STRUCTURAL STUDIES ON THE COMPLEXES OF DI-AND TRIORGANOTIN (IV) HALIDE

ABSTRACT

THESIS SUBMITTED TO THE ALIGARH MUSLIM UNIVERSITY ALIGARH FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY

BY RUKHSANA ILYAS KURESHY

DEPARTMENT OF CHEMISTRY ALIGARH MUSLIM UNIVERSITY ALIGARH (INDIA) 1984
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The composition of the complexes have been established on the basis of elemental analysis. The infrared spectral studies (4000 - 200 cm\(^{-1}\)) have been made to propose probable structure for the complexes. Most of the complexes are soluble in nitromethane or nitrobenzene. Molar conductance of \(10^{-3}\)M solution of these complexes indicate them to be nonionic in nature. To determine the toxicity of the ligands containing sulphur as donor atom and their complexes, experiments have been done on housefly (Musca domestica nobulo), cockroach.
Adducts of the type \( R_2SnX_2-L \) and \( R_2SnX_2-L_2 \) (where \( R = \) methyl, butyl; \( X = \) chloride; acetate and \( L = \) pyrrolidine, acridine, 1,10-phenanthroline, 2,2-bipyridyl and piperazine) have been characterized and site of coordination has been explored. All the adducts have been found to have a 1:1 metal to ligand ratio except pyrrolidine adducts which are formed in 1:2 ratio. Adducts of acridine appear to be trigonal bi-pyramidal while those of piperazine have presumably an octahedral polymeric structure attained through ligand bridging. A cis octahedral geometry for the phenanthroline and 2,2-bipyridyl adducts and a trans octahedral configuration for pyrrolidine adducts have been proposed.

Kinetic measurements of millimolar solutions of dibutyl dichloro bis (pyrrolidine) tin(IV) and dibutyldichloro-(1,10-phenanthroline) tin(IV) in nitrobenzene show an increase in molar conductance with time indicating the solvation of the molecules, in the compounds. The conductance is further enhanced in the presence of nucleophiles namely \( C_6H_5COCl \), \( SOCl_2 \) and \( CH_3COCl \) suggesting the substitution of pyrrolidine or 1,10-phenanthroline by chloride ions. The rate constant for solvation, \( K_s \) and for substitution \( K_1 \) and \( K_2 \) have been obtained from the slope of the plot for three different molar ratios indicating
the 1st order kinetics. The values of rate constants show that solvation is a slower process than substitution and follows SN\(^1\) mechanism.

Substitution compounds of tetramethylene dithiocarbamate, 5-aminoindazolyl dithiocarbamate, α-naphthylamine dithiocarbamate and β-naphthylamine dithiocarbamate of di and tri-organotin(IV) halide of the type R\(_3\)Sn\(_2\)S\(_2\)CNR\(_2\) or R\(_2\)Sn(S\(_2\)CNR\(_2\))\(_2\) have been synthesized to examine whether they act as a unidentate or bidentate ligand and to propose a possible structure for the complexes. All the complexes, except dimethyl- and dibutyltin(5-aminoindazolyl) dithiocarbamate, which are insoluble in nitromethane or nitrobenzene show their covalent nature. The dithiocarbamates of diorganotin(IV) are assumed to have octahedral geometry and those of triorganotin(IV) are five coordinated. Experiments have been done on housefly (Musca domestica nobulo) and fish (Heteropneustes fossilis) in order to determine the biocidal activity of individual dithiocarbamates and their complexes. The LD\(_{50}\) and LC\(_{50}\) for housefly and fish are calculated and the toxicity has been found to decrease in the order TMdtc > Pzdtc > α-Naph.dtc > 5-Amino dtc.

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phenyl and \( L = \) cyclohexanone spirothiazolidinone or 3-aminorhodanine) has been carried out. Both the molecules have three active coordination sites namely, nitrogen, sulphur and carbonyl oxygen atom. A tetrahedral geometry has been proposed for both the di- and triorganotin(IV) complexes of cyclohexanone spirothiazolidinone while those of 3-aminorhodanine are trigonal bipyramidal or octahedral.

The toxic effect of the ligand and those of the complexes has been determined in an experiment on fish (Heteropneustes fossilis) and cockroach (Periplaneta americana). The complexes showed an enhancement in the % mortality of the animals as compared to that of the ligands alone. The \( LC_{50} \) and \( LD_{50} \) in case of the complexes was obviously low. The triorganotin(IV) complexes of both the ligands are more toxic than those of diorganotin(IV).
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BY RUKHSANA ILYAS KURESHY

DEPARTMENT OF CHEMISTRY ALIGARH MUSLIM UNIVERSITY ALIGARH (INDIA) 1984
Department of Chemistry  
Aligarh Muslim University  
Aligarh

Dated:

Certified that the work embodied in this thesis entitled, "Structural studies on the complexes of di- and triorganotin(IV) halide" is the result of original researches carried out under my supervision by (Miss) Rukhsana Ilyas Kureshy and is suitable for submission for the award of the Ph.D. degree of Aligarh Muslim University, Aligarh.

(K. S. Siddiqi).
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Rukhsana Ilyas Kureshy
(Rukhsana Ilyas Kureshy)
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1. Complexes of diorganotin(IV) dichloride and diacetate with some nitrogen heterocyclic

2. Kinetics and Mechanism of substitution of dibutyl dichloro bis(pyrrolidine) tin(IV).

3. Structural and biocidal studies on some di- and tri-organotin(IV) dithiocarbamates.
   K. S. Siddiqi, R. I. Kureshy, N. H. Khan and S. A. A. Zaidi, Indian Journal of Chemistry (Communicated).

4. Characterization and toxicity of organotin(IV) halide complexes of cyclohexanone spirothiazolidinone and 3-aminorhodamine.

5. Substitution mechanism and kinetics of dibutyl dichloro (1,10-phenanthroline) tin(IV).
   K. S. Siddiqi, R. I. Kureshy, N. H. Khan and S. A. A. Zaidi, Indian Journal of Chemistry (Communicated).
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CHAPTER I
INTRODUCTION
INTRODUCTION

Synthesis of novel compounds of metal ions with various donor molecules has been a favourite pursuit of inorganic chemist since long. While these studies on transition metal compounds are quite extensive\(^1,2\) such investigations on organotin compounds are scarce\(^3\).

Many significant advances have been made in the field of coordination chemistry in general and organotin chemistry in particular in the last few decades\(^4,5\). The keen interest in the field of organotin chemistry has been evidenced because of one or more than one of the following reasons:

(i) Its skeleton is usually stable towards nucleophilic reagents and air whereas the group attached to tin through more electronegative atom reacts readily. The organotin compounds present a convenient system for studying the reaction of other ligands where the metal can exist in two different oxidation states and at least four different coordination numbers.

(ii) Because of nuclear properties of tin the organotin compounds are particularly suited to physicochemical methods of investigations.
They are used as catalysts for preparing polyurethanes, as stabilizer for polyvinyl chloride and as biocides.

The importance of organotin compounds is also due to their commercial and industrial applications. A study of their toxicity is of particular interest as organotin pesticides have some advantage over other pesticides owing to the following reasons:

a) They can be used as antifeedants and selective pesticides without affecting the beneficial and non target insects and

b) They readily breakdown to non toxic (residue) inorganic tin compounds and do not harm the environment and the soil.

Organotin compounds are classified as mono, di, tri, and tetraorganotins depending on the number of tin carbon bonds in the molecule. Each class of compound has specific properties. Mono-and diorganotins have catalytic properties and can stabilise plastics such as polyvinylchloride against the degradative effects of heat and light while triorganotins are generally powerful biocides. The biocidal property of the compounds typified by $R_3SnX$ where $R = \text{methyl, ethyl or butyl group}$, $X = \text{chloride}$ is independent of the group $X$. 
but mainly depends upon the length of the carbon chain of the R group in $\text{R}_3\text{SnX}$. Trimethyltin is the most toxic for insects, triethyltin for mammals and tributyltin has maximum toxicity for fungi.

Joyce and co-workers$^8$ performed direct reaction of 2,2-dilithiobenzenyl with $(\text{CH}_3)_2\text{MCl}_2$ or $(\text{C}_6\text{H}_5)_2\text{MCl}_2$ ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$) and obtained 10,11 dihydro-5H dibenzo metallepins (1).

$$\text{Li Li} + \text{R}_2\text{MCl}_2 \rightarrow \begin{array}{c}
\text{M} \\
\text{R} \hspace{0.5cm} \text{R}
\end{array}$$

(I)

The structure and stereochemistry of Sn(IV) derivatives with potentially chelating ligands is also a subject of recent interest$^{9-15}$. A series of diorganotin(IV)dichloride and diisothiocyanate complexes of 3- (2-pyridyl)-5, 6-diphenyl-1,2,4-triazine (11) have been reported$^{16}$. This ligand bears a close structural relationship to 1,10-phenanthroline and 2,2-bipyridyl. Its behaviour as a chelating agent is reported to be closely parallel to that of phenanthroline and 2,2-bipyridyl.
Some more chelate of organotin dihalides and diisothiocyanate with planar tridentate chelating agents\textsuperscript{17} 3- 2-(1,10-phenanthrolyl )-5,6 diphenyl 1,2,4 triazine(III) and 3- 2-(1,10-phenanthrolyl )-5,6 dimethyl-1,2,4 triazine(IV) have been studied, both of which bear close structural relationship to ter-pyridyl
Some donor acceptor type complexes of triphenyltin-, trimethyltin chloride and dimethyltin dichloride with sulphoxide\textsuperscript{18}, $\text{BX}_3$\textsuperscript{19} ($X = \text{Cl}, \text{Br}$) and some heterocyclic bases namely dimethylaminomethyl ferrocene\textsuperscript{20}, piperidine\textsuperscript{21}, 4 phenylpyridine, isoquinoline\textsuperscript{22} have also been reported to yield 1:1 adducts.

Several 1:2 adducts with monodentate ligands\textsuperscript{23} may give a cis or trans octahedral geometry which can be confirmed by the $M$-$X$ stretching frequency. 1:1 adducts with
bidentate ligands are logically expected to have a cis octahedral geometry.

Organotin(IV) halides form complexes with \( \beta \)-keto-amine\(^{24}\) and Schiff bases. Tanaka et al.\(^{25}\) prepared a series of adducts of diorganotin dichloride with \( N,N \)-ethylene and \( N, N' \)-propylene bis (Salicylideneimines) and on the basis of spectroscopic evidences suggest a weak coordination of nitrogen atoms of the neutral ligand to the tin atom(V).

Recently Pelizzi\(^{26}\) has reported the preparation of 1:1 adducts of SnCl\(_4\) and Ph\(_2\)SnCl\(_2\) with some acylhydrazones. A heptacoordination for Sn(IV) and tridentate behaviour for acyl hydrazones from IR spectral studies has been shown.

Certain organotin compounds are used in agriculture as fungicides and acaricide due to their relatively low mammalian and plant toxicity and favourable environmental breakdown conditions. Already triphenyltin hydroxide and acetate have emerged as major chemicals for control of potato blight fungus. Tricyclohexyltin hydroxide is well-known for its acaricidal\(^{27}\) activity. The class of compounds have general formula(VI).

\[
\begin{align*}
&\text{R}_m^1 \\
\begin{array}{c}
\text{C} \\
\text{R'} \\
\text{R}
\end{array} \\
\text{CH}_2 &\quad \text{Sn} \quad \text{X}
\end{align*}
\]

(VI)
where $R$ and $R''$ are a lower alkyl group, $R'$ is hydrogen or a lower alkyl group, $m$ is an integer from 0 to 2, $n$ is an integer from 1 to 2 and $X$ is an electronegative group whose valency is equal to the value of $n$.

The miticidal properties of organotins are apparently related to the alkyl substituent on carbon atom adjacent to the phenyl ring and also to the two carbon bridge between the tin atom and phenyl ring. The preferred compound contains the neophyl group (VII).

\[
\begin{array}{c}
\text{CH}_3 \\
\text{C--CH}_2 \\
\text{CH}_3 \\
\end{array}
\]  
(VII)

and has the structure (VIII).

\[
\begin{array}{c}
\text{CH}_3 \\
\text{C--CH}_2 \\
\text{CH}_3 \\
\end{array}
\begin{array}{c}
\text{O--Sn--Sn--O} \\
\text{Sn--Sn--Sn} \\
\end{array}
\begin{array}{c}
\text{CH}_3 \\
\text{C--CH}_2 \\
\text{CH}_3 \\
\end{array}
\begin{array}{c}
\text{CH}_3 \\
\text{C--CH}_2 \\
\text{CH}_3 \\
\end{array}
\]  
(VIII)

Tributyltin oxide has a major use as a wood preservative and it has been found to be an effective fungicide but it is normally used in combination with a powerful insecticide like gamma benzene hexachloride in order to provide complete protection of the wood. Tributyltin oxide with quaternary ammonium compound gives an aqueous product.
in which the water insoluble organotin is emulsified. The product so obtained has been used for eradicating and inhibiting the growth of algae, mosses and bacterial slum on stonework and masonry.

Triphenyltin acetate (Fentin acetate, IX) and triphenyltin hydroxide (Fentin hydroxide, X) are tenfold more effective than copper fungicides. They have been used for the control of leaf spot on sugarbeet and celery, blast on rice, berry disease on coffee and for algal control on paddy.

\[
\begin{align*}
&\begin{array}{c}
\text{SnOCOCH}_3 \\
\text{(IX)}
\end{array} \\
&\begin{array}{c}
\text{SnOH} \\
\text{(X)}
\end{array}
\end{align*}
\]

Tricyclohexyltin hydroxide(XI) called plictran has been used for control of phytophagous mites which cause extensive damage to orchards and ornamental plants.

\[
\begin{array}{c}
\text{SnOH} \\
\text{(XI)}
\end{array}
\]

Recently, two more miticides called Fenbutatin oxide(XII) and Azocyclotin(XIII) have been introduced. All these pesticides are compatible with other pesticides and do not harm predacious mites, insects and honey-bees. They also
include antifeedant effects on insects like caterpillars etc.

The study of addition compounds of di- and triorgano-tin(IV) halide and acetate with nitrogen containing ligands such as acridine, piperazine, pyrrolidine, 2,2-bipyridyl and phenanthroline has been undertaken in this project with a view to studying the effect of coordination with increasing number of nitrogen atoms in various ligands. Conductometric titrations were carried out to find if there occurred the formation of more than one species in the solution, which ultimately yielded the stable solid adducts.

Substantial work on nucleophilic substitution reaction in octahedral complexes of transition metal ions and those of group (IV) metal halides have been done while such studies on organotin compounds are scarce. However, the kinetics of substitution in \([\text{SnCl_4(Py)_2}], [\text{Bu_3SnCl(Py)}]\) and \([\text{Et_3SnCl(Py)}]\) have been studied conductometrically showing an increase in molar conductance with time which attains a final value equal to that of an uni-univalent electrolyte.
Presently the kinetics of solvation and substitution reaction of the complexes $R_2SnCl_2L_2$ ($L = \text{pyrrolidine, 1, 10-phenanthroline and } R = \text{butyl group}$) in nitrobenzene have been investigated to see the possible nucleophilic substitution mechanism and the order of the reaction. The rate constants for solvation $K_{s1}$, $K_{s2}$ and that of substitution $K_1$ and $K_2$ of pyrrolidine, and 1, 10-phenanthroline by chloride ion, originating from different nucleophilic reagents such as $C_6H_5COCl$, $SOCl_2$ and $CH_3COCl$ have also been calculated. A possible mechanism has been suggested.

An appreciable amount of work has also been done on ligands containing both nitrogen and sulphur as donor atoms. Dithiocarbamates are a class of one such ligand which is a well-known chelating agent. Its importance lies in having insecticidal properties.

Experiments have proved that most of these dithiocarbamates are of practical value in the control of fungal diseases in plants. Several investigators have concluded that the antifungal activity of salts, esters and oxidation products of di-N substituted dithiocarbamate derivatives is higher if the substituent on the nitrogen atom are methyl groups (XIV) and gradually decreases with increasing bulk of alkyl groups. The antifungal activity also depends on the solubility of various metal salts and it is
generally greater for sodium salts owing to its greater solubility in water.

The dithiocarbamate group is capable of acting both as a monodentate or bidentate\textsuperscript{42,43} ligand. In some dialkyltin(IV) dithiocarbamate where the geometry of the tin atom is intermediate between tetrahedral and octahedral arrangement, the presence of an isobidentate dithiocarbamate group has been suggested\textsuperscript{51}. An octahedral trans configuration has been proposed for bis[methyltin dithiocarbamate Me\textsubscript{2}Sn(SS CN Me\textsubscript{2})\textsubscript{2}].\textsuperscript{52} For dithiocarbamate chelates in general, a partial double bond character for $\text{C} \cdots \text{N}$ group has been confirmed on the basis of IR spectral studies. A splitting of $\text{C} \cdots \text{S}$ band at 1000 cm\textsuperscript{-1} occurs only when dithiocarbamate moiety is unsymmetrically bound while for symmetrically bound dithiocarbamate only one band has been observed in this region\textsuperscript{53-55}.

A comparison of resonance contribution to the ground state electronic structures of dithiocarbamate (XV) with that of monothiocarbamate (XVI) suggests that a wider variety of chemistry might be expected to result from these systems. Dithiocarbamates have also been shown to have the resonance
It is also apparent that the sulphur atom in dialkyl monothiocarbamate has considerable mercaptide character and often yields polymeric complexes\(^{57-59}\). The coordination chemistry of dithiocarbamate and dithiolate ligands can drastically be altered by varying R groups which favour one of the various possible resonance structures\(^{60,61}\).

By an appropriate choice of an aromatic amine, a dithiocarbamate exhibiting rather unusual properties due to major contribution of resonance structures (XVII) have been reported\(^{60}\). The overall chemical and physical properties of these dithiocarbamate are altered when complexed to metal ions.
A series of complexes of the dithiocarbamates obtained from α-naphthylamine, β-naphthylamine, 5-aminolindazole, tetramethylene and piperazine were characterized to examine their symmetrical or unsymmetrical behaviour. Since these compounds have been found to be toxic in nature their toxicity was studied in an experiment on fish (Heteropneustes fossilis) and house flies (Musca domestica nobulo). Their LC₅₀ was calculated.

Thiazolidinone and spirothiazolidinones are the derivatives of thiazolidine which belong to an important group of heterocyclic compounds. Extensive work has been reported in recent past on thiazolidinone with a carbonyl group at position 2, 4 or 5. They have also been used as stabilizer for polymeric materials.

Diverse biological activities such as bactericidal, pesticidal, fungicidal, insecticidal, tuberculostatic and antiinflammatory activities have been found to be associated with thiazolidinone derivatives. The stereochemistry of thiazolidinone complexes has always been a subject of interest since there is a possibility of coordination through carbonyl.
oxygen, nitrogen or sulphur atom. Thiazolidinone in presence of various reagents undergoes different types of reactions to yield other heterocyclic compounds like thiazole, benzimidazole, thiopyranothiazolone, benzodiazepine, triazoles, benzo-thiophene etc.

Rhodanines and their derivatives yield complexes with Cu(I), Au(III), Pd(II) and Hg(II)\textsuperscript{62,66,67}. From IR spectral studies Ag(I) is found to coordinate through the thiocarbonyl and nitrogen of the ligand(XVIII) while a bridged type structure has been reported for Cu(I) complex.

\[
\begin{array}{c}
\text{O} \quad \text{C} \quad \text{N} \quad \text{Ag}^{-} \\
\text{H}_{2}\text{C} \quad \text{C} \quad \text{S} \quad \text{S} \quad \text{Ag} \quad \text{N} \quad \text{C} \quad \text{O} \\
\text{S} \quad \text{C} \quad \text{S} \quad \text{C} \quad \text{CH}_{2}
\end{array}
\]

(XVIII)

From a survey of the chemical literature it appears that the complex forming ability of cyclohexanone spirothiazolidinone and 3-aminorhodanine has not been carried out with organotin (IV) halide. It seems, therefore, of interest to carry out such investigations with organotin(IV) halide
to ascertain the mode of coordination as there is some uncertainty to the site of coordination in such and similar other molecules. Its toxicity has not been investigated although it is expected to be appreciably toxic in nature. A comparative study of the toxicity of cyclohexanone and 3-aminorhodanine along with their complexes has been done on cockroach (Periplaneta americana) and fish (Heteropneustes fossilis). Their LD$_{50}$ and LC$_{50}$ values were calculated by graphical method. It has been noted that the toxicity is enhanced after complexation.
CHAPTER II

EXPERIMENTAL METHODS
EXPERIMENTAL METHODS

The physico-chemical methods used for structural elucidation of newly synthesised complexes described in the present work are infrared spectroscopy and molar conductance measurements. To investigate the toxicity of some complexes in terms of LC$_{50}$ the graphical method has been used.

It seems therefore, appropriate to give a brief description of these techniques.

Infrared Spectroscopy:

The infrared spectroscopy provides extremely valuable information for the elucidation of the molecular structures. The characteristic absorption of radiation by many molecules in the infrared region has been classified into three categories, viz., near i.r., 0.8 to 2.5 $\mu$ (12,500 - 4000 cm$^{-1}$); i.r. 2.5 to 15 $\mu$ (4000 - 667 cm$^{-1}$); and far i.r. 15 to 200 $\mu$ (667 - 50 cm$^{-1}$).

The absorption of energy takes place because of the vibrational and rotational motion of the molecules. The pure rotational spectrum of molecules occur at a very long wavelength in the microwave region well beyond the wave-length limit of about 25 $\mu$. At wave-length below 25 $\mu$ the radi-
ation has sufficient energy to cause changes in the vibrational and of course also the rotational levels of molecule.

According to the quantum theory there are discrete energy states, both rotational and vibrational in which each molecule can exist. For diatomic, linear, polyatomic and spherical top molecules the energy of rotational levels is given by the equation

\[ E_r = \frac{J(J + 1) \hbar^2}{8 \pi^2 I} \]  

where \( J \) is the rotational quantum number which can have any integral value 0, 1, 2, 3, \ldots and \( I \) is the moment of inertia of the molecule above the axis of rotation and \( \hbar \) is the Planck's constant.

For the symmetrical and asymmetrical molecules the formula is somewhat more complex. Transitions between the different rotational levels in the microwave and infrared regions are governed by the selection rule.

(a) For a molecule to be infrared active there must be a change in the dipole moment of the molecule as it vibrates.

(b) In absorption of radiation only transition for which change in the vibrational energy is \( \Delta V = \pm 1 \) can occur.

Molecular symmetry determines whether a particular vibrational transition is allowed or not. The frequency of a
given vibration is determined by the masses of the nuclei involved and the nature of the potential function which is expressed in terms of the various force constants. The vibrational frequency, $\nu$, may be approximately represented by the function.

$$\nu = \frac{1}{2\pi c} \sqrt{\frac{K}{\mu}} \quad (ii)$$

where 'K' is the force constant in dynes cm$^{-1}$ of the vibration and ' $\mu$ ' is the reduced mass.

In the infrared region below 25 $\mu$ changes in the vibrational states of the molecule occur during absorption of radiation for small amplitude of vibration, the vibration may be considered harmonic and the energy of the vibrational quantum level is given as

$$E_V = h \omega (V + \frac{1}{2}) \quad (iii)$$

where ' $\omega$ ' is the fundamental vibrational frequency of the harmonic oscillator and 'V' is the vibrational quantum number which can have any integral value 0, 1, 2, 3 -----. The difference in energy between successive energy levels of the harmonic oscillator is thus always $h\omega$.

In order that a vibrating molecule should interact with the fluctuating electrical field of electromagnetic radiation the molecular electrical dipole moment must change its magni-
tude or orientation with respect to a fixed coordinate system during the motion. It is the magnitude of this change of dipole moment which determines the intensity of a transition. There are $3N-6$ normal vibrations of a non-linear molecule of $N$ atoms and hence the $3N-6$ frequencies associated with them are called fundamental frequencies of the molecules. From the symmetry that a molecule possesses one can determine how many of the $3N-6$ vibrations will be observed in its infrared spectrum, and conversely, from the infrared spectrum the molecular symmetry may be deduced. A vibration will be infrared active if its symmetry species is the same as that of at least one of the dipole moment components. For harmonic oscillators, transitions between the various energy levels are governed by the selection rule $\Delta V = \pm 1$. In actual fact, the purely harmonic conditions do not prevail for real molecules. The frequent observation of overtones and combination tones of these vibrations corresponding to change $\Delta V = 2, 3$ etc. is a consequence of the anharmonic nature of the normal modes. These additional bands are usually very much weaker than the parent fundamentals.

For harmonic oscillation of frequency is related to the force $F$ binding the vibrating groups together and the reduced mass $\mu$ by the relationship

$$2\pi \omega = \left( \frac{F}{\mu} \right)^{\frac{1}{2}}, \quad \mu = \frac{m_A \cdot m_B}{m_A + m_B}$$

(iv)
Where \( m_A \) and \( m_B \) are the masses attached to either of the vibrating system. In terms of the frequency \( \nu_r \), in wave number, eq (V) becomes

\[
\nu_r = \frac{1}{2\pi c} \sqrt{\frac{\nu}{\mu}}
\]  

(V)

Thus the frequencies of vibration of a molecule are related to the masses and binding forces. In many of the normal modes of vibrations of a molecule the main participants in the vibration are two atoms held together by a chemical bond. The frequencies are only a slightly affected by another atom, attached to the atoms concerned, and thus these vibrational modes are characteristic of the group in the molecule and very useful in identifying a compound, especially in deducing the structure of an unknown compound or substance. In this work only those frequencies which are pertinent to the discussion of the newly synthesized compounds will be discussed.

**N-H stretching vibrations:**

The N-H stretching vibrations occur in the region 3500 - 3300 cm\(^{-1}\) in dilute solution. Primary amines in dilute solutions of non polar solvents give two absorption bands in this region. The first which is due to symmetric stretching usually found near 3500 cm\(^{-1}\) and the second which arises from the corresponding asymmetric mode is found near
3400 cm\(^{-1}\). The position and intensity of both these bands are sensitive to substitution. Secondary amines show only a single N-H stretching absorption in dilute solution in the above mentioned region. The intensity and frequency of N-H stretching vibrations of secondary amines are very sensitive to structural changes. The band is found in the range 3350 - 3310 cm\(^{-1}\) (low intensity) in aliphatic secondary amines, and near 3490 cm\(^{-1}\) (much higher intensity) in heterocyclic secondary amines such as pyrrole and indoles. Flourine substitution generally seems to enhance the intensity of the bands. Ring strains seems to have little effect on N-H stretching vibration as can be seen by the values of ethyleneimine (3367 - 3341 cm\(^{-1}\)) and diethylamine (3384 cm\(^{-1}\)).

The N-H stretching absorption shifts to lower values in the solid state due to extensive hydrogen bonding. At a very low concentration pyrrolidine shows a band at 3367 cm\(^{-1}\) due to the monomeric N-H stretching frequency\(^{72}\). As the concentration increases, a new band appears at 3268 cm\(^{-1}\) due to intermolecular association (N-H \cdots N bonding). The intensity of the low frequency band increases with increasing concentration until complete association occurs in the ligand state. Hydrogen bonding is very common in ureas and thioureas\(^{73}\). In concentrated solutions of thioureas in CCl\(_4\) and CHCl\(_3\) two to four bands in the 3500 - 3300 cm\(^{-1}\) region are present. The
highest frequency band is much sharper than any of the others, the broadness of which can reach $\sim 200$ cm$^{-1}$. Further, the molar extinction of the highest frequency band increases with decreasing concentration, the trend being opposite for the other bands. In very dilute solutions only, the highest energy band is visible. In the spectra of solids, however, there is always a strong broad band together with weaker and narrower bands on the lower frequency side. This suggests a strongly associated condition for thioureas in the solid state.

Valuable information have been obtained on the structure and tautomerism of many heterocyclic molecules and their substituted derivatives from a study of the N-H stretching absorption. The $\alpha$- and $\gamma$-mercapto pyrimidines and other mercapto-aza-aromatic compounds exist in the thione form, both in the solid state and in solvents of low polarity. In the solid state a weak band in the range 3160 - 3190 cm$^{-1}$ is regarded as an evidence for the presence of $\text{-NH}$ group. In solution a broad band is found in the range 3350 - 3420 cm$^{-1}$, due to N-H stretching in unassociated molecules (weaker bands also appear at lower frequencies, due to associated molecules).

The IR spectra of 2- and 4- hydroxypyrimidines in the solid state and in CHCl$_3$ solution give absorption bands due
to N-H stretching vibrations, indicating their existence in the tautomeric keto form\textsuperscript{75}. However, aminopyrimidines, generally exist in the non tautomeric form, and in solution (CHCl\textsubscript{3}, CCl\textsubscript{4}) give two bands characteristic of amino group\textsuperscript{76,77}.

**N-H deformation vibrations:**

For the deformation frequencies of the NH\textsubscript{2} group in primary amines four characteristic peaks should appear, but the only definite assignment has been done in the case of scissoring vibration, generally observed in the region 1650 - 1590 cm\textsuperscript{-1} \textsuperscript{78}. The lower frequency deformation vibration of the NH\textsubscript{2} group has not been investigated in detail. The NH\textsubscript{2} twisting, wagging and torsional vibrations in methylamine have, however, been assigned to 1455, 780 and 264 cm\textsuperscript{-1} respectively. Secondary aliphatic amines show an extremely weak band in the range 1650 - 1550 cm\textsuperscript{-1} due to N-H deformation vibration and it is difficult to detect this band readily. The assignment of this vibration is very difficult in case of aromatic amines because of the presence of aromatic ring vibrations in this region.

**C-H stretching vibrations:**

These vibrations are usually observed in the 3100-3000 cm\textsuperscript{-1} region in carbocyclic system\textsuperscript{72}. Some aromatic compounds give rise to three bands near 3038 cm\textsuperscript{-1}. Pyridine shows C-N
absorption in the range 3070 – 3020 cm\(^{-1}\) which appear as a series of multiple absorption under high resolutions\(^7\). In pyrimidines this band is observed near 3050 cm\(^{-1}\). A weak band is observed in the case of trisubstituted pyrimidines, since only one free ring hydrogen atom is present. This band is absent in tetrasubstituted pyrimidines.

**C-H in-plane and out-of-plane deformation vibrations:**

A number of characteristic absorption bands in the region 1250 – 1000 cm\(^{-1}\) exhibited by most of the heterocyclic compounds are attributed to C-H in-plane deformation and the ring breathing modes\(^6\). In diazines these bands are observed in the range 1239 – 1021 cm\(^{-1}\)\(^8\). Bands appearing in the region 900 – 700 cm\(^{-1}\) have been attributed to the C-H out of plane deformation vibrations, and the position of these bands depends on the number of free hydrogen atoms adjacent to one another.

**C = N stretching vibrations:**

A band of variable intensity in the region 1690 – 1640 cm\(^{-1}\) is attributed to (C = N) stretching vibrations in open-chain systems or in non-conjugated ring systems\(^3\). With conjugated cyclic systems the position is much less clear, and the C = N absorption bands have been assigned as being within the range 1660 – 1480 cm\(^{-1}\). In cyclic compound and cyclic
materials without internal conjugation the C-N absorption is assigned to the 1650 cm\(^{-1}\) region. The C = N absorption band occurs near 1667 cm\(^{-1}\) region in oxazines, oxazolines, oximes and imines. However, the C = N absorption bands are difficult to identify for two reasons. Firstly owing to the considerable changes in intensity which follow changes in its environment, and secondly because information available on the effects of conjugation in ring systems is often conflicting and indecisive.

**C-N stretching vibrations:**

The C-N stretching absorptions give rise to strong bands in the region 1360 - 1250 cm\(^{-1}\) in aromatic amines. In aliphatic amines the absorption are in the 1220-1020 cm\(^{-1}\) range and are often of low intrinsic intensity. In aromatic primary amines there is one band in the region 1340 - 1250 cm\(^{-1}\) but in secondary amines two bands have been observed in the region 1350 - 1280 cm\(^{-1}\) and 1280 - 1230 cm\(^{-1}\). The position of C-N absorption does not differ much from C-C absorption, but the intensity is relatively large because of C-N polarity.

**Ring stretching vibrations:**

Characteristic aromatic ring vibrations appear in the region 1600 - 1350 cm\(^{-1}\) in most of the heterocyclic compounds. The position and intensity of these vibrations
is dependent on the nature of the ring and type of substitution. Six membered ring shows four bands around 1605, 1575, 1480 and 1430 cm⁻¹, whereas five membered rings show three bands around 1590, 1490 and 1400 cm⁻¹. The intensities of these bands give an idea of the pattern and nature of substitution in the ring. Thus in 4-substituted pyridine-1-oxides and 3-substituted pyridines the intensity of the band around 1605 cm⁻¹ is high for both electron-withdrawing and electron-donating substituents, whereas in the case of 2- and 4-substituted pyridines and 3-substituted pyridine-1-oxides, the intensity is high with electron donor groups and low with electron acceptor groups. The intensity of the band at around 1575 cm⁻¹ also shows similar variations with substitution. Electron donating substituents increase the intensity of the band around 1480 cm⁻¹, whereas the band near 1430 cm⁻¹ is unaffected by the nature of the substituents. This particular trend in the change of intensities has been explained as being due to the charge disturbances in the molecule.

The characteristic pattern of absorption of the ring stretching vibrations result from the complete interaction of the C = C, C = N and N = N vibrations (e.g., in 1,2-diazine) and it is therefore, very difficult to isolate the different vibrations. This is due to the fact that the lone pair of electrons on the nitrogen atom will be able to conjugate with the ring, the magnitude of which depends on the
coplanarity of the system. Therefore, these vibrations are sensitive to minor alterations in molecular geometry and are difficult to distinguish from other vibrations. Even though a band of variable intensity in the region 1660 - 1630 cm\(^{-1}\) is attributed to C = N stretching in open chain \(\alpha,\beta\)-unsaturated compound in cyclic conjugated system the appearance of bands in this region can only be attributed to the ring stretching modes.

Substituted pyrimidines, generally show four bands in the 1590 - 1375 cm\(^{-1}\) region\(^{80,81-83}\), which is probably due to NH\(_2\)-deformation mode. The hydroxy pyrimidines are also not suitable for the development of correlations for the ring vibrations of this type, as they may act in the tautomeric keto form, in which the double bond absorptions of the ring would be expected to be different from the fully aromatic systems.

\(\text{C} = \text{O}\) stretching vibrations:

The \(\text{C} = \text{O}\) stretching vibrations of various carbonyl groups\(^{84}\) absorb in the region 1900 - 1600 cm\(^{-1}\). A more specific range is defined by the type of carbonyl (e.g., ketones, esters etc.) and the position is further affected by a variety of effects. The frequency of carbonyl absorption is determined almost wholly by the nature of its immediate environment, and the structure of the rest of the molecule is of little importance unless it is such as to give rise to chelation or some similar
effect. Thus, the carbonyl shifts away from the normal position in \( \alpha, \beta \)-unsaturated materials and in carbonyl compounds with strongly electronegative substituents on the \( \alpha \)-carbon atom, whilst in cyclic ketones the frequency shifts and its direction is related to the degree of strain of the ring. The frequency shifts due to chelation and to mutual interference effects can also be considerable in some cases. However, in each of these cases the extent of the frequency shift to be expected is known and new range of frequencies falls within comparatively narrower limits.

A carbonyl group situated between two methylene groups represents the simplest case of an undisturbed \( C = O \) stretching vibrations. The studies by many workers have shown that in solution the frequency of the carbonyl absorption of simple ketones of this type always lies within the narrow range 1725 - 1706 cm\(^{-1}\), provided that no hydrogen bonding or other interference effects occur\(^{81}\). Carbonyl groups in unstrained saturated rings absorb within the same overall frequency range 1720 - 1706 cm\(^{-1}\).

The physical state has a direct effect on the carbonyl frequency. Acetone, for example, absorbs at 1742 cm\(^{-1}\) in the vapour phase, whereas in solution the frequency lies between 1728 cm\(^{-1}\) and 1718 cm\(^{-1}\) depending on the solvent. Similarly, dodecyl ketone absorbs at 1740 cm\(^{-1}\) in the vapour state, and
between 1724 cm\(^{-1}\) and 1717 cm\(^{-1}\) in solution. It is probable that some form of dipolar association is occurring in the condensed phase, resulting in a low frequency shift of the order of 20 cm\(^{-1}\) conjugation of a carbonyl group with a \(C = C\) linkage results in a lowering of the frequency by an amount depending on the nature of the double bond. An aliphatic \(C = C\) bond in conjugation with a carbonyl group reduces its frequency by about 40 cm\(^{-1}\) and the absorption occurs in the range 1685 - 1665 cm\(^{-1}\). When an aryl group is directly attached to the carbon atom of the carbonyl group, the frequency shift of the carbonyl is less than that occurring with a full double bond in conjugation, and the absorption band occurs in the range 1700 - 1680 cm\(^{-1}\), with two aryl groups directly attached. However, there is a further fall in the frequency to 1670 - 1660 cm\(^{-1}\). The influence of an\(\alpha\)-aryl group is additive with that of any other structure which is capable of influencing the C=O frequency. With a six membered ring C = O with an\(\alpha\)-aryl group, the frequency is found to be 1695 - 1687 cm\(^{-1}\), which is the same as with similar open chain materials. With a five membered ring C = O, however, the frequency increases to 1715 - 1706 cm\(^{-1}\), the strain of the five membered ring being offset to some extent by the aromatic conjugation. Halogen substitution in the immediate vicinity of carbonyl group results in a high frequency shift, of the carbonyl absorption. This is parti-
cularly marked in the acid chlorides where a chlorine is
directly attached to the carbonyl group, but there is still
an appreciable effect when the helogen is situated on the α-
carbon atom. Thus α-propionic acid, for example, absorbs
at 1730 cm\(^{-1}\) as against 1710 cm\(^{-1}\) for β-chloropropionic acid.

When intramolecular hydrogen bonds are formed, the
carbonyl absorption bands may be lowered by 50 cm\(^{-1}\) according
to hydrogen bond strength\(^{84}\). 1-Hydroxyanthraquinone shows
two C = O bands at 1680 - 1675 cm\(^{-1}\) and 1630 - 1622 cm\(^{-1}\)
corresponding to free and bonded carbonyl groups. With two
hydroxyl groups in each of the β-positions only one band is
shown at 1639 - 1623 cm\(^{-1}\) whilst in the extreme case of 1,4,
5,8-tetra hydroxyanthraquinone the carbonyl frequency has
fallen to 1525 cm\(^{-1}\). Similarly fumaric acid absorbs at
1680 cm\(^{-1}\), in contrast to the normal value of 1705 cm\(^{-1}\) of
maleic acid. Salicylic acid absorbs at 1655 cm\(^{-1}\) which is
comparable with the shifts experienced in the case of the α-
hydroxy-α,β-unsaturated ketones. 3-Amino-2-naphthoic acid
absorbs at 1665 cm\(^{-1}\).

Amides generally show a strong absorption band near
1640 cm\(^{-1}\) when examined in the solid state\(^{85}\). The fact that
the absorption is at an appreciably lower frequency than the
carbonyl absorption of normal ketones must be due to the effect
of resonance with the ionic form. This is enhanced by the
strong association effects in the solid state and the corresponding vapours absorb at considerably higher frequencies. The amide first absorptions subject to a considerable alteration on change of state in which hydrogen bonding is broken, and is also liable to variations in solution depending on the polarity of the solvent employed. Thus hexo-amide absorbs at 1655 cm\(^{-1}\) in the solid state, at 1668 cm\(^{-1}\) in concentrated solutions and at 1680 cm\(^{-1}\) in dilute chloroform solutions. The corresponding values of 1692 cm\(^{-1}\) and 1672 cm\(^{-1}\) given for this absorption band in dioxane and in methanol indicate the degree of frequency shifts likely to be associated with alteration in the type of solvent employed. The carbonyl absorption of N-ethyl-acetamide ranges from 1687 to 1663 cm\(^{-1}\) over a series of solvents, even at concentrations at which hydrogen bonding effects are precluded. At higher concentrations the frequency varies continuously with the concentration due to change in strengths of the intermolecular hydrogen bonds. Formamide absorbs at 1740 cm\(^{-1}\) as vapour and at 1709 cm\(^{-1}\) in dilute chloroform solutions. Therefore, carbonyl frequencies are much closer to these of ketones and suggest that the contribution of the ionic form is quite small under these conditions.

\[ N,N\text{-disubstituted amides are incapable of forming hydrogen bonds, and the carbonyl absorption band is consequently not much influenced by changes in physical state. In} \]
these cases the amide first band usually fall near 1650 cm$^{-1}$ unless a phenyl group is substituted on the nitrogen atom, when it is raised to 1690 cm$^{-1}$. This is due to the competitive effect of the ring for the lone pair electrons of nitrogen ring. In consequence the contribution of the ionic form of the amide is reduced and the carbonyl frequency is raised. A similar effect may account for the high frequencies shown by N-nitrosoamides, which absorbs near 1740 cm$^{-1}$ in solution. The inverse effect occurs in dimethyl urea, in which the ionic character of the carbonyl is reinforced by the second nitrogen atom so that in the solid state the frequency fall to 1610 cm$^{-1}$.

Infrared studies have$^{83,86-92}$ shown that a large number of $\alpha$- and $\gamma$- hydroxy-aza-aromatic derivatives are amides both in solid state and in solution. A very strong band in the range 1620 - 1750 cm$^{-1}$ shows the presence of a carbonyl group. 2-Hydroxy-pyrimidine and 4-isomer in the solid state and in solution show absorption bands in the 1600 - 1700 cm$^{-1}$ region which have no counterpart in the spectra of the methoxy derivatives and must be due to the C = O bond stretching vibrations. Thus these compounds in the states examined exist predominantly in the amide form.

$C = S$ stretching vibration:

The identification of the position of the $C = S$ absorption has been a matter of some difficulty. In carbon disulphide
the C = S stretching modes have been assigned to 1522 cm\(^{-1}\) and 650 cm\(^{-1}\), whilst in carbonyl sulphide it is given at 859 cm\(^{-1}\). These are unusual cases in which the carbon is doubly unsaturated, and they do not offer any guidance to the likely position of the C = S vibration in saturated thioureas and similar compounds. Preliminary calculations indicated that the ratio C = O/ C = S would be about 1.5 and that the C = S frequency would be found in the 1200-1050 cm\(^{-1}\) region. Just as is the case with the carbonyl group, the C = S absorption is found to be sensitive to the nature of the surrounding structure but the relative effects of various substituents are not always the same, and the ratio between the carbonyl and thio-carbonyl frequencies varies over the range 1.6 to 1.14.

Systematic correlations of the available data on thio-carbonyl stretching frequency indicate that when it is unambiguously identifiable, e.g., in \((-\text{CH} = \text{CH}-)_2\), C = S and -CS-SR derivatives, it is at 1150 ± 70 cm\(^{-1}\) 94,95.

However, in some molecules, notably thioamides and thioureas, the thiocarbonyl stretching frequency is uncertain, as there is complete mixing between the C = S stretching mode and other vibrations\(^\text{96,97}\) of similar frequencies. This frequency is hardly susceptible to polar effects. It has been calculated\(^\text{98}\) that the C = S stretching frequency in
thioformaldehyde should be $1120 \pm 40 \text{ cm}^{-1}$, while in thio-
carbonyl chloride it is at $1140 \pm 40 \text{ cm}^{-1}$. By contrast, the
carbonyl stretching frequency in carbonyl chloride (1827 cm$^{-1}$)
is considerably higher than that in formaldehyde (1744 cm$^{-1}$).
Presence of thiocarbonyl stretching frequency in mercapto
compounds, provide a direct evidence for their existence in
the thioamide form. Spinner$^{98}$ observed an intense band in the
range 1100-1190 cm$^{-1}$ in several $\alpha$- and $\gamma$-mercaptoaza-aromatic
compounds attributable to C=S stretching frequency indicating
them to be in the thioamide form. There has been great
uncertainty with regard to the assignment of the C=S stretching
frequency in nitrogen containing compounds and the assign-
ments$^{99}$ in these compounds vary in the wide range of 850-1570
cm$^{-1}$. Elmore$^{100}$ has shown that the band which is generally
assigned to C=S stretching vibration in such compounds results
from the coupling of the C-N and C=S stretching vibrations.
Normal coordinate analysis of N-methylthio formamide, N-methyl-
thioacetamide, N,N'-dimethylthiourea and tetramethylthiourea$^{100,101}$
shows a clear evidence for vibrational mixing in these compounds.
In secondary thioamides the bands with considerable contribution
from the C=S stretching vibration$^{103}$ are found in the region
870-700 cm$^{-1}$. This is considerably lower than in simple thio-
carbonyl compounds, where the C=S vibration is localised. In
thiourea, two bands in the region 1080-730 cm$^{-1}$ are found to
have appreciable contribution from the C=S stretching vibra-
Suzuki's calculations\textsuperscript{102} show that the 843 cm\textsuperscript{-1} band for HCSNH\textsubscript{2} corresponds to an almost pure C=S mode and the intrinsic frequency of the C=S vibrations vary from 900 to 850 cm\textsuperscript{-1}. Gosavi et al.\textsuperscript{101} performed a normal coordinate analyses on N,N\textsuperscript{-}dimethylthiourea and tetra methylthiourea and assigned various mixed C=S stretching frequency bands. The mixed vibration bands of N,N dimethylthiourea have the contribution from C=S stretching vibrations as: 1504 cm\textsuperscript{-1}, 10%; 1420 cm\textsuperscript{-1}, 18% and 752 cm\textsuperscript{-1}, 83% similarly, in tetramethyl thiourea the contribution from C=S stretching vibrations is as: -1408 cm\textsuperscript{-1}, 25%; 1013 cm\textsuperscript{-1}, 50%; 990 cm\textsuperscript{-1}, 50% and 462 cm\textsuperscript{-1}, 37%. Since the force constants FCN and FCS are quite similar, the major contribution from C-N and C=S vibrations are found in the bands which are quite close to each other (e.g., 850 and 752 cm\textsuperscript{-1} in N-N\textsuperscript{-}dimethyl thiourea). The mixed vibration bands are in the region of so called N-C=S bands\textsuperscript{103}.

**C-S stretching vibrations:**

The C-S stretching frequency generally appear as a band of weak and moderate intensity in the range 720-570 cm\textsuperscript{-1}. In the Raman spectra this band is very strong. There appear to be a progressive decrease in the frequency in aromatic derivatives the C-S frequency is found towards the top of this range and some difficulty is experienced in recognizing the C-S frequency due to the presence of the intense CH-out of plane deformation band in this region. In phenyl sulphonyl-
halides the C-S vibration is found between 715 and 706 cm\(^{-1}\).
In organic thiocyanate it appears in the region 740-680 cm\(^{-1}\).
In thioketols, broad bands with several maxima are found probably due to vibrational coupling.

**M-S stretching vibrations:**

The metal sulphur stretching frequency is of particular interest as it gives a direct evidence for coordination through the sulphur atom. It appears in the low frequency region, viz., 480 to 210 range\(^{104}\). In many instances two bands are observed, one of medium to strong intensity, and a weaker band at a frequency 10 to 40 cm\(^{-1}\) lower than the stronger band. The Sn-S frequencies earlier reported appear in this range.

**Metal-halogen vibrations:**

Metal halogen vibration which appear in the low frequency infrared region, are quite useful in determining the stereochemistry of coordination compounds. In a tetrahedral MX\(_4\) molecule (T\(_d\)) there are four modes of vibration. All the four vibrations are Raman active whereas only two (\(\nu_3, \nu_4\)) are infrared active, and their position depends upon the mass of the metal and halogen\(^{105}\). For an octahedral ML\(_6\) molecule (O\(_h\)) (e.g., GeCl\(_6\)^\(^{-2}\), SnCl\(_6\)^\(^{-2}\), etc.) there are six possible normal modes of vibration. These (\(\nu_1, \nu_2\) and \(\nu_5\)) are Raman active whereas only two (\(\nu_3, \nu_4\)) are infrared active\(^{106}\). In octa-
hedral ions \((\text{GeX}_6^{-2}, \text{SnX}_6^{-2}, \text{etc.})\) the \(M-X\) vibrations are found at lower frequency than those found for similar vibrations in tetrahedral environment. When metal tetrahalides, \(\text{MX}_4\), form octahedral complexes, \(\text{MX}_4:2\) donor, the \(M-X\) stretching vibrations by analogy with these octahedral ions, are considerably shifted to lower frequencies relative to those of the free tetrahalides. In many addition compounds metal-halogen vibrations are much more intense than ligand vibrations. In group(IV), this is most marked for adducts of tin tetrahalides and least marked for adducts of silicon tetrahalides where intensities are frequently comparable. Ligands may occupy either cis or trans positions in the octahedron. The use of infrared spectroscopy in the far IR region to study the cis trans isomerism of the adducts of type \(\text{MX}_4\cdot\text{L}_2\) (where \(M = \text{tin, silicon or germanium, X is halogen and L is a monodentate ligand}\)) has been outlined by many workers. Neglecting the coupling between the \(M-X\) and the ligand vibration, the trans-adduct is considered to be similar to a perturbed square planar \(\text{MX}_4\) unit, so that only one infrared active fundamental \(M-X\) stretching vibration (\(\Sigma_u\) symmetry) is predicted, however, for the cis configuration there would be at least two fundamentals. There are numerous flaws in this simple approach. Fermi resonance may make a combination band intense enough to be accepted as a fundamental. Alternatively, certain fundamentals may be very weak as for gaseous
antimony trichloride, whose $\omega_e$ fundamental is very strong relative to the weak $e$ fundamental. Accidental degeneracies may occur or bands may be unresolved. Electronic transactions and lattice vibrations may appear. Calcium fluoride, for example, has a broad infrared absorption band at about 270 cm$^{-1}$. Crystal field effects may resolve degeneracies, thus only triply degenerate $F_{1u}$ fundamental of symmetrical $\text{SiF}_6^{2-}$ is resolved into two peaks in the crystalline compound $\text{BaSiF}_6$, probably owing to elongation of octahedron along the three fold axis, causing a lowering of the symmetry from $O_h$ to $D_{3d}$.

Beattie and coworkers$^5$ carried out normal coordinate analysis of the octahedral species cis- and trans- $\text{MX}_4$, $\text{L}_2$ by Wilson's F-G matrix method, and calculated vibrational frequencies for coordination compounds of some tetrahalides of group(IV). The calculations show that for a cis-adduct three high frequency bands are to be expected, the next nearest band lying considerably below this group (all the bands are infrared and Raman active). In the case of the trans adducts if the metal-ligand force constant is low as compared with the metal-halogen, there will be one main band in the same region as the set of three absorptions mentioned for the cis adducts. However, where the metal-ligand force constant is high, the $e_u$ and $a_{2u}$ vibrations (both IR active) will occur in
similar regions of the spectrum. Thus in a crystalline compound, crystal field resolution of the $e_u$ vibration to doublet, plus the presence of an $a_{2u}$ vibration could lead to a spectrum similar to that of a cis adduct. The $e_u$ vibration (anti symmetric stretch) is relatively insensitive to the value of $F_{M-L}$ and also to the value of the bending force constants. Thus, identification of cis- and trans isomers by infrared spectroscopic examination is helpful in favourable cases, particularly when solution spectra can be obtained.

Metal ligand vibrations:

The metal ligand stretching frequency is of particular interest since it provides direct information regarding the coordinate bond. It appears in the low frequency region and depends on the following factors:

1. Mass of the metal and ligand
2. Oxidation number of metal ion
3. Coordination number of metal ion
4. Geometry of the complex
5. Basicity of the ligand molecule
6. Bridging or non bridging anions
7. Ligand field stabilization energy.

M-C stretching frequencies:

IR spectroscopy is quite valuable as it provides information on the configuration of organotin compounds. Particularly
important is the criterion established for determining the configuration of SnC₃ and SnC₂ moieties in trimethyltin and dimethyltin derivatives. If the spectrum reveals two Sn-C stretching vibrations (both the symmetric and asymmetric modes) the configuration of SnC₃ group is non planar or that of SnC₂ is non linear. However, if there is only one band assignable to an Sn-C stretching vibration the configuration of SnC₃ group is planar or that of SnC₂ is linear. This criterion has been further supported by x-ray studies.

**Molar Conductance**

The conductivity measurement is one of the simplest and easily available technique used in a research laboratory, for the characterization of coordination compounds. It gives direct information regarding whether a given complex is ionic or covalent, i.e., whether the anions satisfy the primary or the secondary valency of the metal ion in the coordination compound, several studies of molar conductivities of different kind of electrolytes in different solvents are now available and it is useful to compare molar conductance (\( \Lambda_M \)) value of a given complex with that of the similar electrolyte. Conventionally solutions of 10⁻³M strength is used for the conductance measurements. Molar conductance values for different type of electrolytes in nitrobenzene at this concentration are as 1:1, 20-30, 2:1, 50-60, 3:1, 70-80, 4:1,
90-100 ohm\(^{-1}\) cm\(^2\) mole\(^{-1}\) 120.

A good description of electrolytic behaviour of coordination compounds in various organic solvents is given in a review\(^{120}\). Molar conductance values for complexes of the various electrolyte types of 10\(^{-3}\)M concentrations in nitromethane are as 1:1, 75-95; 2:1, 150-180; 3:1, 220-260, 4:1 290-330 ohm\(^{-1}\) cm\(^2\) mole\(^{-1}\). Reference values for non-complex electrolytes lead to an average \(\Lambda = \bar{M}\) value for 1:1 electrolytes of \(\approx\) 91.5 ohm\(^{-1}\) cm\(^2\) mole\(^{-1}\). However, the values for the tetraphenylborate and tetraisoamylborate salts are very low because of the low ionic mobilities and if these values are excluded from the overall average, a value of \(\approx\) 96 ohm\(^{-1}\) cm\(^2\) mole\(^{-1}\) is obtained. Average values for complexes of unidentate ligands are for 1:1 electrolytes 88.5 ohm\(^{-1}\) cm\(^2\) mole\(^{-1}\) and for 2:1 electrolytes 167 ohm\(^{-1}\) cm\(^2\) mole\(^{-1}\). For the whole range of complexes which has been studied, values claimed for 1:1 electrolytes range from 60-115 ohm\(^{-1}\) cm\(^2\) mole\(^{-1}\), with an average value of \(\approx\) 83 ohm\(^{-1}\) cm\(^2\) mole\(^{-1}\). For 2:1 electrolytes, values claimed cover the range 115-250 ohm\(^{-1}\) cm\(^2\) mole\(^{-1}\) have been given for 3:1 electrolytes. A reasonable average value is 242 ohm\(^{-1}\) cm\(^2\) mole\(^{-1}\). For 4:1 electrolytes (115-118), values cover a range 244-341 ohm\(^{-1}\) cm\(^2\) mole\(^{-1}\) with an average value of 307 ohm\(^{-1}\) cm\(^2\) mole\(^{-1}\). An unusual electrolyte type is the compound \((\text{CrL}_3)_2(\text{SO}_4)_3\), where \(L = 2\)-amino ethyl pyridine, for which a value of 419 ohm\(^{-1}\) cm\(^2\) mole\(^{-1}\) is quoted.
Toxicity and probit analysis:

In order to find out the toxicity of a chemical in terms of probit the effect of the stimulus is determined according to the reaction of living organism against that chemical. Usually the stimulus is applied at a series of experimental range and the reaction of each range determined from its application to a set of experiments.

Instead of speaking in general term it is more convenient in describing the kind of data to refer to one type of experiment such as the determination of the toxicity of a chemical preparation to a given type of insect. In such experiments various concentrations of the compound are prepared and a set of insects assigned at random to each concentration level. The compound is applied, and for each set a count is made at the total number of insects (n) and the number killed (r). The results can be expressed either as a proportion (r/n) or as a percentage 100 (r/n). Such data may then be applied for probit analysis in assessing the various toxic substances and lethal doses.

Tolerance limit

For any one subject there is a certain level of intensity of the stimulus below which response does not occur and above which it does occur. For example, in considering a given insect there is a limit of concentration for a certain chemical
such that if the concentration is below this limit the insect will survive, but if the concentration exceeds this limit the insects will die. This tolerance is represented by $\lambda$. For most of the biological preparation the distribution of $\lambda$ is not normal but is at least approximately normal for $X = \log_{10}$. In probit analysis therefore the log of the concentration is usually used. Following Finney is referred to as the dose in terms of actual concentration expressed in milligram/liter and the $\log_{10}$ concentration is referred to as the dosage. A plot of the percentages killed against dosage gives a sigmoid curve. The analysis of results from the sigmoid curve presents some rather serious difficulties. It would therefore, seem to be desirable to use a transformation of the percentages such that with a normal distribution the transformed percentages would lie in a straight line. Any variation from the normal curve will cause the plotted probits to vary from a straight line. Generally, the observed variations from a straight line are of two types.

(I) In the first place the sets of experiments may not be all uniform or the conditions for the sets may not be uniform. This will tend to produce an abnormal scatters of the points about the straight line.

(II) In the second place the transformation of the dose to dosage may not be suitable.
Practical application of probit analysis:

Since we expect to get a straight line when probits are plotted against dosage, the methods of linear regression are suggested.

To measure the potency of the preparation it has been found that the dose giving a 50% kill is the most statistic and referred to as LD$_{50}$ (median lethal dose). In experiments where the response is not death we refer to the ED$_{50}$ (median effective dose). Whatever practical advantages there may be in knowing the LD$_{90}$ or some similar value, the fact is that much greater precision can be obtained in the measure of the LD$_{50}$ which is corresponding to a probit value of 5.

Another factor to be measured is the range of the dosage required for a given range of percentage kill. This might be referred to as the sensitivity of the preparation tested. Obviously if small changes in concentrations give a wide range in the percentage kill, the sensitivity is high and represented by the slope of the line. The greater the slope the narrower the range in dosage for a given range in the percentage kill.

The geometry of the line would seem to give therefore the required measure of potency and sensitivity. Taking two points $X_1$ and $X_2$, representing the dosage, on the abscissa of
the graph and finding the corresponding points \( Y_1 \) and \( Y_2 \) on
the probit scale, will give the slope of the line. If \( b \) rep­
resents the slope, then

\[
b = \frac{Y_2 - Y_1}{X_2 - X_1}
\]

This makes it possible to set up a regression equation
of the type \( Y = a + bx \) where \( a = Y_1 - bX_1 \) or \( Y_2 - bX_2 \).
Experimental Techniques used

All the newly synthesized complexes were characterized by their melting points, elemental analysis and conductance measurements. The site of coordination and probable geometry of the complexes was proposed on the basis of IR spectroscopy. Their toxic behaviour was studied in an experiment on fish (Heteropneustes fossilis), house flies (musca domestica nobulo and cockroach (Periplaneta Americana) in term of LC50.

Elemental analyses for carbon, hydrogen and nitrogen were done on a Coleman analyser in the microanalytical laboratory of the Chemistry Department at the University of Calcutta. The estimation of metal, sulphur and halogen were done volumetrically or gravimetrically. For the metal estimation a weighed amount of the compound was taken in a silica crucible and a few drops of HCl were added to decompose it. It was heated slowly till the fumes disappeared and further heating was done with concentrated nitric acid for about half an hour. The dry powder thus obtained was cooled to room temperature and weighed as SnO2. The halogen and sulphur were estimated gravimetrically by known methods.

The infrared and far infrared spectra were recorded on a Perkin Elmer 621 (4000 - 200 cm⁻¹) spectrophotometer at the
instrumentation centre of the Department of Chemistry, Aligarh Muslim University, Aligarh and at R. R. Lab., Hyderabad.

The molar conductivity of the soluble compounds were measured in the nitrobenzene or nitromethane on a Systronics conductivity bridge type 302.

In order to investigate the toxicity experiments on fish, house flies and cockroach were done in the Department of Zoology, A.M.U., Aligarh.
CHAPTER III

COMPLEXES OF DIORGANOTIN(IV) DICHLORIDE AND DIACETATE

WITH SOME NITROGEN HETERO CYCLIC
COMPLEXES OF DIOrganotin(IV) Dichlorides and DiAcetate with Some Nitrogen Heterocyclic

EXPERIMENTAL

Materials and methods:

Dimethyltin dichloride (DMT) dibutyltin dichloride (DBT) and dibutyltin diacetate (DBA) (Fluka, A.G.), piperazine hexahydrate (Pz) (E. Merck), acridine (Acr), pyrrolidine (Pyrr), O-phenanthroline (O-Phen) and 2,2-Bipyridyl (Bipy) (B.D.H.) were used without further purification. The solvent ethanol, nitromethane, nitrobenzene and chloroform were distilled and dried by conventional methods.

Preparation of complexes:

Piperazine complexes:

Piperazine 0.002 mol dissolved in 20 ml of ethanol was added to ethanolic solutions of (a) dimethyltin dichloride 0.0018 mol, (b) dibutyltin dichloride 0.002 mol and (c) dibutyltin diacetate 0.002 mol respectively. White crystalline adducts were obtained within 10 minutes. These were dried in vacuo.

Acridine complexes:

The ligand 0.002 mol was dissolved in 25 ml of ethanol and was added to ethanolic solutions containing (a) 0.0018 mol
of dimethyltin dichloride, (b) 0.002 mol of dibutyltindichloride and (c) 0.002 mol of dibutyltin diacetate respectively. The reaction mixture was dried under vacuum till a brown crystalline or a yellowish solid compound was obtained.

**Pyrrolidine complexes:**

All the complexes were prepared by the method detailed above. A cream coloured complex was immediately obtained in the case of dibutyltin diacetate while dimethyltin dichloride yielded a white crystalline adduct. These were washed several times with hot ethanol and dried in vacuo.

**Phenanthroline adducts:**

These compounds were also synthesized by the usual methods mentioned above. The reaction mixture on standing overnight yielded shining white crystals in case of dimethyltin dichloride while a pink solid was obtained in case of DBT and DBA.

**2,2-Bipyridyl adducts:**

The two components were mixed and stirred for few hours when light pink and white needle like crystals or solid were obtained. They were dried in vacuo.
RESULTS AND DISCUSSION

Dialkyltin dihalides form two types of adducts (1) $R_gSnX_g-L$ (2) $R_gSnX_g-L_g$ depending upon whether the ligand is bidentate or monodentate. When the complex is formed with a bidentate ligand L, it may achieve a trigonal bipyramidal structure or it may have an octahedral geometry depending upon whether both or one coordination site is engaged in coordination.

The alkyltin halides can form adducts with monodentate ligands either in a 1:1 or a 1:2 ratio. It is known that if the ligand is bidentate the complex will be octahedral while with the monodentate ligand the central atom may assume a trigonal bipyramidal geometry in the case of 1:1 complex and an octahedral structure in the case of a 1:2 complex.

Tin(IV) halides are wellknown Lewis acids and interact with various Lewis bases to form adducts. The group(IV) alkylhalide adducts with some donor molecules have been studied less extensively as compared to that of group(IV) metal tetrahalides.

All the complexes studied in this work are stable to oxidation by air and have a 1:1 metal:ligand ratio except for pyrrolidine adducts which have a 1:2 ratio. Their molar conductance of $10^{-3} M$ solution in nitromethane or nitrobenzene
<table>
<thead>
<tr>
<th>Complexes</th>
<th>m.p. °C</th>
<th>%C Found (Calc)</th>
<th>%H Found (Calc)</th>
<th>%N Found (Calc)</th>
<th>%Sn Found (Calc)</th>
<th>%Cl Found (Calc)</th>
<th>Molar Conductance Ohm⁻¹ cm² mole⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMT(Pyrr)₂</td>
<td>195</td>
<td>43.09 (43.08)</td>
<td>8.15 (8.13)</td>
<td>6.28 (6.28)</td>
<td>26.61 (26.60)</td>
<td>-</td>
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<tr>
<td>DBA(Pyrr)₂</td>
<td>300</td>
<td>48.89 (48.70)</td>
<td>5.85 (5.58)</td>
<td>5.69 (5.68)</td>
<td>24.08 (24.06)</td>
<td>-</td>
<td>0.69 x 10⁻¹</td>
</tr>
<tr>
<td>DMT(Pz)</td>
<td>225</td>
<td>23.59 (23.57)</td>
<td>5.28 (5.28)</td>
<td>9.18 (9.16)</td>
<td>38.80 (38.81)</td>
<td>23.20</td>
<td>2.73 x 10⁻¹</td>
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<td>36.98 (36.96)</td>
<td>7.26 (7.24)</td>
<td>7.19 (7.18)</td>
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<td>18.19</td>
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<td>43.97 (43.96)</td>
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<td>6.43 (6.41)</td>
<td>27.16</td>
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<td>3.80 (3.79)</td>
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<td>17.75</td>
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<td>DBT(Acr)</td>
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<td>52.20 (52.22)</td>
<td>5.60 (5.63)</td>
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<td>56.60 (56.63)</td>
<td>6.26 (6.27)</td>
<td>2.63 (2.64)</td>
<td>22.29</td>
<td>-</td>
<td>0.7 x 10⁻¹</td>
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<th>%H Found</th>
<th>%N Found</th>
<th>%Sn Found</th>
<th>%Cl Found</th>
<th>Molar Conductance Ohm⁻¹ cm² mole⁻¹</th>
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<td>DMT(Phen)</td>
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<td>42.06</td>
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<td>7.00</td>
<td>29.66</td>
<td>17.72</td>
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<td></td>
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<td>(42.05)</td>
<td>(3.53)</td>
<td>(7.01)</td>
<td>(29.68)</td>
<td>(17.73)</td>
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<td>49.67</td>
<td>5.41</td>
<td>5.77</td>
<td>24.50</td>
<td>14.62</td>
<td>0.6 x 10⁻¹</td>
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<td></td>
<td></td>
<td>(49.66)</td>
<td>(5.41)</td>
<td>(5.79)</td>
<td>(24.52)</td>
<td>(14.65)</td>
<td></td>
</tr>
<tr>
<td>DBA(Phen)</td>
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<td>54.23</td>
<td>6.03</td>
<td>5.29</td>
<td>22.30</td>
<td>-</td>
<td>0.9 x 10⁻¹</td>
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<td></td>
<td></td>
<td>(54.26)</td>
<td>(6.07)</td>
<td>(5.27)</td>
<td>(22.34)</td>
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<tr>
<td>DMT(Bipy)</td>
<td>55</td>
<td>38.34</td>
<td>3.76</td>
<td>7.42</td>
<td>31.55</td>
<td>18.85</td>
<td>2.8 x 10⁻¹</td>
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<tr>
<td></td>
<td></td>
<td>(38.35)</td>
<td>(3.75)</td>
<td>(7.45)</td>
<td>(31.58)</td>
<td>(18.87)</td>
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<tr>
<td>DBT(Bipy)</td>
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<td>47.01</td>
<td>5.69</td>
<td>6.35</td>
<td>25.81</td>
<td>15.40</td>
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<td></td>
<td></td>
<td>(47.00)</td>
<td>(5.70)</td>
<td>(6.09)</td>
<td>(25.80)</td>
<td>(15.41)</td>
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<tr>
<td>DBA(Bipy)</td>
<td>50</td>
<td>52.11</td>
<td>6.34</td>
<td>5.53</td>
<td>23.41</td>
<td>-</td>
<td>1.3 x 10⁻¹</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(52.10)</td>
<td>(6.36)</td>
<td>(5.52)</td>
<td>(23.40)</td>
<td></td>
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</table>
exhibit their non-electrolytic nature (Table 1).

**Piperazine adducts.**

Piperazine shows a tendency to form unstable compounds with group(IV) metal halides\textsuperscript{125} in varying ratios. Dimethyltin dichloride, dibutyltin dichloride and dibutyltin diacetate form 1:2 complexes (R\textsubscript{2}SnX\textsubscript{2}\cdot2Pz) with piperazine in solution (detected by conductometric titration) but they could not be isolated. However, the solid complexes of piperazine with the above dialkyltin dichlorides and diacetate synthesized had only a 1:1 molar ratio. The IR spectrum of piperazine shows absorption at 3328 cm\(^{-1}\) and 1444 cm\(^{-1}\) attributed to \(\nu\) (N-H) and \(\nu\) (C-N) stretching frequencies respectively. After complexation the enhancement in \(\nu\) (C-N) is negligible but the decrease in \(\nu\) (N-H) is substantial\textsuperscript{122}. This is due to an electronic shift from nitrogen atom towards tin atom after coordination which necessarily weakens the N-H bond with a consequent decrease in N-H stretching frequencies\textsuperscript{126}.

The (C-N) absorption modes appeared at 1560 cm\(^{-1}\), 1590 cm\(^{-1}\) and 1580 cm\(^{-1}\) in dimethyltindichloride, dibutyltindichloride and dibutyltindiacetate adducts respectively. These adducts show M-N stretching frequency at 290 cm\(^{-1}\) and M-Cl bands at 305 cm\(^{-1}\).
The 1:1 piperazine compound apparently seems to be five coordinated but the possibility of the formation of an octahedral polymeric species through ligand bridging (XIX) can also be envisaged.

\[ \text{Acridine adducts:} \]

Acridine exhibits two prominent absorption bands at 1515 cm\(^{-1}\) and 1555 cm\(^{-1}\) attributed to \(\nu(C=\text{N})\) and \(\nu(C=C)\) stretching frequencies. As \(\nu(C=C)\) and \(\nu(C=\text{N})\) appear approximately in the same region of spectrum they could not be distinguished. In all the adducts coordination caused a marked increase in \((C=\text{N})\) and \((C=C)\) stretching frequencies (Table 2). These shifts are in agreement with those reported for adducts with similar donor molecules \(^{127,128}\).

The M-Cl absorption bands are stronger and appear at higher wave numbers as compared to M-N absorption bands. A weak band at 290 cm\(^{-1}\) in all adducts has been assigned to \(\nu(M-N)\). The M-Cl stretching frequencies for all adducts have been observed at 350 cm\(^{-1}\). A probable structure (XX) is proposed.
<table>
<thead>
<tr>
<th></th>
<th>( \nu(N-H) )</th>
<th>( \nu(C-N) )</th>
<th>( \nu(C=O) ) and ( \nu(C=O) )</th>
<th>( \nu(M-N) )</th>
<th>( \nu(M-X) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrrolidine</td>
<td>3268 (b)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>DMT (Pyrr)(_2)</td>
<td>3100 (b)</td>
<td>-</td>
<td>-</td>
<td>285 (w)</td>
<td>310 (m)</td>
</tr>
<tr>
<td>DBT (Pyrr)(_2)</td>
<td>3150 (b)</td>
<td>-</td>
<td>-</td>
<td>320 (w)</td>
<td>330 (m)</td>
</tr>
<tr>
<td>DBA (Pyrr)(_2)</td>
<td>3150 (b)</td>
<td>-</td>
<td>-</td>
<td>285 (w)</td>
<td>-</td>
</tr>
<tr>
<td>Piperazine</td>
<td>3328 (b)</td>
<td>1444 (s)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>DMT (Pz)</td>
<td>3230 (w)</td>
<td>1560 (b)</td>
<td>-</td>
<td>290 (w)</td>
<td>300 (vww)</td>
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<td>DBT (Pz)</td>
<td>3160 (b)</td>
<td>1590 (b)</td>
<td>-</td>
<td>290 (w)</td>
<td>300 (vww)</td>
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<td>3170 (w)</td>
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<td>Acridine</td>
<td>-</td>
<td>-</td>
<td>1555 (s)</td>
<td>1515 (s)</td>
<td>-</td>
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<td>-</td>
<td>-</td>
<td>1565 (w)</td>
<td>1515 (m)</td>
<td>290 (m)</td>
</tr>
<tr>
<td>DBT (Acr)</td>
<td>-</td>
<td>-</td>
<td>1560 (m)</td>
<td>1515 (m)</td>
<td>280 (m)</td>
</tr>
<tr>
<td>DBA (Acr)</td>
<td>-</td>
<td>-</td>
<td>1560 (m)</td>
<td>1515 (m)</td>
<td>280 (w)</td>
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</table>

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<table>
<thead>
<tr>
<th></th>
<th>$\nu$ (N-H)</th>
<th>$\nu$ (C-N)</th>
<th>$\nu$ (C=N)</th>
<th>and $\nu$ (C=C)</th>
<th>$\nu$ (M-N)</th>
<th>$\nu$ (M-X)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenanthroline</td>
<td>-</td>
<td>-</td>
<td>1499 (b)</td>
<td>1415 (s)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>DMT (Phen)</td>
<td>-</td>
<td>-</td>
<td>1570 (b)</td>
<td>-</td>
<td>330 (s)</td>
<td>330 (m)</td>
</tr>
<tr>
<td>DBT (Phen)</td>
<td>-</td>
<td>-</td>
<td>1590 (sb)</td>
<td>-</td>
<td>290 (m)</td>
<td>330 (m)</td>
</tr>
<tr>
<td>DBA (Phen)</td>
<td>-</td>
<td>-</td>
<td>1565 (vs)</td>
<td>1555 (vw)</td>
<td>310 (w)</td>
<td>-</td>
</tr>
<tr>
<td>2,2-bipyridyl</td>
<td>-</td>
<td>-</td>
<td>1500 (b)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>DMT (Bipy)</td>
<td>-</td>
<td>-</td>
<td>1560 (sb)</td>
<td>-</td>
<td>290 (w)</td>
<td>300 (m)</td>
</tr>
<tr>
<td>DBT (Bipy)</td>
<td>-</td>
<td>-</td>
<td>1580 (b)</td>
<td>-</td>
<td>280 (m)</td>
<td>310 (m)</td>
</tr>
<tr>
<td>DBA (Bipy)</td>
<td>-</td>
<td>-</td>
<td>1565 (vs)</td>
<td>-</td>
<td>320 (m)</td>
<td>-</td>
</tr>
</tbody>
</table>
Pyrrolidine adducts:

An absorption band at 3368 cm\(^{-1}\) in the IR spectrum of pyrrolidine is assignable to \(\nu\) (N-H). Coordination of tin through nitrogen atom of pyrrolidine results in an increase in electron density at tin atom causing a decrease in (N-H) stretching frequencies\(^{129}\).

The spectra of dimethyltin dichloride dibutyltin dichloride and dibutyltin diacetate show \(\nu\) (N-H) in the range 3100 - 3150 cm\(^{-1}\). The appearance of only one (M-Cl) band at 330 cm\(^{-1}\) is indicative of a trans configuration while for a cis octahedral compound two closely associated (M-Cl) bands appear in the same region of spectrum\(^5,122\). Following the criterion of Beattie and coworkers\(^{23}\) based on the normal coordinate analysis, these compounds may reasonably be suggested to have a trans octahedral geometry (XXI).
Phenanthroline adducts:

The (C=C) and (C=N) absorption bands at 1499 cm\(^{-1}\) and 1415 cm\(^{-1}\) in phenanthroline undergo a shift to higher wave numbers\(^{128}\) after chelation. A weak band at 1130 cm\(^{-1}\) with a shoulder at 876 cm\(^{-1}\) is further weakened. Besides this, the appearance of a new absorption band at 1150 cm\(^{-1}\) is also a characteristic of chelation of phenanthroline\(^{128}\). However, this absorption band appears at 1140 cm\(^{-1}\) in the present case. In the far i.r. region the \(\nu(M-N)\) appeared at 310 cm\(^{-1}\) while M-Cl bands are observed at 330-350 cm\(^{-1}\).
2,2-Bipyridyl adducts:

The position of the nitrogen atom in 2,2-bipyridyl is similar to that in phenanthroline and hence a similar pattern of IR spectrum is observed. The $\nu(C-C)$ and $\nu(C-N)$ in free ligand are shifted to higher wave numbers after complexation. Of all the vibrations the bands at 995 cm$^{-1}$ and 759 cm$^{-1}$ in free ligand are most sensitive to chelation (XXIII) and have been found to be shifted to higher wave numbers. The first band has been shifted to 1010 cm$^{-1}$ in DMT and 1035 cm$^{-1}$ in DBT and DBA chelates while the second one has been observed at 760 cm$^{-1}$ with increased intensity.

The far IR region of dimethyltin dichloride dibutyltin dichloride and dibutyltin diacetate adducts show $\nu(M-N)$ at 290 cm$^{-1}$, 280 cm$^{-1}$ and 320 cm$^{-1}$ and $\nu(M-Cl)$ at 300 cm$^{-1}$ and 310 cm$^{-1}$ respectively.

(XXIII)
Contradiction to the assignment of appropriate configuration in octahedral complexes arises probably due to the distortion of its true octahedral environment. Replacement of the halide ion by an alkyl group would cause more distortion. Further, if the alkyl groups attached to tin are different the distortion would be further enhanced. The configuration proposed so far for the hexa-coordinated complexes of dialkyltin dichlorides generally possess the alkyl groups in trans position.

In addition to $\nu$(Sn-N) and $\nu$(Sn-Cl), the $\nu$(Sn-C) is also helpful in determining the configuration of SnC$_3$ and SnC$_2$ moieties in R$_3$SnX and R$_2$SnX$_2$ derivatives. It is known that if the spectrum in the region 580-500 cm$^{-1}$ exhibits two Sn-C stretching frequencies symmetric and asymmetric, the configuration of SnC$_3$ group is non planar or that of SnC$_2$ group is non linear. However, if there is only one band assigned to $\nu$(Sn-C) in the above region, the SnC$_3$ group is planar or SnC$_2$ group is linear$^{117}$. This criterion has been further supported by x-ray diffraction studies. In the present case all the addition compounds revealed only one Sn-C band in the region 580-500 cm$^{-1}$ which confirms that the configuration of SnC$_2$ group in diorganotin compounds is linear.
For an octahedral compound with bidentate ligands like 1,10-phenanthroline and 2,2-bipyridyl two types of configurations$^{117,124}$ (XXIV) and (XXV) are possible.

\[ (XXIV) \quad (XXV) \]

Configuration (XXV) is ruled out on the basis of occurrence of only one Sn-C band at 525 in both the cases. The resulting molecule has a symmetry lower than octahedral and structure (XXIV) may therefore, be proposed for phenanthroline and 2,2 bipyridyl chelates.

On the basis of these limited studies it is concluded that the small ligands, like pyrrolidine yielded a 1:2 trans octahedral complexes while bulky ligands give a 1:1 trigonal bipyramidal or an octahedral complex.
CHAPTER IV

KINETICS AND MECHANISM OF SUBSTITUTION OF DIBUTYL-
DICHLOROBIS(PYRROLIDINE) TIN(IV) AND DIBUTYL-
DICHLORO(1,10-PHENANTHROLINE) TIN(IV).
KINETICS AND MECHANISM OF SUBSTITUTION OF DIBUTYLDICHLOROBIS (PYRROLIDINE)TIN(IV) AND DIBUTYLDICHLORO-(1,10-PHENANTHROLINE)TIN(IV)

EXPERIMENTAL

Materials and Method:

Dibutyltindichloride (R₂SnCl₂)(Fluka, A. G.) pyrrolidine (L)(BDH), 1,10-phenanthroline (E. Merck) benzoylchloride, acetyl chloride, thionyl chloride and nitrobenzene (Riedel) were all used as such. Ethanol was distilled over KOH.

Millimolar solutions of dibutyltindichlorobis(pyrrolidine) tin(IV) and dibutyltindichloro (1,10-phenanthroline)tin(IV) were prepared in nitrobenzene and an increase in conductance was measured as a function of time. A plot of molar conductance, ΑΜ versus time gave a curve and from the slope of the linear portion of these curves specific rate constant for solvation Kₛ, was calculated (XXVI, XXVII). The value of Kₛ for dibutyltindichlorobis (pyrrolidine)tin(IV) (1.2 x 10⁻³ sec⁻¹) is slightly greater than that obtained in the case of dibutyltindichloro (1,10-phenanthroline)tin(IV) (1 x 10⁻³ sec⁻¹).

Millimolar solutions of the nucleophiles, namely, C₆H₅COCl, SOCl₂ and CH₃COCl were prepared in nitrobenzene.
Molar conductance time curve for L₂:R₂SnCl₂ in Nitrobenzene (XXVI)
Molar conductance time curve for $\left( \frac{N}{N} \right): R_2 SnCl_2$ in Nitrobenzene

(XXVII)
Solutions of the nucleophile and those of the complexes were mixed separately in three different molar ratios. The conductance of each mixture was measured (i) immediately, (ii) after successive intervals of five minutes for a period of one hour and (iii) after 24 hours to get the value of $\Lambda_\infty$. The increase in conductance was faster in the presence of a nucleophile than without. The molar conductance, $\Lambda_M$ versus time curve for substitution (XXVII,XXIX) was similar to that obtained for solvation.

On plotting $\log \frac{\Lambda_\infty}{(\Lambda_\infty - \Lambda_M)}$ against time two linear plots were obtained (XXX, XXXI) for different molar ratios indicating that both reactions follow first order kinetics. In the substitution reaction by chloride ions two mutually intersecting linear portions of the graph were obtained. The specific rate constants, $K_1$ and $K_2$ for stepwise replacement of pyrrolidine and phenanthroline in the complex were calculated from the slope of the first and second linear portion of the curves using the method of two mutually intersecting lines$^{131,132}$.

The integrated equation for calculation of 1st order rate constant is as follows

$$K = \frac{-2.303}{t} \log \left( \frac{\Lambda_\infty}{\Lambda_\infty - \Lambda_M} \right)$$
Molar conductance time curve for \( \text{L}_2: \text{R}_2 \text{SnCl}_2 \) (i) by \( \text{CH}_3 \text{COCl} \) (ii) by \( \text{SOCl}_2 \)

(XXVIII)
Molar conductance time curve for \( \frac{N_{>3}}{N} \):

1. \( \text{R}_2\text{SnCl}_2 \) by \( \text{CH}_3\text{COCl} \)
2. \( \text{by C}_6\text{H}_5\text{COCl} \)

\( (XXIX) \)
RESULTS AND DISCUSSION

The kinetic study of the complexes were done in nitrobenzene due to the following two reasons - (i) solubility of the complexes and (ii) the non self ionizing character of the solvent$^{34}$. The conductance of millimolar solution of the complexes in nitrobenzene increase with time (XXVI, XXVII). The calculated values of the first order rate constant, $K_g$ show that it depends upon the original concentration of the complex. The participation of solvent however, makes it pseudo first order reaction.

In order to explain these results the following reactions leading to the formation of an ion pair involving nitrobenzene are assumed to take place in the solution. During solvation the rate of increase in molar conductance value in the initial stage is very low (mechanism A & B) which may be explained on the basis of the reaction (I,IV) and (III, VI) which generate ionic species.

\[
\begin{align*}
R_2SnCl_2 L_2 + S & \xrightleftharpoons{K_g} [R_2SnSClL_2]^+ + Cl^- \quad (I) \\
R_2SnCl_2 L_2 + S & \xrightarrow{\text{no shift}} [R_2SnSCl_2L] + L \quad (II) \\
R_2SnCl_2 L_2 + Cl^- & \xrightarrow{\text{no shift}} [R_2SnCl_3L]^- + L \quad (III)
\end{align*}
\]
The replacement of the stronger nucleophile, the chloride ion and pyrrolidine or 1,10-phenanthroline by the solvent, (S) is due to the mass effect. The addition of pyrrolidine or 1,10-phenanthroline, however, effects reaction (III, VI).
First order plots for substitution of 
C₆H₅COCl in different molar ratios for 
L₂ : R₂SnCl₂
First order plots for substitution of SOCl\(_2\) in different molar ratios for \(\frac{N_1}{N_2} : R_2SnCl_2\)
so that the consumption of chloride ion is suppressed as a result of which the equilibrium is shifted in backward direction in reaction (I, IV). Consequently less ionic species are produced which decrease the rate of solvation. As the reactions (I, IV) and (III, VI) are fast, reaction (II, and V) become the rate determining steps.

The study of the kinetics of substitution of pyrroliidine and 1,10-phenanthroline in $[R_2SnCl_2-L_2]$, $[R_2SnCl_2-N]$ by chloride ions generated by nucleophilic reagents provides interesting data. The following mechanisms (C, D) are proposed for the substitution reaction.

Substitution mechanism (SN1) in $R_2SnCl_2L_2$

\[
\begin{align*}
&\text{(VII)} \\
&\text{(VIII)} \\
&\text{(IX)} \\
&\text{(X)}
\end{align*}
\]

\[RCl = R^+ + Cl^-\]

\[R^+ = C_6H_5CO^+, CH_3CO^+, SOCl^+\]
The reaction of chloride ion with $[R_2SnCl_2]^{N}$ complex may follow two paths:

(a) The first order dissociation of 1,10-phenanthroline from the complex followed by rapid addition of chloride ion.

(b) The second path is a second order reaction with direct chloride ion attack followed by rapid addition of another chloride ion.

However, in the present case it has been found to follow first order (SN$_1$) reaction for which the proposed mechanism is as under:

Substitution mechanism (SN$_1$) in $[R_2SnCl_2]^{N}$

\[
\begin{align*}
\text{(XI)} & \quad \xrightarrow{\text{Cl}^-} \quad \text{(XII)} & \quad \text{Cl}^- \quad \text{(XIII)} \\
\text{(XIV)} & \quad \rightarrow \quad \text{(XV)}
\end{align*}
\]
The rate of increase in conductance during substitution indicates that the chloride ion is a stronger nucleophile than pyrrolidine, 1,10-phenanthroline and nitrobenzene. The replacement of the base molecule (L) or the breaking of one of the two bonds in 1,10-phenanthroline complex by the chloride ion resulting in the formation of \([L-R_2SnCl_3]^-\) and \([R_2SnCl_4]^-\) as final product, indicates an increase in molar conductance of the solution as a function of time which attains a maximum value of conductance after 24 hours. The pathway shown, however, involves a trigonal bipyramidal intermediate. The dissociation of \([L-R_2SnCl_3]^-\) or \([R_2SnCl_4]^-\) in step (VIII, XIII) seems to be faster than the corresponding dissociation in step (VII, XII) because of the negative charge on the former which assists the breaking of tin-ligand bond. However, an equilibrium point is attained after 24 hours. From the calculation (Table-3) of specific rate constant, \(K_1\) and \(K_2\) it has been found that it is independent of the concentration as well as the molar ratios.

The dissociation of pyrrolidine (L) or phenanthroline (N) in step (VII, XII) and (IX, XIII) are slow processes and hence it is the rate determining step. The first order plots (XXXI, XXXII) consist of two intersecting straight lines suggesting that there are two different rate determining steps, the first step corresponds to the reaction (VII, XII) and the second for reaction (IX, XIII).
From this study it has been concluded that the rate of substitution is faster than the rate of solvation. Both the reactions follow $\text{SN}_1$ mechanism and the nucleophilic reagents may be arranged in decreasing order of their rate constants, $K_1$ and $K_2$.

$$\text{SOCl}_2 \succ \text{C}_6\text{H}_5\text{COCl} \succ \text{CH}_3\text{COCl}.$$
Table 3

Rate Constant for Substitution of Base Molecule by Chloride Ion in the Complexes

<table>
<thead>
<tr>
<th>Complex : Nucleophilic reagent</th>
<th>Ratio</th>
<th>$K_1 \times 10^{-2}$ sec$^{-1}$</th>
<th>$K_2 \times 10^{-2}$ sec$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_2'SnCl_2L_2 : SOCl_2$</td>
<td>1:1</td>
<td>2.8</td>
<td>7.2</td>
</tr>
<tr>
<td></td>
<td>1:2</td>
<td>2.7</td>
<td>7.2</td>
</tr>
<tr>
<td></td>
<td>1:large</td>
<td>2.8</td>
<td>7.1</td>
</tr>
<tr>
<td>$R_2'SnCl_2L_2 : C_6H_5COCl$</td>
<td>1:1</td>
<td>2.3</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>1:2</td>
<td>2.3</td>
<td>4.9</td>
</tr>
<tr>
<td></td>
<td>1:large</td>
<td>2.5</td>
<td>5.0</td>
</tr>
<tr>
<td>$R_2'SnCl_2L_2 : CH_3COCl$</td>
<td>1:1</td>
<td>1.4</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td>1:2</td>
<td>1.3</td>
<td>3.8</td>
</tr>
<tr>
<td></td>
<td>1:large</td>
<td>1.4</td>
<td>3.9</td>
</tr>
<tr>
<td>$R_2'SnCl_2L_2 : SOCl_2$</td>
<td>1:1</td>
<td>1.4</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td>1:2</td>
<td>1.4</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td>1:large</td>
<td>1.4</td>
<td>2.3</td>
</tr>
<tr>
<td>$R_2'SnCl_2L_2 : C_6H_5COCl$</td>
<td>1:1</td>
<td>1.1</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>1:2</td>
<td>1.1</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>1:large</td>
<td>1.1</td>
<td>1.6</td>
</tr>
<tr>
<td>$R_2'SnCl_2L_2 : CH_3COCl$</td>
<td>1:1</td>
<td>1.0</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>1:2</td>
<td>1.0</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>1:large</td>
<td>1.0</td>
<td>1.2</td>
</tr>
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</table>
CHAPTER V

STRUCTURAL AND BIOCIDAL STUDIES ON SOME DI- AND TRIORGANOTIN(IV) DITHIOCARBAMATES
STRUCTURAL AND BIOCIDAL STUDIES ON SOME DI- AND TRIORGANOTIN(IV)
DITHIOCARBAMATES

EXPERIMENTAL

Material and methods:

Tetramethylene dithiocarbamate (TMdtc), (B.D.H.) m.p. = 150°C, 5-aminoindazole (5-Indz), m.p. = 175°C, α-naphthylamine (α-naph.), m.p. = 50°C, β-naphthylamine (β-naph.), m.p. = 110°C (Koch Light) and piperazine (Pz), (E. Merck) m.p. = 104°C, carbon disulphide (B.D.H.), dimethyltindichloride (DMT), dibutyltindichloride (DBT), trimethyltinchloride (TMT), tributyltinchloride (TBT), triphenyltinchloride (TPT) (E. Merck) were used as such.

Preparation of the complexes:

There are two well-known methods for the synthesis of a dithiocarbamate derivative:

(a) by insertion reaction (A) or
(b) by replacement reaction (B)

However, in the present work all alkyltin(IV) dithiocarbamates were synthesized by the first method except for ammonium tetramethylene dithiocarbamate complexes, by mixing
M:L:CS₂ in 1:2:2 or 1:1:1 ratios. The reaction mixture was vigorously stirred at room temperature and allowed to stand for fifteen days when a solid compound was obtained.

**Toxic effect:**

In order to investigate the toxicity of individual dithiocarbamate experiments were carried out on fish. Specimens of *Heteropneustes fossilis* measuring 10-15 cm were acclimated to laboratory aquaria for 48 hours before the experiment. A stock solution containing 0.1 g of ammonium tetramethylene dithiocarbamate was prepared in 3ml of ethylalcohol and was made up to 100ml with water. A set of four jars were taken for four different concentration of the ligands and one for the control. Specimens were exposed to each concentration (1 ppm, 3 ppm, 5 ppm and 7 ppm) by taking equal numbers of individuals (4 fish) in equivalent volume of water (2 litres). Media of all experimental jars were renewed daily. During the period of exposure the fish were observed for an abnormali
and the number of individuals killed in 96 hours was recorded. The dead specimens were removed immediately from the test containers. After 96 hours it was found that none of the fish died in the jar containing 1 ppm solution while 100% mortality was recorded in the solution containing 3 ppm of the compound. This indicates that the mortality range of the dithiocarbamate lies between 1 ppm to 3 ppm. This experiment was repeated and the fish were exposed to a narrow concentration range of the dithiocarbamate starting from 1.5, 1.8, 2.1 and 2.4 ppm and the % kill value was recorded.

For further investigation of the toxicity of the dithiocarbamate and their corresponding complexes a series of experiments were carried out on house flies (Musca Domestica nobulo). Specimens were exposed to four different concentrations of dithiocarbamate (0.05% to .2%) mixed with a palatable base. The control set was also run simultaneously by taking equal number of individuals (10 flies). Their percent mortality values were obtained after 24 hours.
### Table - 4

Analytical data and some Physical Properties of the Complexes

<table>
<thead>
<tr>
<th>Complexes</th>
<th>M.P. C</th>
<th>Colour</th>
<th>%C Found (Calc)</th>
<th>%H Found (Calc)</th>
<th>%N Found (Calc)</th>
<th>%Sn Found (Calc)</th>
<th>%S Found (Calc)</th>
<th>Molar Conductance ohm⁻¹ cm² moles⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMT(TMdte)₂</td>
<td>185°</td>
<td>Yellow</td>
<td>32.64</td>
<td>5.01</td>
<td>6.33</td>
<td>26.90</td>
<td>29.05</td>
<td>1.13 x 10⁻¹</td>
</tr>
<tr>
<td>DBT(TMdte)₂</td>
<td>110°</td>
<td>Yellow</td>
<td>41.12</td>
<td>6.52</td>
<td>5.32</td>
<td>22.60</td>
<td>24.40</td>
<td>1.2 x 10⁻¹</td>
</tr>
<tr>
<td>TBT(TMdte)</td>
<td>195°</td>
<td>White</td>
<td>46.79</td>
<td>8.09</td>
<td>3.21</td>
<td>27.20</td>
<td>14.69</td>
<td>0.46 x 10⁻¹</td>
</tr>
<tr>
<td>TMT(TMdte)</td>
<td>250°</td>
<td>White</td>
<td>30.95</td>
<td>5.51</td>
<td>4.50</td>
<td>38.27</td>
<td>20.65</td>
<td>1.28 x 10⁻¹</td>
</tr>
<tr>
<td>TPT(TMdte)</td>
<td>115°</td>
<td>White</td>
<td>55.63</td>
<td>4.66</td>
<td>2.82</td>
<td>23.90</td>
<td>12.93</td>
<td>0.38 x 10⁻¹</td>
</tr>
<tr>
<td>DMT(Pzdtc)₂</td>
<td>d.260°</td>
<td>White</td>
<td>30.70</td>
<td>4.71</td>
<td>11.90</td>
<td>27.32</td>
<td>25.27</td>
<td>1.3 x 10⁻¹</td>
</tr>
<tr>
<td>DBT(Pzdtc)₂</td>
<td>170°</td>
<td>White</td>
<td>26.27</td>
<td>7.47</td>
<td>12.20</td>
<td>28.03</td>
<td>25.90</td>
<td>0.5 x 10⁻¹</td>
</tr>
<tr>
<td>TBT(Pzdtc)</td>
<td>d.255°</td>
<td>White</td>
<td>45.32</td>
<td>7.82</td>
<td>6.20</td>
<td>26.35</td>
<td>14.22</td>
<td>0.25 x 10⁻¹</td>
</tr>
<tr>
<td>TMT(Pzdtc)</td>
<td>300°</td>
<td>White</td>
<td>42.86</td>
<td>7.63</td>
<td>12.51</td>
<td>52.96</td>
<td>28.60</td>
<td>1.2 x 10⁻¹</td>
</tr>
</tbody>
</table>

...contd.......

75
<table>
<thead>
<tr>
<th>Complexes</th>
<th>M.P.</th>
<th>Colour</th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
<th>%Sn</th>
<th>%S</th>
<th>Molar Conductance ohm$^{-1}$ cm$^{2}$ moles$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPT(Pzdtc)</td>
<td>d. 260°</td>
<td>White</td>
<td>54.12</td>
<td>4.53</td>
<td>5.47</td>
<td>23.25</td>
<td>12.57</td>
<td>1.2 x 10$^{-1}$</td>
</tr>
<tr>
<td>DMT(5-Indzdtc)$_2$</td>
<td>above 300°</td>
<td>Brown</td>
<td>26.85</td>
<td>2.93</td>
<td>7.21</td>
<td>40.84</td>
<td>22.05</td>
<td>Insoluble</td>
</tr>
<tr>
<td>DBT(5-Indzdtc)$_2$</td>
<td>180°</td>
<td>Brown</td>
<td>40.06</td>
<td>5.50</td>
<td>5.61</td>
<td>31.62</td>
<td>17.15</td>
<td>Insoluble</td>
</tr>
<tr>
<td>TBT(5-Indzdtc)</td>
<td>250°</td>
<td>Brown</td>
<td>48.19</td>
<td>6.65</td>
<td>8.44</td>
<td>23.80</td>
<td>12.85</td>
<td>0.5 x 10$^{-1}$</td>
</tr>
<tr>
<td>TMT(5-Indzdtc)</td>
<td>330°</td>
<td>Brown</td>
<td>35.52</td>
<td>4.04</td>
<td>11.25</td>
<td>31.85</td>
<td>17.22</td>
<td>0.2 x 10$^{-1}$</td>
</tr>
<tr>
<td>TPT(5-Indzdtc)</td>
<td>d. 250°</td>
<td>Brown</td>
<td>55.95</td>
<td>3.77</td>
<td>7.13</td>
<td>21.24</td>
<td>11.49</td>
<td>0.4 x 10$^{-1}$</td>
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<tr>
<td>DMT(α-Naphdtc)$_2$</td>
<td>360°</td>
<td>Dark</td>
<td>49.30</td>
<td>3.78</td>
<td>4.79</td>
<td>20.27</td>
<td>21.90</td>
<td>1.2 x 10$^{-1}$</td>
</tr>
<tr>
<td>DBT(α-Naphdtc)$_2$</td>
<td>d. 210°</td>
<td>Dark</td>
<td>53.80</td>
<td>5.10</td>
<td>4.19</td>
<td>17.70</td>
<td>13.14</td>
<td>2.5 x 10$^{-1}$</td>
</tr>
<tr>
<td>TBT(α-Naphdtc)</td>
<td>220°</td>
<td>Dark</td>
<td>54.44</td>
<td>6.73</td>
<td>2.74</td>
<td>23.37</td>
<td>12.62</td>
<td>1.02 x 10$^{-1}$</td>
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<tr>
<td>TMT(α-Naphdtc)</td>
<td>210°</td>
<td>Dark</td>
<td>44.02</td>
<td>4.49</td>
<td>3.65</td>
<td>31.05</td>
<td>16.76</td>
<td>1.28 x 10$^{-1}$</td>
</tr>
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..... contd .....
<table>
<thead>
<tr>
<th>Complexes</th>
<th>M.P.</th>
<th>Colour</th>
<th>%C Found (Calc)</th>
<th>%H Found (Calc)</th>
<th>%N Found (Calc)</th>
<th>%Sn Found (Calc)</th>
<th>%S Found (Calc)</th>
<th>Molar Conductance ohm^{-1} cm^{2} moles^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPT(α-Naphdte)</td>
<td>360°</td>
<td>Dark Brown</td>
<td>61.37</td>
<td>3.91</td>
<td>2.45</td>
<td>20.90</td>
<td>11.31</td>
<td>1.5 x 10^{-1}</td>
</tr>
<tr>
<td>D'TT(β-Naphdte)_{2}</td>
<td>d.180°</td>
<td>Pink</td>
<td>49.27</td>
<td>3.77</td>
<td>4.79</td>
<td>20.29</td>
<td>21.85</td>
<td>0.5 x 10^{-1}</td>
</tr>
<tr>
<td>DST(β-Naphdte)_{2}</td>
<td>230°</td>
<td>Pink</td>
<td>53.80</td>
<td>5.12</td>
<td>4.17</td>
<td>17.70</td>
<td>19.14</td>
<td>2.06 x 10^{-1}</td>
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<tr>
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<td>310°</td>
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<td>54.43</td>
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<td>2.75</td>
<td>23.37</td>
<td>12.60</td>
<td>0.7 x 10^{-1}</td>
</tr>
<tr>
<td>TVT(β-Naphdte)</td>
<td>d.360°</td>
<td>White</td>
<td>44.01</td>
<td>4.47</td>
<td>3.64</td>
<td>31.05</td>
<td>16.77</td>
<td>1.79 x 10^{-1}</td>
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<td>TPT(β-Naphdte)</td>
<td>215°</td>
<td>White</td>
<td>61.40</td>
<td>3.92</td>
<td>2.47</td>
<td>20.91</td>
<td>11.32</td>
<td>1.38 x 10^{-1}</td>
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</tbody>
</table>
RESULTS AND DISCUSSION

All the complexes are fairly stable at room temperature and decompose between 115 - 360°C. The molar conductance value (0.2 x 10^-1 - 1.9 x 10^-1 Ohm^-1 cm^2 mole^-1) of their millimolar solution in nitromethane or nitrobenzene indicate them to be covalent (Table - 4).

IR spectra:

A broad band at 3410 cm^-1, 3450 cm^-1 and 3350 cm^-1 in \( \alpha \)-naphthylamine-, \( \beta \)-naphthylamine-, 5-aminoindazolyl- and piperazine dithiocarbamate has been assigned to \( \nu (N-H) \). The (N-H) deformation band has been found to appear at 1640 cm^-1 in all cases. There is, however, no change in the (N-H) stretching frequency on passing from the free ligand spectrum to those of the complexes (Table - 5). This supports the non-involvement of the (N-H) group in the coordination with the metal ions.

The distinction between a symmetrically and an unsymmetrically bound dithiocarbamate group is clearly based on the C-S stretching frequency. A symmetrically bound dithiocarbamate group exhibits only one band around 1000 cm^-1 while splitting of this band in 1000 ± 70 cm^-1 indicates the presence of an unsymmetrical dithiocarbamate.
### Table 5

IR spectra of the complexes and their assignments

<table>
<thead>
<tr>
<th>Complexes</th>
<th>$\nu$(C=S)</th>
<th>$\nu$(C=N)</th>
<th>$\nu$(M=S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMT(TMdtc)$_2$</td>
<td>1000 (s)</td>
<td>1440 (s)</td>
<td>385 (m)</td>
</tr>
<tr>
<td>DBT(TMdtc)$_2$</td>
<td>1000 (s)</td>
<td>1450 (s)</td>
<td>390 (m)</td>
</tr>
<tr>
<td>TBT(TMdtc)</td>
<td>1000 (s)</td>
<td>1460 (s)</td>
<td>385 (m)</td>
</tr>
<tr>
<td>TMT(TMdtc)</td>
<td>1015 (s)</td>
<td>1450 (s)</td>
<td>385 (m)</td>
</tr>
<tr>
<td>TPT(TMdtc)</td>
<td>1020 (s)</td>
<td>1451 (s)</td>
<td>395 (m)</td>
</tr>
<tr>
<td>DMT(5-Indzdtc)$_2$</td>
<td>996 (s)</td>
<td>1465 (s)</td>
<td>390 (m)</td>
</tr>
<tr>
<td>DBT(5-Indzdtc)$_2$</td>
<td>999 (s)</td>
<td>1460 (s)</td>
<td>385 (m)</td>
</tr>
<tr>
<td>TBT(5-Indzdtc)</td>
<td>1000 (s)</td>
<td>1480 (s)</td>
<td>390 (m)</td>
</tr>
<tr>
<td>TMT(5-Indzdtc)</td>
<td>1000 (s)</td>
<td>1465 (s)</td>
<td>395 (m)</td>
</tr>
<tr>
<td>TPT(5-Indzdtc)</td>
<td>1025 (s)</td>
<td>1480 (s)</td>
<td>380 (m)</td>
</tr>
<tr>
<td>TBT(α-Naphdtc)</td>
<td>1000 (s)</td>
<td>1495 (s)</td>
<td>375 (m)</td>
</tr>
<tr>
<td>TMT(α-Naphdtc)</td>
<td>1010 (s)</td>
<td>1485 (s)</td>
<td>380 (m)</td>
</tr>
<tr>
<td>TPT(β-Naphdtc)</td>
<td>999 (s)</td>
<td>1480 (s)</td>
<td>385 (m)</td>
</tr>
<tr>
<td>TMT(β-Naphdtc)</td>
<td>1005 (s)</td>
<td>1460 (s)</td>
<td>375 (m)</td>
</tr>
<tr>
<td>DBT(β-Naphdtc)$_2$</td>
<td>1010 (s)</td>
<td>1450 (s)</td>
<td>395 (m)</td>
</tr>
<tr>
<td>TBT(Pzdtc)</td>
<td>1005 (s)</td>
<td>1460 (s)</td>
<td>380 (m)</td>
</tr>
<tr>
<td>TMT(Pzdtc)</td>
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<td>1475 (s)</td>
<td>390 (m)</td>
</tr>
<tr>
<td>TPT(Pzdtc)</td>
<td>1025 (s)</td>
<td>1460 (s)</td>
<td>395 (m)</td>
</tr>
</tbody>
</table>
A single C-S band in 1000 - 1025 cm\(^{-1}\) range in the present case suggests a symmetrical coordination of the dithiocarbamate moiety. The dithiocarbamates containing heterocyclic systems have less tendency to release electrons to the (C = N) double bond after complexation as a consequence of which the (C-N) stretching frequency is lowered. The lowering of \(\nu(C=\equiv N)\) as well as of \(\nu(C=\equiv S)\) is sensitive to the nature of the substituent on the nitrogen atom\(^{1,140,141}\). In dialkyl dithiocarbamate this band appears at higher wave number than in the corresponding dithiocarbamate containing heterocyclic ring\(^{138}\). It is, because in dialkyl dithiocarbamate there is a pull of electrons towards \(\text{CS}_2\) group through nitrogen atom while in heterocyclic systems the delocalization of electrons minimises the electronic shift towards nitrogen atom. We have observed the \(\nu(C-N)\) at 1440-1480 cm\(^{-1}\) which is intermediate between carbon nitrogen double bond (1690-1640 cm\(^{-1}\)) and carbon nitrogen single bond (1360-1250 cm\(^{-1}\)) showing a partial double bond character.

The far IR region (650 - 200 cm\(^{-1}\)) is very important as the metal halogen and metal ligand (M-L) stretching frequencies appear in this region. The metal sulphur stretching frequency lies in the range 375-395 cm\(^{-1}\) which are absent in free ligands.

It is wellknown fact that the diorganotins are less toxic than triorganotins. This toxicity has been found to increase manyfold when one or more coordination bonds are formed with
Probit kill curve (A) 5-Indzdtc
(B) DMT (5-Indzdtc)

Probit kill curve (C) (TMDtc) on fish

Log concentration in ppm X 100

Probits

XXXII

XXXIII
tin atoms. Unlike the conventional pesticides, organotins are very selective. Since they do not leave any toxic residue they need not be degraded to harmless compounds. Organotins have antifeedant properties and normally make foliage unpalatable. The triorganotin halides and acetates have been used in preventing the damage of potato tuber, tomato, sugarbeet and cottonleaf from various insects and moths. The triorganotins used against larvae in a concentration range of 0.1 g - 0.5 g/litre is fatal. In the present case the experiments on houseflies have shown that the lethal concentration range (0.1% - 0.2%) of di- and triorganotin dithiocarbamates is lower than that mentioned above.

A plot of % mortality versus concentration in ppm was made to give a sigmoid curve. For obtaining LD_{50} value the data pertaining to percentage kill were transformed into probits which were plotted against concentration (XXXII). A perpendicular drawn from a value of probit 5 yields the value of LD_{50}. Probits were also derived from the following equation:

\[ Y = a + bx \]

where

- \( Y \) = probit kill
- \( a \) = constant
- \( b \) = slope
- \( x \) = dosage/concentration
Probit kill curve (D) TMdtc
(E) DMT (TMdtc)
on house flies

Log concentration in ppm x 100

Probits

(XXXIV)
Empirically \( b = \frac{Y_2 - Y_1}{x_2 - x_1} \)

or

\( a = Y_1 - bx_1 \)

\( = Y_2 - bx_2 \)

It is evident from \( LD_{50} \) that the individual dithiocarbamates were less toxic (Table - 6) than their corresponding organotin complexes. It is, therefore, concluded that the organotins increase the toxicity of the dithiocarbamate and the order of decrease in toxicity of their complexes is as follows:

\( TM_{dtc} > PZ_{dtc} > \alpha - Naph_{dtc} > 5 - Amino_{dtc} \)

From (XXXIII) it can be seen that the \( LC_{50} \) value in terms of toxicity for the fish is 1.6 ppm which is slightly greater than the value obtained for flies (XXXIV) The fish were found to bleed through pelvic fins and they also discharged excess of mucus as a protection against the toxic effect of the dithiocarbamate. From \( LC_{50} \) value it has been found that the compound is appreciably toxic to kill the fish even if administered in milligram quantity.
### Table - 6

<table>
<thead>
<tr>
<th>Ligand/Complex</th>
<th>Log Conc. in ppm x 100</th>
<th>% Mortality Ligand/Complex</th>
<th>Probit Values</th>
<th>LD$_{50}$ in ppm Ligand/Complex</th>
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<tbody>
<tr>
<td>TMdte/DMT(TMdte)$_2$</td>
<td>2</td>
<td>20/60</td>
<td>4.1584/5.2533</td>
<td>1.58/0.79</td>
</tr>
<tr>
<td></td>
<td>2.17</td>
<td>40/70</td>
<td>4.7467/5.5244</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.30</td>
<td>60/80</td>
<td>5.2533/5.8416</td>
<td></td>
</tr>
<tr>
<td>Pzdte/TPT(Pzdte)</td>
<td>2</td>
<td>30/50</td>
<td>4.4756/5.0000</td>
<td>1.47/1.00</td>
</tr>
<tr>
<td></td>
<td>2.17</td>
<td>50/70</td>
<td>5.0000/5.5244</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.30</td>
<td>70/80</td>
<td>5.5244/5.8416</td>
<td></td>
</tr>
<tr>
<td>α-Naphdte/</td>
<td>2</td>
<td>30/40</td>
<td>4.4756/4.7467</td>
<td>1.41/1.20</td>
</tr>
<tr>
<td>DBT(α-Naphdte)$_2$</td>
<td>2.17</td>
<td>40/70</td>
<td>4.7467/5.5244</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.30</td>
<td>70/80</td>
<td>5.5244/5.8416</td>
<td></td>
</tr>
<tr>
<td>5-Aminodte/DMT</td>
<td>2</td>
<td>20/30</td>
<td>4.1584/4.4756</td>
<td>1.95/1.31</td>
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<td>(5-Amino.dte)$_2$</td>
<td>2.17</td>
<td>30/60</td>
<td>4.4756/5.2533</td>
<td></td>
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<tr>
<td></td>
<td>2.30</td>
<td>60/80</td>
<td>5.2533/5.8416</td>
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CHAPTER VI
CHARACTERIZATION AND TOXICITY OF ORGANOTIN(IV) HALIDE COMPLEXES OF CYCLOHEXANONE SPIROTHIAZOLIDINONE AND 3-AMINORHODANINE.
CHARACTERIZATION AND TOXICITY OF ORGANOTIN(IV) HALIDE COMPLEXES OF CYCLOHEXANONE SPIROTHIAZOLIDINONE AND 3-AMINORHODANINE

EXPERIMENTAL

Material and methods:

Hydrazine hydrate, mercaptoacetic acid (Fluka A.G.) carbon disulphide (Analar), monochloroacetic acid (Eastman Kodak) ammonium carbonate, cyclohexanone, benzene (BDH), dimethyltin dichloride (DMT), dibutyltin dichloride (DBT), trimethyltin chloride (TMT), tributyltin chloride (TBT) and triphenyltin chloride (TPT) (E. Merck) were used as such.

The IR spectra (600 - 4000 cm\(^{-1}\)) were recorded on a Perkin Elmer 621 spectrophotometer as KBr disc and (200 - 600 cm\(^{-1}\)) as nujol mull. Conductivity measurements were done on a Systronics conductivity bridge type - 302.

Synthesis of Cyclohexanone Spirothiazolidinone:

Cyclohexanone (0.05 mol), mercaptoacetic acid (0.14 mol) and ammonium carbonate (0.15 mol) taken in dry benzene were refluxed for sixty hours. After the completion of the reaction, the benzene solution was washed thrice with water then with 1M NaOH and again with water. The resulting solution was dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure.
further experiments could not be done on fish.

Experiments were also done on cockroaches to see the toxicity of the ligand and their complexes with di- and tri-organotin(IV) halides. Five sets of experiment were done simultaneously. The cockroaches were fed on the ligand and the complexes mixed in a palatable base in the concentration range of 1-5 ppm. Their % mortality was recorded after 96 hours.
Syntheses of 3-Aminorhodanine:

Hydrazine hydrate (1 mol) in methanol was treated with carbon disulphide (0.1 mol) in diethyl ether to get dithiocarbonic acid monohydrazide hydrazine salt by continuous stirring. It was further treated with 0.1 mol of aqueous monochloroacetic acid to yield 3-aminorhodanine. The solid was filtered and washed with water and dried in vacuo.

Preparation of the complexes:

Cyclohexanone spirothiazolidinone (XXXV) and 3-aminorhodanine (XXXVI) dissolved in 20 ml alcohol were mixed with \( \text{R}_2\text{SnCl}_2 \) and \( \text{R}_3\text{SnCl} \) in 1:2 and 1:1 molar ratios respectively. The resulting compounds were filtered, washed with alcohol and dried in vacuo.

Toxicity:

To examine the toxicity of the compounds a stock solution containing 0.1 g of the ligands was prepared in 100 ml of water. Four sets of fish were taken along with the control. Six fish in each set were exposed to the solution in concentration range of 1 ppm to 7 ppm. The media were renewed after every twenty-four hours. The fish were found to discharge an excess of mucus during this treatment probably in order to prevent damage from the compounds. It probably inhibits the protein syntheses in the body. The mortality was recorded after 96 hours. As all the organotin complexes were water insoluble
RESULTS AND DISCUSSION

The syntheses of the complexes involves the following reaction:

\[
R_2SnCl_2 + R_3SnCl + 2HCl \rightarrow \text{Product} + 2HCl
\]
The molar conductance of 10⁻³M solution of the complexes in nitromethane or nitrobenzene suggests that they are covalent (Table - 7). Apparently cyclohexanone spirothiazolidinone and 3-aminorhodanine molecules have three active coordination sites namely, the nitrogen, carbonyl group or sulphur. However, it has been reported that for steric reasons and weak bonding ability of oxygen in carbonyl group, all the three sites cannot simultaneously be involved in coordination.
IR Spectrum of Cyclohexanone Spirothiazolidinone Complexes:

The (N-H) stretching frequency at 3400 cm⁻¹ in the ligand does not appear in the complexes showing the replacement of aminohydrogen by tin atom. The υ(C-N) is negligibly enhanced on complexation, which is due to the electronic shift towards tin through nitrogen¹²⁹ (Table-8). The persistent appearance of υ(C=O) at 1710 cm⁻¹ in both the ligand and the complexes rules out the involvement of carbonyl oxygen in coordination. In addition, a band has also been found to appear constantly at 1660 cm⁻¹ in the ligand as well as in the complexes which is probably due to the coupling of υ(C=O) with υ(C-N). Such coupling has been observed in ureas⁶²,⁶⁶,⁶⁷ and their derivatives which appears to be analogous to thiazolidinones.

IR Spectrum of 3-Aminorhodanine Complexes:

The IR spectrum of 3-aminorhodanine shows (N-H) stretching frequency at 3320 cm⁻¹ which is shifted to lower wave number after complexation (Table-9) showing coordination through nitrogen atom. The υ(C=O) in both the ligand and the complexes remains unaltered ruling out the possibility of coordination through carbonyl group. The thioamide group (H-N-C=S) generally gives¹⁴⁵-¹⁴⁷ four thioamide bands. These bands have contributions from δ(C-N) + δ(N-H), υ(C=S + υ(C=N) + δ(C=H), δ(C-N) + υ(C-S) and υ(C-S) as reported for 2-mercaptoquinazoline-4 ones. If the coordination occurs through the sulphur atom all the thioamide bands except
the \( I \) band shifts to lower wave numbers. In the present case
the \( \nu (C=S) \) mixed vibrational frequency at 1080 cm\(^{-1}\) is de-
creased to some extent due to the formation of tin-sulphur bond.
The lowering of this frequency may be attributed to the reduced
double bond character of the \( (C-S) \) linkage. The band around
780 cm\(^{-1}\) is considered to correspond to the 731 cm\(^{-1}\) band in
2-thiourea and is assigned to the thioamide band (IV).

In the far IR region a strong band in 580 - 555 cm\(^{-1}\)
range is due to \( (Sn-C) \) asymmetric stretching\(^{148-150}\) vibrations.
However, the corresponding bands due to symmetric stretching
could not be detected in diorganotin(IV) halide\(^{151}\). It may,
therefore, be assumed that in these complexes the two alkyl
groups attached to tin occupy trans position which is quite
reasonable. The \( (Sn-N) \) band in all the complexes are observed
in 420 - 440 cm\(^{-1}\) range while that of \( (Sn-S) \) is observed at
370 - 340 cm\(^{-1}\). It is clear from these studies that of all
the sites only the nitrogen is coordinated to tin atom in
cyclohexanone spirothiazolidinone while in 3-aminorhodanine
the nitrogen as well as the sulphur atom are coordinated to
the tin atom.

The compounds containing sulphur are more toxic than
organotins themselves but their mammalian toxicity is too
low\(^{152}\). The studies on rats have established an acute oral
LD\(_{50}\) of 2630 mg/kg, and an acute dermal LD\(_{50}\) of 1000 mg/kg.
<table>
<thead>
<tr>
<th>Complexes</th>
<th>m.p. °C</th>
<th>%C Found (Calc)</th>
<th>%H Found (Calc)</th>
<th>%N Found (Calc)</th>
<th>%Sn Found (Calc)</th>
<th>%S Found (Calc)</th>
<th>Molar Conductance 0hm⁻¹ cm² mole⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMT (CST)₂</td>
<td>175</td>
<td>44.20 (44.18)</td>
<td>6.17 (6.18)</td>
<td>5.71 (5.72)</td>
<td>24.22 (24.25)</td>
<td>13.11 (13.10)</td>
<td>3.57 x 10⁻²</td>
</tr>
<tr>
<td>DBT (CST)₂</td>
<td>160</td>
<td>50.28 (50.27)</td>
<td>7.40 (7.38)</td>
<td>4.85 (4.88)</td>
<td>20.67 (20.69)</td>
<td>11.19 (11.18)</td>
<td>1.03 x 10⁻²</td>
</tr>
<tr>
<td>TMT (CST)</td>
<td>290</td>
<td>39.54 (39.55)</td>
<td>6.32 (6.33)</td>
<td>4.19 (4.19)</td>
<td>35.52 (35.53)</td>
<td>9.58 (9.59)</td>
<td>0.514 x 10⁻²</td>
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<tr>
<td>TPT (CST)</td>
<td>80</td>
<td>60.00 (60.02)</td>
<td>5.23 (5.23)</td>
<td>2.70 (2.69)</td>
<td>22.50 (22.51)</td>
<td>6.16 (6.17)</td>
<td>0.128 x 10⁻²</td>
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<tr>
<td>TBT (CST)</td>
<td>45</td>
<td>52.19 (52.18)</td>
<td>8.55 (8.54)</td>
<td>3.05 (3.04)</td>
<td>25.77 (25.78)</td>
<td>6.97 (6.96)</td>
<td>0.159 x 10⁻²</td>
</tr>
<tr>
<td>DMT (ARh)₂</td>
<td>120</td>
<td>21.65 (21.68)</td>
<td>2.70 (2.73)</td>
<td>12.60 (12.63)</td>
<td>26.77 (26.78)</td>
<td>28.90 (28.94)</td>
<td>0.60 x 10⁻²</td>
</tr>
<tr>
<td>DBT (ARh)₂</td>
<td>135</td>
<td>31.80 (31.59)</td>
<td>4.56 (4.58)</td>
<td>10.60 (10.62)</td>
<td>22.50 (22.51)</td>
<td>24.30 (24.32)</td>
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<tr>
<td>TMT (ARh) liquid</td>
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<td>23.15 (23.17)</td>
<td>3.86 (3.89)</td>
<td>9.01 (9.00)</td>
<td>38.11 (38.17)</td>
<td>20.60 (20.62)</td>
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</tr>
<tr>
<td>TBT (ARh) liquid</td>
<td></td>
<td>41.21 (41.20)</td>
<td>6.30 (6.91)</td>
<td>6.42 (6.40)</td>
<td>27.10 (27.14)</td>
<td>14.62 (14.66)</td>
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<tr>
<td>TPT (ARh)</td>
<td>150</td>
<td>50.72 (50.73)</td>
<td>3.60 (3.64)</td>
<td>5.59 (5.63)</td>
<td>23.81 (23.87)</td>
<td>3.00 (3.21)</td>
<td>0.75 x 10⁻²</td>
</tr>
<tr>
<td>Compounds</td>
<td>$\nu$(N-H)</td>
<td>$\nu$(C-N)</td>
<td>$\nu$(C=O)</td>
<td>$\nu$(Sn-N)</td>
<td></td>
<td></td>
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<td>-----------</td>
<td>------------</td>
<td>------------</td>
<td>-------------</td>
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</tr>
<tr>
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<td>3400 (s)</td>
<td>1230 (w)</td>
<td>1710 (s)</td>
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<td></td>
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<tr>
<td></td>
<td></td>
<td>1350 (w)</td>
<td>1660 (s)</td>
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<tr>
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<td>1245 (s)</td>
<td>1650 (s,b)</td>
<td>420 (s)</td>
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<tr>
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<td></td>
<td>1375 (s)</td>
<td>1700 (v,b)</td>
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<tr>
<td>DBT (CST)$_2$</td>
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<td>1655 (s)</td>
<td>420 (s)</td>
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<td>1375 (s)</td>
<td>1700 (s,b)</td>
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<tr>
<td>TMT (CST)</td>
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<td>1265 (s)</td>
<td>1660 (s)</td>
<td>440 (s)</td>
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<tr>
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<td></td>
<td>1380 (s)</td>
<td>1710 (s)</td>
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</tr>
<tr>
<td>TPT (CST)</td>
<td></td>
<td>1260 (s)</td>
<td>1660 (s)</td>
<td>440 (s)</td>
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<td>1380 (s)</td>
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<td>TBT (CST)</td>
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<td>1265 (s)</td>
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<td>1380 (s)</td>
<td>1710 (s)</td>
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<tr>
<td>Compounds</td>
<td>$\nu$(N-H)</td>
<td>$\nu$(C=O)</td>
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<td>Thioamide II</td>
<td>Thioamide III</td>
<td>Thioamide IV</td>
<td>$\nu$(M-S)</td>
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<tr>
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<td>-------------</td>
<td>-------------</td>
<td>-------------</td>
<td>-------------</td>
<td>------------</td>
</tr>
<tr>
<td>(ARh)</td>
<td>3320(m)</td>
<td>1700(m)</td>
<td>1560(m)</td>
<td>1390(s)</td>
<td>1080(m)</td>
<td>790(m)</td>
<td>-</td>
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<tr>
<td>DBT (ARh)</td>
<td>3100(m)</td>
<td>1700(m)</td>
<td>1560(m)</td>
<td>1385(s)</td>
<td>1040(m)</td>
<td>780(m)</td>
<td>370(s)</td>
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<tr>
<td>DBT (ARh)</td>
<td>3100(m)</td>
<td>1700(m)</td>
<td>1560(m)</td>
<td>1380(s)</td>
<td>1030(m)</td>
<td>770(m)</td>
<td>360(s)</td>
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<tr>
<td>THT (ARh)</td>
<td>3110(m)</td>
<td>1700(m)</td>
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<td>1390(s)</td>
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<td>THT (ARh)</td>
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<td>1040(m)</td>
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<tr>
<td>THT (ARh)</td>
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<td>1560(m)</td>
<td>1385(s)</td>
<td>1060(m)</td>
<td>770(m)</td>
<td>370(s)</td>
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</table>
Table - 10

\% Mortality Data of Cyclohexanone spirotiazolidinone and 3-Aminorhodanine on fish

<table>
<thead>
<tr>
<th>Ligands</th>
<th>Concentration in ppm</th>
<th>Log concentration in ppm x 100</th>
<th>% Mortality</th>
<th>Probit values</th>
<th>LC\textsubscript{50}</th>
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</thead>
<tbody>
<tr>
<td>CST</td>
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<td></td>
</tr>
<tr>
<td>1</td>
<td>2.00</td>
<td>20.0</td>
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<td>4.1584</td>
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<tr>
<td>3</td>
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<tr>
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<td>80.0</td>
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<td>5.8416</td>
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<tr>
<td>(ARh)</td>
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</tr>
<tr>
<td>1</td>
<td>2.00</td>
<td>33.3</td>
<td></td>
<td>4.5684</td>
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</tr>
<tr>
<td>3</td>
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<td>50.0</td>
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<td>5.0000</td>
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<td>70.0</td>
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<tr>
<td>7</td>
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<td>80.0</td>
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<td>5.3416</td>
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</table>
### Table - 11

% Mortality data of Cyclohexanone Spirothiazolidinone and 3-Aminorhodanine on Cockroach

<table>
<thead>
<tr>
<th>Ligand/Complex</th>
<th>Concentration in ppm</th>
<th>Log concentration in ppm x 100</th>
<th>% Mortality</th>
<th>LC50</th>
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<td>20/20, 33.3</td>
<td>3.16/2.51</td>
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<td></td>
<td>2</td>
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<td>33.3/33.3, 40</td>
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<tr>
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<td>3</td>
<td>2.47</td>
<td>40/50, 60</td>
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<tr>
<td></td>
<td>4</td>
<td>2.60</td>
<td>50/70, 70, 70</td>
<td>1.99</td>
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<td></td>
<td>5</td>
<td>2.69</td>
<td>80/80, 90</td>
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</tr>
<tr>
<td>ARh/DMT, TMT</td>
<td>1</td>
<td>2</td>
<td>20/33.3, 33.3</td>
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</tr>
<tr>
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<td>2</td>
<td>2.30</td>
<td>33.3/40, 50</td>
<td>2.51/1.99</td>
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<tr>
<td></td>
<td>3</td>
<td>2.47</td>
<td>50/60, 70</td>
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<td></td>
<td>4</td>
<td>2.60</td>
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<td>1.77</td>
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<td>5</td>
<td>2.69</td>
<td>90/90, 99.9</td>
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</table>
Probit kill curve (F) DMT (CST) on cockroach

Probit kill curve (G) (CST) on cockroach

Probit kill curve (H) (CST), (I) (ARh) on fish

Log concentration in ppm x 100

Probits
Probit kill curve (J) TMT (ARh) on cockroach

Probit kill curve (L) TMT (CST) on cockroach

Probit kill curve (L) (DMT) on cockroach

Log concentration in ppm X 100

Probits

3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0
Wild life studies have shown that the acute oral LD$_{50}$ in millard ducks and ringnecked pheasants is greater than 2000 mg/kg body weight. Median tolerance limit, TL$_{50}$ after 96 hours exposure for bluegill flathead minnow and rainbowtrout were 0.0048, 0.0019 and 0.0017 ppm respectively.

To calculate LC$_{50}$, LD$_{50}$ for fish and cockroach the % mortality was plotted against concentration in ppm to get a sigmoid curve. Since it was not a straight line the slopes at different points did not yield the same value. For obtaining LC$_{50}$, LD$_{50}$ the data pertaining to percentage mortality were transformed into probits (Table 10, 11) which were plotted against log concentration in ppm x 100 (XXXVII, XXXVIII, XXXIX) and a perpendicular was drawn from a value of probit 5 equivalent to 50% mortality.

It is evident from our experiments on fish and cockroaches that di-and triorganotin(IV) complexes of 3-amino-rhodanine are more toxic (XXXX, XXXXI, XXXXII) than those of cyclohexanone spirothiazolidinone.
REFERENCES
REFERENCES


142. K. R. S. Ascher, M. E. Nervy, M. Wysoki, L. Gurtelzak,
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