(74)	8328(23)	4282(12)	-898(7)	128(6)
C(75A)	8166(48)	3994(32)	-208(20)	138(12)
C(75B)	7258(22)	3981(14)	-458(9)	59(4)
C(80)	7958(11)	2642(7)	3030(4)	57(2)
C(81)	6833(13)	2450(10)	3362(5)	75(3)
C(82)	7072(19)	3131(15)	3964(7)	107(5)
C(83)	8358(23)	3948(13)	4232(6)	109(5)
C(84)	9510(21)	4121(10)	3898(7)	106(5)
C(85)	9298(14)	3490(9)	3304(6)	81(3)

Table 13. Crystal data and structure refinement for $Bu_2Sn(SCH_2CONHPh)_2$

Empirical formula	C24 H34 N2 O2 S2 Sn
Formula weight	565.38
Temperature	293(2) K
Wavelength	0.71069 A
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 12.4920(10) A alpha = 82.3440(10) deg. b = 13.5550(10) A beta = 81.3450(10) deg. c = 15.3930(10) A gamma = 81.4470(10) deg.
Volume	2531.7(3) A^3
Z	4
Density (calculated)	1.552 Mg/m^3
Absorption coefficient	1.201 mm^-1
F(000)	1216
Crystal size	0.1 x 0.2 x 0.2 mm^3
Theta range for data collection	1.92 to 24.71 deg.
Index ranges	0<=h<=14, -15<=k<=15, -16<=l<=16
Reflections collected	7435
Independent reflections	7435 [R(int) = 0.0000]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7423 / 0 / 600
Goodness-of-fit on F^2	1.053
Final R indices [I>2sigma(I)]	R1 = 0.0495, wR2 = 0.1230
R indices (all data)	R1 = 0.0731, wR2 = 0.1734
Extinction coefficient	0.0049(4)
Largest diff. peak and hole	0.683 and -0.850 e.A^-3

Table 14. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

$Bu_2Sn(SCH_2CONHPh)_2$

	x	y	z	U(eq)
Sn(1)	1195(1)	2283(1)	4746(1)	47(1)
S(1)	199(1)	3434(1)	5725(1)	49(1)
S(2)	-432(2)	1540(1)	4575(1)	60(1)
O(1)	2623(4)	3049(3)	5268(3)	58(1)
O(2)	-1902(5)	3946(4)	3331(4)	82(2)
N(1)	2973(4)	4284(4)	5981(4)	49(1)
N(2)	-932(4)	2588(4)	2812(4)	50(1)
C(1)	1157(5)	4273(5)	5744(6)	59(2)
C(2)	2323(5)	3801(5)	5643(5)	50(2)
C(3)	-1439(6)	2592(6)	4375(5)	63(2)
C(4)	-1445(5)	3100(5)	3465(5)	57(2)
C(11)	2085(7)	952(5)	5247(6)	69(2)
C(12A)	3225(15)	643(14)	4906(12)	61(8)
C(13A)	3366(43)	466(33)	4086(21)	158(24)
C(12B)	2835(18)	483(30)	4426(26)	193(20)
C(13B)	3481(32)	-52(26)	4357(36)	194(22)
C(14)	4417(9)	-187(10)	3690(9)	129(5)
C(21)	1736(7)	3004(6)	3478(5)	71(2)
C(22)	1277(9)	4040(8)	3290(7)	112(4)
C(23)	1715(12)	4530(13)	2434(11)	174(8)
C(24)	1164(19)	5010(22)	1970(12)	276(17)
C(51)	4621(6)	4823(5)	6152(6)	62(2)
C(52)	5713(6)	4655(6)	6196(6)	74(2)
C(53)	6280(6)	3727(6)	6114(5)	68(2)
C(54)	5765(6)	2984(6)	5971(6)	68(2)
C(55)	4657(6)	3142(5)	5908(5)	61(2)
C(56)	4095(5)	4058(4)	6005(4)	45(1)
C(61)	-32(6)	2323(5)	1397(5)	64(2)
C(62)	144(8)	2567(8)	501(6)	93(3)
C(63)	-421(12)	3373(11)	113(7)	135(5)
C(64)	-1196(13)	3953(10)	633(8)	146(6)
C(65)	-1381(8)	3693(8)	1516(7)	96(3)
C(66)	-798(5)	2884(5)	1914(5)	53(2)
Sn(2)	-2691(1)	1505(1)	8691(1)	51(1)
S(3)	-1048(1)	836(2)	9282(1)	72(1)
S(4)	-1883(1)	1504(1)	7126(1)	54(1)
O(3)	-3189(4)	1591(4)	10302(3)	70(2)
O(4)	812(3)	-293(3)	7448(3)	50(1)
N(3)	-2557(4)	1304(4)	11614(4)	50(1)
N(4)	433(4)	1380(4)	7346(4)	45(1)
C(5)	-1524(6)	516(7)	10423(5)	70(2)
C(6)	-2501(5)	1206(5)	10768(5)	53(2)
C(7)	-900(5)	415(5)	7061(5)	48(2)
C(8)	209(4)	469(4)	7312(4)	40(1)
C(31)	-3187(6)	3059(6)	8666(6)	74(2)
C(32)	-4390(7)	3352(6)	8789(8)	89(3)
C(33)	-4741(9)	4425(7)	8799(9)	109(4)
C(34)	-5930(9)	4693(9)	8879(13)	165(7)
C(41)	-3910(9)	558(8)	8837(7)	98(3)
C(42A)	-3883(21)	-402(21)	8962(40)	174(22)
C(43A)	-3118(22)	-1104(26)	9068(34)	177(22)
C(42B)	-3057(42)	-678(32)	8846(29)	184(25)
C(43B)	-3844(37)	-1321(32)	9145(25)	164(20)
C(44)	-3176(15)	-2201(14)	9213(12)	164(6)
C(71)	-3314(5)	1641(5)	13047(5)	53(2)
C(72)	-4088(6)	2102(6)	13636(5)	64(2)
C(73)	-4962(6)	2699(6)	13344(6)	68(2)
C(74)	-5042(6)	2837(6)	12485(6)	76(2)
C(75)	-4245(6)	2418(6)	11871(6)	72(2)
C(76)	-3384(4)	1792(4)	12179(4)	44(1)
C(81)	2346(5)	1123(6)	7551(5)	66(2)
C(82)	3184(7)	1481(9)	7810(7)	96(3)
C(83)	3038(9)	2362(11)	8123(8)	115(4)
C(84)	2053(9)	2931(10)	8171(8)	116(4)
C(85)	1191(7)	2583(7)	7937(6)	76(2)
C(86)	1316(5)	1688(5)	7611(4)	50(2)

Table 15. Selected bond lengths (A) and angles (deg.) for $Bu_2Sn(SCH_2CONHPh)$.

Sn(1)-C(11)	2.092(7)
Sn(1)-C(21)	2.125(7)
Sn(1)-S(1)	2.395(2)
Sn(1)-S(2)	2.460(2)
Sn(1)-O(1)	2.472(4)
S(1)-C(1)	1.776(6)
S(2)-C(3)	1.782(8)
O(1)-C(2)	1.220(8)
O(2)-C(4)	1.209(9)
N(1)-C(2)	1.317(8)
N(2)-C(4)	1.327(8)
C(1)-C(2)	1.495(9)
C(11)-C(12A)	1.46(2)
C(12A)-C(13A)	1.30(4)
C(13A)-C(14)	1.56(4)
C(21)-C(22)	1.445(13)
C(22)-C(23)	1.461(14)
C(53)-C(54)	1.331(11)
C(54)-C(55)	1.385(10)

Contd..

Table 15 (Contd..)

C(11)-Sn(1)-C(21)	119.93(3)
C(11)-Sn(1)-S(1)	120.4(2)
C(21)-Sn(1)-S(1)	112.8(2)
C(11)-Sn(1)-S(2)	96.6(2)
C(21)-Sn(1)-S(2)	106.0(2)
S(1)-Sn(1)-S(2)	93.80(6)
C(11)-Sn(1)-O(1)	82.5(3)
C(21)-Sn(1)-O(1)	85.5(3)
S(1)-Sn(1)-O(1)	75.71(11)
S(2)-Sn(1)-O(1)	166.89(13)
O(1)-C(2)-C(1)	122.0(6)
O(2)-C(4)-C(3)	120.6(6)

Symmetry transformations used to generate equivalent atoms.

Table 16. Anisotropic displacement parameters (A^2 x 10^3) for $Bu_2Sn(SCH_2CONHPh)_2$
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Sn(1)	55(1)	45(1)	40(1)	-5(1)	-3(1)	-3(1)
S(1)	47(1)	44(1)	56(1)	-13(1)	-7(1)	-2(1)
S(2)	71(1)	57(1)	57(1)	-13(1)	-2(1)	-20(1)
O(1)	53(3)	39(2)	86(4)	-23(2)	-17(2)	5(2)
O(2)	80(4)	61(3)	107(5)	-44(3)	-13(3)	12(3)
N(1)	46(3)	42(3)	60(4)	-19(2)	-8(2)	2(2)
N(2)	49(3)	45(3)	55(4)	-15(2)	-6(2)	0(2)
C(1)	47(4)	45(4)	89(6)	-20(3)	-18(3)	2(3)
C(2)	44(3)	38(3)	69(5)	-6(3)	-13(3)	-2(3)
C(3)	53(4)	92(6)	50(5)	-29(4)	-4(3)	-12(4)
C(4)	39(3)	59(4)	80(6)	-37(4)	-8(3)	-5(3)
C(11)	80(5)	50(4)	71(6)	-16(4)	-9(4)	13(4)
C(12A)	60(12)	79(13)	41(13)	-9(8)	-26(8)	21(9)
C(13A)	219(42)	132(32)	55(17)	48(21)	23(19)	106(30)
C(12B)	63(12)	296(42)	250(39)	-197(35)	-88(18)	93(18)
C(13B)	171(31)	110(24)	281(53)	-117(27)	111(34)	-10(21)
C(14)	101(8)	136(10)	152(12)	-61(9)	29(8)	-32(8)
C(21)	70(5)	83(5)	54(5)	-2(4)	11(4)	-17(4)
C(22)	103(8)	106(8)	97(8)	42(6)	17(6)	3(6)
C(23)	132(11)	193(15)	147(13)	122(12)	0(9)	-5(10)
C(24)	253(24)	435(39)	156(17)	166(22)	-91(16)	-209(27)
C(51)	53(4)	54(4)	83(6)	-14(4)	-20(4)	3(3)
C(52)	52(4)	70(5)	108(7)	-32(5)	-22(4)	-1(4)
C(53)	48(4)	92(6)	65(5)	-24(4)	-12(3)	6(4)
C(54)	51(4)	66(5)	85(6)	-25(4)	-16(4)	16(3)
C(55)	59(4)	50(4)	76(6)	-19(3)	-14(4)	5(3)
C(56)	42(3)	47(3)	47(4)	-9(3)	-12(3)	1(3)
C(61)	59(4)	58(4)	67(5)	-3(3)	-1(3)	7(3)
C(62)	103(7)	94(7)	68(7)	-7(5)	8(5)	14(6)
C(63)	181(13)	164(12)	32(6)	6(6)	-3(6)	43(10)
C(64)	199(14)	128(10)	76(9)	22(7)	-24(8)	66(10)
C(65)	91(7)	94(7)	87(8)	-7(5)	-4(5)	25(5)
C(66)	56(4)	47(4)	60(5)	-6(3)	-12(3)	-9(3)
Sn(2)	34(1)	65(1)	51(1)	-5(1)	-10(1)	9(1)
S(3)	35(1)	127(2)	44(1)	-5(1)	-6(1)	24(1)
S(4)	40(1)	70(1)	46(1)	0(1)	-13(1)	14(1)
O(3)	48(3)	104(4)	47(3)	-10(3)	-11(2)	30(3)
O(4)	41(2)	48(2)	58(3)	-3(2)	-13(2)	11(2)
N(3)	35(3)	68(4)	43(4)	-5(2)	-4(2)	9(2)
N(4)	38(3)	44(3)	53(3)	2(2)	-12(2)	-1(2)
C(5)	50(4)	100(6)	47(5)	-8(4)	-7(3)	32(4)
C(6)	40(3)	66(4)	45(5)	0(3)	-6(3)	9(3)
C(7)	38(3)	56(4)	49(4)	-3(3)	-12(3)	-2(3)
C(8)	36(3)	49(4)	31(3)	-3(2)	-4(2)	-1(3)
C(31)	64(5)	63(5)	89(6)	-6(4)	-2(4)	-1(4)
C(32)	57(5)	66(5)	139(9)	-5(5)	-14(5)	6(4)
C(33)	94(7)	75(6)	150(11)	-22(6)	-6(7)	18(5)
C(34)	88(8)	85(8)	315(23)	-46(10)	-33(10)	33(6)
C(41)	103(7)	112(8)	88(8)	-37(6)	22(5)	-51(6)
C(42A)	46(14)	64(19)	406(63)	2(23)	-28(23)	-19(11)
C(43A)	50(14)	135(28)	342(56)	111(32)	-73(23)	-71(18)
C(42B)	187(44)	142(32)	209(35)	-21(25)	114(33)	-118(32)
C(43B)	167(37)	138(36)	167(32)	-39(23)	36(24)	7(26)
C(44)	154(14)	166(16)	165(16)	19(12)	-17(11)	-33(13)
C(71)	48(4)	57(4)	57(5)	-15(3)	-6(3)	-3(3)
C(72)	67(5)	66(5)	61(5)	-26(4)	-3(4)	-3(4)
C(73)	56(4)	59(4)	84(7)	-29(4)	12(4)	1(3)
C(74)	62(5)	74(5)	72(6)	-3(4)	3(4)	32(4)
C(75)	55(4)	76(5)	70(6)	-2(4)	-3(4)	25(4)
C(76)	32(3)	46(3)	51(4)	-8(3)	-3(2)	3(2)
C(81)	44(4)	84(5)	71(6)	2(4)	-11(3)	-13(4)
C(82)	48(5)	143(9)	102(8)	-27(7)	-11(4)	-23(5)
C(83)	76(7)	171(12)	121(10)	-48(9)	-20(6)	-53(8)
C(84)	95(8)	140(10)	135(11)	-70(8)	-6(7)	-47(7)
C(85)	70(5)	95(6)	69(6)	-27(5)	-8(4)	-13(4)
C(86)	48(4)	66(4)	35(4)	0(3)	-5(3)	-12(3)

Table 17. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for $Bu_2Sn(SCH_2CONHPh)_2$

	x	y	z	U(eq)
H(1)	2663(4)	4811(4)	6219(4)	59
H(2)	-644(4)	1987(4)	2971(4)	60
H(1A)	1065(5)	4816(5)	5272(6)	83(9)
H(1B)	995(5)	4563(5)	6300(6)	83(9)
H(3A)	-2150(6)	2374(6)	4567(5)	83(9)
H(3B)	-1362(6)	3090(6)	4752(5)	83(9)
H(11A)	2059(7)	982(5)	5876(6)	82
H(11B)	1683(7)	410(5)	5189(6)	82
H(14A)	4325(9)	-334(10)	3114(9)	193
H(14B)	4539(9)	-803(10)	4070(9)	193
H(14C)	5032(9)	174(10)	3641(9)	193
H(21A)	2524(7)	2972(6)	3416(5)	85
H(21B)	1567(7)	2627(6)	3033(5)	85
H(22A)	1408(9)	4413(8)	3751(7)	134
H(22B)	493(9)	4072(8)	3312(7)	134
H(23A)	2230(12)	4951(13)	2549(11)	209
H(23B)	2136(12)	4006(13)	2106(11)	209
H(24A)	1602(19)	5271(22)	2448(12)	414
H(24B)	753(19)	5556(22)	2264(12)	414
H(24C)	670(19)	4607(22)	1810(12)	414
H(51)	4233(6)	5455(5)	6221(6)	107(7)
H(52)	6075(6)	5179(6)	6282(6)	107(7)
H(53)	7024(6)	3611(6)	6159(5)	107(7)
H(54)	6153(6)	2350(6)	5913(6)	107(7)
H(55)	4304(6)	2622(5)	5800(5)	107(7)
H(61)	381(6)	1764(5)	1657(5)	107(7)
H(62)	664(8)	2165(8)	159(6)	107(7)
H(63)	-296(12)	3542(11)	-496(7)	107(7)
H(64)	-1593(13)	4524(10)	375(8)	107(7)
H(65)	-1920(8)	4079(8)	1857(7)	107(7)
H(3)	-1994(4)	1023(4)	11855(4)	60
H(4)	-53(4)	1858(4)	7180(4)	54
H(5A)	-1708(6)	-164(7)	10505(5)	83(9)
H(5B)	-938(6)	527(7)	10768(5)	83(9)
H(7A)	-1206(5)	-133(5)	7440(5)	83(9)
H(7B)	-796(5)	242(5)	6459(5)	83(9)
H(31A)	-2882(6)	3303(6)	9127(6)	89
H(31B)	-2884(6)	3388(6)	8103(6)	89
H(32A)	-4691(7)	3125(6)	8317(8)	107
H(32B)	-4694(7)	3004(6)	9343(8)	107
H(33A)	-4476(9)	4649(7)	9291(9)	131
H(33B)	-4412(9)	4779(7)	8258(9)	131
H(34A)	-6109(9)	5406(9)	8885(13)	247
H(34B)	-6262(9)	4356(9)	9418(13)	247
H(34C)	-6197(9)	4493(9)	8385(13)	247
H(41A)	-4434(9)	793(8)	9322(7)	118
H(41B)	-4268(9)	756(8)	8312(7)	118
H(44A)	-2458(15)	-2557(14)	9251(12)	246
H(44B)	-3465(15)	-2398(14)	8728(12)	246
H(44C)	-3644(15)	-2357(14)	9753(12)	246
H(71)	-2728(5)	1215(5)	13251(5)	107(7)
H(72)	-4017(6)	2008(6)	14235(5)	107(7)
H(73)	-5500(6)	3009(6)	13741(6)	107(7)
H(74)	-5656(6)	3229(6)	12291(6)	107(7)
H(75)	-4290(6)	2557(6)	11269(6)	107(7)
H(81)	2451(5)	503(6)	7334(5)	107(7)
H(82)	3872(7)	1104(9)	7769(7)	107(7)
H(83)	3620(9)	2591(11)	8312(8)	107(7)
H(84)	1967(9)	3563(10)	8364(8)	107(7)
H(85)	502(7)	2956(7)	8003(6)	107(7)

4.4.3.8. Biocidal Properties:

Introduction:

We discuss below the phytotoxicity and fungicidal activity of the synthesised compounds. Search for new pesticides is essential as even successful pesticides can loose their effectiveness due to growth of resistance of pests towards these pesticides. Moreover, consideration of environmental pollution may lead to the discontinuance of some successful pesticides in future course of time. In the search for new pesticides, organometallic compounds are gaining much more importance day by day. Many organotin compounds are reportedly toxic to various organisms and a number of them have limited but significant uses as biocidal agents in agriculture and technology[32,33]. The main advantages of organotin agrochemicals, which mainly possess prophylactic action are their relatively low phytotoxicity, low toxicity to non target organisms[34,35], lack of resistance to crop pests to these chemicals, and degradation in environmental situation to harmless inorganic tin residues[36]. Much work has yet not been done for controlling the plant pathogenic fungi by using organotin compounds. Therefore, study of fungicidal activity of the synthesised compounds is important.

The fungicidal activity of any compound will be of real value if the compound has negligible phytotoxicity. For this reason, the compounds were tested also for their phytotoxicity level.

Experimental

Fungicidal activity

Materials and Method:

The fungal isolates used are given in the following table :

Species	Code	Host of origin	Source of isolate
Alternaria alternata	ITCC[a]-3022	brinjal, tobacco	Plant Pathology Laboratory, Centre for Life Sciences, N.B.U.
Helminthosporium sativum	ITCC-2684	Wheat	"

[a]ITCC = Indian Type Culture Collection. All the apparatus used were sterilised before use.

i) Preparation of the culture media; 40 gms of potato was extracted with boiling water, 2 gms agar-agar (KDBA, Japan) and 2 grms dextrose were added to the water extract, volume made up to 100 ml and boiled for few minutes until a clear solution resulted. 0.01 gm of streptomycin sulphate was added to the potato-destrose-agar (PDA) medium as anti-bacterial agent. Then slants for culture of fungi were prepared with this media by pouring about 2 ml of this molten media in each test tube and held in slanting condition till the media

solidified. Then the media was impregnated with spore and kept in incubator at 28 ± 1°C for 15 days.

ii) Preparation of spore suspension: After 15 days, spore suspensions were prepared by using sterile double distilled water which were used subsequently for experiments.

iii) Study of the inhibitory effects: The *in vitro* fungicidal activities were determined following spore germination method as described by Rouxel *et al*[37]. Compound solutions (two drops) were placed on two spots, 3 cm apart in a clean, grease free glass slide and the solvent was allowed to evaporate. Then a drop (0.02 ml) of spore suspension, prepared from 15 days old culture was added to these treated spots. In this way sets for various concentrations of the compounds were prepared. The slides were left for 24 hours under humid condition. Finally, one drop of a cotton blue-lactophenol mixture was added to each spot to fix the germinated spores. The number of spores germinated compared to control was then calculated considering an average of 500 spores per treatment. The percentage of inhibition with respect to control was calculated using the Vincent[38] equation:

$$\% \text{ inhibition} = \frac{C-T}{C} \times 100$$

where C and T are germination of spores under control and treated spore suspensions respectively. The % of spores inhibited from germination were determined at different concentrations. Then from the percentage of inhibition graph plotted against

concentration, the ED_{50} (effective dose for 50% inhibition) values were calculated in microgram per millilitre (ppm) unit and presented in Table - 5.

Results

The detailed experimental results are given below in tabular form:

Table - 5

ED_{50} values *in vitro* of the compounds in µg/ml

Compounds	Name of fungi	
	H. sativum	*A. alternata*
Ph_3SnL	0.12	39.80
Bz_3SnL	316.20	1.58
Ph_2SnL_2	20.95	0.90
Bu_2SnL_2	19.95	1.25
Cy_3SnL	3.16	0.89

L = $-S-CH_2CONHPh$.

Phytotoxicity:

Materials and Method:

The *in vitro* phytotoxicity study of these compounds were done on rice seeds of PUSA 2-21 variety, collected from Chinsurah rice Research Institute, Hooghly, West Bengal, India.

Rice seeds were dipped in compound suspensions at different concentrations (25, 50 and 100 µg/ml) for 1, 4 and 8 hours. The treated seeds were allowed to germinate, sowed over a mat of moist filter papers arranged in covered petriplates. One hundred seeds were treated for each experiment. After seven days the germinated seeds were counted against control; seeds producing a root, or coleophile were considered as germinated. Each experiment was repeated in triplicate.

All apparatus and materials were sterilised where necessary using standard procedures.

Results:

Table -6

The results of phytotoxicity study are given below in tabular form:

Compound	Concentration (ppm, ug/ml)	% of germinated seeds treated for 1 hr.	4 hr.	8 hr.	% of germinated seeds in control
Ph_3SnL	100	86	84	75	
	50	89	87	83	92
	25	90	89	86	
Bz_3SnL	100	85	85	82	
	50	89	86	86	94
	25	92	92	90	

Contd..

Table - 6 (Contd..)

Compound	Concentration (ppm, ug/ml)	% of germinated seeds treated for 1 hr.	4 hr.	8 hr.	% of germinated seeds in control
Ph_2SnL_2	100	87	83	78	
	50	88	86	86	91
	25	88	87	87	
Bu_2SnL_2	100	75	72	65	
	50	88	85	83	91
	25	91	89	87	
Cy_3SnL	100	90	88	84	
	50	93	93	91	96
	25	96	94	94	

L = $-S-CH_2CONHPh$

Discussion:

From table 5 it is clear that against H. sativum, $Ph_3SnSCH_2CONHPh$ is the most effective while against A. alternata $Ph_2Sn(SCH_2CONHPh)_2$ is the most effective. $Ph_2Sn(SCH_2CONHPh)_2$ and $Bu_2Sn(SCH_2CONHPh)_2$ although being R_2SnX_2 type, show a high anti fungal activity comparable to that of R_3SnX types. The presence of 'S' atom in the ligand probably has enhanced the fungicidal activity of the $R_2Sn(SCH_2CONHPh)$ series. It is worth mentioning that studies show that $Bz_3SnSCH_2CONHPh$ is more active against the fungus A. alternata than H. sativum.

Rice seed germination studies (Table - 6) showed that the germination is somewhat more inhibited in case of $Ph_3Sn(SCH_2CONHPh)$ and $Bu_2Sn(SCH_2CONHPh)_2$, if the rice seeds are treated for a longer period, the latter having a greater inhibiting effect. Amongst the compounds, $Bu_2Sn(SCH_2CONHPh)_2$ is the most phytotoxic. As a whole, the compound tested have a negligible phytotoxicity.

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Chapter - 5

Synthesis, Characterisation and Biocidal Properties of Organotin (IV) hydantoates.

5.1. Introduction :

Hydantoic acid, $NH_2CONHCH_2COOH$ is a compound having functional groups of the anti tumor and biocidal agent urea[1] as well as of the biocidal agent glycine[2-4].

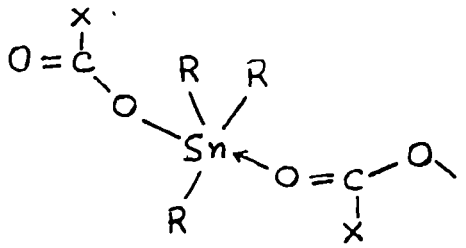
Various organotin carboxylates are now known to have significant biological properties[5,6]. Organotin derivatives of amino acids have been of interest as possible biocides[2-4], for example, tricyclohexyltin alaninate has been found to act as a fungicide and bactericide for seeds and plants[7] and as intermediates in peptide syntheses[8,9]. Triorganotin (IV) complexes are biologically more active than diorgano- and monoorganotin (IV) complexes, owing to their ability to bind protein[10-12]. In cat haemoglobin, both cystein and histidine residues are associated with the triorganotin (IV) moiety[12,13]. It has been observed that some drugs increases the activity when administered as metal complex, more so their metal chelates[45].

Being potentially polydentate ligands, amino acids present interesting structural possibilities when substituted with triorganotin groups at oxygen, since triorganotin compounds adopt higher coordination whenever favourable

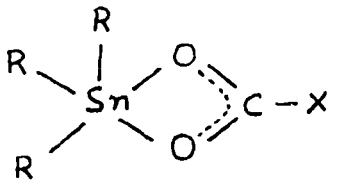
conditions exist[14]. Five coordinated triorganotin (IV) carboxylates are well known, and the one-dimensional polymeric structure with the most electronegative groups in the axial positions of a trigonalbipyramidal arrangement has been confirmed by X-ray study[14,15]. The size of the substituent groups at tin[14] and the degree of branching in the ligand[16] governs the coice of coordination number and geometry around the Sn atom. On the basis of the ambient temperature ^{119m}Sn Mössbauer spectrum the trimethyltin (IV) glycylglycinate was assigned a pentacoordinated, bridged polymeric trigonal bipyramidal geometry whereas tricyclohexyltin (IV) glycylglycinate has hexacoordinated arrangement with octahedral structure[17,18].

G.K. Sandhu and S. Kaur[19] reported that triorganotin (IV) derivatives of N-benzoylglycine have pentacoordinate trigonal bipyramidal structure of tin (IV) with chelating bidentate carboxylate group in the solids and in chloroform solution. Triorganotin (IV) derivatives of N-benzoylglycylglycine are penta-coordinate and are polymers in the solid state. The tin atom in triorganotin (IV) groups, R_3Sn- are coordinated by the unidentate carboxylic group and by the oxygen atoms of the amidocarboxyl group of the adjacent molecule. The complexes are monomers in non-coordinating solvents.

(i)



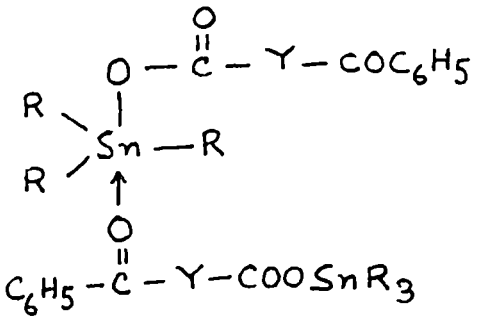
(SOLID)



(IN SOLUTION)

$X = C_6H_5CONHCH_2$

(ii)



(SOLID)

$Y = -NHCH_2CONHCH_2$

The complexes of amino acids and peptides are important in the study of biofluids, particularly when hyper accumulated metal ions are present for physiological or pathological reasons[43]. In vivo, the effective metal ion concentrations are interrelated and their mutual influence may be one of antagonism or stimulation[44].

Very little is known in literature about the biological activity of metal complexes of urea[20]. Recently,

it has been reported that some platinum (II) complexes of urea have strong antitumor and biological activity, but no further observations have been made in this direction[1]. Earlier studies on the metal complexes of urea and its alkyl or aryl derivatives have shown that they are monodentate and bind to the central metal ion through the oxygen atom[39-41]. The few exceptions are their platinum (II), tellurium (II) and copper (I) complexes where metal to nitrogen bond has been reported[42].

5.2. Scope and Objective :

The synthesis of new organotin (IV) hydantoates, designed primarily with the aim of combining the structural features of both urea and glycine i.e., α-amino acid. From the above discussions, it appears that hydantoic acid, $NH_2CONHCH_2COOH$, should be biologically active and in fact hydantoic acid and some of the derivatives are known to possess biological activity[21]. It is expected that incorporation of biologically active molecule in triorganotin (IV) moiety will lead to the formation of potential biocides because in these cases the effects are mutually combined and complemented. Apart from its carboxylate binding site, this molecule has other additional donor atoms suitable for metal coordination which presents interesting structural possibilities. Besides, their is a broad spectrum of

industrial applications of organotin carboxylates[11,22,23], such as, organo chemicals (fungicidal, antifeedants), antifouling biocides (in plants), disinfectants, PVC stabiliser, homogeneous catalysts, anthelmintics etc.

Recently synthesis of Co(II) and Ni (II) complexes of N-acylurea of the general formula $ML_2X_2 \cdot nH_2O$ [M = Ni (II), Co(II), L = N-acyl urea, X = Cl and n = 6] and their enhanced antimicrobial activity than the metal chloride salts have been reported by Famurewa et al.[20]

Keeping these facts in view and in the line with our interest in the structure-activity relationship[24] of organotin (IV) carboxylates[55], it was, therefore, thought of interest to synthesise and characterise the hydantoic acid derivatives of organotin (IV) and to investigate their biocidal properties.

5.3. Experimental and Characterisation :

The solvents were purified and dried before use by standard methods[25]. Triphenyltin chloride, bis (tributyltin) oxide and hydantoic acid were procured from Aldrich and were used as received.

Infrared specta were recorded by using PYE UNICAM SP3-300S Infrared Spectrophotometer (Philips). ^1H NMR spectra were recorded by VA-EM 390(90 MHz) machine and

UV by SHIMADZU, UV-240. ^{1}H and ^{13}C NMR were also recorded, on Varian XL-300 spectrometer.

The micro analyses were performed at RSIC, Punjab University, India and Sn was estimated by standard conventional procedure as SnO_2 in our laboratory.

Manipulations involving benzene were carried out with due precautions and care.

All the melting points reported here are uncorrected.

Physical data including elemental analysis are presented in Table - 1.

Crystallography

The intensity data for the crystals were measured at room temperature using a Rigaku AFC6R diffractometer fitted with grafite monochromatized MoKα radiation, $\lambda = 0.71073$ A^{o}, up to θ_{max} 27.5^{o} employing the $w : 2\theta$ scan technique. The data were corrected for Lorentz and polarization effects[46] and absorption employing the DIFABS program[47]. The measured data which satisfied the $I \geq 3.0\ \sigma(I)$ criterion of observability were used in the subsequent analysis. The crystal data are presented in Table-6.

Direct methods[48] were used to solve the structures and were refined by a full-matrix least-squares procedure based on F [46]. Non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen-atoms were included in the models at their calculated positions (C-H, N-H 0.97 A^{o}) with the following exception. In the refinement of [$Cy_3Sn(OCOCH_2NHCONH_2)$], disorder (high thermal motion) was noted in the cyclohexyl ring C(31)-C(36) with two positions being detected for the C(36) atom; this group was refined with isotropic thermal parameters and hydrogen atoms were not included. Final refinement details (Sigma weights[46]) are listed in Table-6; the analysis of variance showed no special features in either case. The crystallographic numbering scheme used is shown in Figures 1 and 2 (drawn with ORTEP[49]) and fractional atomic coordinates are listed in Tables 7 and 8.

5.3.1. Preparation of Starting Materials:

5.3.1.1. Preparation of Triphenyltin hydroxide:

Triphenyltin hydroxide was prepared according to the method of Gilman et al[26] by alkaline hydrolysis of triphenyltin chloride, m.p. 119°C [lit (27) m.p. 119-120°C].

(Analysis found : C = 58.87; H = 4.30%;
Calcd. for $C_{18}H_{16}SnO$: C = 58.9%, H = 4.36%).

5.3.1.2. Preparation of Tricyclohexyltin hydroxide:

Tricyclohexyltin hydroxide was prepared[28] by treating $SnCl_4$ with CyMgCl in a mol ratio 1:3, hydrolysing unreacted CyMgCl, dehydrating the organic portion, then adding additional CyMgCl, in an overall ratio of 3.5-3.9:1 to initial $SnCl_4$, to convert intermediate Cy_2SnCl_2 to Cy_3SnCl, then hydrolysing the Cy_3SnCl, m.p. 219°C [lit (27) m.p. 220-221°C].

(Analysis found : C = 56.32%, H = 8.80%

and Calcd. for $C_{18}H_{34}SnO$: C = 56.15%, H = 8.84%).

5.3.2. Synthesis of the new Organotin (IV) hydantoates:

5.3.2.1. Synthesis of Triphenyltin (IV) hydantoate:

A 250 ml round bottomed flask was placed on a heating mantle and provided with a Dean-Stark apparatus and a double surface, water cooled reflux condenser. The entire apparatus was flushed with nitrogen to exclude moisture and the reaction was carried out under nitrogen atmosphere. Ph_3SnOH (1.4 gm, 3.8 mmol), hydantoic acid (0.45 gm, 3.8 mmol) and dry benzene (150 ml) were placed in the round bottomed flask. The reaction was carried out by heating under reflux. The water formed during the reaction was azeotropically distilled out by the Dean-Stark apparatus. Refluxation was continued for 24 hours. The

resulting solution was concentrated and lef overnight. A white solid was precipitated, filtered and the residue was washed successively with petroleum ether (60-80°C) and chloroform. Then recrystallisation of the solid from methanol afforded pure crystals of $Ph_3SnOCOCH_2NHCONH_2$, m.p. 203°C, yield, 0.71 gm, 40%.

Elemental analysis : Found (Calcd.)

C	H	N	Sn
53.81 (53.99)	3.94 (4.28)	5.90 (5.99)	25.29 (25.43)

Relevant spectral data:

I.R. (cm^{-1}): (Vide Table -2) 250(w), 280(w), 1525(s), 1555(vs,b) 1600(s,b), 3120(vw), 3260(sh,m), 3310(m,b), 3415(m).

^1H NMR (δ ppm): δ(SnPh : 7.96-7.06 (m,15H), δ(NH): 5.96(b,1H), $\delta(NH_2)$:5.48(S,2H), $\delta(CH_2)$: 3.62(d,2H) J = 5 Hz.

5.3.2.2. Synthesis of Tricyclohexyltin (IV) hydantoate:

Tricyclohexyltin hydroxide (1.4 gm, 3.64 mmol), hydantoic acid (0.43 gm, 3.64 mmol) and 150 ml of dry benzene were taken in a 250 ml round bottomed flask. The flask was fitted with a Dean-Stark apparatus and a water-cooled condenser. Nitrogen was used to flush the whole assemblage. The reaction was started by heating to reflux the mixture and the water formed during the reaction was azeotropically distilled out by the Dean-Stark apparatus. After 24 hours of refluxation the solution was concentrated and left for overnight. A white solid was separated. The solid was washed with benzene and extracted in cold chloroform. From the chloroform extract, solvent was evaporated off. Then repeated recrystallisation of the residue from methanol gave pure crystals of $Cy_3SnOCOCH_2NHCONH_2$, m.p. 194°C, yield 0.88 gm, [illegible]

Elemental analysis : Found (Calcd.):

C	H	N	Sn
53.71	7.50	6.38	23.92
(51.99)	(7.84)	(5.77)	(24.49)

Relevant spectral data:

I.R. (cm^{-1}): 470(w), 500(w), 1580(vs,b), 1615(s,b), 1525(s,b), 3150(m), 3270(m), 3340(m), 3430(m).

^1H NMR (δ ppm): δ(SnCy): 2.50-0.63(m, 33H), δ(NH): 5.66(b, 1H), $\delta(NH_2)$ 4.77(S, 2H), $\delta(CH_2)$: 4.03 (d, 2H) J = 5 Hz.

5.3.2.3. Synthesis of Tributyltin (IV) hydantoate :

Moisture was excluded by flushing nitrogen, from the glass apparatus consisting of a round bottomed flask (250 ml), a Dean-Stark apparatus and a double surface water cooled condenser. Bis(tributyltin) oxide (1 gm, 1.69 mmol), hydantoic acid (0.4 gm, 3.39 mmol) and 150 ml of dry benzene were taken in the reaction flask and were reacted together by heating under reflux. The water formed during the reaction was azeotropically distilled out. After 24 hours of refluxation, the reaction mixture was concentrated and left overnight. Next day some solid was found, filtered. The residue was washed with petroleum ether (60-80°C). The petroleum ether washing was found to contain a negligible amount of liquid which may be unreacted bis(tributyltin) oxide. The solid left was extracted with dichloromethane. Solvent was removed from

the extract. The residue was recrystallised from petroleum ether (60-80°C) - dichloromethane which afforded the product $Bu_3SnOCOCH_2NHCONH_2$, m.p. 112°C, yield, 0.44 gm, 65%.

Elemental analysis : Found (Calcd.)

C	H	N	Sn
44.44 (44.25)	7.71 (7.86)	6.96 (6.88)	29.09 (29.18)

Relevant spectral data :

I.R. (cm^{-1}) : (Vide Table 2) 430(w), 480(w), 1530(vs,b), 1585(vs,b), 1620(vs), 3180(m), 3300(sh,m), 3320(m), 3480(m).

^1H NMR (δ ppm) : δ(SnBu) : 2.20-0.20 (m, 27H), δ(NH) : 5.06 (t, 1H), J = 5 Hz, $\delta(NH_2)$: 5.02(s, 2H), $\delta(CH_2)$: 3.97(d, 2H), J = 5 Hz.

5.4. Results and discussion

5.4.1. I.R. spectra:

The assignment of the relevant bands have been made tentatively on the basis of comparison of the spectra of triorganotin compounds and the free acid and its sodium salt.

The NH_2 and NH stretching frequencies appear between 3480 to 3120 cm^{-1} in solid phase. These bands do not change significantly in solution indicating their minor involvement if at all in hydrogen bonding, association or coordination in solid state.

The spectra are rather complicated in the region between 1650-1500 cm^{-1} due to the expected Amide I, Amide II bands and the carboxylate stretching frequencies. Considering the hydantoic acid to be a mono substituted derivative of urea, e.g., $RHNCONH_2$, following literature[29], in each case it seems that the NH_2 deformation and C=O stretching vibrations appear together as very strong but slightly broad band which in solutions split[5] (see table-2). The Amide I (CO) band in $Ph_3SnOCOCH_2NHCONH_2$ appear at 1555 cm^{-1}, is a clear indication that the C=O group is involved in coordination. The corresponding frequencies in $Bu_3SnOCOCH_2NHCONH_2$ and $Cy_3SnOCOCH_2NHCONH_2$ appear at 1585 cm^{-1} and 1580 cm^{-1} respectively in solid state.

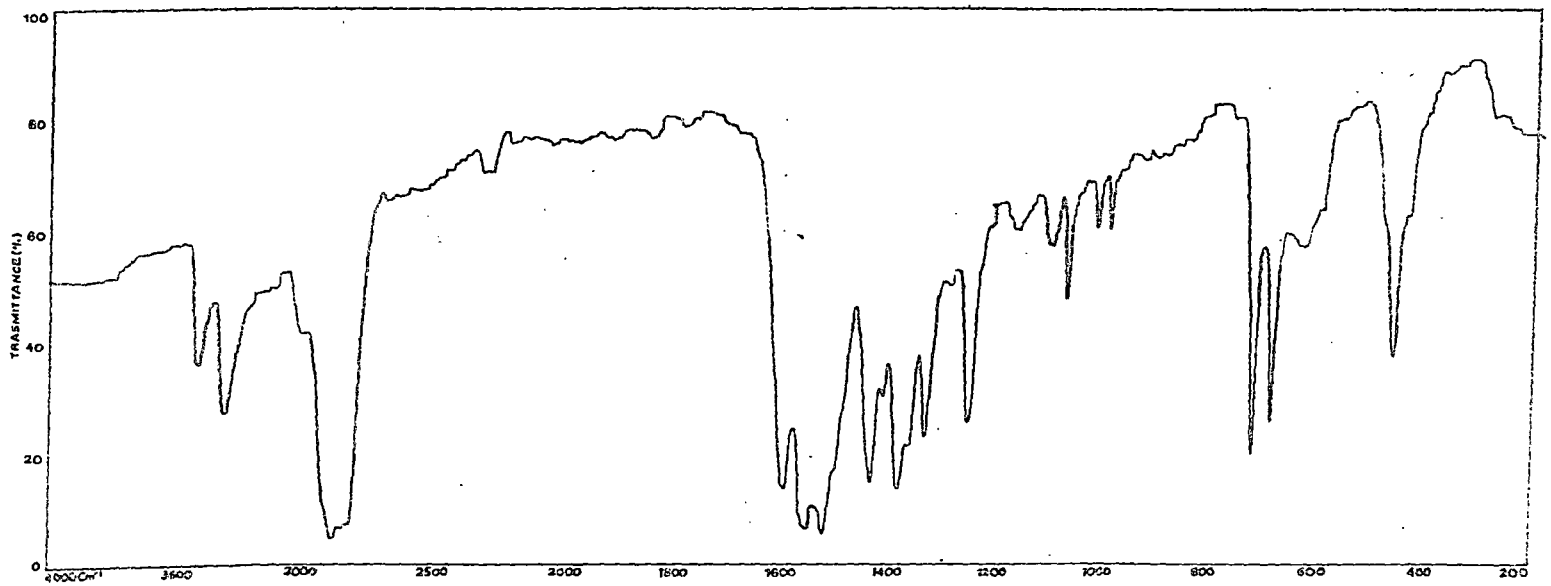


Fig. 5.3 IR spectrum of triphenyl tin (IV) hydantoate

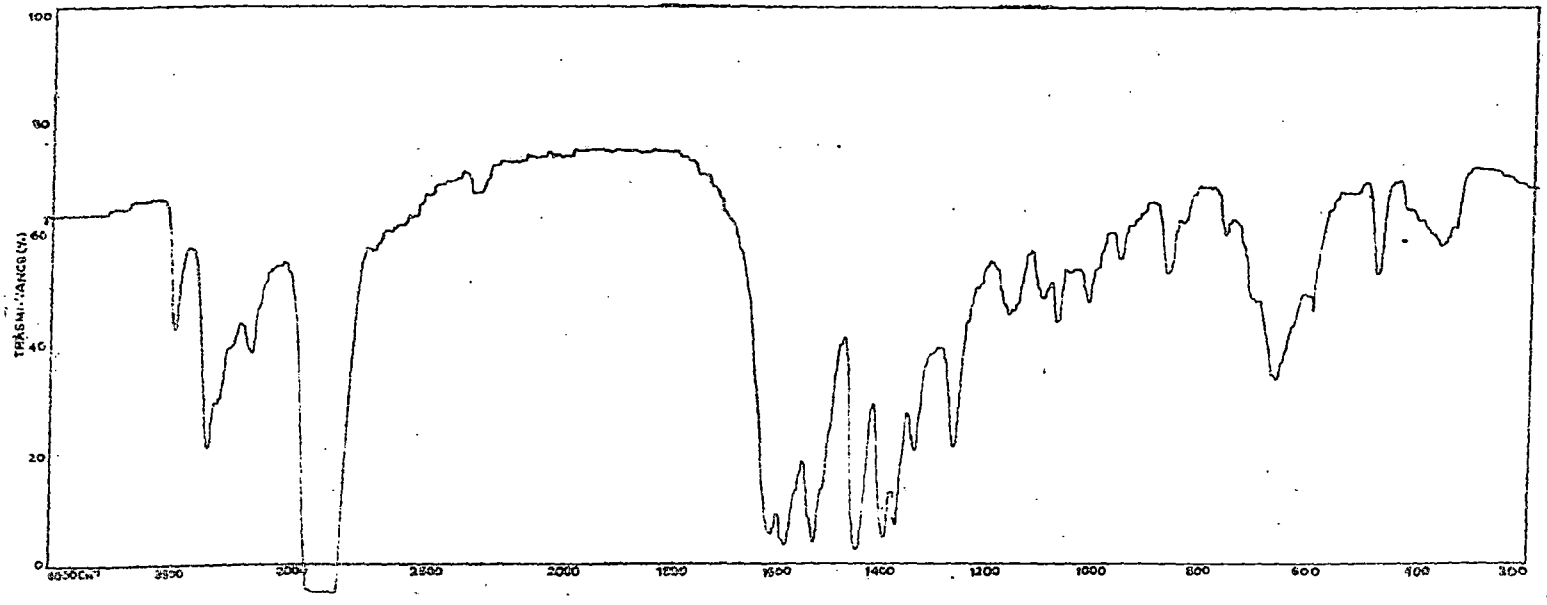


Fig. 5.4 IR spectrum of tributyl tin (IV) hydantoate

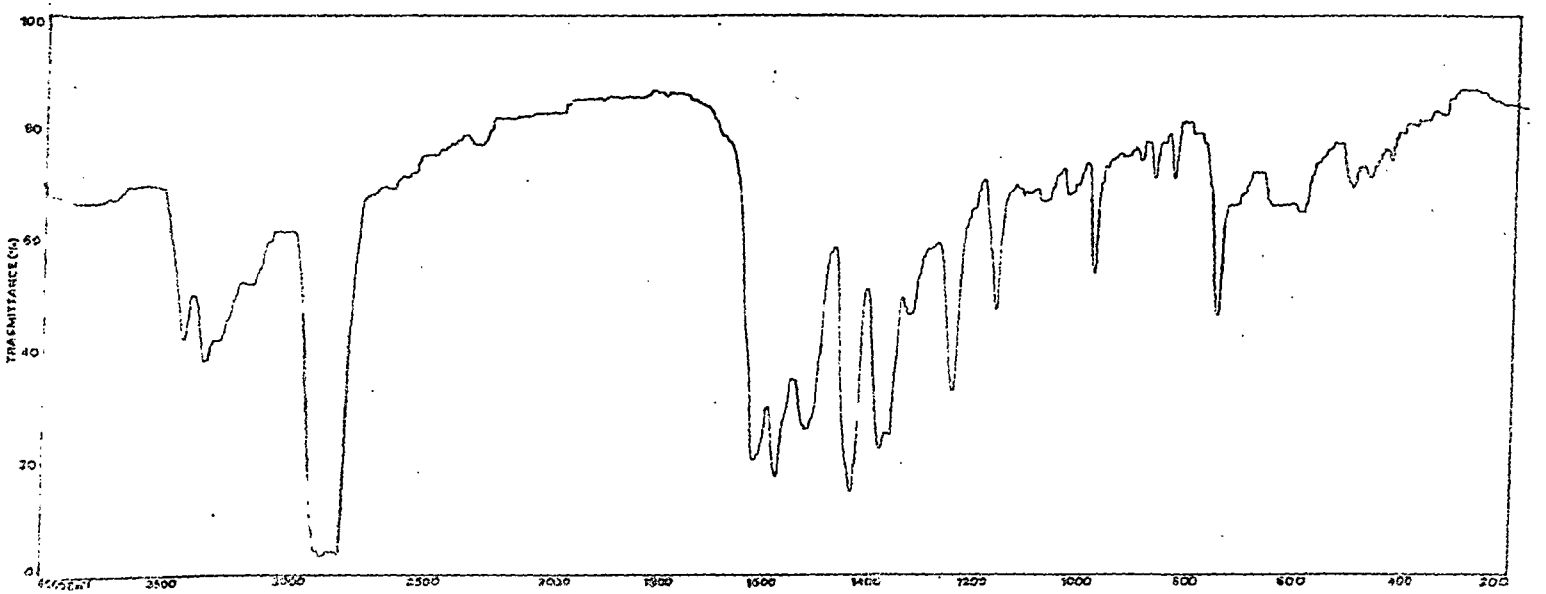


Fig. 5.5 IR spectrum of tricyclohexyl tin (IV) hydantoate

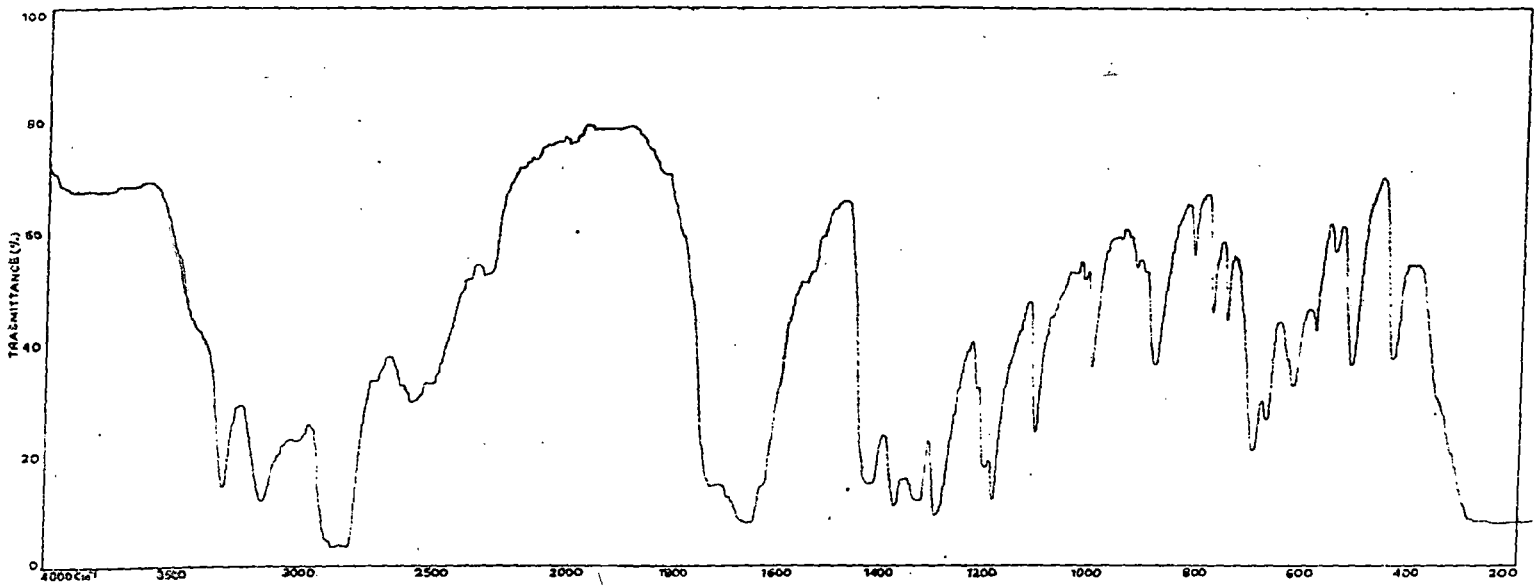


Fig. 5.6 IR spectrum of hydatoic acid

The carboxylate stretching frequency, however, is much lower than normally expected for a free ester type vibration. It is interesting to note that the OCO frequency does not shift in solution confirming the non involvement of the OCO group in intra or inter molecular coordination.

5.4.2. NMR Spectroscopy :

5.4.2.1. ^{1}H NMR spectra (90 MHz)

In all the compounds the expected signals due to the ligand protons and Sn - R (R = Ph, Bu and Cyhex) protons are observed with satisfactory proton integration. The values for the compounds are presented in Table - 3. Because of the insolubility of $Ph_3SnOCOCH_2NHCONH_2$ in $CDCl_3$ it was recorded in d_6 - DMSO. The large difference in the chemical shifts of the ligand protons in $Ph_3SnOCOCH_2NHCONH_2$ on one hand and $Bu_3SnOCOCH_2NHCONH_2$ and $Cy_3SnOCOCH_2NHCONH_2$ on the other may be attributed to solvent effect[30] and also likely C=O coordination in $Ph_3SnOCOCH_2NHCONH_2$.

5.4.2.2 ^{1}H NMR spectra (300 MHz) :

The ^{1}H NMR spectra of the compounds were also recorded at 300 MHz. All the spectra showed the expected proton peaks with satisfactory proton integrations as shown in figures 5.7 to 5.12 (Table - 11).

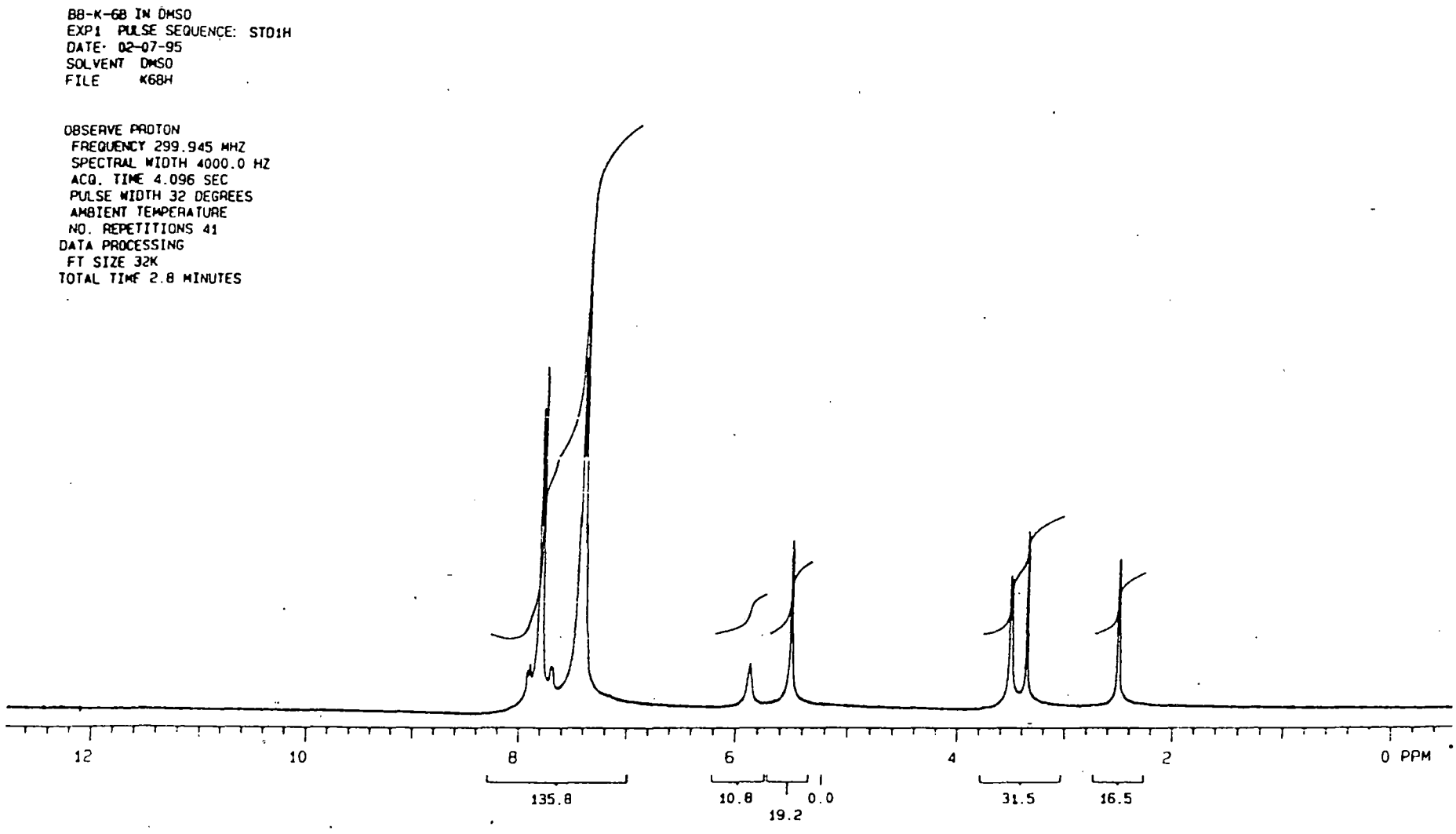


Fig. 5.7 ^{1}H NMR spectrum of triphenyl tin (IV) hydantoate in DMSO.

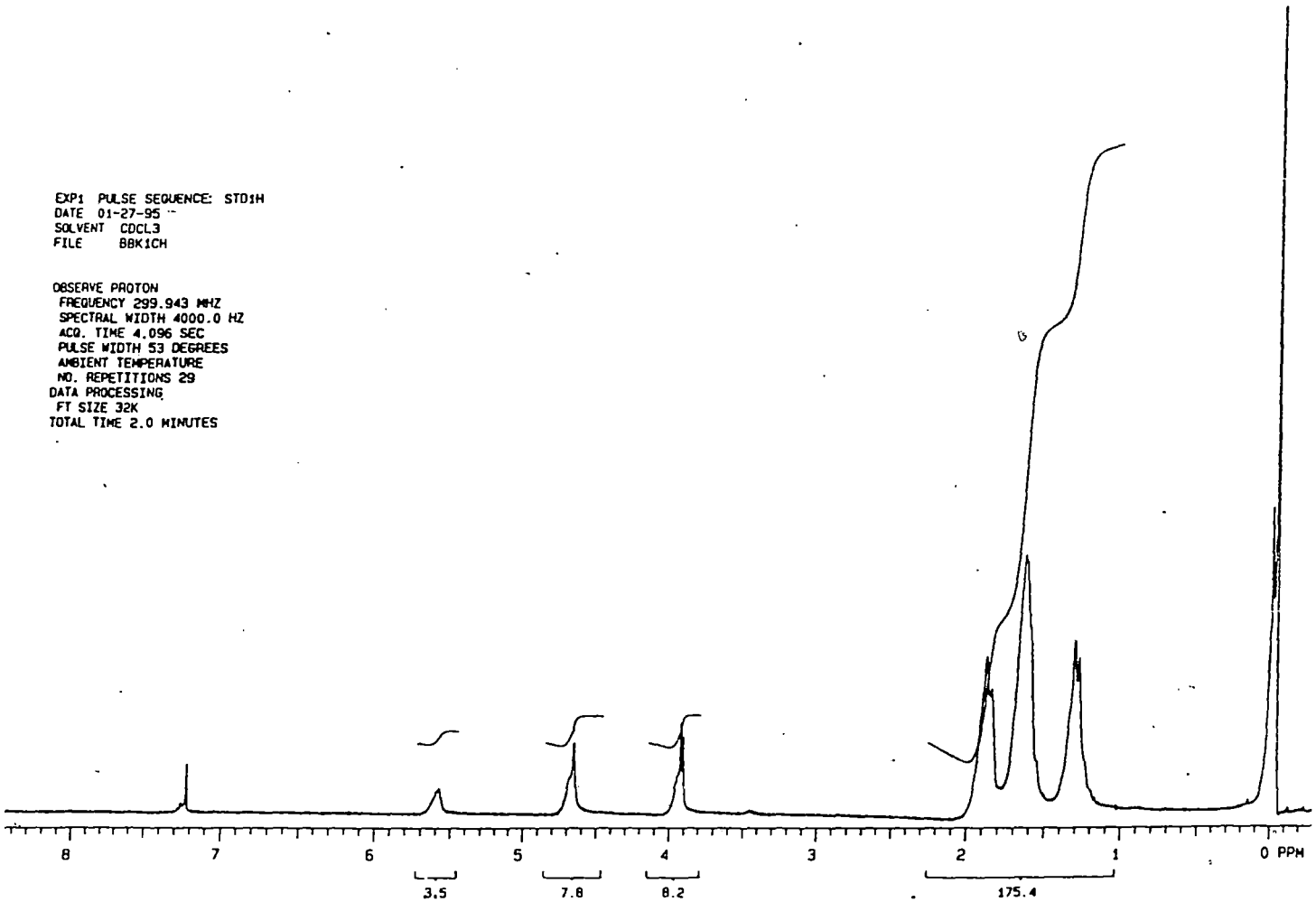


Fig 5.8 ^{1}H NMR spectrum of tricyclohexyl tin (IV) hydantoate in $CDCl_3$

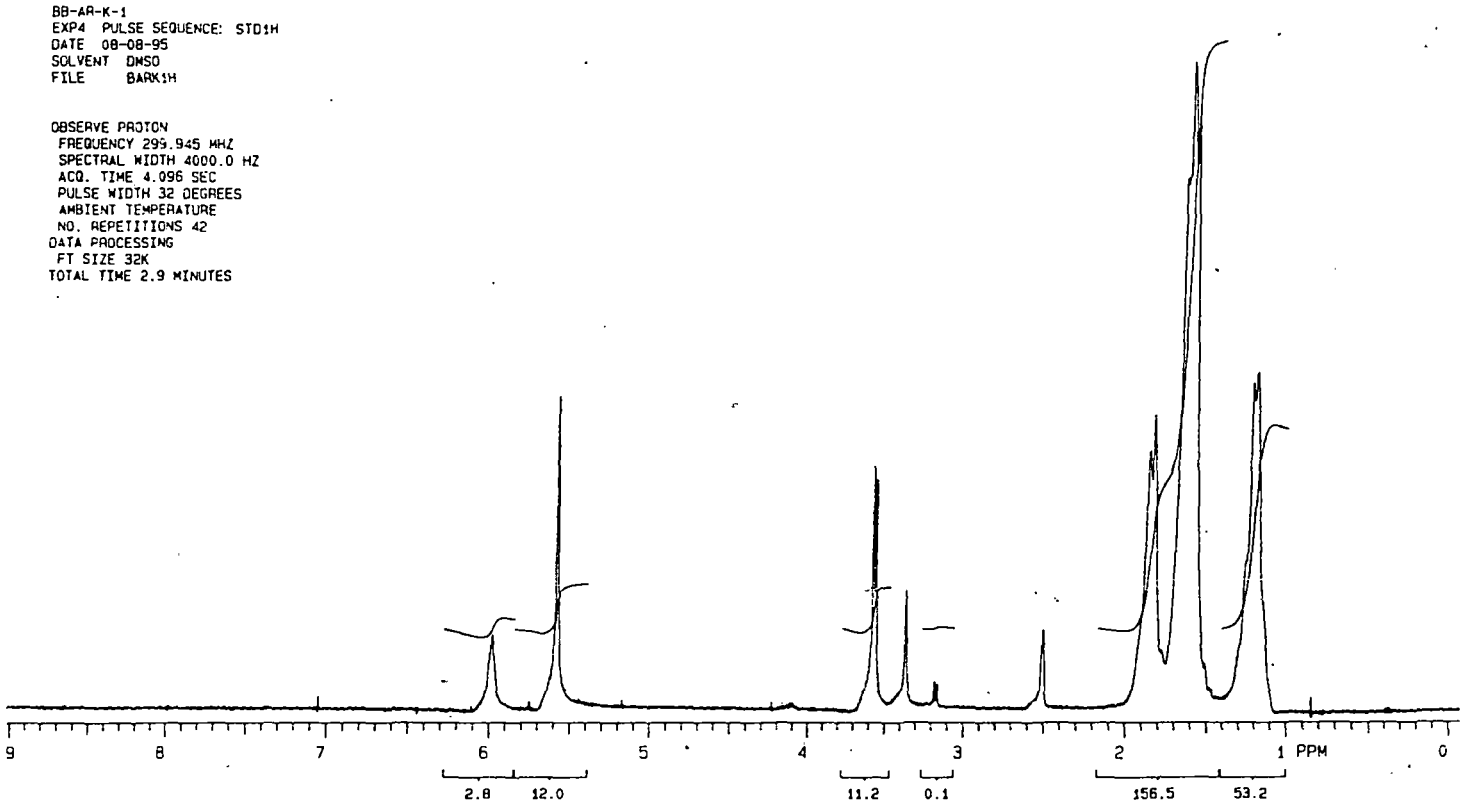


Fig 5.9 ^{1}H NMR spectrum of tricyclohexyl tin (IV) hydantoate in DMSO

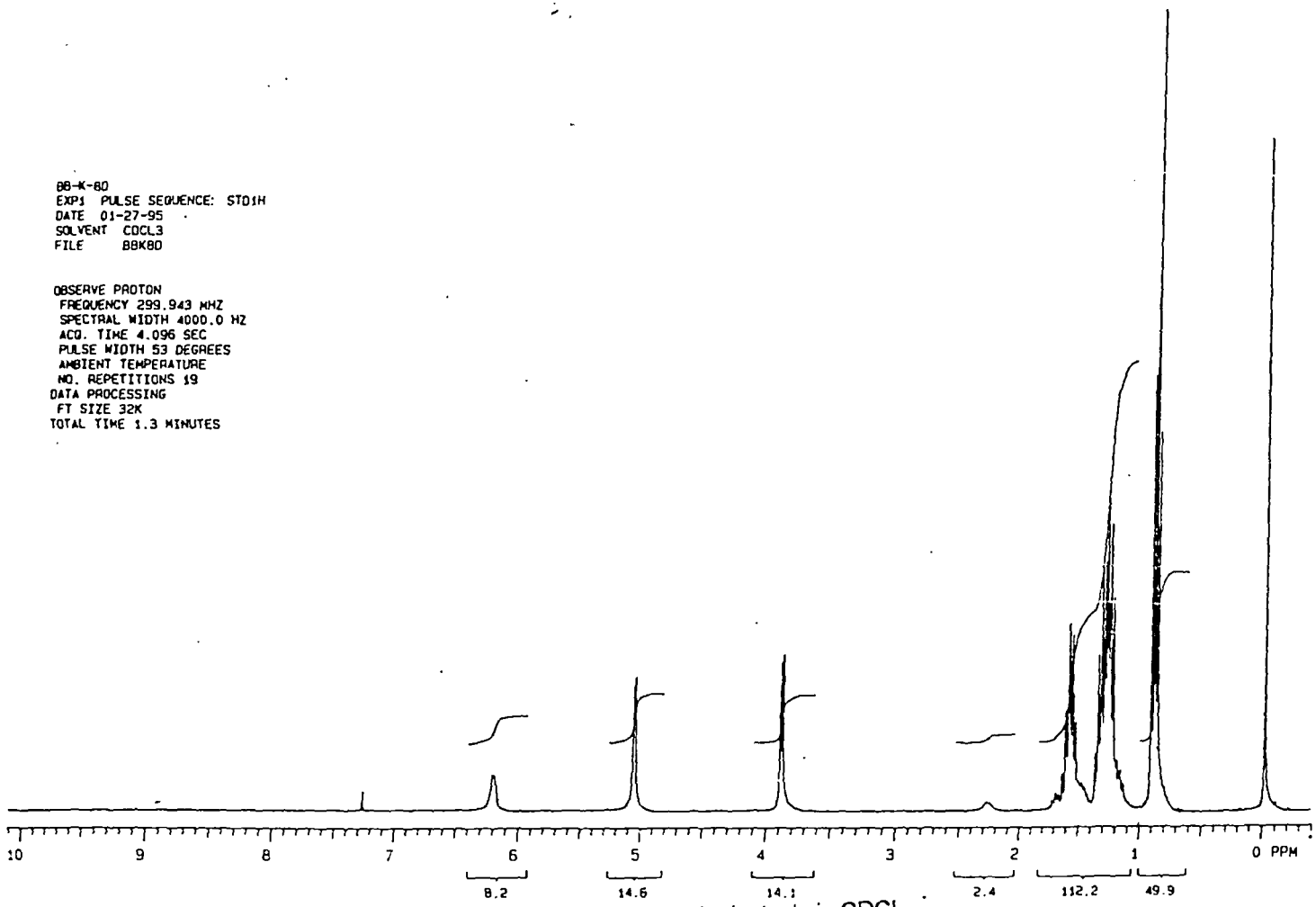


Fig. 5.10 ^{1}H NMR spectrum of tributyl tin (IV) hydantoate in $CDCl_3$

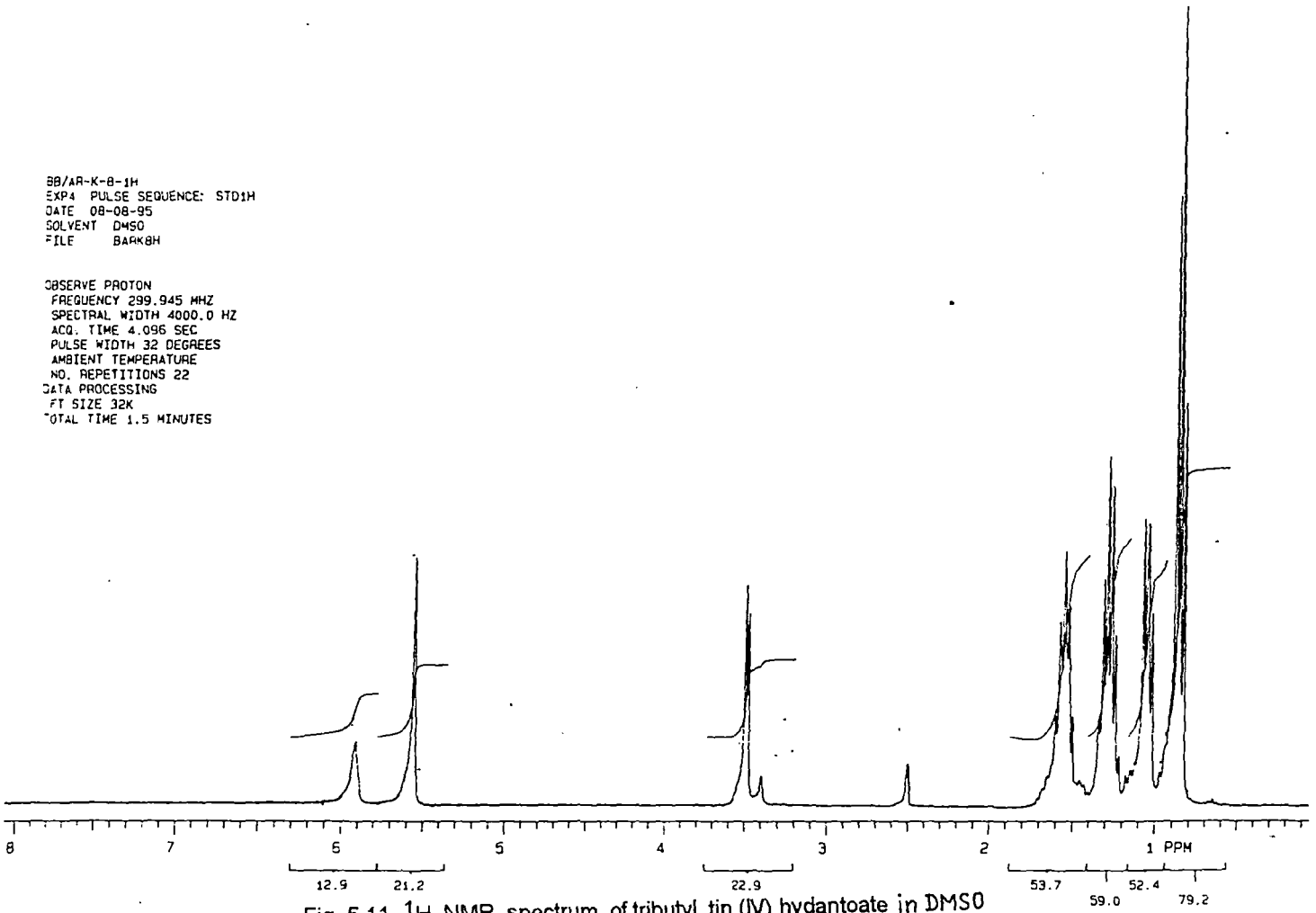


Fig. 5.11 ^{1}H NMR spectrum of tributyl tin (IV) hydantoate in DMSO

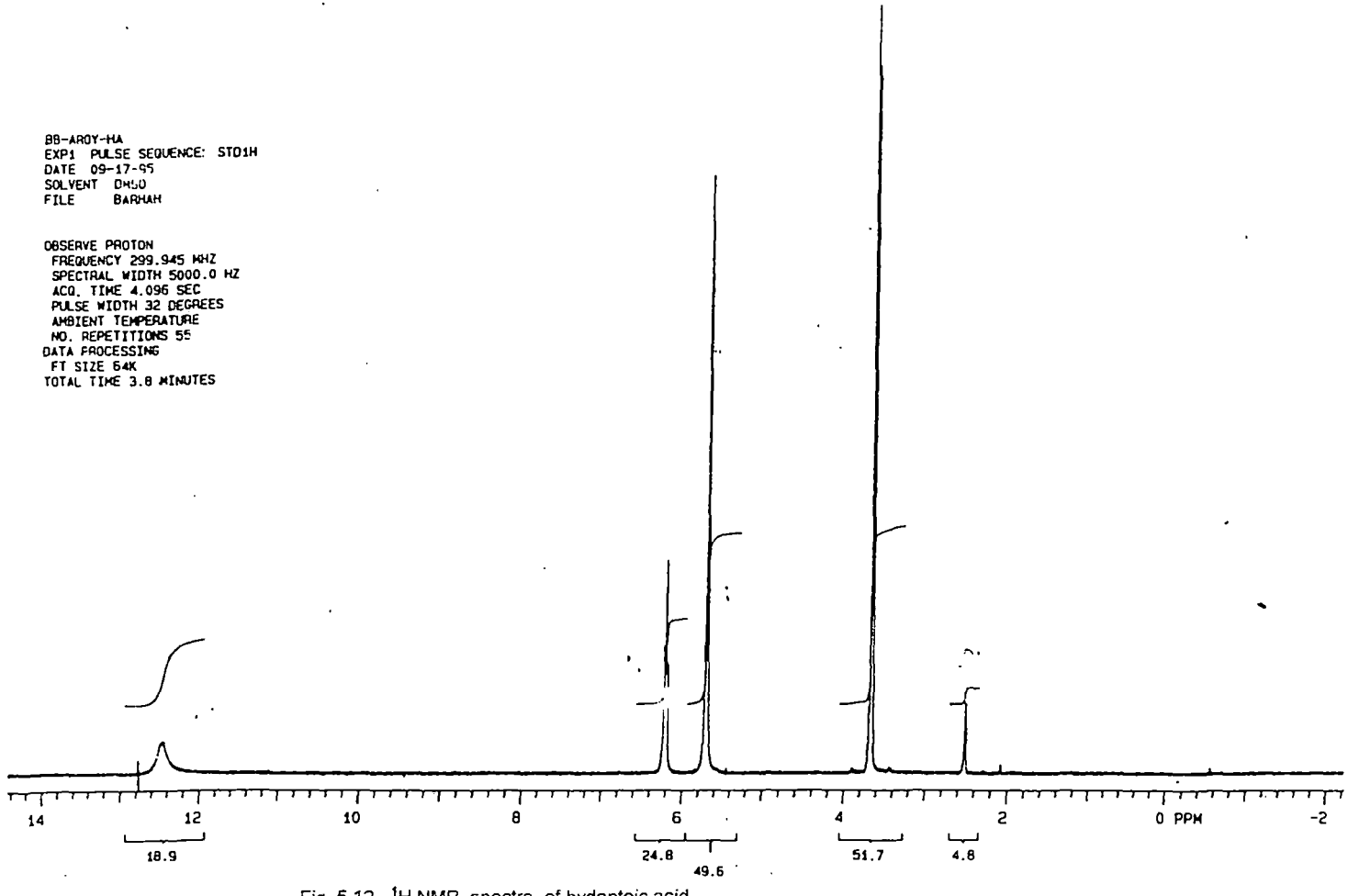


Fig. 5.12 ^{1}H NMR spectra of hydantoic acid

5.4.2.3 ^{13}C NMR Spectroscopy :

The ^{13}C NMR spectral data are presented in Table 10. The C_1 carbon ($NH-CONH_2$) of the ligand appears at around 159 ppm whereas the C_3 (O-CO) appears around 175 ppm. The C_2 ($C-CH_2-N$) appears around 43 ppm. It is evident from the X-ray crystallographic data that the CO group ($NH-CO-NH_2$) of Ph_3SnL is involved in intermolecular coordination leading to a penta-coordinated environment around tin atom. For Cy_3SnL, the CO group ($NH-CO-NH_2$) is free, providing a tetrahedral coordination around tin atom in this compound. Since, the ^{13}C NMR spectra for both Ph_3SnL and Cy_3SnL could not be recorded in $CDCl_3$ solution because of the lack of solubility of the former, the effect of involvement of the CO group in coordination in case of Ph_3SnL can not be concluded with certainly from the ^{13}C NMR spectral data.

5.4.3. UV Spectra

UV spectra were recorded in methanol. The data are presented in the following Table -

Compound	λ_{max} (nm)	ϵ_{max}
Ph_3SnL	209	5.3×10^4
Cy_3SnL	210	1.6×10^4
Bu_3SnL	203	0.6×10^4
HL	202	1.4×10^4

L = $-OCOCH_2NHCONH_2$

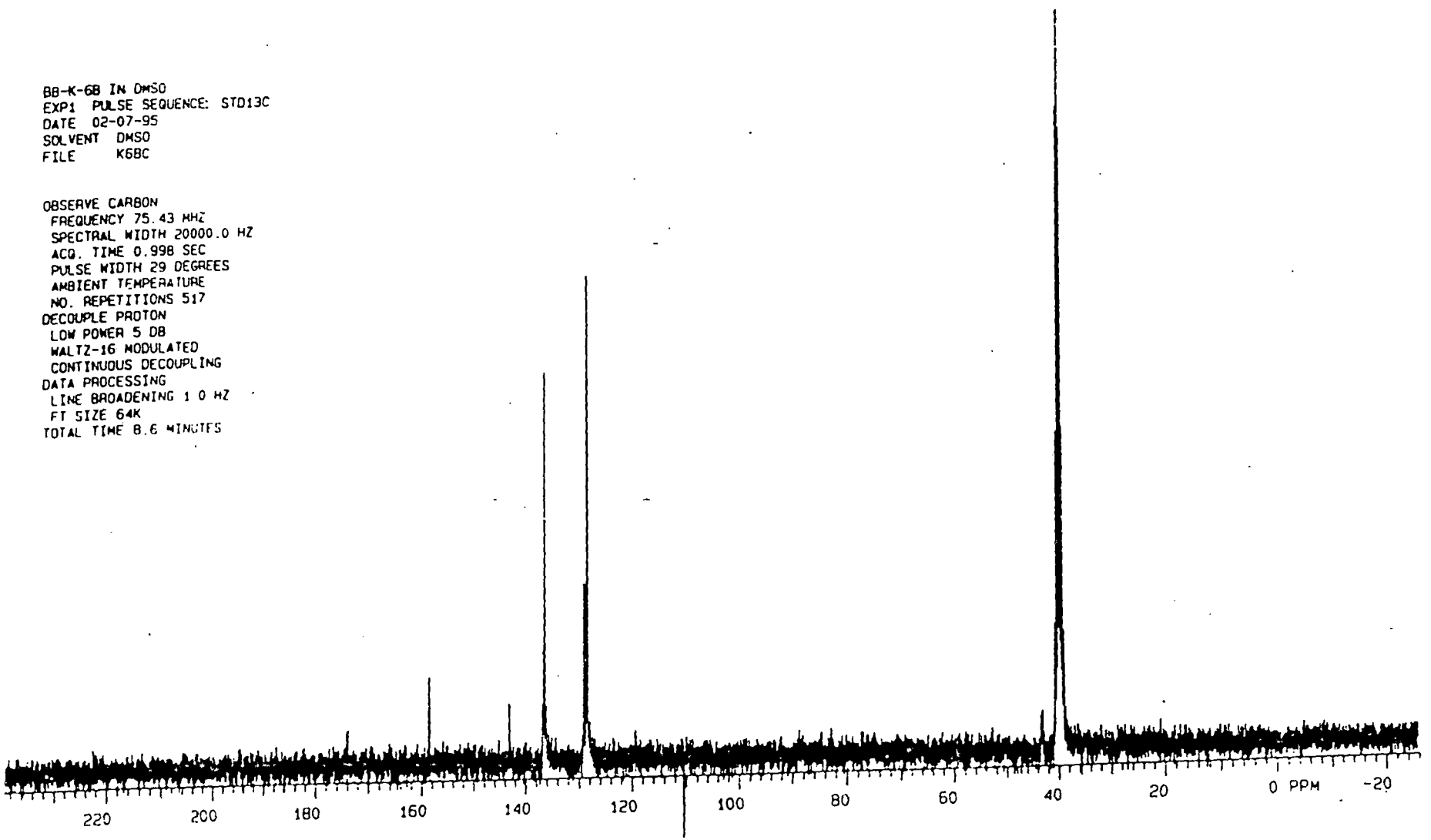


Fig. 5.13 ^{13}C NMR spectra of triphenyl tin (IV) hydantoate

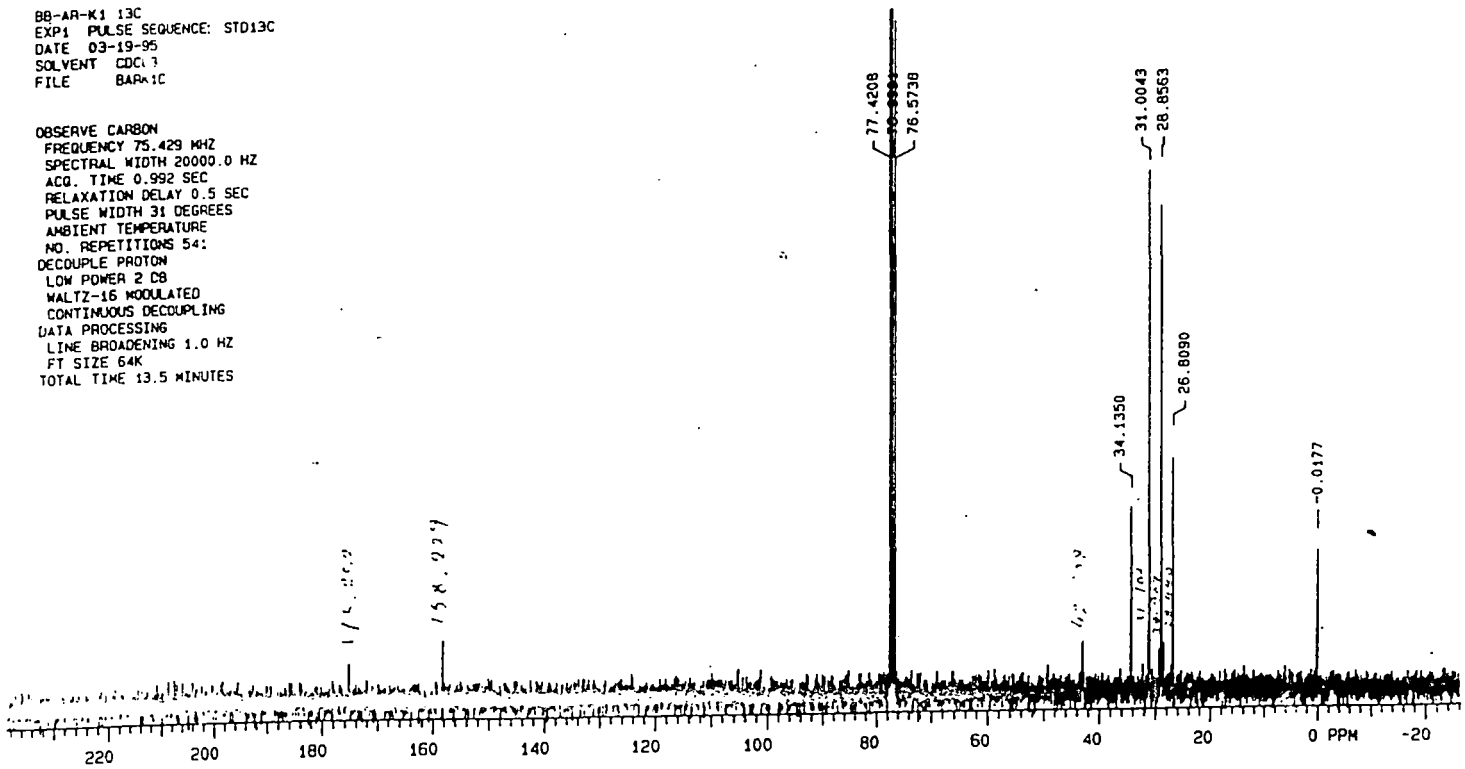


Fig. 5.14 ^{13}C NMR spectrum of tricyclohexyl tin (IV) hydantoate

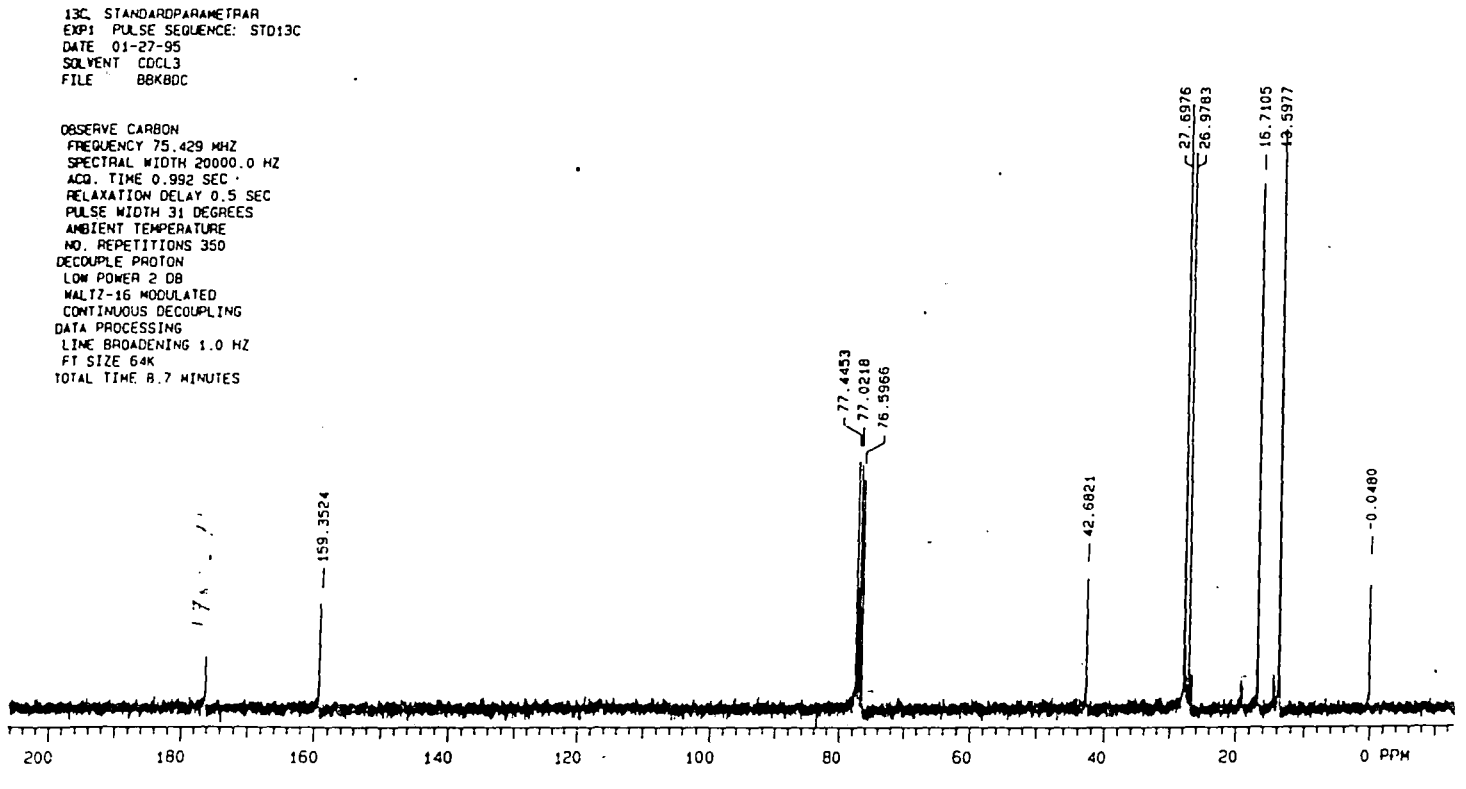


Fig. 5.15 ^{13}C NMR spectrum of tributyl tin (IV) hydantoate

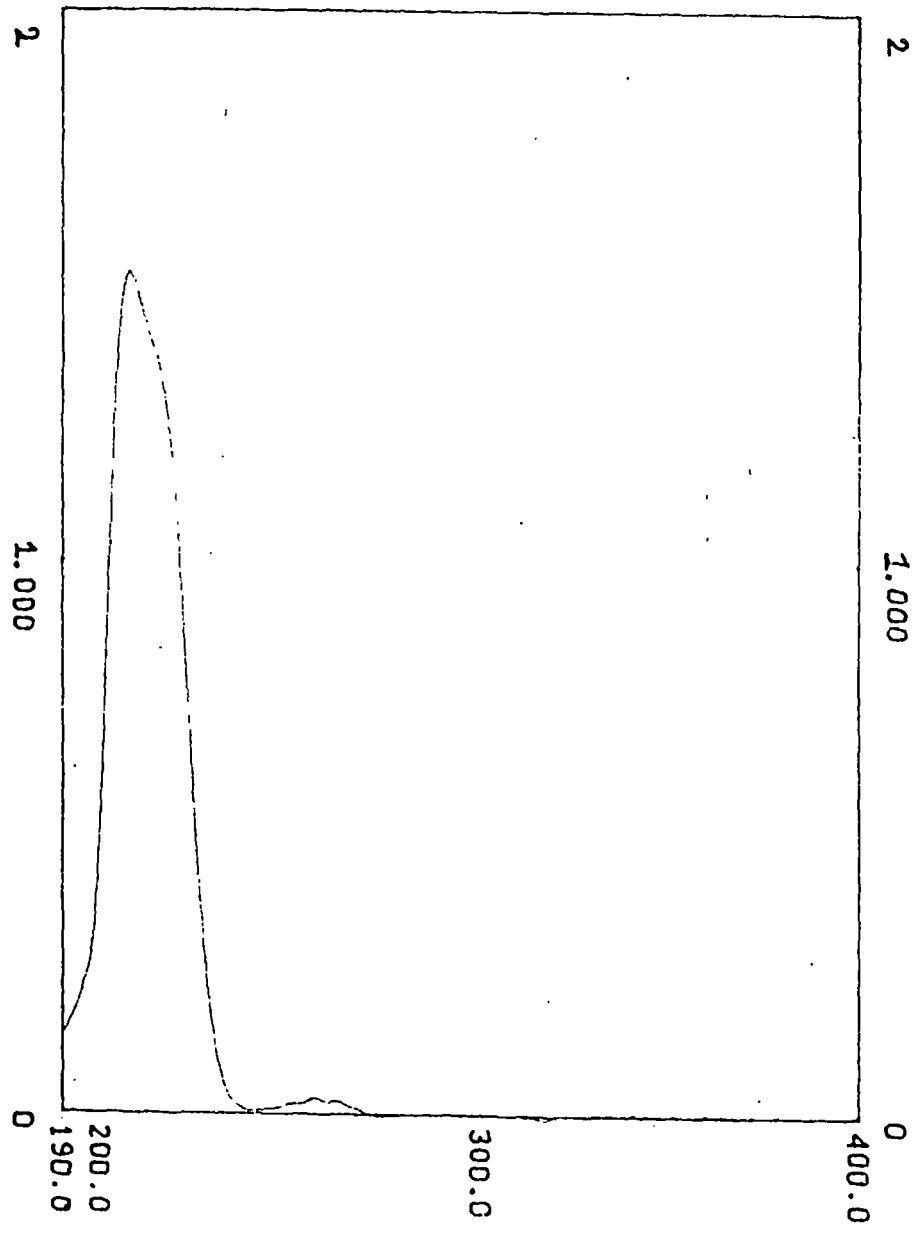


Fig. 5.16 UV spectrum of tri phenyl tin (IV) hydantoate

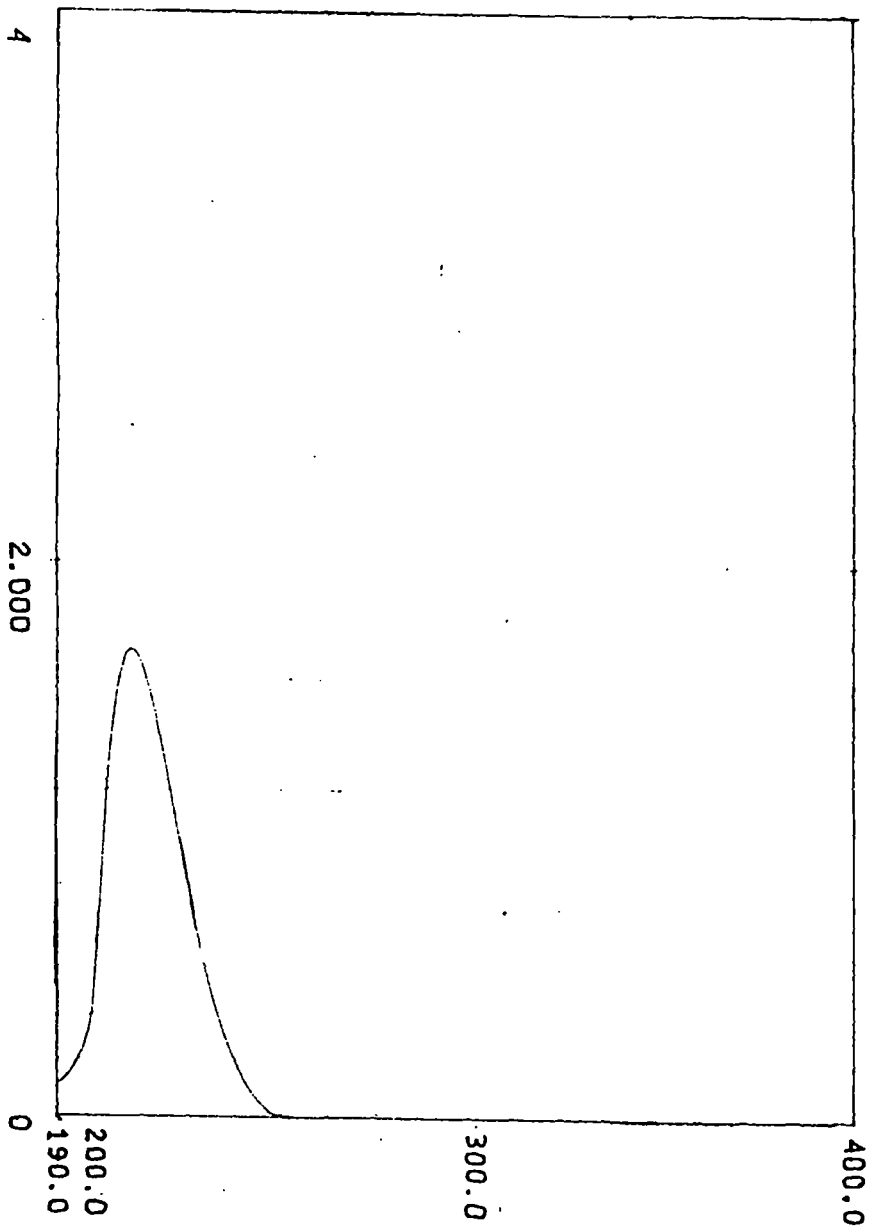


Fig. 5.17 UV spectrum of tricyclohexyl tin(IV)hydantoate

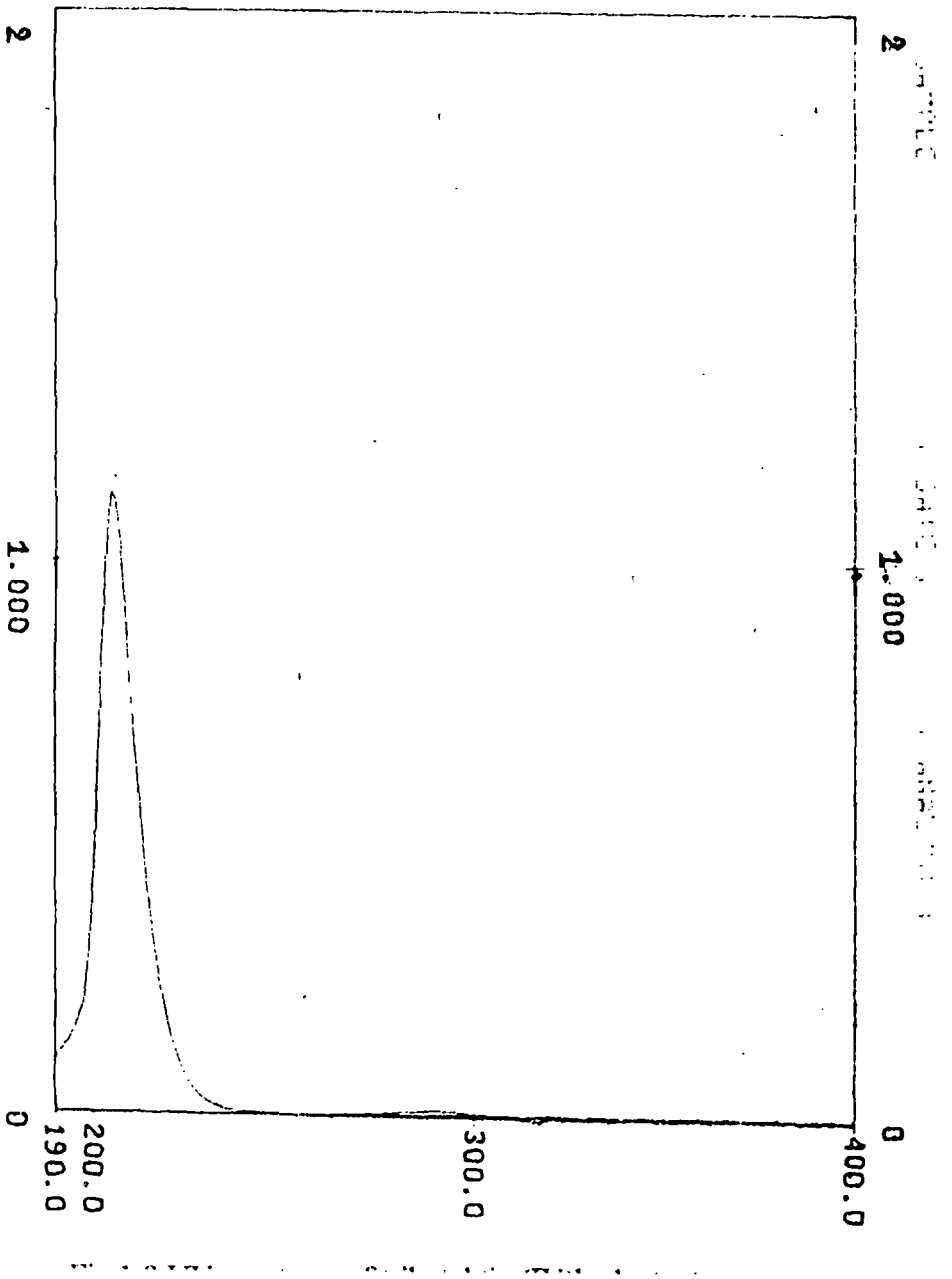


Fig. 5.8 UV spectrum of tributyl tin (IV)hydantoate

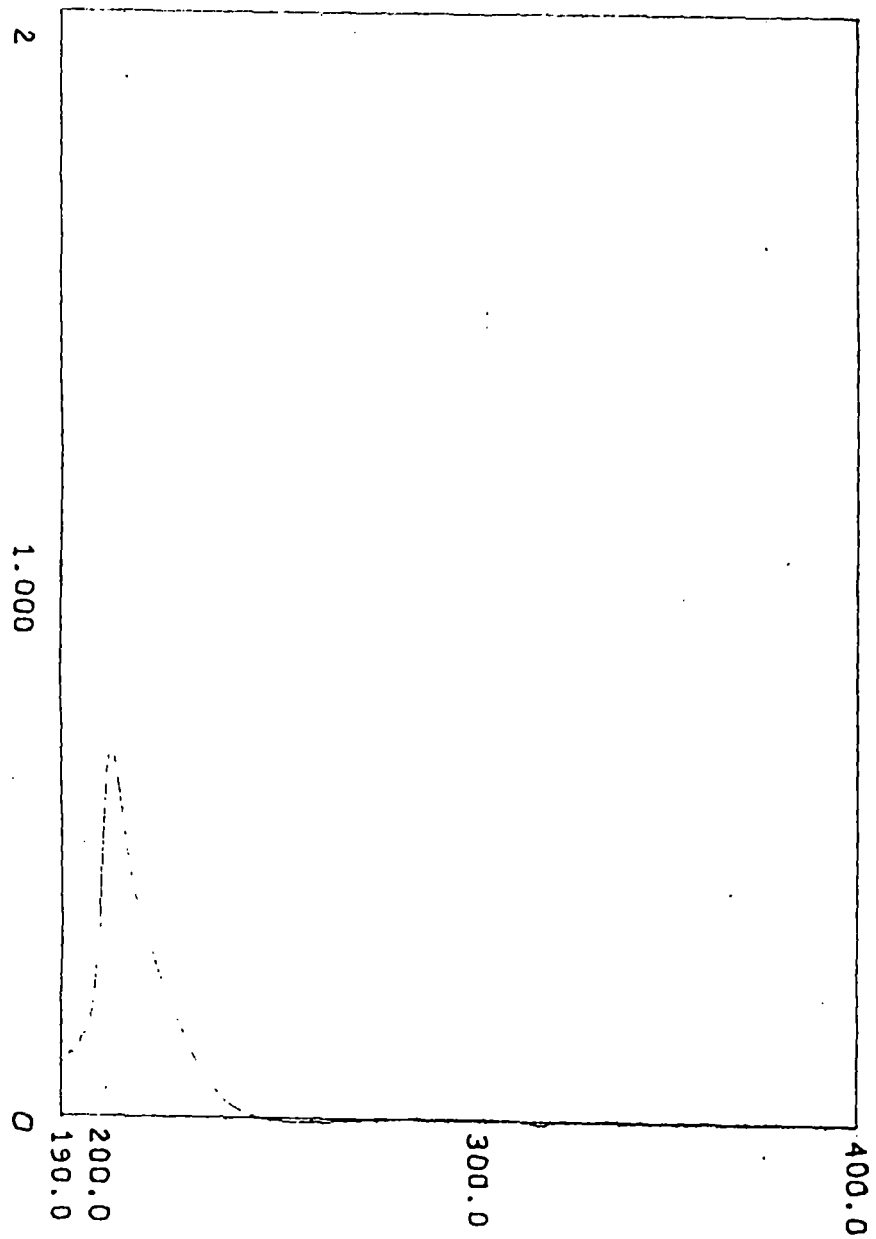


Fig. 5.19 UV spectrum of hydantoic acid

5.4.4 Crystal Structures

5.4.4.1 $[Ph_3Sn(O_2CCH_2N(H)C(O)NH_2)]$

The structure of $[Ph_3Sn(O_2CCH_2N(H)C(O)NH_2)]$ is shown in Fig. 1 and selected interatomic parameters are collected in Table 9. The crystallographic asymmetric unit is comprised of two independent : $[Ph_3Sn(O_2CCH_2N(H)C(O)NH_2)]$ entities, labelled a and b that do not differ significantly from each other. The structure is polymeric owing to the presence of bridging hydantoate ligands. The carboxylate end of the hydantoate anion coordinates a tin atom via one oxygen atom only whereas the other end coordinates another tin atom via the carbonyl group. The Sn(1)....O(2a) and Sn(2)....O(2b) separations of 3.544(3) and 3.549(3) Å, respectively are not representative of significant interactions and the same is true for the Sn(1)....N(4b) and Sn(2)...N(4a) separations of 3.861(4) and 3.886(3) Å respectively. The coordination geometry about each tin atom is completed by the ipso carbon atoms derived from three phenyl groups which define an equatorial plane in the distorted trigonal bipyramidal environments about the tin atoms. In this description, the Sn(1)[Sn(2)] atom lies 0.1093(3) Å [0.0965(3) Å] out of the trigonal plane in the direction of the carboxylate O(1) atom. The Sn-O separation are non-equivalent with the Sn-O(carboxylate) distances of 2.174(2) and 2.174(2)Å, respectively being significantly

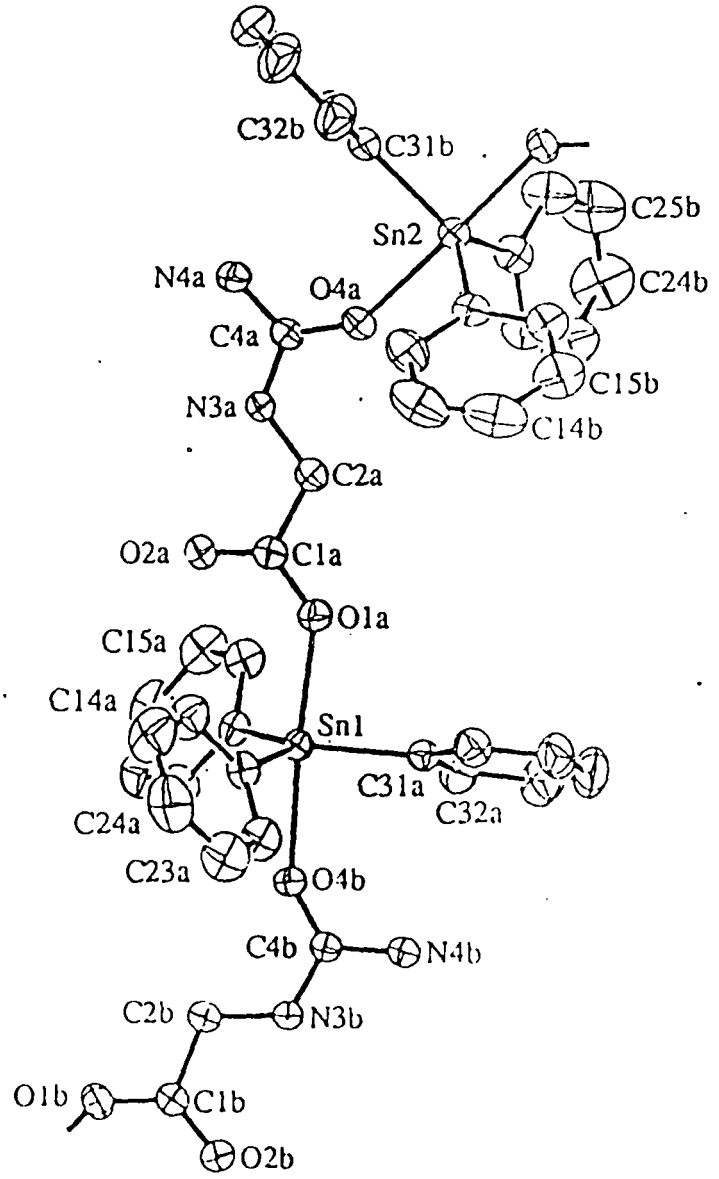


Figure 1 A portion of the polymeric structure and crystallographic numbering scheme for $[Ph_3Sn(O_2CCH_2N(H)C(O)NH_2)]$.

shorter than the Sn-O(carbonyl) interactions of 2.319(2) and 2.315(2) Å, respectively; the axial angles are 175.63(8) and 177.4(1)°, respectively. The dihedral angles formed between the three phenyl groups, i.e. C(11-16), C(21-26) and C(31-36), are 93.8, 108.6 and 115.8°, respectively (81.4, 113.6 and 124.6°, respectively for molecule b). In the lattice the polymeric chains are associated via significant hydrogen bonding contacts. Each of the non-coordinating carbonyl groups forms two O···H-N interactions such that O(2a)····· H(4b1) is 2.01 Å (the O(2a)····N(4b) separation is 2.901(4) Å and the O(2a)···· H-N(4b) angle is 151°) and O(2a)···· H(3b) is 2.11 Å (O2(a)··· N(3b) 2.977(4) Å and O(2a)····· H-N(3b) is 148°) and for molecule b, O(2b)··· H(4a1) is 2.11 Å (symmetry operation : 0.5-x, -0.5+y, 0.5-z, O(2b)····N(4a) is 2.920(4) and O(2b) ···· H-N(4a) is 140°) and O(2b)··· H(3a) is 2.19 Å (O(2b)··· N(3a) is 3.005(4) Å and O(2b)··· H-N(3a) is 141°). The H(4a2) and H(4b2) atoms do not participate in significant hydrogen bonding contacts. The polymeric structure f for $\lfloor Ph_3Sn(O_2CCH_2N(H)C(O)NH_2)\rfloor$ contrasts the monomeric structure found for the R = c-Hex analogue.

5.4.4.2 $\lfloor c\text{-}Hex_3Sn(O_2CCH_2N(H)C(O)NH_2)\rfloor$

The molecular structure of $\lfloor c\text{-}Hex_3Sn(O_2CCH_2N(H)C(O)NH_2)\rfloor$ is shown in Fig. 2 and selected interatomic parameters are collected in Table 9. The hydantoate anion

coordinates the tin atom via one of the carboxylate oxygen atoms forming a Sn-O(1) interaction of 2.090(4) Å ; the separation is shorter than the comparable bonds in the R = Ph derivative. The Sn ... O(2) separation of 2.948(5) Å is not indicative of a significant interaction between these atoms. The absence of other significant inter- or intra-molecular interactions involving the tin atom confirms the monodentate mode of coordination of the hydantoate ligand. The tin atom environment is thus distorted tetrahedral with the maximum distortion from the ideal tetrahedral geometry being manifested in the C(11)-Sn-C(31) angle of 125.6(3) Å which may be traced to the proximity of the non-coordinating O(2) atom. As for the R = Ph derivative there are significant intermolecular hydrogen bonding contacts in the lattice, this time involving both the O(2) and O(4) atoms, the latter owing to the non-coordination of this atom to tin; in this structure all three acidic hydrogen atoms participate in hydrogen bonding. The O(2) ... H(4a) separation is 2.06 Å (symmetry operation; 1.5-$\underline{x}$, 0.5+$\underline{y}$, 0.5-$\underline{z}$, the O(2) ...N(4) separation is 3.010(7) Å and the O(2)... H-N(4) angle is 168°), O(4)...H(4b) is 2.10 Å (symmetry operation : 1.5-$\underline{x}$, -0.5+$\underline{y}$, 0.5-$\underline{z}$, O(4)...N(4) is 2.993(7) Å and O(4)...H-N(4) is 153°) and O(4)...H(3) is 2.19 Å (symmetry operation : 1.5-$\underline{x}$, -0.5+$\underline{y}$, 0.5-$\underline{z}$, O(4)...N(3) is 3.058(7) Å and O(4)...H-N(3) is 149°).

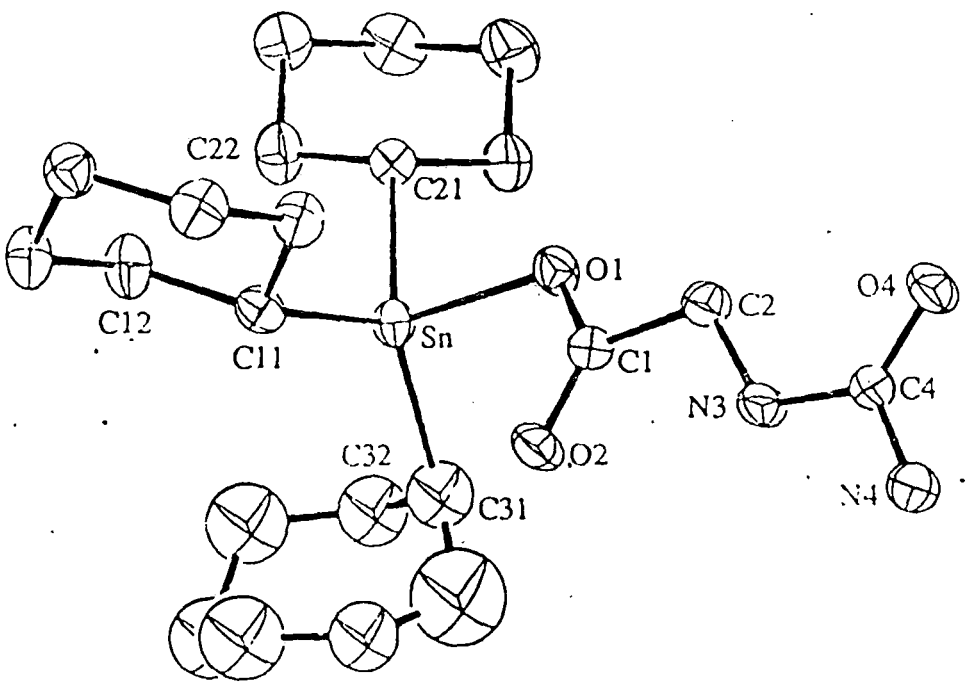


Figure 2 The molecular structure and crystallographic numbering scheme for [c-Hex$_3$Sn(O$_2$CCH$_2$N(H)C(O)NH$_2$)].

Hydantoate coordination

The different modes of coordination of the hydantoate ligands in the R = Ph and R = c-Hex structures are reflected in systematic variations of the derived interatomic parameters (Table 9). The ligands in molecule a and b of the R = Ph structure and in the R = c-Hex structure are essentially planar as reflected in the O(1)/C(1)/C(2)/N(3), C(1)/C(2)/N(3)/C(4) and C(2)/N(3)/C(4)/O(4) torsion angles (Table 9). The shorter Sn-O(1) interaction in the R = c-Hex compound leads to a longer C(1)-O(1) bond, i.e. 1.299(6) Å vs 1.277(4) Å (molecule a) and 1.269(4) Å (molecule b), and, concomittantly, shorter C(1)-O(2) interactions, i.e. 1.205(7) Å vs 1.227(4) and 1.222(4) Å, respectively in the R = Ph structure. Other changes in the ligand parameters relate in particular to the C(4)-N(4) and C(4)-O(4) interactions. The carbonyl C(4)-O(4) bond distance of 1.220(7) Å in the R = c-Hex structure is shorter owing to the non participation in coordination to tin of this group compared to the situation observed in the R = Ph structure where elongation of this bond is apparent, i.e. 1.243(4) and 1.252(4) Å. As a consequence of the increased bond order of the C(4)-O(4) bond in the R = c-Hex structure, the C(4)-N(4) bond distance is increased [1.352(8) Å] compared to that found in the R = Ph structure [i.e. 1.334(4) and 1.326(4) Å].

General Comments

The structure reported here for $[Ph_3Sn(O_2CCH_2N(H)C(O)NH_2]$ is similar to several other triorganotin carboxylates in which the carboxylate residue contains additional potential donor atoms such as oxygen and nitrogen[50]. The closely related structure $[Ph_3Sn(O_2C(CH_2)_2N(H)C(O)NH_2]$[51] adopts this same motif with important parameters Sn-O(1) 2.143(2), Sn-O(4) 2.352(2) Å and O(1)-Sn-O(4) 171.5(1)°. This motif is similar to that found for many $[R_3Sn(O_2CR')]$ structures where the carboxylate is bidentate bridging, i.e. the trans-R_3SnO_2 motif. The other major structural form found for the $[R_3Sn(O_2CR')]$ compounds isthe isolated, distorted tetrahedral arrangement as seen in the structure of $[c\text{-}Hex_3Sn(O_2C(CH_2)_2N(H)C(O)NH_2]$.

The observation in the present study of different modes of coordination of the hydantoate ligand leading to disparate structural motifs has many precedents in the structural chemistry of organotin carboxylate. It has been highlighted in recent reviews of the subject that very different structures may be found for closely related chemical formulae[50]. No consistent correlation between steric and/or electronic effects associated with the organotin centre and the nature of the structure adopted ultimately in the solid state has been established thus far, however. The presence of multiple potential hydrogen bonding sites in the

hydantoate ligand is another factor that may influence the nature of the structure[52]. It is likely that there is a subtle interplay between all of these factors, as well as the less well defined crystal packing effects, which is responsible for the observed structural variations. It is also noteworthy that the phenomenon of structural diversity found in the organotin carboxylates is indeed found in other main group element system[53,54]

5.5. Biocidal Properties:

5.5.1 Introduction :

There is a broad spectrum of industrial applications of organotin carboxylates[11,22,23], such as, organo chemicals (fungicidal, antifeedants), antifouling biocides (in plants), disinfactants, PVC stabiliser etc. Biocidal properties of organotin compounds and the consequent application to the pest control, ecology problems, human medicine and veterinary medicine, etc. have lead to the observed increase in production of organotin compounds during the past few years. Search for new pesticides is essential as even successful pesticides can loose their effectiveness due to growth of resistance of pests towards these pesticides. Moreover, consideration of environmental pollution may lead to the discontinuance of some successful pesticides in future course of time. The main advantages of organotin agrochemicals, are their relatively low phytotoxicity, low

toxicity to non target organisms[33,34], lack of resistance to crop pests to these chemicals and degradation in the environmental situation to harmless inorganic tin residues[35]. Compounds of the type, R_nSnX_{4-n} where R is an organic substituent and X means a polar group are in general biologically active. The most desirable compounds are those where biocidal properties are due not only to the R_nSn group but also to the X group, because in these cases the effects are mutually combined and complemented.

The first investigation in the field of antifungal activity study dates back to as early as 1954[36]. Fungicidal activity is reportedly strictly dependent upon the extent of alkylation of the tin atom, being at maximum with three tin-carbon bonds. Maximum toxicity is associated with a total number 9 to 12 carbon atoms in the alkyl group[37]. Trialkyltin compounds find restricted application as agricultural fungicides due to high phytotoxicity, to some extent due to their mamalian toxicity and also because of less reactivity in the field than in the laboratory trials[38]. In contast, triphenyltin compounds were found to be less phytotoxic hence greater acceptability as fungicide in agriculture.

It is obvious from the above discussion that to find the fungicidal activity of the newly synthesised compounds has importance. The fungicidal activity of any compound will be of real value if the compound has negligible phytotoxicity. For this reason, the compounds were tested also

for their phytotoxicity level.

5.5.2 Experimental :

Fungitoxicity: The synthesised compounds, namely, $Ph_3SnO_2CCH_2NHCONH_2$, $(n\text{-}Bu)_3SnO_2CCH_2NHCONH_2$ and $(Cyclo\text{-}C_6H_{11})_3SnO_2CCH_2NHCONH_2$ were screened for their antifungal effectiveness in vitro against Alternaria alternata (ITCC - 3022) (causative organism of brown spot disease of tobacco and leaf spot and fruit rot of brinjal, Helminthosporium sativum (ITCC - 2684) (causal agent of spot blotch of wheat), Helminthosporium maydis (ITCC - 2675) (causal agent of brown spot of maize (zea mays)_7 and Piricularia oryzae (ITCC - 3050) (blast disease of rice (oryzae sativa)_7. The virulent culture were obtained from the plant pathology laboratory, Department of Botany, U.N.B. Fungi were grown on potato-dextrose - agar (PDA) medium at 28 $\pm$ 1 ^{o}C prepared as described in Chapter 4.

The fungicidal activities were determined following spore germination method as described by Rouxel et al.[31] Eluents (10 ml) were placed on two spots, 3 cm apart in a clean, grease free glass slide and the solvent was allowed to evaporate. Then a drop of spore suspension (0.02 ml), prepared from 15 days old culture was added to these treated spots. In this way sets for various concentrations of the compounds were prepared. The slids were left for 24 hours

under humid condition. Finally, one drop of a cotton blue-lactophenol mixture was added to each spot to fix the germinated spores. The number of spores germinated compared to control was then calculated considering an average of 500 spores per treatment. The percentage of inhibition with respect to control was calculated using the Vincent[32] equation :

$$\% \text{ inhibition} = \frac{C-T}{C} \times 100,$$ where C and T are germination of spores under control and treated spore suspensions respectively. The % of spores inhibited from germination were determined at different concentrations. From these, the ED_{50} (effective dose for 50% inhibition) values were calculated.

Phytotoxicity study of these compounds were done on rice seeds of PUSA 2-21 variety, collected from Chinsurah Rice Research Institute, Hooghly, West Bengal, India.

Phytotoxicity :

Rice seeds were dipped in compound suspensions at different concentrations (25, 50 and 100 µg/ml) for 1, 4 and 8 hours. The treated seeds were allowed to germinate sowed over a mat of moist filter papers arranged in covered petriplates. One hundred seeds were treated for each experiment. After seven days the germinated seeds were counted

against control ; seeds producing a root, a coleoptile were considered as germinated. Each experiment was repeated in triplicate.

All apparatus and materials were sterilized where necessary using standard procedures.

5.5.3 Discussion :

The results of fungitoxicity and phytotoxicity studies are presented in Table - 4 and Table - 5 respectively. Rice seed germination studies showed that tricyclohexyl and triphenyltin derivatives have practically no phytotoxicity but the tributyltin derivative is comparatively more phytotoxic.

From table - 4, it may be seen that the tributyltin derivative is the most effective against the fungi used in vitro. The fungitoxicities (ED_{50} values) are in the following order :

$$n\text{-}Bu_3Sn \rightarrow Ph_3Sn \rightarrow (Cyclo\text{-}C_6H_{11})_3Sn\text{-}$$

Table - 1

Physical data[a]

Compound	mp (°C)	Yield (%)	C (%)	H (%)	N (%)	Sn (%)	U.V.[b] λ_{max} (nm)	U.V.[b] ϵ_{max}
$Ph_3SnOCOCH_2NHCONH_2$	203	40%	53.81 (53.99)	3.94 (4.28)	5.90 (5.99)	25.29 (25.43)	208	5.3×10^4
$(Cyclo\text{-}C_6H_{11})SnOCOCH_2NHCONH_2$	194	50%	53.71 (51.99)	7.50 (7.84)	6.38 (5.77)	23.92 (24.49)	210	1.6×10^4
$(n\text{-}Bu)_3SnOCOCH_2NHCONH_2$	112	65%	44.44 (44.25)	7.71 (7.86)	6.96 (6.88)	29.09 (29.18)	204	0.6×10^4

[a] Values in the parantheses indicate the theoretically calculated values

[b] Spectra recorded in MeOH.

Table - 2

Relevant I.R. data for the compounds[a]

Compound	νNH_2	νNH	Amide II NH	Amide II NH_2	νOCO	Amide I CO	νSnC
$Ph_3SnOCOCH_2NHCONH_2$[c]	3415(m) 3310(mb)	3260(sh,m) 3120(w)	1525(s)	1555(vs,b)	1600(s,b)	1555(vs,b)	280(w) 250(w)
$Bu_3SnOCOCH_2NHCONH_2$[b]	3480(m) 3320(m)	3300(sh,m) 3180(m)	1530(vs,b)	1585(vs,b)	1620(vs)	1585(vs,b)	480(w) 430(w)
	3460(s) 3340(s)	3100(s,b)	1525(s,sh)	1565(s,b)	1620(vs)	1650(vs,b)	500(w) 470(w)
$Cy_3SnOCOCH_2NHCONH_2$[b]	3430(m) 3340(m)	3270(m) 3150(m)	1525(s,b)	1580(vs,b)	1615(s,b)	1580(vs,b)	500(w) 470(w)
	3440(m,sh) 3380(m,b)	3280(m) 3230(m)	1510(m,b)	1565(s)	1615(s)	1630(s,b)	500(vw,b) 425(vw)

[a]nujol mull on CsI optics, [b]in $CHCl_3$ solution, [c]solution spectra could not be obtained due to poor solubility in $CHCl_3$, v = very, s = strong, m = medium, w = weak, b = broad, sh = shoulder.

Table - 3

^{1}H NMR Data for the compounds (90 MHz)

Compound	δ(SnPh)	δ(NH)	δ$(NH)_2$	δ$(CH)_2$	δ(SnB^n)	δ(SnCy)
$Ph_3SnOCOCH_2NHCONH_2$ [a]	7.96–7.06 (m, 15H)	5.96 (b, 1H)	5.48 (s, 2H)	3.62 (d, 2H) J= 5 Hz		
$Bu_3SnOCOCH_2NHCONH_2$ [b]		5.06 (t, 1H) j=5 Hz	5.02 (s, 2H)	3.97 (d, 2H) J=5Hz	2.20–0.20 (m, 27H)	
$Cy_3SnOCOCH_2NHCONH_2$ [b]		5.66 (b, 1H)	4.77 (s, 2H)	4.03 (d, 2H) J=5 Hz		2.50–0.63 (m, 33H)

[a] Spectra recorded in saturated solutions of d_6-DMSO and [b] $CDCl_3$ using internal TMS reference. All shifts are in ppm downfield from TMS, m = complex multiplet pattern, b = broad, s = singlet, d = doublet, t = triplet.

Table - 4

Effect of the compounds on spre germination

	Compound	ED_{50} (ug/ml)
of *A. alternata*	$(Cyclo\text{-}C_6H_{11})_3SnL$	100.00
	Ph_3SnL	20.00
	$(n\text{-}Bu)_3SnL$	0.50
of *H. sativum*	$(Cyclo\text{-}C_6H_{11})_3SnL$	595.60
	Ph_3SnL	1.42
	$(N\text{-}Bu)_3SnL$	0.32
of *H. maydis*	$(CyClo\text{-}C_6H_{11})_3SnL$	22.40
	Ph_3SnL	3.55
	$(N\text{-}Bu)_3SnL$	0.005
of *P. oryzae*	$(Cyclo\text{-}C_6H_{11})_3SnL$	94.40
	Ph_3SnL	0.45
	$(n\text{-}Bu)_3SnL$	0.005

L = $-OCOCH_2NHCONH_2$

Table - 5

Effect of the compounds on rice seed germination

Compound	Concentration (µg/ml)	% of germinated seeds with respect to control treated for		
		1 hr.	4 hr.	8 hr.
$(Cyclo\text{-}C_6H_{11})_3SnL$	100	95	93	90
	50	95	93	93
	25	95	95	94
Ph_3SnL	100	94	92	91
	50	95	94	94
	25	95	95	95
$(n\text{-}Bu)_3SnL$	100	84	81	79
	50	87	83	83
	25	87	85	84
	Control	95	95	95

L = $-OCOCH_2NHCONH_2$

Table 6 Crystallographic data for [$Ph_3Sn(O_2CCH_2N(H)C(O)NH_2)$] (1) and [$c\text{-}Hex_3Sn(O_2CCH_2N(H)C(O)NH_2)$] (2)

	1	2
Formula	$C_{21}H_{20}N_2O_3Sn$	$C_{21}H_{38}N_2O_3Sn$
Formula weight	467.1	485.2
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a, Å	16.955(6)	10.718(4)
b, Å	14.954(3)	9.088(3)
c, Å	17.865(2)	22.549(6)
β, deg.	115.08(1)	98.49(2)
V, $Å^3$	4102(1)	2268(1)
Z	8	4
D_{calcd}, g cm^{-3}	1.512	1.421
F(000)	1872	1008
μ, cm^{-1}	12.67	11.48
Crystal size, mm	0.23 x 0.48 x 0.48	0.08 x 0.13 x 0.32
Transmission coefficients	0.939 - 1.029	0.870 - 1.056
No. data measured	10199	5803
No. unique data	9879	5517
No. observed data	6839	3188
R	0.033	0.049
R_w	0.035	0.057
ρ_{max}, e $Å^{-3}$	0.48	0.88

Table 7 Fractional atomic coordinates for $[Ph_3Sn(O_2CCH_2N(H)C(O)NH_2)]$

Atom	x	y	z
Sn(1)	0.24925(2)	0.12325(2)	0.17665(1)
Sn(2)	0.28465(2)	0.19923(2)	-0.31119(1)
O(1a)	0.2692(2)	0.1617(2)	0.0686(1)
O(1b)	0.2963(2)	0.1506(2)	0.5793(1)
O(2a)	0.2768(2)	0.3111(2)	0.0691(1)
O(2b)	0.2469(2)	0.0101(2)	0.5581(1)
O(4a)	0.2686(2)	0.2565(2)	-0.1981(2)
O(4b)	0.2275(2)	0.0711(2)	0.2887(1)
N(3a)	0.2839(2)	0.3154(2)	-0.0780(2)
N(3b)	0.2453(2)	0.0050(2)	0.4072(2)
N(4a)	0.2924(3)	0.4058(2)	-0.1763(2)
N(4b)	0.2181(3)	-0.0801(2)	0.2945(2)
C(1a)	0.2751(2)	0.2374(2)	0.0382(2)
C(1b)	0.2688(3)	0.0799(2)	0.5368(2)
C(2a)	0.2794(3)	0.2294(2)	-0.0440(2)
C(2b)	0.2649(4)	0.0884(3)	0.4508(2)
C(4a)	0.2808(2)	0.3237(2)	-0.1535(2)
C(4b)	0.2298(3)	0.0009(2)	0.3277(2)
C(11a)	0.1526(2)	0.2204(2)	0.1634(2)
C(11b)	0.3874(3)	0.1216(3)	-0.2230(2)
C(12a)	0.1422(3)	0.2520(3)	0.2319(2)
C(12b)	0.4397(3)	0.1553(3)	-0.1454(3)
C(13a)	0.0788(3)	0.3142(3)	0.2238(3)
C(13b)	0.5035(4)	0.1031(5)	-0.0868(3)
C(14a)	0.0247(3)	0.3452(3)	0.1468(4)
C(14b)	0.5165(4)	0.0178(5)	-0.1049(3)
C(15a)	0.0346(3)	0.3155(3)	0.0789(3)
C(15b)	0.4667(4)	-0.0166(3)	-0.1808(3)
C(16a)	0.0981(3)	0.2538(3)	0.0867(2)
C(16b)	0.4022(3)	0.0351(3)	-0.2402(3)
C(21a)	0.3818(3)	0.1409(2)	0.2602(2)

C(21b)	0.1534(3)	0.1576(3)	-0.3559(2)
C(22a)	0.4232(3)	0.0799(3)	0.3226(3)
C(22b)	0.1215(3)	0.1164(3)	-0.3055(3)
C(23a)	0.5096(3)	0.0899(4)	0.3776(3)
C(23b)	0.0357(4)	0.0839(4)	-0.3374(4)
C(24a)	0.5560(4)	0.1622(4)	0.3706(3)
C(24b)	-0.0171(4)	0.0922(5)	-0.4188(4)
C(25a)	0.5170(4)	0.2228(4)	0.3093(4)
C(25b)	0.0131(4)	0.1320(5)	-0.4701(4)
C(26a)	0.4303(3)	0.2120(3)	0.2535(3)
C(26b)	0.0978(3)	0.1643(4)	-0.4396(3)
C(31a)	0.2050(3)	-0.0019(2)	0.1183(2)
C(31b)	0.3106(3)	0.3296(2)	-0.3423(2)
C(32a)	0.1193(3)	-0.0274(3)	0.0917(3)
C(32b)	0.3921(4)	0.3548(3)	-0.3300(3)
C(33a)	0.0917(4)	-0.1104(4)	0.0563(3)
C(33b)	0.4089(5)	0.4395(4)	-0.3526(4)
C(34a)	0.1485(5)	-0.1674(3)	0.0450(3)
C(34b)	0.3416(7)	0.4980(4)	-0.3883(4)
C(35a)	0.2329(4)	-0.1435(3)	0.0697(3)
C(35b)	0.2607(6)	0.4751(4)	-0.4003(3)
C(36a)	0.2614(3)	-0.0608(3)	0.1064(2)
C(36b)	0.2437(4)	0.3916(3)	-0.3782(3)

Table 8 Fractional atomic coordinates for [c-Hex$_3$Sn(O$_2$CCH$_2$N(H)C(O)NH$_2$)]

Atom	x	y	z
Sn	0.23034(4)	0.28672(5)	0.11052(2)
O(1)	0.3303(3)	0.1051(5)	0.1479(2)
O(2)	0.4916(4)	0.2549(5)	0.1691(2)
O(4)	0.6864(5)	-0.1946(5)	0.2505(2)
N(3)	0.6393(4)	0.0397(5)	0.2243(2)
N(4)	0.8226(5)	-0.0133(6)	0.2819(3)
C(1)	0.4474(5)	0.1329(7)	0.1679(3)
C(2)	0.5223(5)	-0.0007(7)	0.1897(3)
C(4)	0.7140(6)	-0.0643(7)	0.2518(3)
C(11)	0.3267(5)	0.3339(7)	0.0386(3)
C(12)	0.2353(6)	0.3945(8)	-0.0129(3)
C(13)	0.3039(7)	0.4294(8)	-0.0637(3)
C(14)	0.3718(7)	0.2962(8)	-0.0816(3)
C(15)	0.4613(7)	0.2344(9)	-0.0321(3)
C(16)	0.3968(7)	0.1998(8)	0.0196(3)
C(21)	0.0556(5)	0.1678(7)	0.0874(3)
C(22)	-0.0485(6)	0.2578(9)	0.0517(3)
C(23)	-0.1706(6)	0.1689(9)	0.0372(4)
C(24)	-0.2157(6)	0.1121(10)	0.0899(4)
C(25)	-0.1148(7)	0.0190(9)	0.1252(4)
C(26)	0.0064(6)	0.1082(8)	0.1405(3)
C(31)	0.2111(10)	0.4376(12)	0.1809(4)
C(32)	0.0922(9)	0.5282(12)	0.1740(5)
C(33)	0.0787(12)	0.6250(16)	0.1279(6)
C(34)	0.1717(13)	0.7407(15)	0.1342(6)
C(35)	0.2867(14)	0.6914(16)	0.1308(6)
C(36a)[a]	0.3474(10)	0.5969(13)	0.1723(5)
C(36b)[a]	0.3058(16)	0.5072(21)	0.2051(7)

[a] site occupancy factor = 0.5.

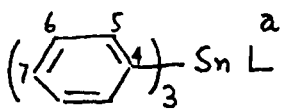
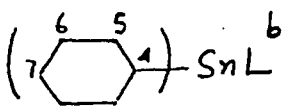
Table 9 Selected bond distances (Å) and angles (°) for $R_3Sn(O_2CCH_2N(H)C(O)NH_2)$

Parameter	R = Ph molecule a	R = Ph molecue b	R = c-Hex
Sn-O(1)	2.174(2)	2.174(2)[a]	2.090(4)
Sn-O(4)	2.319(2)[b]	2.315(2)[c]	
Sn-C(11)	2.127(4)	2.131(4)	2.153(6)
Sn-C(21)	2.122(4)	2.114(5)	2.161(6)
Sn-C(31)	2.118(3)	2.124(4)	2.19(1)
C(1)-O(1)	1.277(4)	1.269(4)	1.299(6)
C(1)-O(2)	1.227(4)	1.222(4)	1.205(7)
C(4)-O(4)	1.243(4)	1.252(4)	1.220(7)
C(2)-N(3)	1.439(4)	1.434(5)	1.438(7)
C(4)-N(3)	1.334(4)	1.331(4)	1.342(7)
C(4)-N(4)	1.334(4)	1.326(4)	1.352(8)
C(1)-C(2)	1.508(5)	1.514(5)	1.503(8)
O(1)-Sn-O(4)	175.63(8)[b]	177.4(1)[a,c]	
O(1)-Sn-C(11)	97.1(1)	97.2(1)[a]	102.3(2)
O(1)-Sn-C(21)	94.3(1)	92.5(1)[a]	94.7(2)
O(1)-Sn-C(31)	87.3(1)	87.9(1)[a]	106.0(3)
O(4)-Sn-C(11)	85.9(1)[b]	85.3(1)[c]	
O(4)-Sn-C(21)	86.7(1)[b]	86.8(1)[c]	
O(4)-Sn-C(31)	88.5(1)[b]	90.1(1)[c]	
C(11)-Sn-C(21)	122.0(1)	121.2(1)	113.6(2)
C(11)-Sn-C(31)	117.0(1)	119.9(2)	125.6(3)

C(21)-Sn-C(31)	120.3(1)	118.2(2)	109.2(3)
Sn-O(1)-C(1)	132.9(2)	131.8(2)	114.0(4)
Sn-O(4)-C(4)	141.7(2)[b,d]	143.9(2)[c,e]	
C(2)-N(3)-C(4)	121.5(3)	121.0(3)	120.2(5)
O(1)-C(1)-O(2)	126.7(3)	127.5(3)	122.9(6)
O(1)-C(1)-C(2)	112.8(3)	112.5(3)	114.0(5)
O(2)-C(1)-C(2)	120.5(3)	120.0(3)	123.1(5)
N(3)-C(2)-C(1)	111.9(3)	112.3(3)	111.4(5)
O(4)-C(4)-N(3)	119.8(3)	120.1(3)	123.1(6)
O(4)-C(4)-N(4)	123.7(3)	123.6(3)	122.2(6)
N(3)-C(4)-N(4)	116.5(3)	116.3(3)	114.7(6)
O(1)/C(1)/C(2)/N(3)	178.7(3)	172.0(4)	-165.1(5)
C(1)/C(2)/N(3)/C(4)	-174.2(3)	172.7(4)	174.0(6)
C(2)/N(3)/C(4)/O(4)	4.3(6)	-3.9(7)	-2(1)

[a] Atom related by the symmetry operation: x, y, -1+z. [b] O(4b). [c] O(4a). [d] C(4b). [e] C(4a).

Table 10 ^{13}C NMR spectroscopic data (δ ppm)

Compound	C_1	C_2	C_3	C_4	C_5	C_6	C_7
	159.22	43.15	174.11	142.85	136.55	128.84	128.65
	158.22	42.90	175.25	34.13	31.00	28.85	26.80
$(CH_3-CH_2-CH_2-CH_2-)_3SnL^b$	159.35	42.68	176.27	27.69	26.97	16.71	13.59

L = $-OCOCH_2NHCONH_2$ (3 2 1)

a = Spectra recorded in d_6-DMSO

b = Spectra recorded in $CDCl_3$

Table 11 ^{1}H NMR spectroscopic data[a] (300 MHz)

Compound	δ NH	δ NH_2	δ CH_2	δ Sn-Ph/Cy/Bu	δ OH
Ph_3SnL[e]	5.88(1),s,b	5.56(2),s	3.57(2),d J=0.02 Hz	7.83-7.42(15),m	
Cy_3SnL[C,e]	5.58(1),s,b 5.98(1),s,b	4.68(2),s 5.58(2),s	3.84(2),d 3.57(2),d J=0.02 Hz	1.91-1.32(33),m 1.86-1.21(33),m	
Bu_3SnL[C,e]	6.20(1),s,b 5.91(1),s,b	5.08(2),s 5.56(2),s	3.91(2),d 3.49(2),d J=0.02 Hz	1.60-0.85(27),m 1.60-0.83(27),m	
$HOCOCH_2NHCONH_2$[e]	6.19(1),t J=0.02 Hz	5.69(2),s	3.66(2),d J=0.02 Hz		12.46(1),s,b

L = $-OCOCH_2NHCONH_2$

a = Chemical shift in ppm downfield relative to Me_4Si as internal standard

C = Spectra recorded in $CDCl_3$

e = Spectra recorded in d_6 - DMSO

s = Singlet, b = broad, d = doublet, m = multiplet

R E F E R E N C E S

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Biocidal Organotin Compounds. Part 2. Synthesis, Characterization and Biocidal Properties of Triorganotin(IV) Hydantoic Acid Derivatives and the Crystal Structures of Triphenyltin- and Tricyclohexyltin- Hydantoate

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The preparation and spectroscopic (^{1}H NMR, UV and IR) characterization of three $R_3Sn(O_2CCH_2N(H)C(O)NH_2)$, R = Ph, c-Hex or nBu, compounds is reported. A different mode of coordination is indicated for the hydantoate ligand in the R = Ph compound compared with the R = c-Hex and R = nBu compounds as confirmed by a crystallographic analysis. The structure of $[Ph_3Sn(O_2CCH_2N(H)C(O)NH_2)]$ is polymeric owing to the presence of bridging hydantoate ligands such that each ligand coordinates one tin atom

via one of the carboxylate oxygen atoms and a symmetry related tin atom via the carbonyl group of the other end of the molecule. The structure features distorted trigonal bipyramidal tin atom geometries with a <u>trans</u>-R_3SnO_2 motif. The structure of [c-$Hex_3Sn(O_2CCH_2N(H)C(O)NH_2)$] by contrast is monomeric, distorted tetrahedral as the carboxylate group is again monodentate and there are no additional tin-ligand interactions. The structures are each stabilized by a number of intermolecular hydrogen bonds. Fungitoxicity and phytotoxicity studies indicate that the R = nBu derivative is the more active compound.

Keywords: Triorganotin, carboxylate, crystal structure, fungitoxicity

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INTRODUCTION

Various triorganotin carboxylates are known to have significant biocidal properties [1,2] and it is expected that the incorporation of biologically active entities into a triorganotin system would lead to the formation of potent biocides. Hydantoic acid, $H_2NC(O)N(H)CH_2C(O)OH$, and some of its derivatives are known to possess biological activity [3] and in the above context, its reactions with triorganotin moieties have been investigated in the present study. In addition to the carboxylate binding site, the anion derived from hydantoic acid has other potential donor sites available for coordination. Continuing previous work into the structure/activity relationship of organotin(IV) carboxylates,[4] the present report details a study of the interaction of triorganotin centres with hydantoic acid employing spectroscopic and crystallographic methods, as well as the biocidal properties of the new compounds.

EXPERIMENTAL

General

The solvents were purified and dried before use by standard procedures. Ph_3SnCl, $(nBu_3Sn)_2O$, c-Hex_3SnOH and hydantoic acid were used as received from commercial sources. Ph_3SnOH was prepared by alkaline hydrolysis of Ph_3SnCl.[5] The ^1H NMR spectra were recorded on a VA-EM-390 (90MHz) spectrometer. The IR spectra were recorded on a Pye-Unicam SP-300S spectrophotometer using CsI optics and UV spectra on a Shimadzu-240 spectrophotometer. Microanalyses were performed at RSIC, Punjab University and tin was estimated gravimetrically as SnO_2. Analytical data are presented in Table 1.

Syntheses

[$Ph_3Sn(O_2CCH_2N(H)C(O)NH_2)$]. A 250 ml round bottomed flask was placed on a heating mantle and fitted with a Dean-Stark apparatus with a double surface, water cooled reflux condenser. The entire apparatus was flushed with N_2 to exclude moisture and the reaction was carried out under N_2. Ph_3SnOH (1.4 g, 3.8 mmol), hydantoic acid (0.45 g, 3.8 mmol) and dry benzene (150 ml) were placed in the reaction vessel. The reaction was perfomed under reflux for 24 h with water produced being removed azeotropically. The resultant solution was concentrated and left to stand overnight. The white solid that precipitated was filtered off and washed successively with petroleum ether (60-80 °C) and chloroform. Recrystallization from methanol solution afforded colourless crystals. The other compounds were prepared using similar procedures; analytical data are given in Table 1.

Crystallography

Intensity data for colourless crystals were measured at room temperature on a Rigaku AFC6R diffractometer fitted with graphite monochromatized MoKα radiation, $\lambda = 0.71073$ Å, up to θ_{max} 27.5° employing the ω:2θ scan technique. The data were corrected for Lorentz and polarization effects [6] and for absorption employing the DIFABS program.[7] Of the data measured, those that satisfied the $I \geq 3.0\sigma(I)$ criterion of observability were used in the subsequent analysis. Crystal data are summarized in Table 2.

The structures were solved by direct methods [8] and each refined by a full-matrix least-squares procedure based on F.[6] Non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen-atoms were included in the models at their calculated positions (C-H, N-H 0.97 Å) with the following exception In the refinement of [c-$Hex_3Sn(O_2CCH_2N(H)C(O)NH_2)$], disorder (high thermal motion) was noted in the cyclohexyl ring C(31)-C(36) with two positions being detected for the C(36) atom; this

group was refined with isotropic thermal parameters and hydrogen atoms were not included. Final refinement details (sigma weights [6]) are listed in Table 2; the analysis of variance showed no special features in either case. The crystallographic numbering scheme used is shown in Figs 1 and 2 (drawn with ORTEP [9]) and fractional atomic coordinates are listed in Tables 3 and 4. Other crystallographic details comprising thermal parameters, hydrogen-atom parameters, all bond distances and angles, and tables of observed and calculated structure factors are available on request from ERTT.

Biological studies

The new compounds were screened for their antifungal effectiveness in vitro against Alternaria alternata (ITCC 3022), a causative organism of brown spot disease of tobacco, leaf spot and fruit rot of brinjal, Helminthosporium sativum (ITCC 2684), causal agent of spot blotch of wheat, Helminthosporium maydis (ITCC 2675), causal agent of brown spot of maize (zea mays), and Piricularia oryzae (ITCC 3050), blast disease of rice (oryzae sativa). The virulent cultures were obtained from the plant pathology laboratory, Department of Botany, U.N.B. Fungi were grown on potatoe-dextrose-agar (PDA) medium at 28 ± 1°C.

The fungicidal activities were determined following the spore germination method as described by Rouxel et al.[10] Eluents (10 µl) 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), prepared from 15-day-old culture was added to the treated spots. In this way sets for various concentrations of the compounds were prepared. The slides were left for 24 hours under humid conditions. Finally, one drop of a cotton blue-lactophenol mixture was added to each spot to fix the germinated spores. The number of spores germinated compared to the control was calculated considering an average of 500 spores per treatment. The percentage of inhibition with respect to the control was calculated using the Vincent equation:[11]

$$\text{inhibition} = \frac{C - T}{T} \times 100\%$$

where C is the number of spores germinated in control and T is the total number of spores germinated after treatment. The percentage of spores inhibited from germination were determined at different concentrations. From these, the effective doses for 50% inhibition, ED_{50}, were calculated in units of $\mu g\ l^{-1}$.

Phytotoxicity of the tin compounds were determined on healthy rice seeds of PUSA-2-21 variety, collected from Chinsurah Rice Research Institute, Hooghly, West Bengal.

Rice seeds were dipped in suspensions of the compounds of different concentrations (25, 50 and 100 $\mu g\ ml^{-1}$) for 1, 4 and 8 hours. The treated seeds were allowed to germinate sowed over a mat of moist filter papers arranged in covered petriplates. One hundred seeds were treated for each experiment. After seven days the germinated seeds were counted against the control and those seeds which had produced a coleoptile were considered as germinated. Each experiment was repeated in triplicate. All apparatus and materials were sterilized where necessary using standard procedures.

DISCUSSION

Synthesis and Spectroscopy

The $R_3Sn(O_2CCH_2N(H)C(O)NH_2)$, R = Ph, c-Hex and nBu, compounds have been prepared in moderate yield from the respective reactions of the triorganotin hydroxides (R = Ph, c-Hex) and oxides (R = nBu) with hydantoic acid; physical data are collected in Table 1.

The ^1H NMR chemical shifts of the resonances, and their integration, observed in the spectra (Table 5) confirm the stoichiometry of the compounds. The assignments of the

important absorptions in the infrared spectra of the new compounds are collected in Table 6. The NH_2 and NH stretching frequencies appear between 3480 and 3120 cm^{-1} in a CsI matrix. The spectra are rather complicated in the region 1650 to 1500 cm^{-1} owing to the presence of amide I, amide II and carboxylate streching frequencies. Considering hydantoic acid to be a mono substituted derivative of urea, i.e. $RHNC(=O)NH_2$, following the literature precedent,[12] in each case the NH_2 deformation and C=O stretching vibrations appear together as very strong, but slightly broad bands; in solution these split (Table 6). The amide I (CO) band in $Ph_3(O_2CCH_2N(H)C(O)NH_2)$ occurs at 1555 cm^{-1}, a clear indication that the N-C(=O)-N carbonyl group is involved in coordination in contrast to the other R = c-Hex and R = nBu derivatives for which the equivalent frequencies occur at 1580 and 1585 cm^{-1}, respectively in the solid state. The crystal determination of R = Ph and R = c-Hex compounds have been undertaken to examine in detail the mode of coordination of the hydantoate ligands.

Crystal structures

[$Ph_3Sn(O_2CCH_2N(H)C(O)NH_2)$]

The structure of [$Ph_3Sn(O_2CCH_2N(H)C(O)NH_2)$] is shown in Fig. 1 and selected interatomic parameters are collected in Table 7. The crystallographic asymmetric unit is comprised of two independent [$Ph_3Sn(O_2CCH_2N(H)C(O)NH_2)$] entities, labelled a and b, that do not differ significantly from eachother. The structure is polymeric owing to the presence of bridging hydantoate ligands. The carboxylate end of the hydantoate anion coordinates a tin atom via one oxygen atom only whereas the other end coordinates another tin atom via the carbonyl group. The Sn(1)...O(2a) and Sn(2)...O(2b) separations of 3.544(3) and 3.549(3) Å, respectively are not representative of significant interactions and the same is true for the Sn(1)...N(4b) and Sn(2)...N(4a) separations of 3.861(4) and 3.886(3) Å, respectively. The coordination geometry about each tin atom is completed by the ipso carbon atoms derived from three phenyl groups which define an equatorial plane in

the distorted trigonal bipyramidal environments about the tin atoms. In this description, the Sn(1) [Sn(2)] atom lies 0.1093(3) Å [0.0965(3)Å] out of the trigonal plane in the direction of the carboxylate O(1) atom. The Sn-O separations are non-equivalent with the Sn-O(carboxylate) distances of 2.174(2) and 2.174(2) Å, respectively being significantly shorter than the Sn-O(carbonyl) interactions of 2.319(2) and 2.315(2) Å, respectively; the axial angles are 175.63(8) and 177.4(1)°, respectively. The dihedral angles formed between the three phenyl groups, i.e. C(11-16), C(21-26), and C(31-36), are 93.8, 108.6 and 115.8°, respectively (81.4, 113.6 and 124.6°, respectively for molecule b). In the lattice the polymeric chains are associated via significant hydrogen bonding contacts. Each of the non-coordinating carbonyl groups forms two O...H-N interactions such that O(2a)...H(4b1) is 2.01 Å (the O(2a)...N(4b) separation is 2.901(4) Å and the O(2a)...H-N(4b) angle is 151°) and O(2a)...H(3b) is 2.11 Å (O2(a)...N(3b) 2.977(4) Å and O(2a)...H-N(3b) is 148°) and for molecule b, O(2b)...H(4a1) is 2.11 Å (symmetry operation: 0.5-x, -0.5+y, 0.5-z, O(2b)...N(4a) is 2.920(4) and O(2b)...H-N(4a) is 140°) and O(2b)...H(3a) is 2.19 Å (O(2b)...N(3a) is 3.005(4) Å and O(2b)...H-N(3a) is 141°). The H(4a2) and H(4b2) atoms do not participate in significant hydrogen bonding contacts. The polymeric structure found for [$Ph_3Sn(O_2CCH_2N(H)C(O)NH_2)$] constrasts the monomeric structure found for the R = c-Hex analogue.

[$c\text{-}Hex_3Sn(O_2CCH_2N(H)C(O)NH_2)$]

The molecular structure of [$c\text{-}Hex_3Sn(O_2CCH_2N(H)C(O)NH_2)$] is shown in Fig. 2 and selected interatomic parameters are collected in Table 7. The hydantoate anion coordinates the tin atom via one of the carboxylate oxygen atoms forming a Sn-O(1) interaction of 2.090(4) Å; this separation is shorter than the comparable bonds in the R = Ph derivative. The Sn...O(2) separation of 2.948(5) Å is not indicative of a significant interaction between these atoms. The absence of other significant inter- or intra-molecular interactions involving the tin atom confirms the monodentate mode of coordination of the

hydantoate ligand. The tin atom environment is thus distorted tetrahedral with the maximum distortion from the ideal tetrahedral geometry being manifested in the C(11)-Sn-C(31) angle of 125.6(3) Å which may be traced to the proximity of the non-coordinating O(2) atom. As for the R = Ph derivative there are significant intermolecular hydrogen bonding contacts in the lattice, this time involving both the O(2) and O(4) atoms, the latter owing to the non-coordination of this atom to tin; in this structure all three acidic hydrogen atoms participate in hydrogen bonding. The O(2)...H(4a) separation is 2.06 Å (symmetry operation; 1.5-x, 0.5+y, 0.5-z, the O(2)...N(4) separation is 3.010(7) Å and the O(2)...H-N(4) angle is 168°), O(4)...H(4b) is 2.10 Å (symmetry operation: 1.5-x, -0.5+y, 0.5-z, O(4)...N(4) is 2.993(7) Å and O(4)...H-N(4) is 153°) and O(4)...H(3) is 2.19 Å (symmetry operation: 1.5-x, -0.5+y, 0.5-z, O(4)...N(3) is 3.058(7) Å and O(4)...H-N(3) is 149°).

Hydantoate coordination

The different modes of coordination of the hydantoate ligands in the R = Ph and R = c-Hex structures are reflected in systematic variations of the derived interatomic parameters (Table 7). The ligands in molecule a and b of the R = Ph structure and in the R = c-Hex structure are essentially planar as reflected in the O(1)/C(1)/C(2)/N(3), C(1)/C(2)/N(3)/C(4) and C(2)/N(3)/C(4)/O(4) torsion angles (Table 7). The shorter Sn-O(1) interaction in the R = c-Hex compound leads to a longer C(1)-O(1) bond, i.e. 1.299(6) Å vs 1.277(4) Å (molecule a) and 1.269(4) Å (molecule b), and, concomittantly, shorter C(1)-O(2) interactions, i.e. 1.205(7) Å vs 1.227(4) and 1.222(4) Å, respectively in the R = Ph structure. Other changes in the ligand parameters relate in particular to the C(4)-N(4) and C(4)-O(4) interactions. The carbonyl C(4)-O(4) bond distance of 1.220(7) Å in the R = c-Hex structure is shorter owing to the non participation in coordination to tin of this group compared to the situation observed in the R = Ph structure where elongation of this bond is apparent, i.e. 1.243(4) and 1.252(4) Å. As a consequence of the increased bond order of the C(4)-O(4) bond in the

R = c-Hex structure, the C(4)-N(4) bond distance is increased [1.352(8) Å] compared to that found in the R = Ph structure [i.e. 1.334(4) and 1.326(4) Å].

General Comments

The structure reported here for [$Ph_3Sn(O_2CCH_2N(H)C(O)NH_2)$] is similar to several other triorganotin carboxylates in which the carboxylate residue contains additional potential donor atoms such as oxygen and nitrogen.[13] The closely related structure [$Ph_3Sn(O_2C(CH_2)_2N(H)C(O)NH_2)$] [14] adopts this same motif with important parameters Sn-O(1) 2.143(2), Sn-O(4) 2.352(2) Å and O(1)-Sn-O(4) 171.5(1)°. This motif is similar to that found for many [$R_3Sn(O_2CR')$] structures where the carboxylate is bidentate bridging, i.e. the trans-R_3SnO_2 motif. The other major structural form found for the [$R_3Sn(O_2CR')$] compounds is the isolated, distorted tetrahedral arrangement as seen in the structure of [c-$Hex_3Sn(O_2C(CH_2)_2N(H)C(O)NH_2$].

The observation in the present study of different modes of coordination of the hydantoate ligand leading to disparate structural motifs has many precendents in the structural chemistry of organotin carboxylates. It has been highlighted in recent reviews of the subject that very different structures may be found for closely related chemical formulae.[13] No consistent correlation between steric and/or electronic effects associated with the organotin centre and the nature of the structure adopted ultimely in the solid state has been established thus far, however. The presence of multiple potential hydrogen bonding sites in the hydantoate ligand is another factor that may influence the nature of the structure.[15] It is likely that there is a subtle interplay between all of these factors, as well as the less well defined crystal packing effects, which is responsible for the observed structural variations. It is also noteworthy that the phenomenon of structural diversity found in the organotin carboxylates is indeed found in other main group element system.[16,17]

Biocidal activity

The results of the fungitoxicity and phytotoxicity studies are presented in Tables 8 and 9, respectively. Rice seed germination studies showed that the R = c-Hex and R = Ph derivatives have practically no phytotoxicity but that the R = nBu derivative is comparatively more phytotoxic.

From Table 9 it may be seen that the R = nBu derivative is the most effective against the fungi used in vitro. The fungiotoxicities (ED_{50} values) of the $R_3Sn(O_2CCH_2N(H)C(O)NH_2)$ compounds are in the following order:

$$R = nBu > Ph > c\text{-}Hex$$

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Table 1 Physical data for $R_3Sn(O_2CCH_2N(H)C(O)NH_2)$

Compound	Yield (%)	M. pt (°C)	λ_{max} (nm) [a]	Elemental analysis (%)[b] C	H	N	Sn
R = Ph [c]	40	203	208	53.8 (54.0)	3.9 (4.3)	5.9 (6.0)	25.3 (25.4)
R = c-Hex [d]	50	194	210	53.7 (52.0)	7.5 (7.8)	6.4 (5.8)	23.9 (24.5)
R = nBu [d]	65	112	204	44.4 (44.3)	7.7 (7.9)	7.0 (6.9)	29.1 (29.2)

[a] Spectra recorded in methanol solution. [b] Calculated values in parentheses. [c] recrystallized from methanol solution. [d] recrystallized from $CHCl_3$-petroleum ether (60-80 °C) solution.

Table 2 Crystallographic data for [$Ph_3Sn(O_2CCH_2N(H)C(O)NH_2)$] (**1**) and [$c\text{-}Hex_3Sn(O_2CCH_2N(H)C(O)NH_2)$] (**2**)

	1	**2**
Formula	$C_{21}H_{20}N_2O_3Sn$	$C_{21}H_{38}N_2O_3Sn$
Formula weight	467.1	485.2
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a, Å	16.955(6)	10.718(4)
b, Å	14.954(3)	9.088(3)
c, Å	17.865(2)	22.549(6)
β, deg.	115.08(1)	98.49(2)
V, $Å^3$	4102(1)	2268(1)
Z	8	4
D_{calcd}, g cm^{-3}	1.512	1.421
F(000)	1872	1008
μ, cm^{-1}	12.67	11.48
Crystal size, mm	0.23 x 0.48 x 0.48	0.08 x 0.13 x 0.32
Transmission coefficients	0.939 - 1.029	0.870 - 1.056
No. data measured	10199	5803
No. unique data	9879	5517
No. observed data	6839	3188
R	0.033	0.049
R_w	0.035	0.057
ρ_{max}, e $Å^{-3}$	0.48	0.88

Table 3 Fractional atomic coordinates for [$Ph_3Sn(O_2CCH_2N(H)C(O)NH_2)$]

Atom	x	y	z
Sn(1)	0.24925(2)	0.12325(2)	0.17665(1)
Sn(2)	0.28465(2)	0.19923(2)	-0.31119(1)
O(1a)	0.2692(2)	0.1617(2)	0.0686(1)
O(1b)	0.2963(2)	0.1506(2)	0.5793(1)
O(2a)	0.2768(2)	0.3111(2)	0.0691(1)
O(2b)	0.2469(2)	0.0101(2)	0.5581(1)
O(4a)	0.2686(2)	0.2565(2)	-0.1981(2)
O(4b)	0.2275(2)	0.0711(2)	0.2887(1)
N(3a)	0.2839(2)	0.3154(2)	-0.0780(2)
N(3b)	0.2453(2)	0.0050(2)	0.4072(2)
N(4a)	0.2924(3)	0.4058(2)	-0.1763(2)
N(4b)	0.2181(3)	-0.0801(2)	0.2945(2)
C(1a)	0.2751(2)	0.2374(2)	0.0382(2)
C(1b)	0.2688(3)	0.0799(2)	0.5368(2)
C(2a)	0.2794(3)	0.2294(2)	-0.0440(2)
C(2b)	0.2649(4)	0.0884(3)	0.4508(2)
C(4a)	0.2808(2)	0.3237(2)	-0.1535(2)
C(4b)	0.2298(3)	0.0009(2)	0.3277(2)
C(11a)	0.1526(2)	0.2204(2)	0.1634(2)
C(11b)	0.3874(3)	0.1216(3)	-0.2230(2)
C(12a)	0.1422(3)	0.2520(3)	0.2319(2)
C(12b)	0.4397(3)	0.1553(3)	-0.1454(3)
C(13a)	0.0788(3)	0.3142(3)	0.2238(3)
C(13b)	0.5035(4)	0.1031(5)	-0.0868(3)
C(14a)	0.0247(3)	0.3452(3)	0.1468(4)
C(14b)	0.5165(4)	0.0178(5)	-0.1049(3)
C(15a)	0.0346(3)	0.3155(3)	0.0789(3)
C(15b)	0.4667(4)	-0.0166(3)	-0.1808(3)
C(16a)	0.0981(3)	0.2538(3)	0.0867(2)
C(16b)	0.4022(3)	0.0351(3)	-0.2402(3)
C(21a)	0.3818(3)	0.1409(2)	0.2602(2)

C(21b)	0.1534(3)	0.1576(3)	-0.3559(2)
C(22a)	0.4232(3)	0.0799(3)	0.3226(3)
C(22b)	0.1215(3)	0.1164(3)	-0.3055(3)
C(23a)	0.5096(3)	0.0899(4)	0.3776(3)
C(23b)	0.0357(4)	0.0839(4)	-0.3374(4)
C(24a)	0.5560(4)	0.1622(4)	0.3706(3)
C(24b)	-0.0171(4)	0.0922(5)	-0.4188(4)
C(25a)	0.5170(4)	0.2228(4)	0.3093(4)
C(25b)	0.0131(4)	0.1320(5)	-0.4701(4)
C(26a)	0.4303(3)	0.2120(3)	0.2535(3)
C(26b)	0.0978(3)	0.1643(4)	-0.4396(3)
C(31a)	0.2050(3)	-0.0019(2)	0.1183(2)
C(31b)	0.3106(3)	0.3296(2)	-0.3423(2)
C(32a)	0.1193(3)	-0.0274(3)	0.0917(3)
C(32b)	0.3921(4)	0.3548(3)	-0.3300(3)
C(33a)	0.0917(4)	-0.1104(4)	0.0563(3)
C(33b)	0.4089(5)	0.4395(4)	-0.3526(4)
C(34a)	0.1485(5)	-0.1674(3)	0.0450(3)
C(34b)	0.3416(7)	0.4980(4)	-0.3883(4)
C(35a)	0.2329(4)	-0.1435(3)	0.0697(3)
C(35b)	0.2607(6)	0.4751(4)	-0.4003(3)
C(36a)	0.2614(3)	-0.0608(3)	0.1064(2)
C(36b)	0.2437(4)	0.3916(3)	-0.3782(3)

Table 4 Fractional atomic coordinates for [c-$Hex_3Sn(O_2CCH_2N(H)C(O)NH_2)$]

Atom	x	y	z
Sn	0.23034(4)	0.28672(5)	0.11052(2)
O(1)	0.3303(3)	0.1051(5)	0.1479(2)
O(2)	0.4916(4)	0.2549(5)	0.1691(2)
O(4)	0.6864(5)	-0.1946(5)	0.2505(2)
N(3)	0.6393(4)	0.0397(5)	0.2243(2)
N(4)	0.8226(5)	-0.0133(6)	0.2819(3)
C(1)	0.4474(5)	0.1329(7)	0.1679(3)
C(2)	0.5223(5)	-0.0007(7)	0.1897(3)
C(4)	0.7140(6)	-0.0643(7)	0.2518(3)
C(11)	0.3267(5)	0.3339(7)	0.0386(3)
C(12)	0.2353(6)	0.3945(8)	-0.0129(3)
C(13)	0.3039(7)	0.4294(8)	-0.0637(3)
C(14)	0.3718(7)	0.2962(8)	-0.0816(3)
C(15)	0.4613(7)	0.2344(9)	-0.0321(3)
C(16)	0.3968(7)	0.1998(8)	0.0196(3)
C(21)	0.0556(5)	0.1678(7)	0.0874(3)
C(22)	-0.0485(6)	0.2578(9)	0.0517(3)
C(23)	-0.1706(6)	0.1689(9)	0.0372(4)
C(24)	-0.2157(6)	0.1121(10)	0.0899(4)
C(25)	-0.1148(7)	0.0190(9)	0.1252(4)
C(26)	0.0064(6)	0.1082(8)	0.1405(3)
C(31)	0.2111(10)	0.4376(12)	0.1809(4)
C(32)	0.0922(9)	0.5282(12)	0.1740(5)
C(33)	0.0787(12)	0.6250(16)	0.1279(6)
C(34)	0.1717(13)	0.7407(15)	0.1342(6)
C(35)	0.2867(14)	0.6914(16)	0.1308(6)
C(36a)[a]	0.3474(10)	0.5969(13)	0.1723(5)
C(36b)[a]	0.3058(16)	0.5072(21)	0.2051(7)

[a] site occupancy factor = 0.5.

Table 5 ^{1}H NMR data (ppm) for $R_3Sn(O_2CCH_2N(H)C(O)NH_2)$

Compound	δ Sn-aromatic/ ligand ring	δ (NH)	δ (NH_2)	δ (CH_2)	δ (Sn nBu)	δ (Sn c-Hex)
R = Ph [a]	7.96 - 7.06 (m, 15H)	5.96 (b, 1H)	5.48 (s, 2H)	3.62 (d, 2H, J = 5 Hz)		
R = nBu [b]		5.06 (t, 1H, J = 5 Hz)	5.02 (s, 2H)	3.97 (d, 2H, J = 5 Hz)	2.20 - 0.20 (m, 27H)	
R = c-Hex [b]		5.66 (b, 1H)	4.77 (s, 2H)	4.03 (d, 2H, J = 5 Hz)		2.30 - 0.63 (m, 33H)

[a] Spectra recorded in saturated solutions of d_6-DMSO [b] and $CDCl_3$ solution using internal TMS as reference. All shifts are in ppm downfield to TMS. Proton integration are in parentheses. Abbreviations: s = singlet, d = doublet, m = complex multiplet pattern centred at the given δ value, b = broad, t = triplet centred at the given δ value.

Table 6 Selected IR data (cm^{-1}) for $R_3Sn(O_2CCH_2N(H)C(O)NH_2)$

Compound	$\upsilon(NH_2)$	υ(NH)	υ(amide II)		υ(OCO)	υ(amide I)	υ(SnC)
			$\upsilon(NH_2)$	$\upsilon(NH_2)$		CO	
R = Ph[a,b]	3415 m	3260 sh, m	1525 s	1555 vs, b	1600 s, b	1555 vs, b	280 w
	3310 m, b	3120 w					250w
R = nBu[a]	3480 m	3300 sh, m	1530 vs, b	1585 vs, b	1620 vs	1585 vs, b	480 w
	3320 m	3180 m					430 w
R = nBu[c]	3460 s	3100 s, b	1525 s, sh	1565 s, b	1620 vs	1650 vs, b	500 w
	3340 s						470 w
R = c-Hex[a]	3430 m	3270 m	1525 s, b	1580 vs, b	1615 s, b	1580 vs, b	500 w
	3340 m	3150 m					470 w
R = c-Hex[c]	3440 m, sh	3280 m	1510 m, b	1565 s	1615 s	1630 s, b	500 w, b
	3380 m, b	3230 m					425 w

[a] Spectra recorded in CsI optics. [b] The solution spectrum of R = Ph compound was not recorded in solution owing to its poor solubility.

[c] Spectra recorded in $CDCl_3$ solution. Abbreviations: v = very, s = strong, m = medium, w = weak, b = broad, sh = shoulder.

Table 7 Selected bond distances (Å) and angles (°) for $R_3Sn(O_2CCH_2N(H)C(O)NH_2)$

Parameter	R = Ph molecule a	R = Ph molecue b	R = c-Hex
Sn-O(1)	2.174(2)	2.174(2)[a]	2.090(4)
Sn-O(4)	2.319(2)[b]	2.315(2)[c]	
Sn-C(11)	2.127(4)	2.131(4)	2.153(6)
Sn-C(21)	2.122(4)	2.114(5)	2.161(6)
Sn-C(31)	2.118(3)	2.124(4)	2.19(1)
C(1)-O(1)	1.277(4)	1.269(4)	1.299(6)
C(1)-O(2)	1.227(4)	1.222(4)	1.205(7)
C(4)-O(4)	1.243(4)	1.252(4)	1.220(7)
C(2)-N(3)	1.439(4)	1.434(5)	1.438(7)
C(4)-N(3)	1.334(4)	1.331(4)	1.342(7)
C(4)-N(4)	1.334(4)	1.326(4)	1.352(8)
C(1)-C(2)	1.508(5)	1.514(5)	1.503(8)
O(1)-Sn-O(4)	175.63(8)[b]	177.4(1)[a,c]	
O(1)-Sn-C(11)	97.1(1)	97.2(1)[a]	102.3(2)
O(1)-Sn-C(21)	94.3(1)	92.5(1)[a]	94.7(2)
O(1)-Sn-C(31)	87.3(1)	87.9(1)[a]	106.0(3)
O(4)-Sn-C(11)	85.9(1)[b]	85.3(1)[c]	
O(4)-Sn-C(21)	86.7(1)[b]	86.8(1)[c]	
O(4)-Sn-C(31)	88.5(1)[b]	90.1(1)[c]	
C(11)-Sn-C(21)	122.0(1)	121.2(1)	113.6(2)
C(11)-Sn-C(31)	117.0(1)	119.9(2)	125.6(3)

C(21)-Sn-C(31)	120.3(1)	118.2(2)	109.2(3)
Sn-O(1)-C(1)	132.9(2)	131.8(2)	114.0(4)
Sn-O(4)-C(4)	141.7(2)[b,d]	143.9(2)[c,e]	
C(2)-N(3)-C(4)	121.5(3)	121.0(3)	120.2(5)
O(1)-C(1)-O(2)	126.7(3)	127.5(3)	122.9(6)
O(1)-C(1)-C(2)	112.8(3)	112.5(3)	114.0(5)
O(2)-C(1)-C(2)	120.5(3)	120.0(3)	123.1(5)
N(3)-C(2)-C(1)	111.9(3)	112.3(3)	111.4(5)
O(4)-C(4)-N(3)	119.8(3)	120.1(3)	123.1(6)
O(4)-C(4)-N(4)	123.7(3)	123.6(3)	122.2(6)
N(3)-C(4)-N(4)	116.5(3)	116.3(3)	114.7(6)
O(1)/C(1)/C(2)/N(3)	178.7(3)	172.0(4)	-165.1(5)
C(1)/C(2)/N(3)/C(4)	-174.2(3)	172.7(4)	174.0(6)
C(2)/N(3)/C(4)/O(4)	4.3(6)	-3.9(7)	-2(1)

[a] Atom related by the symmetry operation: x, y, -1+z. [b] O(4b). [c] O(4a). [d] C(4b). [e] C(4a).

Table 8 Effect of on the $R_3Sn(O_2CCH_2N(H)C(O)NH_2)$ compounds on spore germination

Spore	R	ED_{50} (mg/ml)
A. alternata	c-Hex	100.00
	Ph	20.00
	nBu	0.50
H. aativum	c-Hex	595.60
	Ph	1.42
	nBu	0.32
H. maydis	c-Hex	22.40
	Ph	3.55
	nBu	0.005
P. oryzae	c-Hex	94.40
	Ph	0.45
	nBu	0.005

Table 9 Effect of on the $R_3Sn(O_2CCH_2N(H)C(O)NH_2)$ compounds on rice seed germination

R	concentration (μg/ml)	% of germinated seeds[a] after treatment for 1 h	4 h	8 h
c-Hex	100	95	93	90
	50	95	93	93
	25	95	95	94
Ph	100	94	92	91
	50	95	94	94
	25	95	95	95
nBu	100	84	81	79
	50	87	83	83
	25	87	85	84
control		95	95	95

[a] with respect to the control.

Captions to Figures

Figure 1 A portion of the polymeric structure and crystallographic numbering scheme for [$Ph_3Sn(O_2CCH_2N(H)C(O)NH_2)$].

Figure 2 The molecular structure and crystallographic numbering scheme for [$c\text{-}Hex_3Sn(O_2CCH_2N(H)C(O)NH_2)$].

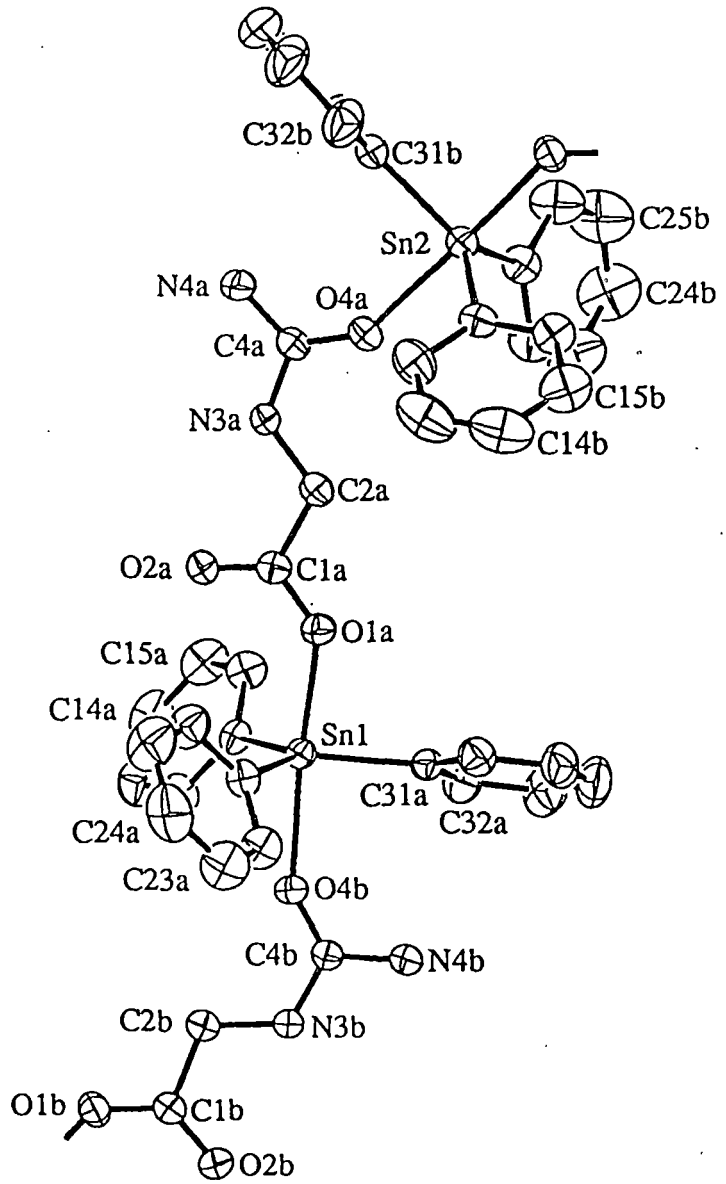

Figure 1 A portion of the polymeric structure and crystallographic numbering scheme for $[Ph_3Sn(O_2CCH_2N(H)C(O)NH_2)]$.

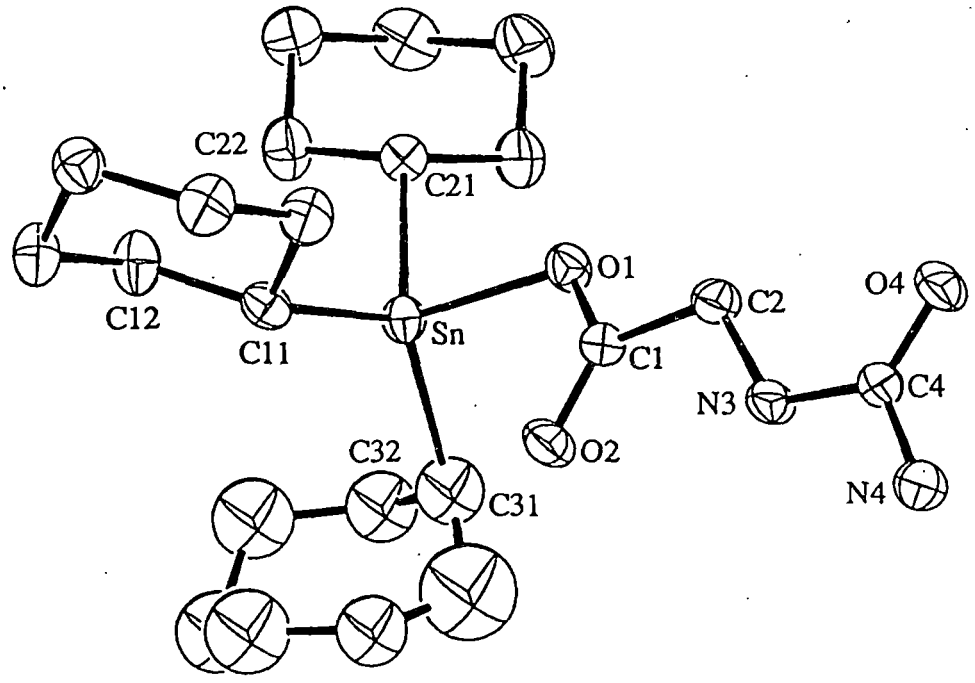

Figure 2 The molecular structure and crystallographic numbering scheme for [c-$Hex_3Sn(O_2CCH_2N(H)C(O)NH_2)$].

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Biocidal Organotin Compounds: Part 1. Preparation and Characterization of Triorganotin(IV) 4-Pyridyl- and 2-Pyrimidyl- thioacetates and the Crystal Structure of Triphenyltin(2-pyrimidylthioacetate)

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The preparation and spectroscopic characterization of $[R_3Sn(O_2CCH_2SC_5H_4N\text{-}4)]$, R = Ph, benzyl (Bz), cyclohexyl (c-Hex) and n-Bu, and of $[R_3Sn(O_2CCH_2SC_4H_3N_2\text{-}2,6)]$, R = Me, Ph and n-Bu, are reported. The 2-pyrimidyl compounds feature trigonal bipyramidal tin centres with *trans*-R_3SnO_2 geometries as was confirmed by X-ray crystallography for $[Ph_3Sn(O_2CCH_2SC_4H_3N_2\text{-}2,6]$.¶ By contrast the 4-pyridyl compounds have trigonal bipyramidal geometries in the solid state (arising from intermolecular Sn···N interaction) and tetrahedral geometries in solution. The biocidal activity of these compounds against the fungi *Helminthosporium maydis* (ITCC 2675) and *H. oryzae* (ITCC 2537), both of which damage crops such as maize and rice, shows promise. Encouraging is the observation that the compounds show no adverse phytotoxicity at concentrations to 10^{-3} M.

Keywords: triorganotin; carboxylate; crystal structure; fungitoxicity; Mössbauer

INTRODUCTION

The biocidal properties of organotin carboxylates are very rich[1–3] and in addition these compounds show an interesting range of structural variations[4] leading to structure–activity relationships.[5] These latter studies have shown that triorganotin carboxylates that have either isolated tetrahedral tin centres or *trans*-R_3SnO_2 tin atom geometries (arising from bridging carboxylate ligands) possess significantly greater biocidal activity than the compounds with the monomeric *cis*-R_3SnO_2 structural type, i.e. compounds with chelating carboxylate ligands spanning both equatorial and axial sites.

The above has led to a study of the biocidal activity of a new series of organotin thiocarboxylates,[6] $R_3Sn(O_2CCH_2SR')$, with varying R groups (R = alkyl or aryl) and containing the biologically important 4-pyridyl and 2-pyrimidyl groups incorporated into the carboxylate ligands. This paper details the preparation, spectroscopic characterization and biocidal activity of these compounds and the single-crystal structure determination of a representative compound. During the preparation of this manuscript the crystal structure of $[Ph_3Sn(O_2CCH_2SC_4H_3N_2\text{-}2,6)]$ was reported by others.[7]

EXPERIMENTAL

General

4-Pyridylthioacetic acid and 2-pyrimidylthioacetic acid were procured from Aldrich. The triorganotin halides Me_3SnCl, $n\text{-}Bu_3SnCl$ and Ph_3SnCl

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¶ Supplementary material is held at the Crystallographic Data Centre, Cambridge, UK.

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Table 1 Analytical and UV data for the triorganotin 4-pyridylthio- (R^1) and 2-pyrimidylthio- (R^2) acetates[a]

Compound	Yield (%)	M. pt (°C)	λ_{max} (nm)[a]	Elemental analysis (%)[b] C	H	N	Sn
$Ph_3Sn(O_2CCH_2R^1)$	90	160	214	57.10 (57.94)	3.59 (4.05)	2.58 (2.70)	23.48 (22.92)
$Bz_3Sn(O_2CCH_2R^1)$	92	154	209	59.22 (60.00)	4.10 (4.82)	2.30 (2.50)	20.65 (21.23)
$(c\text{-Hex})_3Sn(O_2CCH_2R^1)$	88	200	217	55.50 (56.00)	7.12 (7.28)	2.52 (2.61)	20.87 (22.15)
$(n\text{-Bu})_3Sn(O_2CCH_2R^1)$	94	85	264	49.71 (49.81)	7.49 (7.20)	3.06 (3.05)	25.38 (25.93)
$Ph_3Sn(O_2CCH_2R^2)$	60	142	228	55.20 (55.52)	3.74 (3.85)	5.36 (5.39)	22.91 (22.83)
$Me_3Sn(O_2CCH_2R^2)$	90	137	248	31.93 (32.46)	4.15 (4.20)	7.98 (8.41)	35.26 (35.67)
$(n\text{-Bu})_3Sn(O_2CCH_2R^2)$	90	53	247	47.30 (47.08)	6.82 (6.97)	5.98 (6.10)	25.68 (25.87)

Abbreviation: Ph, phenyl; Bz, benzyl; c-Hex, cyclohexyl; n-Bu, n-butyl; Me, methyl.
[a] Spectra recorded in methanol solution: [b] Calculated values in parentheses.

were purchased from Aldrich/Fluka AG and were used after crystallization or distillation where necessary. Tribenzyltin chloride was prepared following the literature method.[8] All solvents were purified and dried before use. The reactions were carried out under an inert atmosphere; however, other manipulations were performed under aerobic conditions.

Instrumentation

The IR spectra were recorded on a Pye–Unicam SP-300S spectrophotometer using CsI optics both for solid and solution spectra. ^1H NMR spectra were recorded on a VA-EM-390 90 MHz spectrometer. The UV spectra were recorded on a Shimadzu-240 spectrophotometer. Microanalyses were performed at the National Chemical Laboratory, Pune, India. Tin was estimated gravimetrically as SnO_2.

Syntheses

The sodium salts of 4-pyridylthioacetic acid and 2-pyrimidylthioacetic acid were prepared by titrating a methanolic solution/suspension of the acid with 0.5 M methanolic sodium hydroxide in the presence of an indicator. The sodium salts were isolated as crystals upon concentration of their respective solutions.

The triorganotin(IV) carboxylates were obtained in good yields by refluxing (4–6 h) the appropriate triorganotin chloride with the sodium salts of the carboxylates in methanol solution. The air-stable products were precipitated along with sodium chloride and were purified by recrystallization from acetonitrile. Tables 1–4 summarize the analytical and spectroscopic data for these compounds. The $[Ph_3Sn(O_2CCH_2SC_4H_3N_2\text{-}2,6)]$ compound was also investigated crystallographically.

Crystallography

Intensity data for a colourless crystal (0.16 mm × 0.19 mm × 0.32 mm) were measured at room temperature on a Rigaku AFC6R diffractometer fitted with graphite monochromatized MoKα radiation, $\lambda = 0.71073$ Å, up to θ_{max} 27.5° employing the $\omega:2\theta$ scan technique. The data were corrected for Lorentz and polarization effects[9] and for absorption employing the DIFABS program[10] which resulted in a range of transmission coefficients of 0.856–1.031. Of the 11 442 data measured, 10 906 were unique and 6823 satisfied the $I \geq 3.0\sigma(I)$ criterion of observability and were used in the subsequent analysis.

Crystal data for $C_{24}H_{23}N_2O_2SSn$: $M = 522.2$, monoclinic, space group $P2_1/c$, $a = 21.341(7)$, $b = 11.688(6)$, $c = 19.004(4)$ Å, $\beta = 110.53(2)°$, $V = 4439(5)$ Å^3, $Z = 8$, $D_{calcd} = 1.563$ g cm^{-3}, $F(000) = 2104$, $\mu = 12.68$ cm^{-1}.

The structure was solved by direct methods[11] and refined by a full-matrix least-squares procedure based on *F*.[9] Non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were included in the model at their calculated positions (C–H 0.97 Å). At convergence $R=0.037$ and $R_w=0.043$ (sigma weights[9]). The analysis of variance showed no special features and the maximum residual in the final difference map was 0.52 e Å^{-3}. The crystallographic numbering scheme used is shown in Fig. 1 (drawn with ORTEP[12]) and selected interatomic parameters are listed in Table 5. Other crystallographic details comprising fractional atomic coordinates, thermal parameters, H-atom parameters, all bond distances and angles, and tables of observed and calculated structure factors are available on request from ERTT.

Biological studies

Virulent cultures of *Helminthosporium maydis* (ITCC 2675) and *H. oryzae* (ITCC 2537), causal agents of brown spot of maize (*Zea mays*) and rice (*Oryzae sativa*), respectively, and *Bacillus cereus* (IMI no. 359387) were obtained from the Plant Pathology Laboratory, Department of Botany, University of North Bengal. Fungi were grown on potato–dextrose–agar (PDA) medium at 28 ± 1 °C, whereas *B. cereus*, isolated from tea leaves (CP-1), were grown on nutrient agar (NA) supplemented with 2 μg ml^{-1} nystatin.

In vitro fungitoxicity was ascertained following spore germination assay as described by Rouxel *et al.*[13] Purified eluents (10 μl) were placed separately at two points 3 cm apart on a clean, grease-free slide. The solvent was allowed to evaporate. One drop of spore suspension (0.02 ml per drop), prepared from 15-day-old cultures of either *H. maydis* or *H. oryzae*, were mounted separately on the glass slide. The slides were incubated on moist Petri plates for 24 h at 25 ± 1 °C. Finally, one drop of a lactophenol–Cotton Blue mixture was added to each spot to fix the germinated spores. The number of spores germinated compared with the control was calculated considering an average of 500 spores per treatment. The percentage of inhibition over the control was calculated using the Vincent equation:[14]

$$\text{Inhibition} = \frac{C-T}{T} \times 100\%$$

where C is the number of spores germinated in control and T is the total number of spores germinated after treatment. From these, the effective

Table 2 Selected IR data (cm^{-1}) for the triorganotin 4-pyridylthio- (R^1) and 2-pyrimidylthio- (R^2) acetates[a]

	Solid				Solution				
Compound	ν_{as}(OCO)	ν_s(OCO)	$\Delta\nu$[b]	ν_{as}(SnC)	ν_{as}(OCO)	ν_s(OCO)	$\Delta\nu$[b]	ν_{as}(SnC)	ν_s(SnC)
$Na(O_2CCH_2R^1)$	1590 (vs)	1420 (s)	170						
$Ph_3Sn(O_2CCH_2R^1)$	1625 (m)	1320 (s)	305	515 (w)	1640 (m)	1320 (m)	320	550 (m)	490 (m)
$Bz_3Sn(O_2CCH_2R^1)$	1628 (s)	1355 (s)	273	520 (m)	1650 (m)	1320 (m)	330	545 (m)	490 (m)
$(c\text{-Hex})_3Sn(O_2CCH_2R^1)$	1615 (s)	1355 (s)	260	515 (m)	1640 (s)	1315 (m)	325	545 (m)	500 (m)
$(n\text{-Bu})_3Sn(O_2CCH_2R^1)$	1615 (s)	1335 (m)	280	515 (m)	1645 (s)	1320 (s)	—325	545 (m)	490 (m)
$Na(O_2CCH_2R^2)$	1570 (s)	1410 (s)	160						
$Ph_3Sn(O_2CCH_2R^2)$	1575 (s)	1380 (s)	195	515 (m)	1635 (m)	1325 (m)	310	542 (m)	485 (s)
$Me_3Sn(O_2CCH_2R^2)$	1570 (s)	1380 (s)	190	515 (m)	1650 (m)	1325 (m)	325	555 (m)	475 (s)
$(n\text{-Bu})_3Sn(O_2CCH_2R^2)$	1590 (vs)	1400 (s)	190	520 (w)	1630 (s)	1315 (s)	325	550 (m)	495 (m)

Abbreviations: vs, very strong; s, strong; m, medium; w, weak. [a] Spectra recorded in CsI optics, solids in a Nujol mul and solutions in CCl_4. [b] $\Delta\nu = [\nu_{as}(OCO) - \nu_s(OCO)]$ cm^{-1}.

Table 3 ^{1}H NMR data (ppm) for the triorganotin 4-pyridylthio- (R^1) and 2-pyrimidylthio- (R^2) acetates[a,b]

Compound	δ(Sn–aromatic/ligand ring)	δ-(CH_2—)[c]	δ-(CH_2—)[d]	δ-(Sn–alkyl)
$Ph_3Sn(O_2CCH_2R^1)$	8.01 (d)[e] (2H) J = 5 Hz 7.52 (m) (17H)	3.62 (s) (2H)		
$Bz_3Sn(O_2CCH_2R^1)$	8.43 (d)[e] (2H) J = 5 Hz 7.33 (m) (17H)	3.62 (m) (2H)	2.61 (s) (6H) $^2J(^{119}Sn—CH)$ = 63 Hz $^2J(^{117}Sn—CH)$ = 57 Hz	
$(c\text{-Hex})_3Sn(O_2CCH_2R^1)$	8.55 (d) (2H) J = 5 Hz 7.44 (d) (2H) J = 5 Hz	3.55 (s) (2H)		1.53 (m, b) (33H)
$(n\text{-Bu})_3Sn(O_2CCH_2R^1)$	8.52 (d) (2H) J = 5 Hz 7.56 (d) (2H) J = 5 Hz	3.54 (s) (2H)		1.31 (m, b) (27H)
$Ph_3Sn(O_2CCH_2R^2)$	8.62 (d) (2H) J = 4 Hz 7.37 (m) (16H)	2.72 (s) (2H)		
$Me_3Sn(O_2CCH_2R^2)$	8.65 (d) (2H) J = 4 Hz 7.51 (t) (1H) J = 4 Hz	2.63 (s) (2H)		0.55 (s) (9H) $^2J(^{119}Sn—CH)$ = 64 Hz $^2J(^{117}Sn—CH)$ = 61 Hz
$(n\text{-Bu})_3Sn(O_2CCH_2R^2)$	8.34 (d) (2H) J = 4 Hz 7.65 (t) (1H) J = 4 Hz	2.62 (s) (2H)		1.34 (m, b) (27H)

[a] Spectra recorded in saturated solutions of $CDCl_3$ using internal TMS as reference. All shifts are in ppm downfield to TMS. Proton integration in parentheses. [b] Abbreviations: s, singlet; d, doublet; m, complex multiplet pattern centred at the given δ value; b, broad; t, triplet centred at the given δ value. [c] Ligand. [d] Benzyl. [e] The expected second doublet due to ligand protons is masked by the complex multiplet signal patterns of tin–aromatic protons.

doses for 50% inhibition, ED_{50}, were calculated in units of $\mu g\ l^{-1}$.

The fungicidal activity of the compounds was compared with that of triphenyltin acetate[15] (commercially marketed as Fentin acetate).

The bactericidal activity of these compounds was tested following the agar cup bioassay method. Bacterial suspension (1 ml) was mixed with sterilized NA (2 ml per Petri plate) at 45 °C and plated. The plates were chilled for 30 min and then, with the aid of a sterile cork borer, an 8 mm diameter cup was made. The same volume of the solution of the compound was added to each cup and incubated at 37 °C for 24 h. The diameters of the inhibition zones were recorded.

Table 4 ^{119}Sn Mössbauer ($mm\ s^{-1}$) data for selected compounds[a]

Compound	IS	QS	Γ
$Ph_3Sn(O_2CCH_2SC_5H_4N\text{-}4)$	1.20	2.91	0.91, 0.91
$Bz_3Sn(O_2CCH_2SC_5H_4N\text{-}4)$	1.37	2.76	0.92, 0.93
$Ph_3Sn(O_2CCH_2SC_4H_3N_2\text{-}2,6)$	1.26	3.43	0.93, 0.93

[a] Data recorded at 78 K; relative to $CaSnO_3$.

For the study of the phytotoxicity of these compounds, healthy rice seeds of the PUSA-2-21 variety were collected from Chinsurah Rice Research Institute, Hooghly, West Bengal, and were used in the present investigation.

Initially the compounds were dissolved in acetone (2–3 drops), then water suspensions of these compounds were prepared at concentrations of 200, 100, 50 and 25 $\mu g\ ml^{-1}$. Acetone controls for each treatment and one set of water controls were arranged.

Healthy seeds were dipped in the range of water suspensions for each of the compounds tested for 1, 4 and 8 h. The treated seeds were then 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 seven days, the germinated seeds were counted; seeds producing a root or

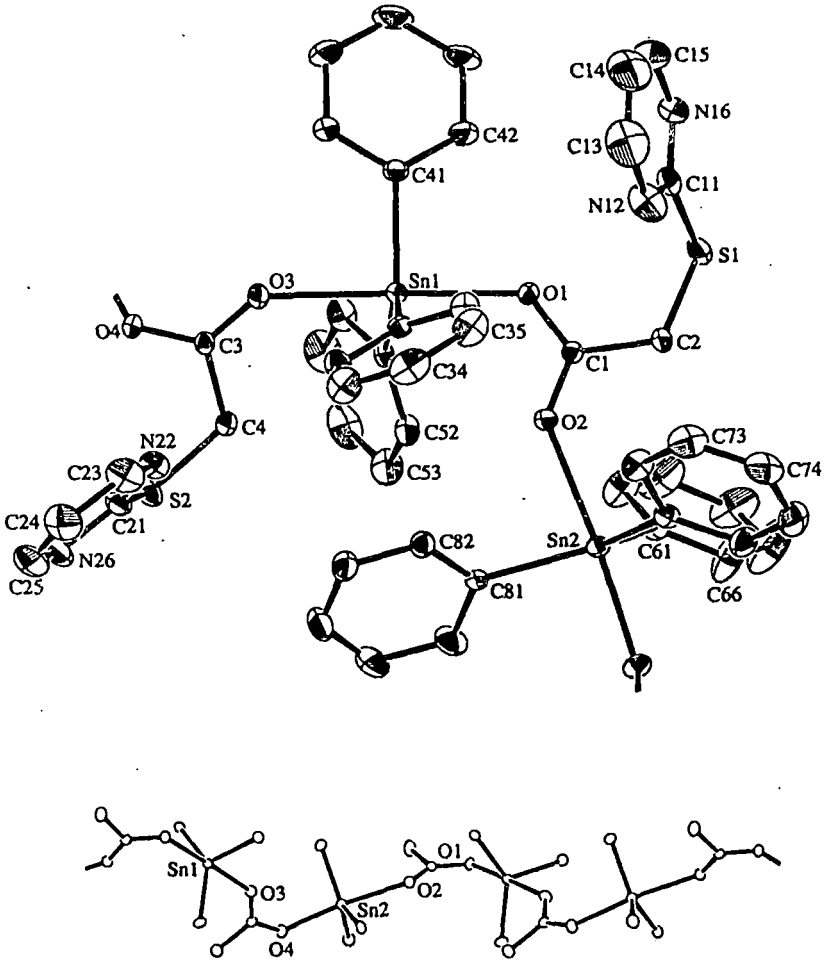

Figure 1 Molecular structure and crystallographic numbering scheme for the two molecules comprising the asymmetric unit in $[Ph_3Sn(O_2CCH_2SC_4H_3N_2\text{-}2,6)]$. The lower view shows the polymeric structure; the R' and all but the *ipso* carbon atoms of the phenyl rings have been omitted for clarity.

coleoptile were considered as germinated. Each experiment (i.e. four concentrations, three time regimes per compound) was repeated in triplicate. All apparatus and materials were sterilized where necessary using standard procedures.

DISCUSSION

Synthesis and spectroscopy

The triorganotin(IV) carboxylates (Table 1) were obtained in good yield via the metathetical reaction between the triorganotin halide and the sodium salts of 4-pyridylthioacetic acid and 2-pyrimidylthioacetic acid.

Infrared data for the compounds are presented in Table 2. The difference in $\nu_{as}(OCO)$ and $\nu_s(OCO)$ (i.e. $\Delta\nu$) in the solid state for the 4-pyridylthioacetates is quite large, i.e. 260–305 cm^{-1}, whereas $\Delta\nu$ is quite low for the 2-pyrimidylthioacetates, i.e. 190–195 cm^{-1}. These results indicate that the 4-pyridylthioacetate ligands coordinate via one oxygen atom only, as confirmed by an independent crystal structure analysis of $[Ph_3Sn(O_2CCH_2SC_5H_4N\text{-}4)]$.[16] In this structure, a trigonal bipyramidal tin centre was observed owing to the presence of weak intermolecular Sn···N interactions. By contrast, a

bidentate bridging mode is indicated for the 2-pyrimidylthioacetates, as revealed by the X-ray analysis of a representative compound, $[Ph_3Sn(O_2CCH_2SC_4H_3N_2\text{-}2,6)]$ (see below). In solution, the $\Delta\nu$ values for the triorganotin 4-pyridylthioacetate complexes are comparable with those observed in the solid state, suggesting a similar coordination mode. In the case of the 2-pyrimidylthioacetates, the rise in the $\Delta\nu$ values suggests a change in coordination about the tin atom, i.e. from a trigonal bipyramid (solid state) to a tetrahedral geometry (solution). In the solid-state spectra the planarity of the C_3Sn moiety is also indicated by the appearance of only one ν(Sn—C) whereas in solution both ν_{as}(Sn—C) and ν_s(Sn—C) are observed.

The ^1H NMR data are summarized in Table 3. The observed shifts and splittings confirm the stoichiometries of the compounds. For all the compounds studied, the PhSn and the signal due to the protons of the heterocyclic rings appear as complex patterns in the region 8.01 to 7.33 ppm. In the 4-pyridyl series, the δ(Sn—CH_2) for the Bz_3Sn derivative appeared as a singlet at 2.61 ppm [$^2J(^{119}Sn—CH_2) = 63$ Hz and $^2J(^{117}Sn—CH_2) = 57$ Hz], whereas the δ(Sn–cyclohexyl) and δ(Sn–butyl) protons appeared as complex patterns centred about 1.53 and 1.31 ppm, respectively. For the 2-pyrimidyl compounds, Sn—CH_3 resonance appeared as a singlet at δ0.55 ppm with $^2J(^{119}Sn—CH_3) = 64$ Hz and $^2J(^{117}Sn—CH_3) = 61$ Hz.

The $\delta(CH_2)$ of the carboxylate ligands merit special comment. The signals for the CH_2 protons of the 4-pyridylthioacetates appeared at approximately δ3.4–3.6 ppm whereas the corresponding

Table 5 Selected bond distances (Å) and angles (°) for $[Ph_3Sn(O_2CCH_2SC_4H_3N_2\text{-}2,6)]$

Atoms	Distance	Atoms	Distance
Sn(1)—O(1)	2.196 (4)	Sn(2)—O(4)'[a]	2.143 (4)
Sn(1)—O(3)	2.326 (4)	Sn(2)—O(2)	2.323 (4)
Sn(1)—C(31)	2.116 (5)	Sn(2)—C(61)	2.109 (5)
Sn(1)—C(41)	2.114 (5)	Sn(2)—C(71)	2.099 (5)
Sn(1)—C(51)	2.098 (5)	Sn(2)—C(81)	2.098 (6)
S(1)—C(2)	1.772 (6)	S(2)—C(4)	1.768 (6)
S(1)—C(11)	1.726 (7)	S(2)—C(21)	1.730 (6)
O(1)—C(1)	1.254 (6)	O(3)—C(3)	1.237 (6)
O(2)—C(1)	1.235 (6)	O(4)—C(3)	1.240 (6)
N(12)—C(11)	1.286 (9)	N(22)—C(21)	1.298 (7)
N(12)—C(13)	1.35 (1)	N(22)—C(23)	1.321 (8)
N(16)—C(11)	1.324 (9)	N(26)—C(21)	1.321 (8)
N(16)—C(15)	1.34 (1)	N(26)—C(25)	1.35 (1)
C(1)—C(2)	1.504 (7)	C(3)—C(4)	1.506 (7)
C(13)—C(14)	1.32 (2)	C(23)—C(24)	1.34 (1)
C(14)—C(15)	1.31 (2)	C(24)—C(25)	1.35 (1)
O(1)–Sn(1)–O(3)	178.7 (1)	O(2)–Sn–O(4)'	174.0 (1)
O(1)–Sn(1)–C(31)	90.7 (2)	O(2)–Sn(2)–C(61)	90.0 (2)
O(1)–Sn(1)–C(41)	89.8 (2)	O(2)–Sn(2)–C(71)	89.4 (2)
O(1)–Sn(1)–C(51)	94.1 (2)	O(2)–Sn(2)–C(81)	84.8 (2)
O(3)–Sn(1)–C(31)	88.9 (2)	O(4)'–Sn(2)–C(61)	88.1 (2)
O(3)–Sn(1)–C(41)	91.5 (2)	O(4)'–Sn(2)–C(71)	96.6 (2)
O(3)–Sn(1)–C(51)	85.3 (2)	O(4)'–Sn(2)–C(81)	91.3 (2)
C(31)–Sn(1)–C(41)	116.5 (2)	C(61)–Sn(2)–C(71)	114.4 (2)
C(31)–Sn(1)–C(51)	134.7 (2)	C(61)–Sn(2)–C(81)	120.7 (2)
C(41)–Sn(1)–C(51)	108.6 (2)	C(71)–Sn(2)–C(81)	124.5 (2)
C(2)–S(1)–C(11)	103.3 (3)	C(4)–S(2)–C(21)	102.1 (3)
Sn(1)–O(1)–C(1)	124.7 (3)	Sn(2)–O(4)'–C(3)'	131.2 (4)
Sn(1)–O(2)–C(1)	136.7 (3)	Sn(2)–O(3)–C(3)	138.0 (3)
C(11)–N(12)–C(13)	114.6 (9)	C(21)–N(22)–C(23)	115.5 (6)
C(11)–N(16)–C(15)	114.7 (8)	C(21)–N(26)–C(25)	113.8 (6)

[a] Atom related by the symmetry operation: x, 1.5 − y, −0.5 + z.

Table 6 Comparative study of the effect of $R_3Sn(O_2CCH_2SC_5H_4N-4)$ on *Helminthosporium maydis* fungus

Concentration (M)	Germination (%)	
	$(n\text{-}Bu)_3Sn(O_2CCH_2R^1)$[a]	$Ph_3Sn(O_2CCH_2R^1)$[a]
Control	92	92
10^{-3}	0	0
10^{-4}	3	5
10^{-5}	61	40
10^{-6}	84	76
ED_{50}(μg l^{-1})	13	3

[a] R^1 = pyridylthio

signals for the 2-pyrimidylthioacetates appeared at δ2.6–2.7 ppm. The downfield shift for the former complexes is probably due to the fact that the pyridine residue is more electron-withdrawing than the pyrimidine residue, which correlates with the enhanced basicity of the 4-pyridylthioacetates.

A selection of the compounds were also subjected to a tin-119 Mössbauer study. Details of the experimental techniques have been reported previously[17] and data are summarized in Table 4. The slight increase in the isomer shift (IS) value for $[Bz_3Sn(O_2CCH_2SC_5H_4N-4)]$ compared with $[Ph_3Sn(O_2CCH_2SC_5H_4N-4)]$ is due to the reduced electron-withdrawing ability of the benzyl substituents compared with the phenyl groups. The quadrupole splitting (QS) of $[Ph_3Sn(O_2CCH_2SC_4H_3N_2\text{-}2,6)]$ (3.43 mm s^{-1}) is typical of five-coordinate organotin carboxylates incorporating a bridging CO_2 moiety, e.g. $[Me_3Sn(O_2CMe)]$[18,19] has QS = 3.68 mm s^{-1}. The lower QS values for $[Ph_3Sn(O_2CCH_2SC_5H_4N-4)]$ and $[Bz_3Sn(O_2CCH_2SC_5H_4N-4)]$ (2.91 and 2.76 mm s^{-1}, respectively) reflect the asymmetric C_3SnON coordination sphere evident in the structure of $[Ph_3Sn(O_2CCH_2SC_5H_4N-4)]$, for which the Sn···N interaction is weak.[16] The similarity of QS values for each of $[Ph_3Sn(O_2CCH_2SC_5H_4N-4)]$ and $[Bz_3Sn(O_2CCH_2SC_5H_4N-4)]$ suggests similar structures featuring a C_3SnON core in contrast to a C_3SnO_2 core in the structure of $[Ph_3Sn(O_2CCH_2SC_4H_3N_2\text{-}2,6)]$.

Table 7 Comparative study of the effect of $R_3Sn(O_2CCH_2SC_4H_3N_2\text{-}2,6)$ on *Helminthosporium oryzae*

Compound	Concentration (M)	Germination (%)	
$Ph_3Sn(O_2CCH_2R^2)$[a]	10^{-3}	0	
	10^{-4}	32	
	10^{-5}	46	ED_{50} = 60 μg l^{-1}
	10^{-6}	80	
$Ph_3Sn(O_2CCH_2R^2)$[a]	10^{-3}	5	
	10^{-4}	67	
	10^{-5}	86	ED_{50} = 200 μg l^{-1}
	10^{-6}	97	

[a] R^2 = pyrimidinylthio

Crystal structure

The structure of $[Ph_3Sn(O_2CCH_2SC_4H_3N_2\text{-}2,6)]$ is shown in Fig. 1, and selected interatomic parameters are listed in Table 5. The structure reported here for $[Ph_3Sn(O_2CCH_2SC_4H_3N_2\text{-}2,6)]$ is in essential agreement with that reported by others.[7] The crystallographic asymmetric unit comprises two independent $[Ph_3Sn(O_2CCH_2SC_4H_3N_2\text{-}2,6)]$ units which associate as a result of intermolecular Sn→O contacts, afforded by bidentate bridging carboxylate groups, as shown in Fig. 1. The resultant structure is therefore polymeric, as shown in the lower view of Fig. 1. There is no evidence of coordination to tin by either the heterocyclic nitrogen atoms or the thioether atoms. Each of the tin atoms exists in a distorted trigonal bipyramidal geometry with the axial positions occupied by the oxygen atoms and the equatorial plane defined by the three phenyl groups. The Sn(1) atom lies 0.0607(4) Å out of the trigonal plane in the direction of O(1) atom and the corresponding distance for the Sn(2) atom is 0.0751(4) Å, in the direction of the O(4)′ atom (symmetry operation: x, $1.5-y$, $-0.5+z$). The difference in the Sn—O bond distances about each of the tin atoms is relatively small, but experimentally significant, at 0.13 and 0.18 Å for the Sn(1) and Sn(2) atoms, respectively, indicating a relatively symmetrical bridging mode for the carboxylate ligands. The near-equivalence in the Sn—O bond distances is reflected in the narrow range of C—O bond distances of 1.235(6)–1.254(6) Å. There is a notable difference in the C–Sn–C angles about the two tin centres, with the range of angles about the Sn(1) atom being 108.6(2)–134.7(2)° and that about the Sn(2) atom being smaller at 114.4(2)–124.5(2)°. The expansion of the C(31)–Sn(1)–C(51) angle to 134.7(2)° and concomitant contraction of the other two angles from the ideal trigonal values may be traced to the relatively close approach of the O(2) atom, i.e. 3.280(5) Å. The weak

Sn(1)···O(2) contact does not represent a significant bonding interaction, however. Whereas the tin atom geometries are in essential agreement with each other, there are some significant differences in the relative orientations of the tin-bound phenyl substituents and of the pyrimidine residues. The dihedral angles between the C(31)–C(36), C(41)–C(46) and C(51)–C(56) rings of 67.7, 100.6 and 100.4°, respectively, i.e. about the Sn(1) atom, may be compared with the angles of 53.7, 102.7 and 147.8° for the C(61)–C(66), C(71)–C(76) and C(81)–C(86) rings, respectively. For the carboxylate ligands, the C(1)/C(2)/S(1)/C(11) and C(2)/S(1)/C(11)/N(12) torsion angles of 74.5(5) and 17.8(6)°, respectively, are significantly different from the comparable C(3)/C(4)/S(2)/C(21) and C(4)/S(2)/C(21)/N(22) angles of −64.2(5) and −1.1(6)°, respectively.

The structure reported here for $[Ph_3Sn(O_2CCH_2SC_4H_3N_2\text{-}2,6)]$ corresponds to one of the major structural motifs found for compounds with the general formula $[R_3Sn(O_2CR')]$.[4] The other main motif for this formula has a monomeric structure in which the tin atom is four-coordinate (i.e. where the carboxylate ligand is monodentate) or approaching five-coordinate (where the carboxylate ligand is coordinating in an asymmetric mode). There are several other $[R_3Sn(O_2CR')]$ structures available in which an additional atom that is incorporated in the carboxylate residue, e.g. oxygen or nitrogen, is also coordinated to the tin atom giving rise to different motifs;[4] however, as mentioned above, no such intra- or inter-molecular interactions are found in the structure of $[Ph_3Sn(O_2CCH_2SC_4H_3N_2\text{-}2,6)]$.

Fungicidal activity

The results of the fungitoxicity and phytotoxicity tests are summarized in Tables 6 and 7, respectively. No fungitoxicity was found for the 4-pyridylthio- and 2-pyrimidylthio-acetic acids at the 10^{-3} M level, whereas their triorganotin complexes showed increased activity. For the 4-pyridylthioacetates tested against *H. maydis*, the triphenyl derivative was more active than the tributyl species. By contrast, the tributyltin 2-pyrimidylthioacetate compound has greater activity than the triphenyltin derivative at different concentrations against *H. oryzae*. However, the activity of the butyl compound decreases markedly at lower concentrations.

The 100 ppm concentration of Fentin acetate was found to inhibit the growth of the fungi when treated *in vitro* and hence it is encouraging to find that the newly synthesized compounds are potentially more active (see Tables 6 and 7). Further testing, *in vivo*, is required to confirm these results.

The bactericidal activity of all the compounds was such that they killed over 95% of the bacterial *Bacillus cereus* under the conditions of the experiment (results not shown).

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