SYNTHESIS, CHARACTERIZATION AND BIOCIDAL ACTIVITY OF NOVEL METAL CHELATES WITH ASYMMETRIC ORGANIC LIGANDS

ABSTRACT

THESIS
SUBMITTED FOR THE AWARD OF THE DEGREE OF
Doctor of Philosophy
IN
CHEMISTRY

BY
FAREEBA ATHAR

DEPARTMENT OF CHEMISTRY
ALIGARH MUSLIM UNIVERSITY
ALIGARH (INDIA)
2001
ABSTRACT
ABSTRACT

Design of new metal complexes bearing optically active auxiliary ligand has attracted much attention in the past decade due to their importance in diverse areas of interdisciplinary nature. Coordination Chemistry plays an important role in providing suitable supramolecular infrastructure which has the possibility of introducing chiral stereogenic center in either the organic ligands or the metal complexes.

The chiral metal complexes have found efficient applications in several asymmetric organic processes-Diels Alder reactions catalyzed by different metal ions [Mn$^{II}$, Fe$^{II}$, Co$^{II}$, Ni$^{II}$, Cu$^{II}$, Zn$^{II}$], cyclopropanation of alcohol [Cu$^{II}$] and selective epoxidation catalysts for olefins. Studies with metalloporphyrins as oxygenating catalysts were stimulated to model the reactivity of cytochrome P-450 family of heme enzymes. The rigid macrocyclic core and alterable periphery of porphyrin makes them attractive template for building asymmetric catalysts.

Chiral groups can be attached in many different geometries aiming at systems which give high enantioselectivities and good yield. Chirality in metal complexes can generate more selective and active metal center which is well tuned to adapt a different stereochemistry. To investigate the mechanism and coordination behavior of these asymmetric
metal complexes, we have synthesized a variety of novel series of metal complexes with first row transition metal ions and organotin chlorides from organic ligands bearing chiral stereogenic center. The complexes are adequately characterized by different spectroscopic techniques. DNA is the primary target responsible for the anticancer activity of cisplatin and X-ray structural and NMR data have identified N_7 of the guanine base as the primary binding site. As a consequence, we have adopted a systematic study of certain asymmetric complexes with CT DNA. Thus design of these artificial biomodels requires a knowledge of the kinetic and binding mechanism. We have kinetically ascertained the mode of binding of CT DNA to these complexes by spectrophotometric techniques. Similarly, the activity of these chiral metal complexes to bind dioxygen reversibly has been probed and the rate constants $K_{obs} / K_{(DNA-complex)}$ at room temperature were calculated using least square regression method.

The change in redox behavior in these complexes is evidenced by sharp difference in voltammetric responses before and after interaction with CT DNA/dioxygen which is observed by taking cyclic voltammograms (CV) of all the free and bound species. The pattern of the voltammetric responses suggest a mechanistic pathway for the coordination of these complexes with CT DNA or as a reversible electrocatalyst for $O_2$ binding.
Synthesis of new asymmetric ligands was done by condensing o-phenylene diamine with carbon disulphide and acetaldehyde/benzaldehyde and their complexes with transition metal ions (Mn^{II}, Co^{II}, Ni^{II}, Cu^{II} and Zn^{II}). These complexes were characterized by elemental analyses, conductivity measurements, IR, UV-Vis., EPR and NMR spectroscopy. On the basis of above studies, it has been concluded that all the complexes possess square-planar geometry and are ionic in nature. Photokinetic studies of the DNA-metal complexes \([C_{10}H_{10}S_4N_2Cu](NO_3)_2\) and \([C_{10}H_{10}S_4N_2Ni](NO_3)_2\) were carried out and the rate constants \(k'_{(DNA-complex)}\) were calculated. The results indicate that DNA reacts with the metal complex in two steps. DNA first undergoes structural degradation and is then completely hydrolysed as indicated by spectral changes consistent with earlier results. The asymmetric \(N_2S_2\) macrocyclic metal complexes show a strong propensity for DNA inhibition and can be used as an intercalating binding model.

Heterobimetallic chemistry has emerged as a challenging field of research. Different applications of heterobimetallic complexes have been thoroughly explored viz. magnetic and electrical properties, catalytic behavior, biomodels or biological model systems. An attempt has been made to synthesize new asymmetric heterobimetallic complexes of the type \([LML'Sn]Cl\) and \([LM'L'Sn]Cl_2\), where \(L = \) ethylene diamine, \(M = Mn^{II}, Co^{II}, Ni^{II}\) and \(Cu^{II}\), \(M' = \) Cr^{III} and Fe^{III}.
and \( L' = \text{l-tryptophan and l-valine.} \) They have been synthesized and characterized by elemental analyses, UV-Vis., IR, EPR, NMR, cyclic voltammetry and conductivity measurements. The Co\(^{III}\) analogue of these complexes which is the air oxidation product of Co\(^{II}\) complex, was characterized by two dimensional NMR COSY data. The oxygen binding affinities of the Co(II) complex have been investigated spectrophotometrically. The kinetic data proves that Co(II) of a coordinated molecule participates in the rate determining step of the dioxygen binding process. The plots of the pseudo-first order rate constant \( k_{\text{obs}} \) versus \([O_2]\) is linear passing through an intercept. The electrochemical properties of \([C_{15}H_{23}N_4O_2SnCo]^{2+}\) and \([C_{15}H_{23}N_4O_2SnCu]^+\) are discussed with respect to the influence of an adjacent metal ion tin(IV) on cobalt(III) and copper(II) redox potential. Comparison of the electrochemical properties of \([\text{Co}^{III}\text{Sn}^{IV}]^{2+}\) and \([\text{Cu}^{II}\text{Sn}^{IV}]^+\) reveal that in both the species one electron transfer reaction takes place. For the \([\text{Co}^{III}\text{Sn}^{IV}]^-\) species \( E^0 = +0.272 \) V and \(-1.1 \) V and for the \([\text{Cu}^{II}\text{Sn}^{IV}]^+\) species \( E^0 = +0.078 \) V and \(-0.300 \) V values were obtained, respectively.

In the past decade, porphyrin-nucleic acid interactions have been studied and a variety of porphyrins and their metal derivatives have shown to bind to single or to double stranded DNA/RNA sequences but chiral porphyrin complexes can induce more effective changes in the conformation of nucleic acids. A new template-directed
chiral porphyrin \([(TPP)Co(Trp)]\), where TPP = tetraphenyl porphyrin and Trp = l-tryptophan, was prepared and characterized by various physico-chemical methods. These chiral template porphyrins can serve as a chiral substrate passage to the metal centre. The conformational changes in DNA by \([(TPP)Co(Trp)]\) have been studied spectrophotometrically.

The complex \([(TPP)Co(Trp)]\), after interaction with calf thymus DNA, shows a shift in the absorption spectrum and a large hypochromicity, indicating an intercalating binding mode. This observation was further confirmed by the electrochemical behavior of \([(TPP)Co(Trp)]\) before and after interaction with calf thymus DNA. The complex experiences a negative shift in \(E_{1/2}\) and a decrease in \(E_p\).

The ratio of cathodic to anodic peak currents \(i_{pc}/i_{pa}\) was \(\approx 1\) for \([(TPP)Co(Trp)]\) while for DNA bound complex \(i_{pc}/i_{pa} < 1\), suggesting that the calf thymus DNA moiety is bound strongly to the complex \([(TPP)Co(Trp)]\).

Kinetic studies of the DNA-porphyrin complex reveal a pseudo-first order rate law as the plot of \(k_{obs}\) versus calf thymus DNA is linear passing through the origin.

A new asymmetric organotin linked porphyrin dimers of the type \([(TPP)M(Trp)\}_{2}M'\) where TPP = tetraphenyl porphyrin, \(M = \text{Co(II)}\) and \(\text{Zn(II)}\), Trp = l-tryptophan and \(M' = \text{dimethyl tin(IV)}\) have been synthesized and characterized by various conventional methods. We have prepared two optically active porphyrin moieties of Co(II)
and Zn(II) which are linked by an organotin group such as dimethyl tin(IV) to achieve optically active porphyrin dimers. These dimers are designed so as to hold two different or same metals in 5-coordinate geometry and possess cooperative binding properties. Besides, 5-coordinate chiral porphyrin dimer arrays are of great interest in specific catalytic reactions by the use of their chiral grooves and vacant sixth site for oxygen binding. The electrochemical behavior of \[\{(TPP)Co(Trp)\}_2Sn(CH_3)_2\] dimer has been studied by cyclic voltammetry. The complex revealed two reversible responses at +0.778 V and -0.421V, assigned to the Co(III/II) and Co(II/I) couples, respectively. Upon oxygenation, the voltammetric responses for both Co(III/II) and Co(II/I) couples shift to more negative potential from an initial potential of +0.778V and -0.421V. The changes in the cyclic voltammetric pattern during the oxygenation reaction reveal that the \[\{(TPP)Co(Trp)\}_2Sn(CH_3)_2\] dimer can act as a catalyst for the electroreduction of O_2. The kinetic studies for the complex \[\{(TPP)Co(Trp)\}_2Sn(CH_3)_2\] were determined by spectrophotometric titration with dioxygen. The experiments carried out in methanol under large excess of oxygen at 20 °C show absorbance changes which correspond to pseudo-first order conditions. A plot of rate constants \(k_{obs}\) versus \([O_2]\) gave a straight line passing through an intercept and clearly indicates that the oxygenated complex
is the predominant species in the reaction as $k_{\text{on}}[O_2] \gg k_{\text{off}}$.

There is an increased interest in the synthesis of tin based antitumor drugs and activity of these complexes is closely related to their structure. Thus, the chiral complexes may have wide spread application in the field of medicine as antitumor, anti HIV agents, as catalysts and also as enzyme model systems. Here, we report the synthesis of novel chiral organotin complexes using amino acids as chiral auxiliaries and 1,10-phenanthroline as a secondary ligand. A series of di and tri organotin(IV) [LSnR^L'\] complexes where $n = 2$ or 3, $L = \text{L-amino acids like L-tryptophan and L-valine and } L' = 1,10\text{-phenanthroline}$.

Structure elucidation has been done by IR, UV, $^1\text{H}$, $^{13}\text{C}$, $^{119}\text{Sn}$ NMR spectroscopy. All the complexes are air stable and electrolytic in nature. On the basis of structural evidences, it has been concluded that the carboxylic acid of the L-amino acid is behaving as a monodentate ligand in all these complexes and complexes are octahedral in shape with a coordination number six around the tin atom. The $^{119}\text{Sn}$ chemical shift at -280.931 ppm for the complex $[\text{C}_{41}\text{H}_{34}\text{N}_3\text{O}_2\text{Sn}]$ is suggestive of six coordinate geometry around the tin(IV) atom.
SYNTHESIS, CHARACTERIZATION AND BIOCIDAL ACTIVITY OF NOVEL METAL CHELATES WITH ASYMMETRIC ORGANIC LIGANDS

THESIS
SUBMITTED FOR THE AWARD OF THE DEGREE OF
Doctor of Philosophy
IN
CHEMISTRY

BY
FAREEDA ATHAR

DEPARTMENT OF CHEMISTRY
ALIGARH MUSLIM UNIVERSITY
ALIGARH (INDIA)
2001
Certificate

The work embodied in this thesis entitled “Synthesis, characterization and biocidal activity of novel metal chelates with asymmetric organic ligands” is the result of original researches carried out by Miss. Fareeda Athar in this Department and is suitable for submission for the award of Ph.D. degree.

Farukh Arjmand
## CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGEMENT</td>
<td>-</td>
</tr>
<tr>
<td>PUBLICATIONS</td>
<td>-</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>i-vii</td>
</tr>
<tr>
<td>CHAPTER I: INTRODUCTION</td>
<td>1-26</td>
</tr>
<tr>
<td>CHAPTER II: EXPERIMENTAL</td>
<td>27-37</td>
</tr>
<tr>
<td>CHAPTER III: NEW ASYMMETRIC $N_2S_2$ MACROCYCLES, THEIR METAL CHELATES</td>
<td>38-56</td>
</tr>
<tr>
<td>AND THE PHOTOKINETICS OF DNA-COMPLEX INTERACTION.</td>
<td></td>
</tr>
<tr>
<td>CHAPTER IV: NOVEL ASYMMETRIC HETEROBIMETALLIC COMPLEXES OF TRANSITION</td>
<td>57-80</td>
</tr>
<tr>
<td>METALS AND KINETICS OF OXYGEN BINDING TO A COBALT(II) COMPLEX.</td>
<td></td>
</tr>
<tr>
<td>CHAPTER V(A): INTERACTION OF A NEW COBALT(II) COMPLEX OF 5-</td>
<td>81-95</td>
</tr>
<tr>
<td>COORDINATED CHIRAL PORPHYRIN WITH CALF THYMUS DNA.</td>
<td></td>
</tr>
<tr>
<td>CHAPTER V(B): SYNTHESIS OF NEW ORGANOTIN-LINKED PORPHYRIN DIMERS:</td>
<td>96-117</td>
</tr>
<tr>
<td>ELECTROCHEMICAL STUDIES AND DIOXYGEN BINDING TO Co(II) PORPHYRIN ARRAY</td>
<td></td>
</tr>
<tr>
<td>CHAPTER VI: SYNTHESIS AND CHARACTERIZATION OF NOVEL CHIRAL ORGANOTIN</td>
<td>118-135</td>
</tr>
<tr>
<td>COMPLEXES.</td>
<td></td>
</tr>
<tr>
<td>REFERENCES</td>
<td>135-155</td>
</tr>
</tbody>
</table>
ACKNOWLEDGEMENT
ACKNOWLEDGEMENT

I feel actuated from within to express my heartfelt gratitude to Allah, The Almighty, The most Merciful and Benevolent for enabling me to submit my Ph.D. thesis.

The topic I undertook was quite challenging but I was fortunate enough to have Dr. (Mrs.) Farukh Arjmand as my supervisor. Without her help and guidance I would not have been able to complete this task. Her able guidance, illustrious advice, keen interest and constructive criticism encouraged me to pursue my work vigorously with the result that I could complete my research work within the minimum possible time.

My humble and sincere gratitude also extend to Dr. Sartaj Tabassum for his kind support during my research work in the light of his vast knowledge and experience.

I pay my thanks to the Chairman, Prof. M. Ilyas for providing me necessary research facilities.

My sincere thanks are also due to Prof. C. Pettinari, University of Camerino, Department of Chemistry, Camerino, Italy for $^{119}$Sn NMR spectral data.

I am also grateful to Dr. Sudha Srivastava, TIFR, Mumbai and Prof. R. J. Singh, Department of Physics, AMU, Aligarh for providing me the NMR and EPR facilities, respectively.

Finally, I must acknowledge the affectionate help I received from my parents- Mr. Atharul Haq Siddiqi and Mrs. Nahid Kauser, who all along inspired me and took upon themselves the task of removing all the hurdles: financial and others which came in my way.

Last but not least I thank to all my colleagues.

FAREEDA ATHAR

FAREEDA ATHAR
PUBLICATIONS
Publications

1. New asymmetric N$_2$S$_2$ macrocycles, their metal chelates and the photokinetics of DNA-complex interaction,
   Fareeda Athar, Farukh Arjmand and Sartaj Tabassum, Transition Met. Chem.,

2. Novel asymmetric heterobimetallic complexes of transition metals
   and kinetics of oxygen binding to a cobalt(II) complex,
   Fareeda Athar, Farukh Arjmand and Sartaj Tabassum, Transition Met. Chem.,

3. Synthesis and characterization of novel chiral organotin complexes,

4. Interaction of a new cobalt(II) complex of five-coordinated chiral porphyrin with calf thymus DNA
   Sartaj Tabassum, Fareeda Athar and Farukh Arjmand, Transition Met. Chem.,
   00, 00-00, 2001.

5. Synthesis of new organotin-linked porphyrin dimers: electrochemical studies and dioxygen binding to Co(II) porphyrin array
   Fareeda Athar and Farukh Arjmand, Bull. Chem. Soc. Jpn. (Communicated)
ABSTRACT
ABSTRACT

Design of new metal complexes bearing optically active auxiliary ligand has attracted much attention in the past decade due to their importance in diverse areas of interdisciplinary nature. Coordination Chemistry plays an important role in providing suitable supramolecular infrastructure which has the possibility of introducing chiral stereogenic center in either the organic ligands or the metal complexes.

The chiral metal complexes have found efficient applications in several asymmetric organic processes-Diels Alder reactions catalyzed by different metal ions \([\text{Mn}^{II}, \text{Fe}^{II}, \text{Co}^{II}, \text{Ni}^{II}, \text{Cu}^{II}, \text{Zn}^{II}]\), cyclopropanation of alcohol \([\text{Cu}^{II}]\) and selective epoxidation catalysts for olefins. Studies with metalloporphyrins as oxygenating catalysts were stimulated to model the reactivity of cytochrome P-450 family of heme enzymes. The rigid macrocyclic core and alterable periphery of porphyrin makes them attractive template for building asymmetric catalysts.

Chiral groups can be attached in many different geometries aiming at systems which give high enantioselectivities and good yield. Chirality in metal complexes can generate more selective and active metal center which is well tuned to adapt a different stereochemistry. To investigate the mechanism and coordination behavior of these asymmetric
metal complexes, we have synthesized a variety of novel series of metal complexes with first row transition metal ions and organotin chlorides from organic ligands bearing chiral stereogenic center. The complexes are adequately characterized by different spectroscopic techniques. DNA is the primary target responsible for the anticancer activity of cisplatin and X-ray structural and NMR data have identified N7 of the guanine base as the primary binding site. As a consequence, we have adopted a systematic study of certain asymmetric complexes with CT DNA. Thus design of these artificial biomodels requires a knowledge of the kinetic and binding mechanism. We have kinetically ascertained the mode of binding of CT DNA to these complexes by spectrophotometric techniques. Similarly, the activity of these chiral metal complexes to bind dioxygen reversibly has been probed and the rate constants $K_{obs}/K_{(DNA-complex)}$ at room temperature were calculated using least square regression method.

The change in redox behavior in these complexes is evidenced by sharp difference in voltammetric responses before and after interaction with CT DNA/dioxygen which is observed by taking cyclic voltammograms (CV) of all the free and bound species. The pattern of the voltammetric responses suggest a mechanistic pathway for the coordination of these complexes with CT DNA or as a reversible electrocatalyst for $O_2$ binding.
Synthesis of new asymmetric ligands was done by condensing o-phenylene diamine with carbon disulphide and acetaldehyde/benzaldehyde and their complexes with transition metal ions (Mn$^{II}$, Co$^{II}$, Ni$^{II}$, Cu$^{II}$ and Zn$^{II}$). These complexes were characterized by elemental analyses, conductivity measurements, IR, UV-Vis., EPR and NMR spectroscopy. On the basis of above studies, it has been concluded that all the complexes possess square-planar geometry and are ionic in nature. Photokinetic studies of the DNA-metal complexes $[C_{10}H_{10}S_{4}N_{2}Cu](NO_{3})_2$ and $[C_{10}H_{10}S_{4}N_{2}Ni](NO_{3})_2$ were carried out and the rate constants $k'_{(DNA-complex)}$ were calculated. The results indicate that DNA reacts with the metal complex in two steps. DNA first undergoes structural degradation and is then completely hydrolysed as indicated by spectral changes consistent with earlier results. The asymmetric $N_2S_2$ macrocyclic metal complexes show a strong propensity for DNA inhibition and can be used as an intercalating binding model.

Heterobimetallic chemistry has emerged as a challenging field of research. Different applications of heterobimetallic complexes have been thoroughly explored viz. magnetic and electrical properties, catalytic behavior, biomodels or biological model systems. An attempt has been made to synthesize new asymmetric heterobimetallic complexes of the type $[LML'Sn]Cl$ and $[LM'L'Sn]Cl_2$, where $L$ = ethylene diamine, $M$ = Mn$^{II}$, Co$^{II}$, Ni$^{II}$ and Cu$^{II}$, $M'$ = Cr$^{III}$ and Fe$^{III}$. 

(iii)
and L' = l-tryptophan and l-valine. They have been synthesized and characterized by elemental analyses, UV-Vis., IR, EPR, NMR, cyclic voltammetry and conductivity measurements. The Co^{III} analogue of these complexes which is the air oxidation product of Co^{II} complex, was characterized by two dimensional NMR COSY data. The oxygen binding affinities of the Co(II) complex have been investigated spectrophotometrically. The kinetic data proves that Co(II) of a coordinated molecule participates in the rate determining step of the dioxygen binding process. The plots of the pseudo-first order rate constant k_{obs} versus [O_{2}] is linear passing through an intercept. The electrochemical properties of [C_{15}H_{23}N_{4}O_{2}SnCo]^{+\_+} and [C_{15}H_{23}N_{4}O_{2}SnCu]^{+} are discussed with respect to the influence of an adjacent metal ion tin(IV) on cobalt(III) and copper(II) redox potential. Comparison of the electrochemical properties of [Co^{III}Sn^{IV}]^{+\_+} and [Cu^{II}Sn^{IV}]^{+} reveal that in both the species one electron transfer reaction takes place. For the [Co^{III}Sn^{IV}]^{+\_+} species E^{\circ} = +0.272 V and -1.1 V and for the [Cu^{II}Sn^{IV}]^{+} species E^{\circ} = +0.078 V and -0.300 V values were obtained, respectively.

In the past decade, porphyrin-nucleic acid interactions have been studied and a variety of porphyrins and their metal derivatives have shown to bind to single or to double stranded DNA/RNA sequences but chiral porphyrin complexes can induce more effective changes in the conformation of nucleic acids. A new template-directed
chiral porphyrin \([(\text{TPP})\text{Co(Trp)}]\), where TPP = tetraphenyl porphyrin and Trp = l-tryptophan, was prepared and characterized by various physico-chemical methods. These chiral template porphyrins can serve as a chiral substrate passage to the metal centre. The conformational changes in DNA by \([(\text{TPP})\text{Co(Trp)}]\) have been studied spectrophotometrically. The complex \([(\text{TPP})\text{Co(Trp)}]\), after interaction with calf thymus DNA, shows a shift in the absorption spectrum and a large hypochromicity, indicating an intercalating binding mode. This observation was further confirmed by the electrochemical behavior of \([(\text{TPP})\text{Co(Trp)}]\) before and after interaction with calf thymus DNA. The complex experiences a negative shift in $E_{1/2}$ and a decrease in $E_p$. The ratio of cathodic to anodic peak currents $i_\text{pc}/i_\text{pa}$ was $\approx 1$ for \([(\text{TPP})\text{Co(Trp)}]\) while for DNA bound complex $i_\text{pc}/i_\text{pa} < 1$, suggesting that the calf thymus DNA moiety is bound strongly to the complex \([(\text{TPP})\text{Co(Trp)}]\). Kinetic studies of the DNA-porphyrin complex reveal a pseudo-first order rate law as the plot of $k_{\text{obs}}$ versus calf thymus DNA is linear passing through the origin.

A new asymmetric organotin linked porphyrin dimers of the type \[\{[(\text{TPP})\text{M(Trp))}_2\text{M'}]\] where TPP = tetraphenyl porphyrin, M = Co(II) and Zn(II), Trp = l-tryptophan and M' = dimethyl tin(IV) have been synthesized and characterized by various conventional methods. We have prepared two optically active porphyrin moieties of Co(II)
and Zn(II) which are linked by an organotin group such as dimethyl tin(IV) to achieve optically active porphyrin dimers. These dimers are designed so as to hold two different or same metals in 5-coordinate geometry and possess cooperative binding properties. Besides, 5-coordinate chiral porphyrin dimer arrays are of great interest in specific catalytic reactions by the use of their chiral grooves and vacant sixth site for oxygen binding. The electrochemical behavior of [{(TPP)Co(Trp)}_2Sn(CH_3)_2] dimer has been studied by cyclic voltammetry. The complex revealed two reversible responses at +0.778 V and -0.421V, assigned to the Co(III/II) and Co(II/I) couples, respectively. Upon oxygenation, the voltammetric responses for both Co(III/II) and Co(II/I) couples shift to more negative potential from an initial potential of +0.778V and -0.421V. The changes in the cyclic voltammetric pattern during the oxygenation reaction reveal that the [{(TPP)Co(Trp)}_2Sn(CH_3)_2] dimer can act as a catalyst for the electroreduction of O_2. The kinetic studies for the complex [{(TPP)Co(Trp)}_2Sn(CH_3)_2] were determined by spectrophotometric titration with dioxygen. The experiments carried out in methanol under large excess of oxygen at 20 °C show absorbance changes which correspond to pseudo-first order conditions. A plot of rate constants k_{obs} versus [O_2] gave a straight line passing through an intercept and clearly indicates that the oxygenated complex
is the predominant species in the reaction as $k_{an}[O_2] > k_{of}$.

There is an increased interest in the synthesis of tin based antitumor drugs and activity of these complexes is closely related to their structure. Thus, the chiral complexes may have wide spread application in the field of medicine as antitumor, anti HIV agents, as catalysts and also as enzyme model systems. Here, we report the synthesis of novel chiral organotin complexes using amino acids as chiral auxiliaries and 1,10-phenanthroline as a secondary ligand. A series of di and tri organotin(IV) [LSnR' L'] complexes where $n = 2$ or $3$, $L = 1$-amino acids like l-tryptophan and l-valine and $L' = 1,10$-phenanthroline. Structure elucidation has been done by IR, UV, $^1H$, $^1^3C$, $^{119}Sn$ NMR spectroscopy. All the complexes are air stable and electrolytic in nature. On the basis of structural evidences, it has been concluded that the carboxylic acid of the l-amino acid is behaving as a monodentate ligand in all these complexes and complexes are octahedral in shape with a coordination number six around the tin atom. The $^{119}Sn$ chemical shift at -280.931 ppm for the complex $[C_4H_{13}N_3O_2Sn]$ is suggestive of six coordinate geometry around the tin(IV) atom.
CHAPTER I

INTRODUCTION
INTRODUCTION

Asymmetric synthesis is the most challenging task in current synthetic chemistry.\(^1\) Chiral metal complexes have not only invoked interest to Organic Chemists but Inorganic Researchers are also actively engaged and have led to a new sub area- Inorganic Asymmetric Synthesis.

In chiral metal complexes, the stereochemistry of the metal center plays a pivotal role in enantioselective catalytic transformations.\(^12\-20\) Brunner et al.\(^21\) have synthesized benzene ruthenium(II) complexes using chiral salicylidene aminato ligand. They demonstrated that there is a correlation between the conformation of 1-phenylethyl group and the configuration of the ruthenium atom. The control of stereochemistry about the metal center is also useful in pursuing the chiral auxiliary, chiral reagent or chiral pool.\(^22\-23\)

Chiral ligands as chiral auxiliaries containing nitrogen, oxygen and phosphorous donor sets have been recognized as highly excellent and efficient building blocks due to their use in many enantioselective transition and nontransition metal catalyzed reactions. Chiral auxiliaries having nitrogen and oxygen donor sets have become a subject of extensive research since past few years.\(^24\-27\)

Chiral \(N_2O_2\) tetradeutate ligands and their complexes were synthesized by Cross et al.\(^28\) with hard (Ti\(^{IV}\), Mn\(^{IV}\), Mo\(^{VI}\)) and borderline (Cu\(^{II}\), Ni\(^{II}\)) transition metal ions (Fig. 1a & b).
These tetradeutate ligands coordinate stereospecifically with the metal ions. The absolute configuration of the resultant complexes (Δ or Λ) mainly depends on the metal ion involved.

Reetz et al.²⁹ have reported the synthesis of asymmetric diiminophosphoranes. They have converted chiral diamines such as (1R, 2R)-1,2-diaminocyclohexane or R'-2,2'-diamino-1,1'-binaphthalene into diimino(triphenyl)phosphoranes (Fig. 2).
Chiral Schiff base metal complexes have also attracted considerable attention as they are capable of catalyzing a number of enantioselective reactions. Leung et al have reported chiral manganese(III) complexes of quadridentate Schiff base (Jacobsen’s catalyst) (Fig. 3).

Fig. 2

Fig. 3
These catalysts are capable of catalyzing epoxidation of unfunctionalized alkenes in excellent enantiomeric excess. Jacobsen and co-workers, have reported the chromium(III) complex [CrL(Cl)] which also catalyzes highly stereoselective ring opening of meso-epoxides such as cyclohexene oxide with trimethylsilyl azide. To design such chiral metal Schiff base complexes, a reasonable data of their redox and structural properties is desirable. Thus, redox behavior of these complexes was studied by electrochemical experiments. Due to the stereoelectronic flexibility and easy availability, they are capable of catalyzing a number of enantioselective reactions. In a similar way, Cheng et al have reported chiral manganese(III) and copper(II) complexes of binaphthyl Schiff base (Fig. 4).

![Diagram](https://example.com/diagram.png)

R¹ = Cl, Me, Et, H, Me, Et, Pr⁺, Bu⁺, Cl, Bu⁺
R² = Cl, NO₂, Me

Fig. 4
The strategy of using chiral $N_2S_2$ macrocyclic ligands as chiral auxiliaries has not been done till date. Thiosemicarbazides, thiosemicarbazones and dithiocarbamates having nitrogen and sulphur ligands have been studied because of their highly interesting chemical and biological properties. These $N_2S_2$ donor sets show distinct spectroscopic properties and have high DNA binding affinity. The binding of metal ion to nucleic acid is important as it helps in determining the primary and secondary structure of nucleic acids and also these binding reactions regulate gene expression and initiate cleavage and linkage reactions. The binding affinities of small molecules give valuable information about the designing of new diagnostic and chemotherapeutic agents. The DNA binds with these metal ions through various binding modes. One mode of noncovalent binding involves intercalation of planar molecules between base pairs of DNA helix. Other mode of binding involves intercalation of planar molecules between the complex cation and anionic backbone phosphodiester residues.

Barton et al. studied the interaction of a $\Delta$ and $\Lambda$ $[\text{Ru(Phen)}_2\text{dppz}]^{2+}$ with DNA where dppz = dipyridophenazine. The studies describe the

(a) Enantioselective binding by the octahedral complexes.

(b) Ligand specific intercalation for dppz and Phi complexes where Phi = phenanthrene quinone diimine.

(c) Intercalation access by these metal complexes from the major grooves.
The DNA binding behavior of copper complexes [Cu(bcp)]^+, [Cu(dmp)]^+ and [Cu(dpsmp)]^2 where bcp = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, dmp = 2,9-dimethyl-1,10-phenanthroline and dpsmp^2 = 2,9-dimethyl-4,7-bis-(sulfonatophenyl)-1,10-phenanthroline was studied by Mahadevan et al using spectroscopic as well as voltammetric techniques. The binding of intercalative drugs to DNA helix was characterized through absorption spectroscopic titrations by following the changes in absorbance (hypochromism/hyperchromism) and shift in wavelength. The percentage hyperchromism observed was found to be independent of the concentration of added dpsmp suggesting that hyperchromism is due to interaction of the complex with DNA. (Fig. 5)

Fig. 5- Charge transfer spectra of [Cu(dpsmp)]^2 (0.035 mM) in the absence (---) and presence (—) of increasing amounts of CT DNA
The electrochemical methods employed to study coordination of metal ions and chelates to DNA provide a useful complement to their spectroscopic data such as UV-Visible spectroscopy.

The nature of DNA binding of the copper complexes was followed by cyclic voltammetry. The Cu(II)/Cu(I) redox potentials of the [CuII(dpsmp)]2- reveal fairly reversible behavior and on addition of DNA, the complexes experience negative shift in $E_{1/2}$ and a decrease in $E_p$. The ratio of cathodic to anodic peak current, $I_{pa}/I_{pc}$ decreases with increasing concentration of DNA suggesting strong absorption of the [CuII(dpsmp)]2- complex in presence of DNA (Fig. 6).

![Fig. 6- Cyclic voltammograms of 0.1 mM [CuII(dpsmp)]2- in the absence (—) and presence (---) of 6 mM NP.](image-url)
In addition to the changes in $E_{1/2}$ the voltammetric peak currents decrease on addition of DNA to $[\text{Cu}^I\text{(dpsmp)}]^3\text{+}$ complex. The decrease in current is mainly due to the diffusion of equilibrium mixture of free and DNA-bound metal complexes to the electrode surface. This suggests strong binding of the Cu complex to the DNA and a square scheme (scheme-I) showing the binding of Cu(II) and Cu(I) form of complexes to DNA for reversible redox behavior is given here.

$$\text{CuL}_2^{2+} + e^- \rightleftharpoons \text{CuL}_2^+$$

$$\text{K}_2^+ \rightleftharpoons \text{K}^+$$

$$\text{CuL}_2^{2+} \text{DNA} + e^- \rightleftharpoons \text{CuL}_2^+ \text{DNA}$$

Scheme -1

Asymmetric ligands have also been used as building blocks in the heterobimetallic complexes. Yet there is scarcity of literature on this subject. In the past decade, heterobimetallic chemistry has emerged as a challenging field of research. Different applications of heterobimetallic complexes have been thoroughly explored viz. magnetic properties, electrical properties, catalytic properties and biomodels or biological model systems. Due to their unique properties, heterodinuclear
complexes can be distinguished from mononuclear or homonuclear complexes. When the two metal ions are bound by same or different ligands in close proximity, they cooperate in catalytic processes. Cheng and Das \textsuperscript{75} have studied the effect of a second metal on the catalytic activity of Mn(III). They illustrated that metal-metal interactions are important in many bimetallic metalloproteins and in transport of dioxygen in biological systems.\textsuperscript{76-78}

The structure and geometry of these heterobimetallic complexes makes them versatile enough to be able to accommodate another metal ion. The formation of heterobimetallic complexes may be attributed to the difference in the set of donor atoms of the adjacent chambers. Macrocyclic Schiff base complexes are excellent for such purposes and allow the coordination of two different metal ions. Lisowski et al \textsuperscript{79} have synthesized heterobimetallic complexes using macrocyclic Schiff bases containing nickel(II) and lanthanide(III) ions.

In a recent report, \textsuperscript{80} the heterodinuclear macrocyclic complex containing both Yb\textsuperscript{3+} and Na\textsuperscript{+} ions was synthesized and characterized by X-ray crystallography and \textsuperscript{1}H and \textsuperscript{23}Na solution NMR. These studies reveal that a suitable ligand should contain a Schiff base chamber for lanthanide coordination and a crown-ether moiety for the coordination of the alkali metal ion (Fig. 7).
Fig. 7 - Schematic representation of the compartmental macrocycle design for coordinating a lanthanide(III) ion into the Schiff base \( \text{N}_2\text{O}_2 \) chamber and an alkali metal ion into the crown ether moiety.

Active sites involving more than one metal center have their own importance e.g. dicopper sites in hemocyanin and tyrosinase, diiron(III) sites in methemerythrin, ribonucleotide reductase and heterobimetallic sites of Fe" and Cu" in respiratory cytochrome oxidase which catalyze the 4e reduction of dioxygen to water in the mitochondria of eukaryotic cells. 81-83

Heterobimetallic complexes of iron(II) and vanadium(III) systems with an oxo transfer reaction were synthesized by Bosnich et al. 84 (Fig. 8) The ligands used in these investigations have two metal-binding sites, one 6-coordinate (closed site) and one 4-coordinate (open site). 85-87 The purpose of this design is to allow a substrate, such as \( \text{O}_2 \), to bind to the open site but to be reduced by both metals.
For a dicobalt(II) complex, similar binding of O$_2$ to the open-site cobalt(II) could lead to the formation of dicobalt(III) peroxide complex analogous to the process in hemerythrin. In hemerythrin, two iron(II) ions are present, dioxygen binds to only one metal but both use reducing power to convert dioxygen to peroxide. When one of the metals in dicobalt(II) complexes was oxidized, the other metal was deactivated to oxidation. This mutual deactivation is not metal dependent and two metal oxidation is expected to occur by sequential electron transfer (eq-1)

$$[\text{Fe}^{II}(L)V^{III}\text{Cl}_2]^+ + \text{O} \rightarrow \text{Fe}^{III}(L)V^{V}(O)\text{Cl}^{2+} \rightarrow [\text{Fe}^{III}(L)V^{IV}O]^{3+}$$

Laccase employes four copper ions for the reduction of dioxygen to water. All the four copper ions take part in the reduction process, though
only two copper ions seem to bind to the dioxygen. \textsuperscript{92}

Various other complexes of diiron(II) and dicobalt(II) containing dinucleating ligands with sterically bulky nitrogen bases were used to study the dioxygen binding. \textsuperscript{93-95} The substituents viz. 4,5-diphenyl weakens the electron donor ability of dinucleating ligand to stabilize the divalent oxidation state of iron and form a hydrophobic cavity for a $O_2$ binding site which suppresses the irreversible oxidation and facilitates the reversible oxygenation (Fig. 9).

![Fig. 9 - Dinucleating ligands](image-url)
In order to study the dynamics of oxygen binding to a cobalt(II) moiety, coordination environment with one vacant site is most suitable. The design of dioxygen carriers using tetradentate ligands, 4-coordinate species is preferred than 6-coordinate species which fails to provide a vacant coordination site. For 6-coordinate cobalt(II) dioxygen carriers, all six coordination sites of the cobalt(II) ion were occupied either by ligand donor atoms or solvent molecules. Thus dissociation of one of the coordinated groups was a requirement for $O_2$ binding. Busch et al. studied the kinetics of dioxygen binding of Co(II) complexes with vacant coordination sites (Fig. 10).

Fig. 10
At low temperature (from -40 to -20 °C) the absorbance changes correspond to completely reversible behavior of the complexes. However, at higher temperature, partial autoxidation takes place. The kinetics of dioxygen binding for cobalt(II) complexes was measured by a spectrophotometric stopped-flow technique in the temperature range (from -75 to 40 °C). For the simple reversible O₂ binding reaction, the observed rate constants depend on both the rate constant for binding and the rate constant for dissociation (k_{on} and k_{off}). When a large excess of dioxygen is present in the reaction mixture eq-2 holds good.¹⁰⁰ Linear plots of \(k_{\text{obs}}\) vs \([O₂]\) were observed for all cobalt(II) complexes (Fig. 11).

\[
\begin{align*}
\text{k}_{\text{obs}} &= \text{k}_{\text{on}}[O₂] + \text{k}_{\text{off}} \quad \text{eq-2}
\end{align*}
\]

Fig. 11
Asymmetric metal complexes have widespread application in the field of medicine as antitumor and anti HIV agents and also as enzyme model systems. Cis-platin \([\text{cis-PtCl}_2(\text{NH}_3)_2]\) is one of the most widely used drugs in the treatment of several cancers. DNA replication is inhibited in the presence of cis-platin but due to problems regarding the resistance and immense side effects, development of new platinum drugs which may be active against a wide range of cancers with fewer side effects have taken place.

Knowledge of biological targets of these platinum drugs was not a hard task as structural X-ray and NMR data have identified N7 of the guanine base as the primary DNA binding site.

In a recent report, cis-platin DNA cross link models were explored with unusual type of chirality-neutral chelate amine carrier ligand (N-N'-Dimethylpiperazine). They proved the anticancer activity of these complexes in terms of DNA binding. They suggest that the guanine N7 is chiral and these bases gives different conformers with the Pt complexes. In distorted cis-platin intrastrand cross-linked DNA adducts, the dominant conformer has guanine in a head-to-head (HH) orientation. Conformation with head-to-tail (HT) orientation favors in cis-PtA2G2 adducts. (A2 = two monodentate or one bidentate amine ligand, G = guanine derivative not linked by a phosphodiester group). The evidence that linked adducts
favor the (HH form) and unlinked adducts favor the (HT form) has been witnessed through extensive studies spanning a quarter of a century. The solid data indicates that in all adducts the bases have either small tilt or large tilt and favor dipole-dipole interactions. Thus, they were proved as highly dynamic anticancer drugs.

Chirality greatly influences the anticancer activity of the metal complexes. It has been proved that the activity is related to NH groups of the cis-Pt(NH$_3$)$_2$ moiety. The NH groups are positioned to interact with the nucleic acid target and simultaneously break the symmetry and influence the position of the nucleic acid bases. Though chiral platinum complexes have been thoroughly studied, no attempt has been taken to synthesize new chiral anticancer organotin complexes. Although many organotin derivatives like diethyl tin(IV) and dibutyl tin(IV) derivatives were found to be effective anticancer agents. It has been proved that the dissociated diorganotin(IV) moieties act as antitumor agents.

Qingshan et al have synthesized diethyl tin(IV) complexes formulated as [Et$_2$Sn(Phen)(AMP)Cl], [Et$_2$Sn(Phen)(CMP)Cl] and [Et$_2$Sn(Phen)(GMP)Cl] where AMP = Adenosine-5'-monophosphate, CMP = Cytidine-5'-monophosphate and GMP = Guanosine-5'-monophosphate (Fig. 12).
The results indicate that diorganotin(IV) complexes coordinate with the phosphate group of the nucleotide and suggest them good anticancer agents.

Recently, a new class of compounds has gained interest due to their unique photochemical and electrochemical properties i.e. asymmetric metalloporphyrins and their dimers bearing chiral groups. Metalloporphyrins and their dimers have been extensively studied due to their role in many biological processes such as oxygen carriers in haemoglobin and myoglobin and as enzyme model systems. For example, cytochrome P-450 and horseradish peroxidase
(HRD) have been recognized as two heme enzymes responsible for the biological oxidation of toxic compounds. \(^{132-136}\) Chiral porphyrin complexes can induce more effective changes in the conformation of nucleic acids. \(^{137}\)

Porphyrin-nucleic acid interactions have been studied. They interact with DNA through both outside binding and intercalation. \(^{138-142}\) They have been recognized as excellent DNA binding and cleavage reagents \(^{143-146}\) and sensitizers for photodynamic therapy. \(^{147-150}\) These metalloporphyrins can be employed for studies as electron transfer agents through DNA, \(^{151}\) nucleic acid directed porphyrin aggregation \(^{152}\) and potential DNA damage induced by photodynamic therapy of neoplastic tissue. \(^{153-155}\) An X-ray structure \(^{156}\) of a tetraarylporphyrin DNA complex reveals that the porphyrin macrocycle is capable of binding to nucleic acids rather than flipping out into solution. The binding of DNA to the porphyrin macrocycle is evidence from changes in UV-Vis. spectroscopy, NMR properties of the porphyrins and redox potentials of the metal centers.

Hoffman et al \(^{157}\) have shown the binding of octa-plus porphyrazines to DNA. The kinetic studies were monitored by electronic absorption spectroscopy. Three binding modes were suggested (Fig.13)

(a) External binding with stacking.
(b) External binding (via. interactions with the phosphates)

(c) Intercalation.

The shift in absorbance maxima and extent of hypochromism suggest that the binding between DNA and porphyrins take place through intercalation or through external stacking of the porphyrazines along the DNA phosphate backbone.

![Diagrams of DNA binding modes](image)

Fig. 13

The biologically active porphyrins usually exist as dimers in solution and protein matrices, e.g. the "special pair" of chlorophylls in solution and photosynthetic reaction centers. Kimura et al have reported chiral twisted porphyrin dimers. They have proposed chiral porphyrin dimers (R)- and (S)- in which two porphyrin moieties are
linked by a chiral binaphthyl spacer (Fig. 14). In another attempt, they have reported the chiral twisted porphyrin dimers and their self assembly through the intermolecular formation of a $\mu$-oxo dimer between the porphyrin moieties (Fig. 15). The absorption spectra in CH$_2$Cl$_2$ changes in response to mixing with aqueous solution at various pH.

![Fig. 14](image-url)
Chiral porphyrin dimers linked through chiral groups have been recognized as good enantioselective catalysts. The multinuclear and dimeric porphyrins have been employed as catalysts for 4-electron reduction of oxygen. These dimers are designed to hold two different or same metals.
in 5-coordinate geometry and possess cooperative binding properties. Besides, 5-coordinate chiral porphyrin arrays are of great interest in specific catalytic reactions by the use of their chiral grooves and vacant site for oxygen binding. Yamamoto et al have investigated the electron transfer processes in dinuclear cobalt porphyrin complex by cyclic voltammetry. The studies gave important information about the redox behavior of the Co(II) dimer and the main objective of these studies was to know whether or not the two metal centers electrochemically interact with each other in the mixed valence state (Co$^{II}$-Co$^{III}$). The dimeric cobalt porphyrin was found to be a good model for elucidating interaction through space or a $\pi$-$\pi$ stacking orbital between each porphyrin ring because the cobalt porphyrins are strongly attracted to each other by the 4 ionic groups on each. Two redox waves were observed at -0.37 V and -0.17 V in the cyclic voltammogram of dinuclear cobalt porphyrin which is different from that of monomeric cobalt porphyrin Co(II)TPPS at -0.33V. The redox couples are ascribed to Co$^{II}$-Co$^{II}$/Co$^{II}$-Co$^{III}$ and Co$^{II}$-Co$^{III}$/Co$^{III}$-Co$^{III}$ on the basis of spectrochemical data (Fig. 16).
Fig. 16- UV-Visible absorption spectra of cobalt porphyrins in DMSO obtained by spectroelectrochemical measurements. (a)Co(II)TPPS-Co(III)TMPyP (b)Co(III)TPPS-Co(II)TMPyP at -0.27 V (c) Co(III)TPPS-Co(III)TMPyP at 0.1 V

Present work

Chiral N₂S₂ macrocyclic complexes of transition metals are novel as they exhibit high DNA binding affinity. New N₂S₂ macrocyclic asymmetric ligands have been synthesized by condensing o-phenylene diamine with CS₂ and benzaldehyde/acetaldehyde and their complexes with Mn²⁺, Co²⁺, Ni²⁺, Cu²⁺ and Zn²⁺ were prepared and characterized by elemental analysis, conductivity measurements, IR, UV-Vis., EPR and NMR spectra.

Photokinetic studies of the DNA-metal complexes [C₁₀H₁₀S₄N₂Cu](NO₃)₂ and [C₁₀H₁₀S₄N₂Ni](NO₃)₂ were carried out and the rate constants k(DNA-complex) were calculated.
In another set of experiments a series of asymmetric heterobimetallic complexes of the type \([\text{LML'Sn}]\text{Cl}\) and \([\text{LM'L'Sn}]\text{Cl}_2\) where \(\text{L} = \text{ethylene diamine}, \text{M} = \text{Mn}^{\text{II}}, \text{Co}^{\text{II}}, \text{Ni}^{\text{II}}\) and \(\text{Cu}^{\text{II}}, \text{M'} = \text{Cr}^{\text{III}}\) and \(\text{Fe}^{\text{III}}\) and \(\text{L'} = \text{l-tryptophan and l-valine}\) have been synthesized and characterized by various physico-chemical methods. The \(\text{Co}^{\text{III}}\) analogue of these complexes was characterized by two dimensional NMR COSY data. The kinetics of oxygen binding with the complex \([\text{C}_{15}\text{H}_{23}\text{N}_2\text{O}_2\text{SnCo}]\text{Cl}\) has also been studied spectrophotometrically. The electrochemical behavior of \([\text{C}_{15}\text{H}_{23}\text{N}_4\text{O}_2\text{SnCo}]^{\text{II}}\) and \([\text{C}_{15}\text{H}_{23}\text{N}_4\text{O}_2\text{SnCu}]^{\text{II}}\) was monitored by cyclic voltammetry to study the influence of an adjacent metal ion \(\text{tin(IV)}\) on \(\text{cobalt(III)}\) and \(\text{copper(II)}\) redox potential as the redox potentials are sensitively modified by the presence of the second metal ion.

Chiral porphyrin complexes are promising chemotherapeutic agents as they can induce more effective changes in the conformation of nucleic acids. In this context, an attempt has been made to synthesize chiral template porphyrins \([(\text{TPP})\text{Co(Trp)}]\) where \(\text{TPP} = \text{Tetraphenyl porphyrin and Trp = l-tryptophan}\) and characterized by various physico-chemical methods. These chiral porphyrin can serve as a chiral substrate passage to the metal center which generates a more active and more selective metal center. The conformational changes in DNA by \([(\text{TPP})\text{Co(Trp)}]\) have been studied spectrophotometrically.
and by kinetic experiments. The binding of CT DNA to the complex [(TPP)Co(Trp)] was further confirmed by the redox behavior of free and CT DNA bound [(TPP)Co(Trp)] which was studied by cyclic voltammetry.

The biologically active dimeric porphyrins are naturally occurring and have attracted considerable attention as they preferentially act as a catalyst. It is observed that catalytic reduction commences with the coordination of $O_2$ to the cobalt(II) center of the metalloporphyrin. This adduct leads to enhanced rates of reduction of $O_2$ and its reformation during the catalytic cycle. With the objective of understanding the catalytic behavior of Co(II)-$O_2$ coordination, we have synthesized novel organotin linked porphyrin dimers of the type [(TPP)M(Trp)$_2$M'] where TPP = Tetraphenyl porphyrin, M = Co(II) and Zn(II), Trp = 1-tryptophan and M' = dimethyl tin(IV) and characterized by various physico-chemical methods. The oxygen binding of [(TPP)Co(Trp)$_2$Sn(CH$_3$)$_2$] was studied by electrochemical experiments (cyclic voltammetry) and kinetic studies were determined by spectrophotometric titration with dioxygen. The experiments were carried out in methanol under large excess of oxygen at 20 °C under pseudo-first order conditions.

There is an increased interest in synthesis of tin based anticancer drugs and activity of these complexes is closely related to their structure. Thus the chiral complexes of organotin have been synthesized
using amino acids as chiral auxiliary and 1,10-Phenanthroline as a secondary ligand. A series of di and tri organotin(IV) $[\text{LSnRnL'}]$ complex where $n = 2$ or $3$, $L = \text{l-amino acids like l-tryptophan, l-leucine and l-valine and } L' = 1,10\text{-phenanthroline}$ have been prepared and structure elucidation was done by IR, UV, $^1\text{H}$, $^{13}\text{C}$, $^{119}\text{Sn}$ NMR spectroscopy.
CHAPTER II

EXPERIMENTAL METHODS
CHAPTER II

EXPERIMENTAL METHODS

The following techniques were employed to characterize the complexes

1. Infra-red spectroscopy
2. Ultra-voilet and visible (ligand-field) spectroscopy
3. Nuclear magnetic resonance spectroscopy
4. Electron paramagnetic resonance
5. Molar conductance measurements
6. Polarimetry
7. Cyclic voltammetry
8. Kinetic studies

Infra-red spectroscopy

The infrared spectroscopy is a useful technique to characterize a compound. It results from transition between vibrational and rotational energy levels. IR region of the electromagnetic spectrum covers a wide range of wavelength from 200 cm$^{-1}$ to 4000 cm$^{-1}$. It has been found that in IR absorption some of the vibrational frequencies are associated with specific groups of atoms and are the same irrespective of the molecules in which this group is present. These are called characteristic frequencies$^{189}$ and their constancy results from the constancy of bond force constants from molecule to molecule. The
important observation that the IR spectrum of a complex molecule consists of characteristic group frequencies which makes IR spectroscopy an unique and powerful tool in structural analysis.

**Ultraviolet and visible spectroscopy**

When a molecule absorbs radiation its energy is increased. This increased energy is equal to the energy of the photon expressed by the relation

\[ E = h\nu \]

\[ = hc/\lambda \]

where \( h \) is Plank's constant, \( \nu \) and \( \lambda \) are the frequency and wavelength of the radiation respectively and \( c \) is the velocity of light. Most of the compounds absorb light in the spectral region between 200 and 1000 nm. These transitions correspond to the excitation of electrons of the molecules from ground state to higher electronic states. In a transition metal, all the five 'd' orbitals viz. \( d_{xy}, d_{yz}, d_{xz}, d_{z^2} \) and \( d_{x^2-y^2} \) are degenerate. However, in coordination compounds due to the presence of ligands, this degeneracy is lifted and d orbitals split into two groups \( t_{2g} \) (\( d_{xy}, d_{yz} \) and \( d_{xz} \)) and \( e_g \) (\( d_{z^2} \) and \( d_{x^2-y^2} \)) in an octahedral complex and \( t \) and \( e \) in a tetrahedral complex. The set of \( t_{2g} \) orbitals goes below the original level of degenerate orbitals in octahedral complexes and the case is reversed in tetrahedral complexes.

Sometime due to transfer of charge from ligand to metal or metal to ligand, bands appear in the ultraviolet region of the spectrum, such spectra are
known as charge transfer spectra or redox spectra.

**Nuclear Magnetic Resonance**

The nuclei of certain isotopes possess a mechanical spin or angular momentum. The NMR spectroscopy is concerned with nuclei having spin quantum number \( I = 1/2 \), examples of which include \(^1\text{H} \), \(^3\text{P} \) and \(^19\text{F} \).

For a nucleus with \( I = 1/2 \) there are two values for the nuclear spin angular momentum quantum number \( m = \pm 1/2 \) which are degenerate in the absence of a magnetic field. However, this degeneracy is destroyed such that the positive value of \( m \) corresponds to the lower energy state and negative value to higher energy state separated by \( \Delta E \).

In an NMR experiment, one applies strong homogenous magnetic field causing the nuclei to precess. Radiation of energy comparable to \( \Delta E \) is then imposed with a radio frequency transmitter equal to the Larmor frequency and the two are said to be in resonance. The energy can be transferred to and from the source and the sample and NMR signal is obtained when a nucleus is excited from low energy to high energy state.

**Electron Spin Resonance**

EPR spectroscopy is the branch of absorption spectroscopy in which radiation having frequency in the microwave region is absorbed by paramagnetic energy levels of electrons with unpaired spins. The magnetic
energy splitting is done by applying a static magnetic field.

For an electron of spin \( S = 1/2 \), the spin angular momentum quantum number will have values of \( m_s = +1/2 \). In absence of magnetic field, the two values of \( m_s \) i.e.\(+1/2\) and \(-1/2\) will give rise to a doubly degenerate spin energy state. If a magnetic field is applied, this degeneracy is lifted and leads to the non-degenerate energy levels. The low energy level will have the spin magnetic moment aligned with the field and correspond to the quantum number \( m_s = -1/2 \). On the other hand, the high energy state will have the spin magnetic moment opposed to the field and correspond to the quantum number \( m_s = +1/2 \).

Conductance measurements

The conductivity measurements is one of the simplest and easily available techniques used to study the nature of complexes. It gives direct information regarding whether a given compound is ionic or covalent. For this purpose, the measurement of molar conductance (\( \Lambda_m \)) which is related to the conductance value in the following manner is made,

\[
\Lambda_m = \frac{\text{cell constant} \times \text{conductance}}{\text{concentration of solute expressed in mol cm}^{-3}}
\]
Conventionally solutions of $10^{-3}$ M strength are used for the conductance measurement. Molar conductance values of different types of electrolytes in a few solvents are given below; A 1:1 electrolyte has a value of 75-95 ohm$^{-1}$ cm$^2$ mol$^{-1}$ in nitromethane, 50-75 ohm$^{-1}$ cm$^2$ mol$^{-1}$ in dimethylformamide 78-80 and 100-160 ohm$^{-1}$ cm$^2$ mol$^{-1}$ in methyl cyanide. Similarly, a solution of 2:1 electrolyte has a value of 150-180 ohm$^{-1}$ cm$^2$ mol$^{-1}$ in nitromethane, 130-170 ohm$^{-1}$ cm$^2$ mol$^{-1}$ in dimethylformamide and 140-220 ohm$^{-1}$ cm$^2$ mol$^{-1}$ in methyl cyanide.

**Polarimetry**

Optical isomerism manifests itself by the rotation that certain molecules impart to the plane of polarized light when in gaseous, liquid or molten state or in solution. This rotation is observed and measured by a rather simple instrument, known as polarimeter. The specific rotation $[\alpha]$ of a dissolved substance is given by the expression

$$[\alpha] = \frac{\alpha}{l \times c}$$

where $\alpha$ is the observed rotation in degrees

- $l$ is the path length of the sample in decimeters
- $c$ is the concentration in grams per milliliter
The dependence on wavelength and temperature is indicated by subscripts and superscripts respectively. Thus \([\alpha]^{25}\) means the specific rotation at 25\(^\circ\) C measured at the wavelength of the sodium D line.

Optical rotation is generally measured using light from a sodium-vapour lamp, which gives essentially monochromatic radiation (the yellow sodium D line is a doublet at 5890 and 5896 A\(^\circ\)). A beam of light is polarized by passage through nicol prism (the polarizer), which consists of two calcite prisms cemented together so that only one of the two rays formed by double refraction is transmitted. The beam of polarized light passes through the solution and then through a second nicol prism. When no optically active material is placed between the prisms (0° rotation), the prisms are positioned at right angles so that no light is transmitted. When an optically active material is placed between the prisms, the analyzer must be turned in order to maintain the darkness in the field of view. The optical rotation is the angle by which the analyzer is turned in order to reach darkness. It is very difficult to determine by eye the setting for complete darkness, because positions near the completely dark position are very dark. Therefore, many instruments are constructed such that the field of view is divided into two equal parts, and the analyzer is adjusted so as to equalize the light intensity in each half of the field.
Cyclic voltammetry

Cyclic voltammetry involves the measurement of current-voltage curves under diffusion controlled, mass transfer conditions at a stationary electrode, utilizing symmetrical triangular scan rates ranging from a few millivolts per second to hundred of volts per second. The triangle returns at the same speed and permits the display of a complete polarogram with cathodic (reduction) and anodic (oxidation) waveforms one above the other. Two seconds or less is required to record a complete polarogram. (Fig. 17).

Consider the reaction

\[ \text{O} + \text{n}e \rightleftharpoons \text{R} \quad \text{(i)} \]

Assuming semi-infinite linear diffusion and a solution containing initially only species O. With the electrode held at a potential \( E_i \), where no electrode reaction occur.

The potential is swept linearly at v v/sec so that the potential at any time is

\[ E(t) = E_i - vt \]

or \( E_{\text{peak}} = E_{1/2} - 0.0285 \)
The rate of electron transfer is so rapid at the electrode surface that species \( O \) and \( R \) immediately adjust to the ratio according to the Nernst equation which is as follows

\[
C_o(0,t) = C_o^* - [nFA(\pi D_o)^{1/2}] \int_0^t i(\tau)(t-\tau)^{1/2} \, d\tau \quad \text{(ii)}
\]

\[
i = nFAC_o^*(\pi D_o \sigma)^{1/2} x (\sigma t) \quad \text{(iii)}
\]

The measured parameters of interest on these \( i-E \) curves (cyclic voltammograms) are \( i_{pa}/i_{pc} \), the ratio of peak currents, and \( E_{pa} - E_{pc} \), the separation of peak potentials. For a Nernstian wave with stable product, the ratio \( i_{pa}/i_{pc} = 1 \) regardless of scan rate, \( E_{\lambda} \) and diffusion coefficients, when \( i_{pa} \) is measured from the decaying current as a base line.
The difference between $E_{pA}$ and $E_{pE}$ ($\Delta E_p$) is a useful diagnostic test of a Nernstian reaction. Although $\Delta E_p$ is slightly a function of $E_p$, it is always close to $2.3RT/nF$.

The technique yields information about reaction reversibility and also offers a very rapid means of analysis for suitable systems. The method is particularly valuable for the investigation of stepwise reactions and in many cases, direct investigation of reactive intermediates.

**Kinetic studies**

In a closed constant volume system, the rate of a chemical reaction is defined as the rate of change with time of the concentration of any of the reactants and products. The concentration can be expressed in any units of quantity per unit volume e.g. moles per liter, moles per cubic centimeter. The rate will be defined as positive quantity regardless of the component whose concentration change is measured.

Consider the general chemical reaction

$$aA + bB \rightarrow cC + dD$$

The rate can be expressed as

$$\frac{-dA}{dt} , \frac{-dB}{dt} , \frac{dC}{dt} \quad \text{or} \quad \frac{dD}{dt}$$

where A, B, C and D designate the concentration in arbitrary units.
The rate of a chemical reaction is not measured directly instead the concentration of one of the reactants or products is determined as a function of time. A common procedure for determining the reaction order is to compare the experimental results with integrated rate equations for reactions of different orders. For a first order rate equation, integrating by separate variables using integration limits such that at \( t = 0 \), \( c = c_o \) and at \( t = t \), \( c = c \):

\[
-kc = \frac{dc}{dt}
\]

or \( \ln\left(\frac{c}{c_o}\right) = kt \)

If the reaction is first order, a plot of \( \ln c \) or \( \log c \) versus time should give a straight line with a slope of \(-k\) or \(-k/2.303\) respectively (Fig. 18). The dependent variable chosen is the decrease in concentration of reactant. If this variable is designated as \( x \) and \( c_o \) is the initial concentration,

\[
\frac{dx}{dt} = k(c_o - x)
\]

\[
\ln\left(\frac{c_o}{c_o - x}\right) = kt
\]
If, however, the conditions for a given reaction are such that one or more of concentration factors are constant or nearly constant during a reaction, these factors are included in the constant $k$. In this case, the reaction is said to be of pseudo-$n$th order or kinetically of $n$th order where $n$ is the sum of the exponents of those concentration factors which alter the reaction. This situation is true for catalytic reactions where the concentration of catalysts remains constant throughout the reaction, if one reactant is in large excess over another so that during the reaction there is only a small percentage change in the concentration of the former reactant.

All kinetic experiments were performed at room temperature under pseudo-first order conditions using a systronic 119 spectrophotometer. For the interaction of the complexes with DNA, the buffer containing tris(hydroxymethyl)aminomethane hydrochloride ($5 \text{mmol dm}^{-3}$), NaCl, pH-7.0 ($50 \text{ mmol dm}^{-3}$) with varying DNA concentrations was used. A solution of Calf Thymus DNA in the buffer gave ca. 1.91:1 ratio of UV absorbances at 260 and 280 nm.

In another set of kinetic experiments, the absorbance changes of Co$^{II}$ complexes at 428 nm and 620 nm ($\lambda_{\text{max}}$ of Co$^{II}$) respectively, under varying concentrations of oxygen ($1 \times 10^{-3}$ to $5 \times 10^{-3}$) mol$^{-1}$ dm$^{-3}$ was monitored spectrophotometrically. Pseudo-first order rate constants ($k_{\text{obs}}$) were obtained by linear least square regression method.
CHAPTER-III

New asymmetric $\text{N}_2\text{S}_2$ macrocycles, their metal chelates and the photokinetics of DNA-complex interaction.
CHAPTER III

Experimental

CS₂, Ni, Cu(NO₃)₂ hydrated, Mn, Co, Ni and Zn(AcO)₂, acetaldehyde and benzaldehyde (BDH) and o-phenylene diamine (Fluka) were used as received. Microanalyses of the complexes were obtained on a Carlo Erba Analyzer Model 1106. Molar conductances were measured at room temperature on a Digisun Electronic Conductivity Bridge. IR spectra (200-4000 cm⁻¹) were recorded on a Carl-Ziess Specord M-80 spectrophotometer in nujol mulls. The electronic spectra were recorded on a Systronic 119 spectrometer (ESP-300). The NMR spectra were recorded on an amx-500 instrument. The kinetic studies were performed on Systronic 119 spectrophotometer.

Synthesis of ligands  \( L = [C_{10}H_{10}N_2S_4] \) and  \( L' = [C_{15}H_{12}N_2S_4] \)

Carbon disulphide (0.1 mol, 5.5 mL) was added dropwise with constant stirring to o-phenylene diamine (5 g, 0.05 mol) in absolute ethanol (75 mL) at 0-5 °C. The reaction mixture was stirred for ca. 1 h and was allowed to stand overnight in refrigerator. A solid brown product was isolated by filtration under vacuum and washed thoroughly with hexane. It was then treated under reflux with acetaldehyde (0.44 g, 0.01 mol) or benzaldehyde (1.06 g, 0.01 mol) in methanol (25 mL) for 3 days. After removing the solvent under vacuum, the dark brown crystalline product was
isolated, washed with hexane and dried in vacuo.

**Synthesis of the complexes** $[C_{16}H_{16}N_4S_4O_6Cu]$ and $[C_{15}H_{12}N_4S_4O_6Cu]$

To a solution of ligand $[L]$ (0.286 g, 0.001 mol) or $[L']$ (0.384 g, 0.001 mol) in methanol (20 mL) was added Cu(NO$_3$)$_2$·3H$_2$O (0.241 g, 0.001 mol). A silver/brown precipitate appears on standing for ca. 3 h which was filtered off, washed thoroughly with hexane and dried in vacuo (Scheme 2).

**Synthesis of the complexes** $[C_{16}H_{16}N_4S_4O_6Ni]$ and $[C_{19}H_{18}N_2S_4O_4Ni]$

Ligand $[L]$ (0.286 g, 0.001 mol) or $[L']$ (0.384 g, 0.001 mol) in methanol (20 mL) and Ni(NO$_3$)$_2$·6H$_2$O (0.290 g, 0.001 mol)/Ni(AcO)$_2$ (0.248 g, 0.001 mol) in methanol (10 mL) were added together. A yellow/grey colour precipitate was obtained after keeping the solution for ca. 3 h which was filtered off, washed thoroughly with hexane and dried in vacuo.

**Synthesis of the complexes** $[C_{14}H_{16}N_2S_4O_4Mn]$ and $[C_{19}H_{18}N_2S_4O_4Mn]$

To a methanolic solution (20 mL) of $[L]$ (0.286 g, 0.001 mol) or $[L']$ (0.384 g, 0.001 mol), a solution of Mn(AcO)$_2$ (0.245 g, 0.001 mol) in methanol (10 mL) was added. The resulting black/grey compound was collected after filtration, washed with hexane and dried in vacuo.
Synthesis of the complex $[C_{14}H_{16}N_{2}S_{4}O_{4}Zn]$ 

A yellow colour precipitate was obtained after mixing [L] (0.286 g, 0.001 mol) in methanol (20 mL) and Zn(AcO)$_2$ (0.219 g, 0.001 mol) in methanol (10 mL). The product isolated after filtration was washed thoroughly with hexane and dried in vacuo. (Table 1).

\[ \text{Scheme 2} \]
Results and discussion

IR spectra

Important IR spectral data of optically active $N_2S_2$ macrocycles and their complexes are listed in Table 2. The optically active $N_2S_2$ macrocyclic ligands were prepared by condensing carbon disulphide and o-phenylene diamine with acetaldehyde/benzaldehyde (1:1 ratio). These ligands exhibit thione-thiol tautomerization since they contain a thioamide (-HN-C=S) functional group. However, the $\nu$(S-H) band at 2570 cm$^{-1}$ is absent from their IR spectra, but $\nu$(N-H) at 3220 cm$^{-1}$ is present indicating that the ligand in solid state remains in thio form. This contention is further confirmed by the $^1$H NMR spectrum in DMSO-$d_6$ which does not show any peak at ca. 4.0 ppm due to S-H proton, suggesting that thiol tautomeric form is absent. A strong band in the 1067-1094 cm$^{-1}$ region and another at 778-780 cm$^{-1}$ have been assigned to $\nu$(C=S) and $\nu$(C-S) respectively. The $\nu$(C-S) value is shifted by ca. 40 cm$^{-1}$ in all the complexes (730-740 cm$^{-1}$) clearly indicating that sulphur is involved in coordination. The spectra of the complexes show a large negative shift in the $\nu$(N-H) frequency (ca. 40 cm$^{-1}$) suggesting coordination of amine group to the metal. Other bands of medium intensity at 1300-1400 cm$^{-1}$ have been assigned to $\nu$(C-C), $\nu$(C-N). The far IR spectra of the complexes show absorption in the 330-370 cm$^{-1}$
and 440-470 cm\(^{-1}\) ranges due to \(v(M-S)\) and \(v(M-N)\) respectively. Thus on the basis of IR spectral data, we conclude that the metal exhibits square-planar geometry.

**Electronic spectra**

The absorption bands in the 23201-32051 cm\(^{-1}\) range in the complexes are attributed to MLCT transitions. However, in some cases, these bands are poorly resolved due to the small energy separation between some of the d orbitals.\(^{196,197}\) For the copper(II) complex, the weak bands at ca. 21,200 and 15243 cm\(^{-1}\) are assigned to \(2B_{1g} \rightarrow 2E_g\) and \(2B_{1g} \rightarrow 2A_{1g}\) transitions respectively, characteristic of square-planar geometry. The nickel(II) complex shows a broad band at 15625 cm\(^{-1}\) typical of square-planar geometry.\(^{198}\) The weak bands at 17241 cm\(^{-1}\), 22421 cm\(^{-1}\) and 21321 cm\(^{-1}\) correspond to \(2A_{1g} \rightarrow 2B_{2g}\) and \(2A_{1g} \rightarrow 2E_g\) in the cobalt(II) and manganese(II) complexes respectively, also supporting square-planar geometry.\(^{199}\)

**EPR spectra**

The EPR spectrum of copper(II) complex shows \(g_\perp (2.02)\) and \(g_\parallel (2.14)\) values, corresponding to square-planar geometry. The \(g\) values (\(g_\parallel > g_\perp\)) suggest the presence of an unpaired electron in the \(dx^2-y^2\) orbital and
the ground state \( (e_{g})^4 (a_{1g})^2 (b_{2g})^2 (b_{1g})^2 \) indicates the square-planar geometry for the copper(II) complex. The manganese(II) complex also shows \( g = 2.00 \) value, indicating square-planar geometry.

NMR spectra

\(^1\text{H} \) and \(^{13}\text{C} \) NMR spectra of the complexes are given in Table 3 and 4 respectively. The multiplets in the range 6.2-7.0 ppm and 6.8-7.4 ppm have been observed corresponding to the aromatic protons of the ligands and complexes respectively. The complex \([C_{14}H_{16}N_2S_4O_6Ni]\) shows a multiplet due to (-S-CH-C) proton in the range 5.9-6.0 ppm and a doublet due to \((CH_3)\) methyl protons in 2.1-2.2 ppm range. A doublet at 5.9,6.0 ppm has been observed for the complex \([C_{19}H_{18}N_2S_4O_4Ni]\), assignable to the (-S-CH-Ph) proton. However, no band has been observed for the aldehydic proton in the ligands and complexes.

\(^{13}\text{C} \) NMR of the ligands and complexes show a band in the range 109-136 ppm assignable to the aromatic carbons. A band in the 168.1-170.8 ppm range due to the \((CS_2)\) carbon has been observed in all the ligands and complexes. The complex \([C_{14}H_{16}N_2S_4O_6Ni]\) exhibit a band at 23.0 ppm for the \((-CH_3)\) methyl carbon. In the complex \([C_{19}H_{18}N_2S_4O_4Ni]\), a band at 136.8 ppm has been observed corresponding to the phenyl carbons.
Kinetic Studies

All experiments were performed at 30 ± 0.1 °C under pseudo-first order conditions (DNA >Complex) and the kinetics were followed by monitoring the absorbance at 260 nm (λ_max for DNA) on a 119 systronic spectrophotometer. Neither complex nor product show any absorbance at this range. The absorption spectra of \([C_{10}H_{10}N_2S_4Cu(NO_3)_2]\) and \([C_{10}H_{10}N_2S_4Ni(NO_3)_2]\) were obtained in DMSO/H_2O v/v 5 mL DMSO and 95 mL H_2O. The spectrum of the complexes exhibit two well resolved bands at 302 and 428 nm (Fig. 19) and 312 nm (Fig. 20), respectively. The band at 302 nm has been attributed to intraligand transitions and the band in the visible region are assigned to MLCT transitions. These bands shift ca. 10 nm after DNA calf thymus interaction. The complex \([C_{10}H_{10}N_2S_4Cu(NO_3)_2]\) and \([C_{10}H_{10}N_2S_4Ni(NO_3)_2]\) with calf thymus DNA recorded isobestic points at 302 and 392 nm (Fig. 21) and 254 and 287 nm (Fig. 22), respectively showing pronounced hypochromism. The observed hypochromism and concomitant red shifts are often associated with intercalative binding.\(^{206-208}\) The above spectral changes indicate that DNA reacts with the metal complexes in two steps. DNA first undergoes structural degradation and is then completely hydrolysed.
Fig. 19

Fig. 20
Fig. 21

Fig. 22
The first order plots of log \((A_\infty - A_t)\) versus time were linear up to 80\% completion of the reaction (Fig 23). The absorption spectra of calf thymus DNA with varying concentrations (1 \times 10^{-5} to 9 \times 10^{-5}) recorded spectrophotometrically by photoirradiation. The effect of varying DNA (range 1 \times 10^{-4} to 9 \times 10^{-5} mol dm^{-3}) on the reaction rate was studied at fixed \([C_{10}H_{10}N_2S_4M](NO_3)_2\) \(c = 0.52 \times 10^{-5} mol dm^{-3}\) at temp. = 30 °C where \(M = Cu^{II}\) or \(Ni^{II}\). The rate constants \((k_{obs})\) are shown graphically in Fig 24 which clearly indicates that the first order kinetics with respect to [DNA].

![Fig. 23]
Consistent with all the experimental data obtained for the complexation of \([C_{10}H_{10}N_2S_4M](NO_3)_2\) with DNA where \(M = Cu^{II}\) or \(Ni^{II}\), we postulate the following mechanism.
On the basis of the Scheme 3 the following rate law has been derived

\[ k_{\text{obs}} = \frac{k_1k_2[D\text{NA}]}{(k_1 + k_2)} \quad (1) \]

According to eqn (1), plot of \( k_{\text{obs}} \) versus [DNA] should be linear with slope \( = k_1k_2/(k_1 + k_2) \), if the proposed mechanism (Scheme 3) is correct. The linearity obtained from the plots of \( k_{\text{obs}} \) versus [DNA] in
Fig 24 is consistent with the proposed mechanism. By using two different metal ions, we have ascertained that the binding mode remains unaffected.
<table>
<thead>
<tr>
<th>Complexes</th>
<th>Colour</th>
<th>M.P.</th>
<th>Yield</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>$\Lambda^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(°C)</td>
<td>(%)</td>
<td></td>
<td></td>
<td></td>
<td>(Ω·cm²·mol⁻¹)</td>
</tr>
<tr>
<td>$C_{10}H_{10}N_2S_4$</td>
<td>brown</td>
<td>258-260</td>
<td>70</td>
<td>41.95</td>
<td>3.48</td>
<td>9.76</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(41.96)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(3.49)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(9.79)</td>
</tr>
<tr>
<td>$C_{10}H_{10}N_4S_4O_6Ni$</td>
<td>yellow</td>
<td>310-312</td>
<td>72</td>
<td>25.59</td>
<td>2.12</td>
<td>11.93</td>
<td>73</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(25.60)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(2.13)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(11.94)</td>
</tr>
<tr>
<td>$C_{10}H_{10}N_4S_4O_6Cu$</td>
<td>silver</td>
<td>332-335</td>
<td>71</td>
<td>25.33</td>
<td>2.10</td>
<td>11.81</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(25.34)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(2.11)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(11.82)</td>
</tr>
<tr>
<td>$C_{14}H_{16}N_2S_4O_4Mn$</td>
<td>black</td>
<td>342-345</td>
<td>70</td>
<td>36.60</td>
<td>3.48</td>
<td>6.09</td>
<td>72</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(36.61)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(3.49)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(6.10)</td>
</tr>
<tr>
<td>$C_{14}H_{16}N_2S_4O_4Co$</td>
<td>blue</td>
<td>291-293</td>
<td>73</td>
<td>36.28</td>
<td>3.45</td>
<td>6.04</td>
<td>76</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(36.29)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(3.46)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(6.05)</td>
</tr>
<tr>
<td>$C_{14}H_{16}N_2S_4O_4Zn$</td>
<td>yellow</td>
<td>270-272</td>
<td>70</td>
<td>35.78</td>
<td>3.40</td>
<td>5.96</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(35.79)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(3.41)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(5.97)</td>
</tr>
</tbody>
</table>
Table 1- Contd.

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Colour</th>
<th>M.P. (°C)</th>
<th>Yield (%)</th>
<th>Found (Calcd.)</th>
<th>Λ* (Ω⁻¹ cm² mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}<em>{15}\text{H}</em>{12}\text{N}<em>{2}\text{S}</em>{4} )</td>
<td>brown</td>
<td>277-279</td>
<td>72</td>
<td>C: 51.71</td>
<td>(51.72)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H: 3.44</td>
<td>(3.45)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>N: 8.04</td>
<td>(8.05)</td>
</tr>
<tr>
<td>( \text{C}<em>{19}\text{H}</em>{18}\text{N}<em>{2}\text{S}</em>{4}\text{O}_{4}\text{Ni} )</td>
<td>grey</td>
<td>260-262</td>
<td>72</td>
<td>C: 43.44</td>
<td>(43.45)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H: 3.42</td>
<td>(3.43)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>N: 5.33</td>
<td>(5.34)</td>
</tr>
<tr>
<td>( \text{C}<em>{15}\text{H}</em>{12}\text{N}<em>{4}\text{S}</em>{4}\text{O}_{6}\text{Cu} )</td>
<td>brown</td>
<td>200-202</td>
<td>70</td>
<td>C: 34.11</td>
<td>(34.12)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H: 2.26</td>
<td>(2.27)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>N: 10.61</td>
<td>(10.62)</td>
</tr>
<tr>
<td>( \text{C}<em>{19}\text{H}</em>{18}\text{N}<em>{2}\text{S}</em>{4}\text{O}_{4}\text{Mn} )</td>
<td>grey</td>
<td>241-243</td>
<td>71</td>
<td>C: 43.76</td>
<td>(43.77)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H: 3.45</td>
<td>(3.46)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>N: 5.36</td>
<td>(5.37)</td>
</tr>
<tr>
<td>( \text{C}<em>{19}\text{H}</em>{18}\text{N}<em>{2}\text{S}</em>{4}\text{O}_{4}\text{Co} )</td>
<td>blue</td>
<td>351-353</td>
<td>72</td>
<td>C: 43.42</td>
<td>(43.43)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H: 3.42</td>
<td>(3.43)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>N: 5.32</td>
<td>(5.33)</td>
</tr>
</tbody>
</table>

\( a = \) Molar conductance in DMSO. 209
Table 2. IR spectra of the complexes (cm\(^{-1}\))

<table>
<thead>
<tr>
<th>Complex</th>
<th>v(NH)</th>
<th>v(CN)</th>
<th>v(C-S)</th>
<th>δ(NH)</th>
<th>v(M-S)</th>
<th>v(M-N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(<em>{10})H(</em>{10})N(_2)S(_4)</td>
<td>3220</td>
<td>1385</td>
<td>778</td>
<td>1570</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C(<em>{14})H(</em>{16})N(_2)S(_4)O(_4)Ni</td>
<td>3180</td>
<td>1368</td>
<td>737</td>
<td>1570</td>
<td>364</td>
<td>460</td>
</tr>
<tr>
<td>C(<em>{10})H(</em>{10})N(_2)S(_4)O(_6)Cu</td>
<td>3178</td>
<td>1371</td>
<td>738</td>
<td>1568</td>
<td>355</td>
<td>440</td>
</tr>
<tr>
<td>C(<em>{14})H(</em>{16})N(_2)S(_4)O(_4)Mn</td>
<td>3175</td>
<td>1370</td>
<td>735</td>
<td>1565</td>
<td>343</td>
<td>450</td>
</tr>
<tr>
<td>C(<em>{14})H(</em>{16})N(_2)S(_4)O(_4)Co</td>
<td>3176</td>
<td>1368</td>
<td>739</td>
<td>1571</td>
<td>333</td>
<td>440</td>
</tr>
<tr>
<td>C(<em>{14})H(</em>{16})N(_2)S(_4)O(_4)Zn</td>
<td>3174</td>
<td>1365</td>
<td>735</td>
<td>1571</td>
<td>331</td>
<td>445</td>
</tr>
<tr>
<td>Complex</td>
<td>$\nu$(NH)</td>
<td>$\nu$(CN)</td>
<td>$\nu$(C-S)</td>
<td>$\delta$(NH)</td>
<td>$\nu$(M-S)</td>
<td>$\nu$(M-N)</td>
</tr>
<tr>
<td>--------------------------</td>
<td>-----------</td>
<td>-----------</td>
<td>------------</td>
<td>--------------</td>
<td>------------</td>
<td>------------</td>
</tr>
<tr>
<td>C$<em>{15}$H$</em>{12}$N$_2$S$_4$</td>
<td>3222</td>
<td>1380</td>
<td>780</td>
<td>1571</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C$<em>{19}$H$</em>{18}$N$_2$S$_4$O$_4$Ni</td>
<td>3184</td>
<td>1370</td>
<td>736</td>
<td>1572</td>
<td>363</td>
<td>470</td>
</tr>
<tr>
<td>C$<em>{15}$H$</em>{12}$N$_2$S$_4$O$_6$Cu</td>
<td>3170</td>
<td>1371</td>
<td>735</td>
<td>1567</td>
<td>354</td>
<td>450</td>
</tr>
<tr>
<td>C$<em>{19}$H$</em>{18}$N$_2$S$_4$O$_4$Mn</td>
<td>3174</td>
<td>1368</td>
<td>731</td>
<td>1566</td>
<td>344</td>
<td>440</td>
</tr>
<tr>
<td>C$<em>{19}$H$</em>{18}$N$_2$S$_4$O$_4$Co</td>
<td>3175</td>
<td>1373</td>
<td>738</td>
<td>1574</td>
<td>336</td>
<td>450</td>
</tr>
<tr>
<td>Complex</td>
<td>Ar protons</td>
<td>Ar-NH-C=S</td>
<td>-S-CH-C-</td>
<td>-C-CH₃</td>
<td>-S-CH-Ph</td>
<td>Ph protons</td>
</tr>
<tr>
<td>---------------</td>
<td>------------</td>
<td>-----------</td>
<td>-----------</td>
<td>--------</td>
<td>----------</td>
<td>------------</td>
</tr>
<tr>
<td></td>
<td>4H(m)</td>
<td>2H(s)</td>
<td>1H(m)</td>
<td>3H(d)</td>
<td>1H(d)</td>
<td>5H(d)</td>
</tr>
<tr>
<td>( \text{C}<em>{10}\text{H}</em>{10}\text{N}_2\text{S}_4 )</td>
<td>6.2-6.8</td>
<td>5.0</td>
<td>5.3-5.3</td>
<td>2.1,2.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( \text{C}<em>{14}\text{H}</em>{16}\text{N}_2\text{S}_4\text{O}_4\text{Ni} )</td>
<td>6.9-7.0</td>
<td>5.9</td>
<td>5.9-6.0</td>
<td>2.4-2.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( \text{C}<em>{13}\text{H}</em>{12}\text{N}_2\text{S}_4 )</td>
<td>6.8-6.9</td>
<td>5.1</td>
<td>-</td>
<td>-</td>
<td>6.6-6.8</td>
<td>7.1-7.2</td>
</tr>
<tr>
<td>( \text{C}<em>{19}\text{H}</em>{18}\text{N}_2\text{S}_4\text{O}_4\text{Ni} )</td>
<td>7.2-7.4</td>
<td>5.9</td>
<td>-</td>
<td>-</td>
<td>5.9-6.0</td>
<td>7.9-8.0</td>
</tr>
</tbody>
</table>

Table 3. \(^1\text{H}\) NMR spectra of the ligands and complexes (ppm)
Table 4. $^{13}$C NMR spectra of the ligands and complexes (ppm)

<table>
<thead>
<tr>
<th>Complex</th>
<th>Ar carbons</th>
<th>CS$_2$</th>
<th>S-C-S</th>
<th>-CH$_3$</th>
<th>-Ph carbons</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{16}H_{16}N_2S_4$</td>
<td>118.0-136.0</td>
<td>170.8</td>
<td>48.9-49.9</td>
<td>24.0</td>
<td>-</td>
</tr>
<tr>
<td>$C_{14}H_{16}N_2S_4O_4Ni$</td>
<td>109.4-132.2</td>
<td>168.1</td>
<td>38.9-39.9</td>
<td>23.0</td>
<td>-</td>
</tr>
<tr>
<td>$C_{15}H_{12}N_2S_4$</td>
<td>112.6-122.7</td>
<td>170.8</td>
<td>50.3-51.3</td>
<td>-</td>
<td>128.9</td>
</tr>
<tr>
<td>$C_{19}H_{18}N_2S_4O_4Ni$</td>
<td>112.5-135.1</td>
<td>170.8</td>
<td>41.6-42.7</td>
<td>-</td>
<td>136.8</td>
</tr>
</tbody>
</table>
CHAPTER-IV

Novel asymmetric heterobimetallic complexes of transition metals and kinetics of oxygen binding to a cobalt(II) complex
CHAPTER - IV

Experimental

L-valine, L-tryptophan (Sisco Research lab. ltd.), CrCl$_3$.2.H$_2$O, MnCl$_2$.4H$_2$O, FeCl$_3$, CoCl$_2$.6H$_2$O, NiCl$_2$.6H$_2$O and CuCl$_2$.2H$_2$O (BDH), ethylene diamine (BDH) were used as received. Microanalyses of the complexes were obtained on a Carlo Erba Analyzer Model 1106. Molar conductances were measured at room temperature on a Digisun Electronic Conductivity bridge. IR spectra (200-4000 cm$^{-1}$) were recorded on a Carl-Ziess specord M-80 spectrophotometer in nujol mulls. The electronic spectra were recorded on a Systronic 119 spectrophotometer. The NMR spectra were recorded on an anix-500 instrument. The optical rotation of the complexes were recorded on ASI, India polarimeter.

Cyclic voltammetric measurements were carried out on a CH instrument electrochemical analyzer. High purity, aqueous DMSO (95:5) solvent was employed for the CV studies with 0.4M KNO$_3$ as a supporting electrolyte. A three electrode configuration was used, comprising platinum disk working electrode, platinum wire counter electrode and Ag/AgCl reference electrode. Experiments were carried out at room temperature.

Kinetic experiments were performed under pseudo-first order conditions using a Systronic 119 spectrophotometer.
Synthesis of the complexes \([C_{15}H_{23}N_4O_2SnCrCl_2]\) and \([C_9H_{22}N_3O_2SnCrCl_2]\)

L-tryptophan (0.204 g, 1 mmol)/l-valine (0.117 g, 1 mmol) was dissolved by heating in methanol (20 mL) and an equivalent amount of ethylene diamine (0.060 g, 1 mmol) was added. In a separate flask, \(\text{CrCl}_3 \cdot 2\text{H}_2\text{O}\) (0.266 g, 1 mmol) and \((\text{Me})_2\text{SnCl}_2\) (0.219 g, 1 mmol) were dissolved in methanol (25 mL). The two solutions were then mixed and heated under reflux for ca. 7 h. After cooling the mixture was concentrated to ca. 20 mL, then stirred for ca. 2 h. to give a dark green/green crystalline solid which was filtered under vacuum and washed thoroughly with ether and dried in vacuo (Scheme 4).

**Synthesis of the complexes \([C_{15}H_{23}N_4O_2SnMnCl]\) and \([C_9H_{22}N_3O_2SnMnCl]\)**

To a methanolic solution (20 mL) of l-tryptophan (0.204 g, 1 mmol)/l-valine (0.117 g, 1 mmol) was added an equivalent amount of ethylene diamine (0.60 g, 1 mmol). In another flask, a solution of \(\text{MnCl}_2 \cdot 4\text{H}_2\text{O}\) (0.198 g, 1 mmol) and \((\text{Me})_2\text{SnCl}_2\) (0.219 g, 1 mmol) were taken in methanol (25 mL). The two solutions were mixed and kept under reflux for 7 h. The mixture was concentrated to ca. 25 mL and then stirred for ca. 3 h to give a yellow/light brown precipitate, which was filtered
under vacuum and washed thoroughly with ether and dried in vacuo.

Synthesis of the complexes \([C_{15}H_{23}N_4O_2SnCoCl]\) and \([C_{9}H_{22}N_3O_2SnCoCl]\)

A solution of l-tryptophan (0.204 g, 1 mmol)/l-valine (0.117 g, 1 mmol) in hot methanol (20 mL) and ethylene diamine (0.060 g, 1 mmol) in 1:1 molar ratio. An equimolar solution of CoCl\(_2\)·6H\(_2\)O (0.238 g, 1 mmol) and (Me)\(_2\)SnCl\(_2\) (0.219 g, 1 mmol) in methanol (20 mL) was slowly added to the above solution. The resulting mixture was kept under reflux for 7 h. After cooling the mixture was concentrated to ca. 20 mL and stirred for ca. 3 h to give a green coloured precipitate which was filtered under vacuum, washed thoroughly with ether and dried in vacuo.

The cobalt(III) analogue was obtained by air oxidation of cobalt(II) complex (Scheme-4').

Synthesis of the complexes \([C_{15}H_{23}N_4O_2SnNiCl]\) and \([C_{9}H_{22}N_3O_2SnNiCl]\)

In a heated solution of l-tryptophan (0.204 g, 1 mmol)/l-valine (0.117 g, 1 mmol) in methanol (20 mL), an equimolar amount of ethylene diamine (0.060 g, 1 mmol) was added. In a separate flask, a solution of NiCl\(_2\)·6H\(_2\)O (0.237 g, 1 mmol) and (Me)\(_2\)SnCl\(_2\) (0.219 g, 1 mmol) in methanol (25 mL) was taken. The above two solutions were mixed together and kept under reflux for 7 h. The resulting solution was concentrated to ca. 20 mL and then stirred
for ca. 2 h to give a light green coloured precipitate which was filtered under vacuum, washed thoroughly with ether and dried in vacuo.  

**Synthesis of the complexes [C_{15}H_{23}N_{4}O_{2}SnFeCl_{2}] and [C_{9}H_{22}N_{3}O_{2}SnFeCl_{2}]**

Equimolar amounts of L-tryptophan (0.204 g, 1 mmol)/l-valine (0.117 g, 1 mmol) in methanol (20 mL) and ethylene diamine (0.060 g, 1 mmol) were added. To this mixture, a solution of FeCl₃ (0.162 g, 1 mmol) and (Me)₂SnCl₂ (0.219 g, 1 mmol) also in methanol (10 mL) was added. The resulting solution was kept under reflux for ca. 7 h. Then the solution was concentrated to 15 mL and stirred for ca. 3 h to give a brown/dark brown coloured precipitate which was filtered under vacuum, washed thoroughly with ether and dried in vacuo.

**Synthesis of the complexes [C_{15}H_{23}N_{4}O_{2}SnCuCl] and [C_{9}H_{22}N_{3}O_{2}SnCuCl]**

L-tryptophan (0.204 g, 1 mmol)/l-valine (0.117 g, 1 mmol) was dissolved in methanol (20 mL) after heating in which ethylene diamine (0.060 g, 1 mmol) was added in 1:1 molar ratio. To the above solution, a solution of CuCl₂·2H₂O (0.170 g, 1 mmol) and (Me)₂SnCl₂ (0.219 g, 1 mmol) in methanol (20 mL) was mixed. The resulting mixture was refluxed for ca. 7 h. After cooling the mixture was concentrated
to ca. 20 min and then stirred for ca. 4 h to give a blue-coloured compound which was filtered under vacuum, washed with ether and dried in vacuo.

\[ \text{Scheme-4} \]

\[ \text{Scheme-4'} \]

\[ \text{\( \text{C}_9\text{H}_8\text{N} \)} \]
Results and discussion

IR spectra

The physical, analytical data and molar conductance measurements of the complexes are given in Table 5. The complexes were formed by the interaction of ethylene diamine, l-amino acids, transition metal salts and dimethyltin dichloride in 1:1:1:1 molar ratio and on the basis of the analytical data, the complexes were formulated as [LML'Sn]Cl and [LM'L'Sn]Cl₂ where L = ethylene diamine, M = MnⅡ, CoⅡ, NiⅡ and CuⅡ, M' = CrⅢ and FeⅢ and L' = l-tryptophan and l-valine. The IR spectra (Table 6) of the complexes exhibit a distinct band in the 3378-3419 cm⁻¹ range due to the v(NH) stretching frequency. The free amino acids show two bands in the 1610-1660 cm⁻¹ and 1395-1430 cm⁻¹ regions, corresponding to the antisymmetric and symmetric (COO⁻) stretching vibrations, respectively. These bands are shifted to lower and higher frequency respectively on complexation, indicating that the amino acid carboxylate group is involved in complex formation. Moreover, the appearance of a symmetric (COO⁻) stretching band in the IR of the complexes at 1350-1400 cm⁻¹ is due to amino acid carboxylic acid group coordinated to the metal ion, through nitrogen and oxygen of the carboxylic group which is further confirmed by the appearance of v(M-O) stretching frequency in the
374-419 cm\(^{-1}\) range respectively. All the complexes show one distinct v(Sn-N) band in the 417-421 cm\(^{-1}\) far IR range indicating coordination of nitrogen atom to tin(IV) metal ion. On the basis of IR spectral data and other physical measurements, we propose the coordination environment of the complexes as in Figs 25a and 25b.

**Electronic spectra**

The electronic spectrum of the complex \([C_{15}H_2N_4O_2SnCu]Cl\) shows two bands at ca. 16,234 cm\(^{-1}\) and 15,625 cm\(^{-1}\) assigned to \(^2\)B\(_{1g}\) \(\rightarrow\) \(^2\)E\(_g\) and \(^2\)B\(_{1g}\) \(\rightarrow\) \(^2\)A\(_{1g}\) transitions respectively, indicating square-planar geometry for the copper(II) complex. The nickel(II) complex shows a broad band at 15630 cm\(^{-1}\) due to the square-planar environments around the nickel(II) ion. The electronic spectrum of cobalt(II) complex displays two bands at ca. 16,234 and 20,661 cm\(^{-1}\) regions which are assigned to \(^2\)A\(_{1g}\) \(\rightarrow\) \(^2\)E\(_g\) transitions, respectively, characteristic of square-planar geometry. In the electronic spectrum of chromium(III), two bands are observed at 15865 and 23792 cm\(^{-1}\) which may be corresponding to \(^4\)A\(_{2g}\)(F) \(\rightarrow\) \(^4\)T\(_{2g}\)(F) and \(^4\)A\(_{2g}\)(F) \(\rightarrow\) \(^4\)T\(_{1g}\)(F) transitions, respectively, are in favor of octahedral geometry. The electronic spectra of iron(III) exhibits three bands at ca. 12,210, 20,000 and 25,000 cm\(^{-1}\) which are assigned to \(^6\)A\(_{1g}\) \(\rightarrow\) \(^4\)T\(_{1g}\)(G), \(^6\)A\(_{1g}\) \(\rightarrow\) \(^4\)T\(_{2g}\)(G) and \(^6\)A\(_{1g}\) \(\rightarrow\) \(^4\)A\(_{1g}\) transitions indicating octahedral geometry for the iron(III) complex.
Fig. 25 a

$M = \text{Mn}^{\text{II}}, \text{Co}^{\text{II}}, \text{Ni}^{\text{II}}, \text{Cu}^{\text{II}}$

Fig. 25 b

$M' = \text{Cr}^{\text{III}}, \text{Fe}^{\text{III}}$
NMR spectra

$^1$H NMR and $^{13}$C NMR spectra of all the complexes are given in Table 7 and Table 8 respectively. On the basis of $^1$H NMR complete resonance assignments have been carried out for the complex $[C_{13}H_{23}N_4O_2SnCo]^{++}$ using 2D NMR technique (Fig 26 a & b) (Table 9). The $^1$H NMR further supports that amino acid carboxylic acid group coordinates to the metal ion through oxygen and nitrogen. The absence of -COOH proton signal in the $^1$H NMR indicates the deprotonation of the -COOH group and its subsequent coordination in the complex formation. A doublet at 3.2-3.5 ppm and 3.8-3.9 ppm has been observed which may be assigned to the -CH$_2$- protons in all the complexes. A multiplet at 5.0-5.8 ppm has been observed corresponding to the -CH- protons of the amino acid moiety present in all the complexes. A singlet has been observed at 1.0 ppm which may be assigned to the -CH$_3$ protons of the dimethyltin(IV) moiety. A singlet at 1.0 ppm has also been observed in the corresponding 2D COSY NMR which also confirms the presence of dimethyltin(IV) moiety.
Fig. 26a
EPR spectra

The EPR spectra recorded on the powdered sample of the copper complex \( [C_{15}H_{23}N_4O_2SnCu]Cl \) gave \( g \) values which are less than 2.3 (\( g_\perp = 2.01 \) and \( g_\parallel = 2.12 \)). The low field side of EPR spectra of the copper(II) complex is less intense than the high field side i.e. \( g_\parallel > g_\perp \) suggesting that the unpaired electron is present in the \( dx^2-y^2 \) orbital which indicates the square-planar geometry around the Cu(II) ion. \(^{218,219}\) For the complex \( [C_{15}H_{23}N_4O_2SnMn]Cl \), \( g = 2.01 \) value clearly indicates square-planar geometry around the Mn(II) ion. \(^{203}\)

Electrochemical properties

Redox properties of the cobalt complexes have been studied by cyclic voltammetry (CV) using a platinum working electrode in DMSO/H_2O solution. The cyclic voltammogram recorded for the Co^{Ill} complex \( [Co^{III}Sn^{IV}]^{2+} \) in DMSO/H_2O (5:95) reveals one electron transfer reaction and a quasi reversible wave occurs with \( E^0 \) value of 0.272 V and -1.1 V as shown in (Fig 27). The \( E^0 \) value confirms cathodic responses for the cobalt complex and may be assigned to Co^{III}-Co^{II} redox couple. \(^{220}\) Cu^{II} complex \( [Cu^{II}Sn^{IV}]^+ \) exhibits in DMSO/H_2O (5:95), a reduction wave \( E^0 \) value of +0.078 V and -0.300 V
respectively. This redox reaction is one electron transfer reaction with quasi reversible system containing Cu$^{II}$-Cu$^{I}$ as shown in Fig 28. For this couple, the difference between the cathodic and anodic potentials $\Delta E$ is of the order of 56 mV. The $\Delta E_p$ value lies within the range of nernstian value ($\Delta E_p = 59$ mV) for one electron redox system. The electrochemical data of these complexes are given in Table 10.

**Table 10. Electrochemical data of the complexes**

<table>
<thead>
<tr>
<th>Complex</th>
<th>$E_{pc}$ (V)</th>
<th>$E_{1/2}$ (mV)</th>
<th>$\Delta E_p$ (mV)</th>
<th>$E_{pa}$ (V)</th>
<th>$E_{1/2}$ (mV)</th>
<th>$\Delta E_p$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Co}^{III}\text{Sn}^{IV}]^{2+}$</td>
<td>+0.272</td>
<td>229</td>
<td>43</td>
<td>-1.10</td>
<td>825</td>
<td>275</td>
</tr>
<tr>
<td>$[\text{Cu}^{II}\text{Sn}^{IV}]^{+}$</td>
<td>+0.078</td>
<td>22</td>
<td>56</td>
<td>-0.30</td>
<td>258</td>
<td>42</td>
</tr>
</tbody>
</table>
Kinetic studies

The UV-Vis. spectral change gave kinetic data of cobalt(II) complex. To study the kinetics, the complex was dissolved in DMSO at room temperature (20-25 °C) under constant dioxygen pressure with varying concentrations of oxygen (1 x 10⁻³ to 5 x 10⁻³) mol⁻¹ dm⁻³. The successive dioxygenation reaction was monitored spectrophotometrically by gauging the absorbance at 660 nm. A plot of the rate constant $k_{obs}$ versus $[O_2]$ gave a straight line through an intercept as shown in Fig. 28.
Fig 29 and Fig. 30. The rate law which can be applied is as follows:

\[ k_{\text{obs}} = k_1 [O_2] + k_1 \]

\[ \text{CoL} + O_2 \xrightarrow{k_{\text{on}}/k_{\text{off}}} \text{CoL}[O_2] \]

\[ \frac{d[\text{CoL}]}{dt} = k_{\text{obs}} [\text{CoL}] \]

\[ k_{\text{obs}} = k_{\text{on}} [O_2] + k_{\text{off}} \]

For the simple reversible \( O_2 \) binding reaction, the observed rate constant depends on both the rate constant for binding and the rate constant for dissociation \([k_{\text{on}} \text{ and } k_{\text{off}}]\). The Pseudo-first order condition was monitored by taking a large excess of oxygen over complex \([C_{15}H_{23}N_4O_2SnCo]Cl\). The Pseudo-first order rate constants were calculated up to 80% completion of the reaction. The value of regression coefficient \([r > 0.9996]\). Since the intercepts of these plots are close to zero and therefore fail to yield precise values for \( k_{\text{off}} \). This clearly indicates that \( k_{\text{on}} [O_2] \gg k_{\text{off}} \) and oxygenated complex is the predominant species in the reaction. However, at higher temperatures, partial autoxidation of the complex was observed during monitoring the procedure. On the basis of above results and discussion, following mechanism (Scheme 5) has been proposed.\(^{225,226}\)
Fig. 29

\[ \log(A_e/A) \]

\([O_2] = \text{mol}^{-1} \text{dm}^{-3}\]

(Time in min.)

Fig. 30

\(10^2 K_{obs} \text{ (s}^{-1}\)
$S = \text{Solvent}$

$X = \text{C}_9\text{H}_8\text{N}$

$R = \text{CH}_3$

**Scheme 5**
Table 5. Physical, analytical data, [α] and conductivity measurements of the complexes

| Complex                  | M.P. (°C) | [α]  | Yield (%) | Found (Calcd.) | Λ *  
|--------------------------|-----------|------|-----------|----------------|------
<p>| C_{15}H_{23}N_{4}O_{2}SnCrCl_{2} | 160-163   | 12.9 | 70        | 33.84 4.32 10.50 | 0    |
|                          |           |      |           | (33.85) (4.33) (10.53) |      |
| C_{15}H_{23}N_{4}O_{2}SnMnCl | 300-305   | 13.5 | 72        | 35.98 4.58 11.19 | 62   |
|                          |           |      |           | (35.99) (4.59) (11.20) |      |
| C_{15}H_{23}N_{4}O_{2}SnFeCl_{2} | 150-153   | 14.2 | 75        | 33.59 4.27 10.44 | 0    |
|                          |           |      |           | (33.61) (4.29) (10.46) |      |
| C_{15}H_{23}N_{4}O_{2}SnCoCl | 163-165   | 13.0 | 74        | 35.69 4.54 11.09 | 60   |
|                          |           |      |           | (35.70) (4.56) (11.11) |      |
| C_{15}H_{23}N_{4}O_{2}SnNiCl | 242-245   | 12.5 | 79        | 35.70 4.54 11.09 | 58   |
|                          |           |      |           | (35.72) (4.56) (11.11) |      |
| C_{15}H_{23}N_{4}O_{2}SnCuCl | 182-185   | 13.8 | 73        | 35.36 4.49 11.00 | 63   |
|                          |           |      |           | (35.38) (4.52) (11.01) |      |</p>
<table>
<thead>
<tr>
<th>Complex</th>
<th>M.P. (°C)</th>
<th>[α]</th>
<th>Yield (%)</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>Ω⁻¹ cm² mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₈H₂₂N₃O₂SnCrCl₂</td>
<td>180-183</td>
<td>15.8</td>
<td>74</td>
<td>24.27</td>
<td>4.94</td>
<td>9.43</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(24.29)</td>
<td>(4.95)</td>
<td>(9.44)</td>
<td></td>
</tr>
<tr>
<td>C₈H₂₂N₃O₂SnMnCl</td>
<td>165-168</td>
<td>16.7</td>
<td>76</td>
<td>26.11</td>
<td>5.29</td>
<td>10.15</td>
<td>62</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(26.12)</td>
<td>(5.32)</td>
<td>(10.16)</td>
<td></td>
</tr>
<tr>
<td>C₈H₂₂N₃O₂SnFeCl₂</td>
<td>182-185</td>
<td>17.1</td>
<td>71</td>
<td>24.06</td>
<td>4.90</td>
<td>9.35</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(24.07)</td>
<td>(4.91)</td>
<td>(9.36)</td>
<td></td>
</tr>
<tr>
<td>C₈H₂₂N₃O₂SnCoCl</td>
<td>300-303</td>
<td>16.3</td>
<td>75</td>
<td>25.87</td>
<td>5.25</td>
<td>10.05</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(25.89)</td>
<td>(5.27)</td>
<td>(10.07)</td>
<td></td>
</tr>
<tr>
<td>C₈H₂₂N₃O₂SnNiCl</td>
<td>310-313</td>
<td>18.0</td>
<td>74</td>
<td>25.90</td>
<td>5.27</td>
<td>10.05</td>
<td>64</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(25.91)</td>
<td>(5.28)</td>
<td>(10.07)</td>
<td></td>
</tr>
<tr>
<td>C₈H₂₂N₃O₂SnCuCl</td>
<td>305-307</td>
<td>19.3</td>
<td>72</td>
<td>26.60</td>
<td>5.19</td>
<td>9.94</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(25.61)</td>
<td>(5.22)</td>
<td>(9.96)</td>
<td></td>
</tr>
</tbody>
</table>
Table 6- IR spectra of the complexes (cm⁻¹)

<table>
<thead>
<tr>
<th>Complex</th>
<th>δ(N-H)</th>
<th>ν(C-O)</th>
<th>ν(C=O)</th>
<th>ν(M–N)</th>
<th>ν(M-O)</th>
<th>ν(Sn-N)</th>
<th>ν(M-Cl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( C_{15}H_{23}N_4O_2SnCrCl_2 )</td>
<td>1247</td>
<td>1357</td>
<td>1625</td>
<td>420</td>
<td>460</td>
<td>410</td>
<td>418</td>
</tr>
<tr>
<td>( C_{15}H_{23}N_4O_2SnMnCl )</td>
<td>1246</td>
<td>1363</td>
<td>1631</td>
<td>470</td>
<td>374</td>
<td>420</td>
<td>-</td>
</tr>
<tr>
<td>( C_{15}H_{23}N_4O_2SnFeCl_2 )</td>
<td>1248</td>
<td>1356</td>
<td>1630</td>
<td>245</td>
<td>419</td>
<td>419</td>
<td>365</td>
</tr>
<tr>
<td>( C_{15}H_{23}N_4O_2SnCoCl )</td>
<td>1245</td>
<td>1366</td>
<td>1632</td>
<td>440</td>
<td>356</td>
<td>421</td>
<td>-</td>
</tr>
<tr>
<td>( C_{15}H_{23}N_4O_2SnNiCl )</td>
<td>1246</td>
<td>1364</td>
<td>1626</td>
<td>430</td>
<td>385</td>
<td>420</td>
<td>-</td>
</tr>
<tr>
<td>( C_{15}H_{23}N_4O_2SnCuCl )</td>
<td>1249</td>
<td>1358</td>
<td>1629</td>
<td>450</td>
<td>390</td>
<td>417</td>
<td>-</td>
</tr>
<tr>
<td>Complex</td>
<td>$\delta$(N-H)</td>
<td>$\nu$(C-O)</td>
<td>$\nu$(C=O)</td>
<td>$\nu$(M-N)</td>
<td>$\nu$(M-O)</td>
<td>$\nu$(Sn-N)</td>
<td>$\nu$(M-Cl)</td>
</tr>
<tr>
<td>------------------------</td>
<td>---------------</td>
<td>-------------</td>
<td>-------------</td>
<td>-------------</td>
<td>-------------</td>
<td>--------------</td>
<td>--------------</td>
</tr>
<tr>
<td>($\text{Ar}$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{C}<em>9\text{H}</em>{12}\text{N}_3\text{O}_2\text{SnCrCl}_2$</td>
<td>1248</td>
<td>1356</td>
<td>1624</td>
<td>430</td>
<td>450</td>
<td>420</td>
<td>420</td>
</tr>
<tr>
<td>$\text{C}<em>9\text{H}</em>{12}\text{N}_3\text{O}_2\text{SnMnCl}$</td>
<td>1247</td>
<td>1367</td>
<td>1630</td>
<td>460</td>
<td>375</td>
<td>410</td>
<td>-</td>
</tr>
<tr>
<td>$\text{C}<em>9\text{H}</em>{12}\text{N}_3\text{O}_2\text{SnFeCl}_2$</td>
<td>1241</td>
<td>1358</td>
<td>1632</td>
<td>250</td>
<td>419</td>
<td>419</td>
<td>370</td>
</tr>
<tr>
<td>$\text{C}<em>9\text{H}</em>{12}\text{N}_3\text{O}_2\text{SnCoCl}$</td>
<td>1244</td>
<td>1361</td>
<td>1634</td>
<td>450</td>
<td>357</td>
<td>420</td>
<td>-</td>
</tr>
<tr>
<td>$\text{C}<em>9\text{H}</em>{12}\text{N}_3\text{O}_2\text{SnNiCl}$</td>
<td>1245</td>
<td>1363</td>
<td>1627</td>
<td>440</td>
<td>390</td>
<td>430</td>
<td>-</td>
</tr>
<tr>
<td>$\text{C}<em>9\text{H}</em>{12}\text{N}_3\text{O}_2\text{SnCuCl}$</td>
<td>1246</td>
<td>1352</td>
<td>1628</td>
<td>450</td>
<td>380</td>
<td>417</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 7- $^1$H NMR of the complexes (ppm)

<table>
<thead>
<tr>
<th>Complex</th>
<th>Aryl</th>
<th>-NH-C=C-</th>
<th>-CH=C-</th>
<th>-CH$_2$-</th>
<th>-CH-</th>
<th>-NH-</th>
<th>-CH$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[C_{15}H_{23}N_4O_2SnCo]^{2+}$</td>
<td>7.0-7.6</td>
<td>7.3, 7.4</td>
<td>7.20</td>
<td>3.5, 3.8</td>
<td>5.0-5.8</td>
<td>6.9-7.0</td>
<td>1.0</td>
</tr>
<tr>
<td>$[C_{15}H_{23}N_4O_2SnNi]^+$</td>
<td>7.1-7.7</td>
<td>7.2, 7.5</td>
<td>7.17</td>
<td>3.2, 3.9</td>
<td>5.2-5.7</td>
<td>6.7-7.1</td>
<td>0.8</td>
</tr>
<tr>
<td>$[C_9H_{22}N_3O_2SnCo]^{2+}$</td>
<td>7.0-7.5</td>
<td>7.3, 7.5</td>
<td>7.12</td>
<td>3.3, 3.8</td>
<td>5.1-5.8</td>
<td>6.9-7.1</td>
<td>1.0</td>
</tr>
<tr>
<td>$[C_9H_{22}N_3O_2SnNi]^+$</td>
<td>7.0-7.6</td>
<td>7.3, 7.4</td>
<td>7.18</td>
<td>3.5, 3.8</td>
<td>5.0-5.8</td>
<td>6.9-7.0</td>
<td>0.9</td>
</tr>
<tr>
<td>Complex</td>
<td>Ar</td>
<td>HN-CH=</td>
<td>Ar-C=</td>
<td>CH₂</td>
<td>-CH-</td>
<td>O-C=O</td>
<td>-CH₃</td>
</tr>
<tr>
<td>-------------------------</td>
<td>--------</td>
<td>--------</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
<td>------</td>
</tr>
<tr>
<td>([C_{15}H_{23}N_{4}O_{2}SnCo])⁺⁺</td>
<td>118-124</td>
<td>111.6</td>
<td>108.2</td>
<td>39.7</td>
<td>54.9</td>
<td>170.6</td>
<td>7.3</td>
</tr>
<tr>
<td>([C_{15}H_{23}N_{4}O_{2}SnNi])⁺</td>
<td>115-123</td>
<td>111.5</td>
<td>108.1</td>
<td>39.6</td>
<td>54.7</td>
<td>170.4</td>
<td>7.7</td>
</tr>
<tr>
<td>([C_{9}H_{22}N_{3}O_{2}SnCo])⁺⁺</td>
<td>116-125</td>
<td>111.3</td>
<td>108.4</td>
<td>39.8</td>
<td>54.8</td>
<td>170.3</td>
<td>7.9</td>
</tr>
<tr>
<td>([C_{9}H_{22}N_{3}O_{2}SnNi])⁺</td>
<td>116-124</td>
<td>111.8</td>
<td>108.9</td>
<td>39.1</td>
<td>54.4</td>
<td>170.1</td>
<td>7.4</td>
</tr>
</tbody>
</table>
Table 9- $^1$H NMR assignment of the complex $[C_{15}H_{23}N_4O_2SnCo]^{++}$ and correlations with 2D COSY NMR spectra in DMSO.

<table>
<thead>
<tr>
<th>Protons</th>
<th>(ppm)</th>
<th>COSY correlations (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-CH$_3$ (A)</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>-N-CH$_2$-CH$_2$-N- (B)</td>
<td>2.4-2.8</td>
<td>2.2-2.9</td>
</tr>
<tr>
<td>-CH$_2$- (C)</td>
<td>3.5, 3.8</td>
<td>3.5, 3.8</td>
</tr>
<tr>
<td>-CH- (D)</td>
<td>5.0-5.8</td>
<td>4.4-5.9</td>
</tr>
<tr>
<td>Aryl protons (E)</td>
<td>7.0-7.6</td>
<td>7.2-7.5</td>
</tr>
<tr>
<td>-NH-C=C- (E)</td>
<td>7.3, 7.4</td>
<td>7.1, 7.2</td>
</tr>
<tr>
<td>-CH=C- (E)</td>
<td>7.2</td>
<td>7.2</td>
</tr>
<tr>
<td>-NH- (E)</td>
<td>6.9-7.0</td>
<td>7.1-7.2</td>
</tr>
</tbody>
</table>
CHAPTER - V(A)

Interaction of a new cobalt(II) complex of 5-coordinated chiral porphyrin with calf thymus DNA
CHAPTER - V(A)

Experimental

Pyrrole (Merck), benzaldehyde, CoCl₂·6H₂O (BDH) and L-tryptophan (Sisco research lab pvt. ltd.) were used as received. Microanalysis of the complex was obtained on a Carlo Erba Analyzer Model 1106. IR spectra (200-4000 cm⁻¹) were recorded on a Carl-Ziess specord M-80 spectrophotometer in nujol mulls. The electronic spectra were recorded on a Systronic 119 spectrophotometer. The NMR spectra were recorded on an amx-500 instrument. The optical rotation of the complexes were recorded on ASI, India polarimeter.

Cyclic measurements were carried out on a CH instruments electrochemical analyzer. High purity, H₂O/MeOH (95:5) solvent was employed for the CV studies with 0.4 M KNO₃ as supporting electrolyte. A three electrode configuration was used comprising a Platinum wire counter electrode and Ag/AgCl reference electrode. Experiments were carried out at room temperature.

Tetraphenylporphyrin [H₂TPP]

A solution of benzaldehyde (0.106 g, 1 mmol) and glacial acetic acid (2:1) was kept under reflux for ca. 1 h. Pyrrole (0.067 g, 1 mmol) was then slowly added to this boiling solution. The resulting dark solution was again refluxed for 30 min. A crystalline black precipitate
was isolated by separating the mixture in diethyl ether and chloroform with the help of separating funnel. The crystalline black product (mixture) was further purified by column chromatography. The mixture was chromatographed successively twice on silica gel columns. Different fractions were obtained and the major product was characterized by various physico-chemical methods.

**Tetraphenylporphyrin cobalt(II) complex [(TPP)Co]**

\([\text{H}_2\text{TPP}] \) (0.614 g, 1 mmol) and \(\text{CoCl}_2\cdot6\text{H}_2\text{O} \) (0.237 g, 1 mmol) were heated to reflux for ca. 6 h in (1:1) molar ratio in methanol (30 mL). The resulting solution was further concentrated to ca. 10 mL and allowed to cool overnight in refrigeration. A cream precipitate was obtained after filtration and washed thoroughly with hexane and dried in vacuo.

\([(\text{TPP})\text{Co(Trp)}]\)

To a heated solution of l-tryptophan (0.214 g, 1 mmol) in methanol (20 mL) was added \([(\text{TPP})\text{Co}] \) (0.828 g, 1 mmol) also in methanol (10 mL). The mixture was refluxed for ca. 8 h. A green precipitate was obtained after refrigeration overnight which was filtered off, washed thoroughly with hexane and dried in vacuo. (Fig. 31). M.P. - 108±3, \([\alpha]\) - 11.25, Found: C, 75.43;
L-tryptophan (0.214 g, 1 mmol) and [(TPP)Ni] (0.671 g, 1 mmol) were mixed together in methanol (20 mL). The resulting solution was refluxed for ca. 10 h. A green colour precipitate was obtained after refrigeration overnight which was filtered off in vacuum, washed thoroughly with hexane and dried in vacuo. M.p. = 92±3, [α] - 12.5, Found : C, 75.42; H, 4.56; N, 9.59. C_{55}H_{40}N_{6}O_{2}Ni calcd.: C, 75.43; H, 4.57; N, 9.60%.

Fig. 31
Results and discussion

IR spectra

On the basis of analytical data, the complex was formulated as [(TPP)Co(Trp)] where TPP = tetraphenyl porphyrin and Trp = l-tryptophan. The IR spectra of the free amino acids show two bands in the 1610-1660 cm\(^{-1}\) and 1395-1430 cm\(^{-1}\) regions, corresponding to the antisymmetric and symmetric (COO\(^{−}\)) stretching vibrations, respectively. The shift in the frequencies of these bands on complexation clearly indicates the involvement of carboxylate group of the tryptophan in chiral porphyrin complex formation. The IR spectra of the complex, displays a band at 1593 cm\(^{-1}\) due to antisymmetric COO\(^{−}\) stretching vibration which is overlapped by the high intensity band of the -C=C- stretching vibration observed in the 1480-1620 cm\(^{-1}\) region.\(^{20}\) The appearance of the symmetric COO\(^{−}\) stretching band at 1352 cm\(^{-1}\) is due to coordination of the carboxyl group of the tryptophan moiety to the metal ion. This is further confirmed by \(^1\)H NMR spectrum of the analogue [Ni] derivative of the chiral porphyrin, where a singlet appears at 11.00 p.p.m due to the carboxylic group of tryptophan which clearly indicates that carboxyl oxygen of the tryptophan is coordinated to the metal ion.\(^{216}\) Furthermore, the appearance of a band at 356 cm\(^{-1}\) of v(Co-O)
confirms the coordination of tryptophan to the chiroporphyrin through oxygen. On the basis of IR spectral results, we propose the five coordinated mode of chiral porphyrin as shown in Fig. 31.

**NMR spectra**

$^1$H and $^{13}$C NMR spectra of the analogue [Ni] derivative of chiroporphyrin are given in Tables 11 and 12 respectively. On the basis of $^1$H NMR, complete resonance assignments have been carried out for the complex [(TPP)Ni(Trp)] using 2D COSY NMR technique (Fig. 32). In the $^1$H NMR spectra of the complex [(TPP)Ni(Trp)] a singlet has been observed at 11.0 ppm which may be assigned to the (-COOH) carboxylic acid group proton confirming the presence of -COOH proton. A singlet has also been observed at 10.9 ppm in the corresponding 2D COSY NMR spectra. A doublet has been observed at 5.3, 5.4 ppm due to the (-NH$_2$) group of the amino acid moiety. All the phenyl protons and pyrrole protons has been observed in the 7.3-8.0 ppm and 7.5-8.0 ppm range respectively. A multiplet has been observed in the 5.3-5.5 ppm range which may be assigned to the -CH- protons. A doublet has been observed due to -CH$_2$- protons of the amino acid group of the complex.
Redox behavior

Cyclic voltammetric studies support the UV spectral results and also provide insight into the mode of calf thymus DNA binding to the complex [(TPP)Co(Trp)]. The cyclic voltammogram of [(TPP)Co] in THF at scan rate 0.1 V/s show reversible process at $E_{1/2} = -0.85$ and -1.86 V. The cyclic voltammogram recorded for the [(TPP)Co(Trp)] complex (Fig. 33) in H$_2$O/MeOH (95:5) reveals two reversible half waves and a one electron transfer reaction Co(II)/Co(I) with $E_p$ values at 0.713 V and -0.400 V at a scan rate of 0.1 V/s, respectively. The profile of the voltammogram obtained at variable scan rates (Fig. 34 a, b, c) is almost similar showing two reversible half waves, however as the scan rate increases, the peak become more sharp proving the reversibility of the process. For a reversible wave $E_p$ is independent of scan rate and $i_p$ (as well as the current at any point of the wave) is proportional to $V^{1/2}$. On addition of calf thymus DNA, the complex experiences a negative shift in $E_{1/2}$ of 32 and 99 mV respectively (Fig. 35) and a decrease in $E_p$ 103 mV at the scan rate of 0.1 V/s. For the [(TPP)Co(Trp)] complex the ratio of cathodic to anodic peak currents $i_p^c/i_p^a$ is 1.46 while for the DNA bound complex the
Fig. 33

Potential / V

Current / 1e-5A

Fig. 34

Potential / V

Current / 1e-5A
cathodic to anodic peak currents $i_{pc}/i_{pa}$ is $< 1(0.29)$ suggesting that the DNA moiety is bound strongly to the complex. In addition to changes in the formal potential, the voltammetric peak currents decrease upon addition of calf thymus DNA to the complex. The decrease in current is due to diffusion of an equilibrium mixture of free and DNA-bound metal complex to the electrode surface. ²³⁶
Absorption spectra

Fig. 36 shows the electronic spectrum of the complex [(TPP)Co(Trp)] at \( c = 2.2 \times 10^{-4} \text{ g/cm}^3 \), \( c = \text{complex concentration} \). A characteristic soret band at 23202 cm\(^{-1}\) in the absence of calf thymus DNA is observed in the complex and is attributed to metal ligand charge transfer (MLCT). During the interaction of the complex with calf thymus DNA, this band completely disappears and a newly formed soret band appears at 23095 cm\(^{-1}\) showing large hypochromicity. In the visible region, a single band which appears at 18484 cm\(^{-1}\) in the complex (Fig. 36) disappears after interaction with calf thymus DNA. The effect on the visible spectrum by adding a large excess of DNA with time is shown in Fig. 37. The extent of hypochromism in the visible and soret bands show strong intercalative binding. Two isobestic points at 24272 cm\(^{-1}\) and 22472 cm\(^{-1}\) have been observed when different concentrations of calf thymus DNA were added. The rate constant \( k = -1.5 \times 10^{-2} \) has been calculated at \( c = 2.4 \times 10^{-4} \text{ g/cm}^3 \) where \( c \) is the concentration of [(TPP)Co(Trp)].
Fig. 36 - Electronic spectra of the complex [(TPP)Co(Trp)] in the absence of DNA at \( c = 2.4 \times 10^{-4} \text{ g/cm}^3 \).

Fig. 37- Electronic spectra of the complex [(TPP)Co(Trp)] in presence of DNA with respect to the time at \( c = 2.4 \times 10^{-4} \text{ g/cm}^3 \).
Kinetic studies

Kinetic experiments were monitored spectrophotometrically at room temperature. The rate constant \( k_{\text{obs}} = -1.5 \times 10^{-2} \) was calculated at varying concentrations (1 \( \times \) \( 10^{-7} \) to 9 \( \times \) \( 10^{-7} \)) of calf thymus DNA and the plot of \( k_{\text{obs}} \) versus calf thymus DNA is linear passing through the origin (Fig. 38) suggesting the pseudo-first order rate law.

\[
k_{\text{obs}} = \frac{k_1 k_2 [\text{DNA}]}{(k_1 + k_2)}
\]

Fig. 38
Our results are consistent with equation (1) which clearly shows the linearity of the plot with slope = $k_1k_2/k_{-1} + k_2$. On the basis of the above results following mechanism is proposed (Scheme 6).

\[
\frac{+ \text{DNA} + \text{H}_2\text{O}}{k_1 \rightleftharpoons k_{-1}} \xrightarrow{k_2} \\
\text{Scheme 6}
\]

$\text{H}_2\text{O}$

$\text{Co}$

$\text{DNA}$

$\text{OH}$

$\text{O} = \text{C} \rightleftharpoons \text{N}$

$\text{O} = \text{C} \rightleftharpoons \text{N}$

$\text{OH}$

$\text{C}_{10}\text{H}_{11}\text{N}_2$
Table 11 - $^1$H NMR assignments of the complex [(TPP)Ni(Trp)] and correlations with 2D COSY NMR spectra (ppm)

<table>
<thead>
<tr>
<th>Protons</th>
<th>$^1$H NMR</th>
<th>COSY correlations</th>
</tr>
</thead>
<tbody>
<tr>
<td>-CH$_2$-</td>
<td>3.3, 3.7</td>
<td>3.5, 3.9</td>
</tr>
<tr>
<td>-CH-</td>
<td>5.3-5.5</td>
<td>5.3-5.5</td>
</tr>
<tr>
<td>-NH-C=C-</td>
<td>7.1, 7.3</td>
<td>7.0, 7.1</td>
</tr>
<tr>
<td>-CH=C-</td>
<td>7.2</td>
<td>7.3</td>
</tr>
<tr>
<td>(Pyrrole protons)</td>
<td>7.5-8.0</td>
<td>7.5-8.0</td>
</tr>
<tr>
<td>-CO$_2$H</td>
<td>11.0</td>
<td>10.9</td>
</tr>
<tr>
<td>-NH$_2$</td>
<td>5.3, 5.4</td>
<td>5.3, 5.4</td>
</tr>
<tr>
<td>-C$_6$H$_5$</td>
<td>7.3-8.0</td>
<td>7.3-7.7</td>
</tr>
<tr>
<td>Carbons</td>
<td>$^{13}$C NMR</td>
<td></td>
</tr>
<tr>
<td>---------------</td>
<td>------------</td>
<td></td>
</tr>
<tr>
<td>Phenyl carbons</td>
<td>118.1-130.9</td>
<td></td>
</tr>
<tr>
<td>COOH</td>
<td>167.2</td>
<td></td>
</tr>
<tr>
<td>-CH-</td>
<td>54.3</td>
<td></td>
</tr>
<tr>
<td>-CH$_2$-</td>
<td>38.2</td>
<td></td>
</tr>
<tr>
<td>Ar-C=</td>
<td>108.6</td>
<td></td>
</tr>
<tr>
<td>NH-CH=</td>
<td>111.2</td>
<td></td>
</tr>
<tr>
<td>Pyrrole C $\alpha$</td>
<td>132.7</td>
<td></td>
</tr>
<tr>
<td>Pyrrole C $\beta$</td>
<td>145.1</td>
<td></td>
</tr>
</tbody>
</table>
CHAPTER - V(B)

Synthesis of new organotin-linked porphyrin dimers: Electrochemical studies and dioxygen binding to Co(II) porphyrin array.
CHAPTER V (B)

Experimental

Pyrrole (Merck), benzaldehyde, CoCl$_2$$\cdot$6H$_2$O, NiCl$_2$$\cdot$6H$_2$O, CuCl$_2$$\cdot$2H$_2$O, ZnCl$_2$ (BDH), (CH$_3$)$_2$SnCl$_2$ (Fluka) and 1-tryptophan (Sisco research lab pvt. ltd.) were used as received. Microanalysis of the complexes were obtained on a Carlo Erba Analyzer Model 1106. IR spectra (200-4000 cm$^{-1}$) were recorded on a Carl-Ziess specord M-80 spectrophotometer in nujol mulls. The electronic spectra were recorded on a Systronic 119 spectrophotometer. The NMR spectra were recorded on an amx-500 instrument. The optical rotation of the complexes were recorded on ASI, India polarimeter.

Cyclic measurements were carried out on a CH instruments electrochemical analyzer. High purity, aqueous MeOH (95:5) solvent was employed for the CV studies with 0.4 M KNO$_3$ as a supporting electrolyte. A three electrode configuration was used comprising platinum wire counter electrode and Ag/AgCl reference electrode. Experiments were carried out at room temperature.

Kinetic experiments were performed under pseudo-first order conditions using a Systronic 119 spectrophotometer. The progress of the reaction was monitored by measuring absorbance changes at 428 nm ($\lambda_{\text{max}}$ of Co$^{II}$) under varying concentrations of oxygen (1 x 10$^{-3}$ to 5 x 10$^{-3}$) mol$^{-1}$ dm$^{-3}$. Pseudo-first order rate constants $k_{\text{obs}}$ were obtained by linear least square regression method.
Tetraphenyl porphyrin [H₂TPP]

The synthesis of tetraphenyl porphyrin [H₂TPP] was carried out by the method described earlier [Chapter V(A)- page 81]

Tetraphenyl porphyrin metal(II) complexes [(TPP)M] where M = Co(II), Ni(II), Cu(II) and Zn(II).

[H₂TPP] (0.614 g, 1 mmol) and CoCl₂.6H₂O (0.237 g, 1 mmol) were heated to reflux for ca. 6 h in (1:1) molar ratio in methanol (30 mL ). The resulting solution was further concentrated to ca. 10 mL and allowed to cool overnight in refrigeration. A cream precipitate was obtained and washed thoroughly with hexane in vacuo.

A similar procedure was also adopted for the Ni(II), Cu(II) and Zn(II) complexes.

[(TPP)Co(Trp)] where Trp = l-tryptophan

To a heated solution of l-tryptophan (0.214 g, 1 mmol) in methanol (20 mL) was added [(TPP)Co] ( 0.671 g, 1 mmol ) in methanol (10 mL ). A green precipitate was obtained after refluxing the solution for few hours and then allowed to cool in refrigeration. The precipitate was then filtered off, washed thoroughly with hexane and dried in vacuo.
L-tryptophan (0.214 g, 1 mmol) was dissolved in methanol (20 mL) after heating and [(TPP)Ni] (0.671 g, 1 mmol) in methanol (10 mL) was added to the above solution. Then the solution was refluxed for few hours and kept in refrigeration for ca. 24 h. A light green colour precipitate was obtained, washed thoroughly with hexane and dried in vacuo.

[(TPP)Cu(Trp)]

A heated solution of L-tryptophan (0.214 g, 1 mmol) and [(TPP)Cu] (0.675 g, 1 mmol) in methanol (20 mL) were mixed together and refluxed for few hours. A dark green colour precipitate was obtained after keeping the solution in refrigeration overnight which was washed thoroughly with hexane and dried in vacuo.

[(TPP)Zn(Trp)]

To a methanolic solution (20 mL) was added [(TPP)Zn] (0.667 g, 1 mmol) in methanol (10 mL). The resulting solution was refluxed for few hours and kept overnight in refrigeration, washed thoroughly with hexane and dried in vacuo.
\[ \{\text{(TPP)Co(Trp)\rangle}_2\text{Sn(CH}_3\text{)}_2\} \]

\[ \{\text{(TPP)Co(Trp)\rangle}_2\text{Sn(CH}_3\text{)}_2\} \] was prepared by adding a solution of \[(\text{TPP)Co(Trp)\rangle}\] (0.087g, 0.1mmol) in methanol (20 mL) to a solution of \((\text{CH}_3\text{)}_2\text{SnCl}_2\) (0.011g, 0.05 mmol) in methanol (10 mL). The resulting solution was refluxed for ca. 8 h. A light green precipitate was obtained after refrigeration for few hours which was filtered off in vacuum, washed thoroughly with hexane and dried in vacuo. (Fig. 39).

\[ \{\text{(TPP)Zn(Trp)\rangle}_2\text{Sn(CH}_3\text{)}_2\} \]

\[ \{\text{(TPP)Zn(Trp)\rangle}_2\text{Sn(CH}_3\text{)}_2\} \] were mixed together in methanol (20 mL) in 1:2 molar ratio. The resulting solution was refluxed for ca. 8 h. A brown colour precipitate was obtained after refrigeration for few hours which was filtered in vacuum, washed with hexane and dried in vacuo. (Table 13).
$M = \text{Co and Zn}$
$R = \text{C}_6\text{H}_5$
$R' = \text{C}_9\text{H}_8\text{N}$

Fig. 39
Results and discussion

IR spectra

The physical and analytical data of the complexes are given in Table 13. On the basis of analytical data, the monometallic complexes were formulated as \([(\text{TPP})M(\text{Trp})]\) where \(\text{TPP} = \text{tetraphenyl porphyrin}, \ M = \text{Co(II), Ni(II), Cu(II) and Zn(II)} \) and \(\text{Trp} = \text{l-tryptophan and }\) \(\left[\left(\text{TPP})M(\text{Trp})\right)_2\text{M'}\right]\) where \(M = \text{Co(II) and Zn(II)}\) and \(M' = \text{dimethyl tin(IV)}\). The IR spectra (Table 14) of all the complexes show a broad band in the 2900-3388 cm\(^{-1}\) range ascribed to the stretching vibration of the free -NH\(_2\) group suggests that -NH\(_2\) moiety of the l-tryptophan has not taken part in the reaction. The IR spectra of the free amino acid show two bands in the region 1610-1660 cm\(^{-1}\) and 1395-1430 cm\(^{-1}\) corresponding to the antisymmetric and symmetric (COO\(^-\)) stretching vibrations, respectively. The shift in the frequencies of these bands on complexation clearly indicate the involvement of carboxylate group of the tryptophan in the formation of chiral porphyrin. The IR spectra of all the complexes display a band at 1590-1620 cm\(^{-1}\) range due to antisymmetric COO\(^-\) stretching vibration which is overlapped by the high intensity band of the -C=\(\text{C-}\) stretching vibration observed in the region 1480-1620 cm\(^{-1}\). \(^{240}\) The appearance of symmetric COO\(^-\) stretching band at 1320-1353 cm\(^{-1}\) region is due to the coordination of the carboxyl group of the tryptophan moiety to the metal ion. This contention
is further confirmed by the appearance of a band in the region
356-390 cm$^{-1}$ due to $\nu$(M-O) stretching vibration confirms the coordination
of the tryptophan to the chiroporphyrin through oxygen. In the
$\{(TPP)M(Trp)\}_{2}M^{+}\}$ complexes, a band appears at 462-473 cm$^{-1}$
range which is assigned to the $\nu$(Sn-O) stretching vibration. The
absence of $\nu$(Sn-N) and $\nu$(Sn-Cl) stretching vibrations at 418 cm$^{-1}$ and
220-242 cm$^{-1}$ respectively suggest the coordination mode as shown in
Figure 39.

**Electronic spectra**

The electronic spectra of the porphyrin complex $\{(TPP)Co(Trp)\}_{2}Sn(CH_{3})_{2}\$ exhibit several d-d bands in the visible and near infrared regions, 16949-23753 cm$^{-1}$, characteristic of five-coordinate complexes. On the contrary six coordinate complexes of cobalt(II) show only two d-d bands at ca. 10000 and 20000-22000 cm$^{-1}$.

**NMR spectra**

$^1$H NMR and $^{13}$C NMR spectra of the $\{(TPP)Zn(Trp)\}_{2}Sn(CH_{3})_{2}\$ complex have been given in Table 15 and 16 respectively. On the basis of $^1$H NMR complete resonance assignments have been carried out for the complex $\{(TPP)Zn(Trp)\}_{2}Sn(CH_{3})_{2}\$ using 2D NMR technique (Figure 40) (Table 17).
Electrochemical Properties

The complex [(TPP)Co(Trp)] and [(TPP)Co(Trp)]$_2$Sn(CH$_3$)$_2$ dimer exhibit almost same voltammetric responses in MeOH/H$_2$O (5:95). Fig.41 displays cyclic voltammogram for [(TPP)Co(Trp)] complex revealing two reversible responses at 0.713 V and -0.307 V that can be assigned to the Co(III/II) and Co(II/I) couples, respectively. These assignments have also been evidenced by Kadish for other cobalt porphyrins. Fig.42 shows the cyclic voltammogram for the complex [(TPP)Co(Trp)]$_2$Sn(CH$_3$)$_2$. The results reveal one electron transfer reaction for the Co(III/II) and Co(II/I) redox couples with $E^0$ value at +0.778 V and -0.427 V respectively at the same scan rate. The coordination of O$_2$ by the complex [(TPP)Co(Trp)]$_2$Sn(CH$_3$)$_2$ was followed spectrophotometrically and also by voltammetric experiments in solution. The affinity of the complex [(TPP)Co(Trp)]$_2$Sn(CH$_3$)$_2$ for oxygen binding is enhanced substantially by coordination in the axial coordination site on the porphyrin ring. Upon oxygenation, the voltammetric responses for both Co(III/II) and Co(II/I) couples shift to more negative potential from an initial potential of 0.778V and -0.421V. The changes in the cyclic voltammetry of [(TPP)Co(Trp)]$_2$Sn(CH$_3$)$_2$ dimer in presence of O$_2$ are shown in Fig.43. The responses obtained differ in following
Figure 41

- Initial E (V) = -0.6
- High E (V) = 2.5
- Low E (V) = -0.8
- Initial PIN = P
- Scan Rate (V/s) = 0.1
- Segment = 3
- Scan Interval (V) = 0.001
- Quiet Time (s) = 2
- Sensitivity (A/V) = 5e-6

Figure 42

- Initial E (V) = -0.6
- High E (V) = 4
- Low E (V) = -0.8
- Initial PIN = P
- Scan Rate (V/s) = 0.1
- Segment = 3
- Scan Interval (V) = 0.001
- Quiet Time (s) = 2
- Sensitivity (A/V) = 5e-6
manners:

(i) The oxidation of Co(II) porphyrin occurs over a broad potential -0.371-0.64 V.

(ii) The multiple splitting occurs in the anodic peaks during oxygenation. After the oxygenation is complete that is when the sixth coordination site is fully occupied, a new anodic peak arises at 0.527 V due to oxidation of \([{(TPP)Co^{II}(Trp)}_2Sn(CH_3)_2] \) dimer to \([{(TPP)Co^{III}(Trp)}_2Sn(CH_3)_2] \) dimer. This latter species is responsible for the cathodic peak at -0.476 V (Fig. 44). The voltammogram of oxygenated \([{(TPP)Co(Trp)}_2Sn(CH_3)_2] \) dimer shows a cathodic response at -0.85 V showing the reduction of O₂ to O₂⁻. The voltammetric responses shown in Fig. 44 predict mechanistic 'square scheme' as shown in scheme 7. The assignment of oxidation states to Co and O₂ in the complex is arbitrary Co(II) and O₂ or Co(III) and O₂⁻ but spectral evidence favors Co(III)-O₂⁻ combination or it may be due to partial oxidation of the complex during monitoring the process. Regarding voltammetric responses of coordinated organotin(IV), these are not accessible by the electrode due to chelate formation, though free dimethyl tin(IV) shows voltammetric responses at -0.67 V and -0.456 V. Thus ability of cobalt porphyrin to serve as an electrocatalyst for the reduction of O₂ is explored.
Scheme-7 (Square Scheme)
Kinetic studies

The kinetic studies between \(\{(TPP)Co(Trp)\}_2Sn(CH_3)_2\) and \(O_2\) was monitored spectrophotometrically in methanol at a temperature 20°C under constant dioxygen pressure with varying concentrations of oxygen \((1 \times 10^{-3} - 5 \times 10^{-3}) \text{ mol}^{-1} \text{ dm}^{-3}\). The successive dioxygenation reaction was carried out by gauging the absorbance at 428 nm. The absorbance recorded wavelength versus time under large excess of dioxygen with respect to the complex \(\{(TPP)Co(Trp)\}_2Sn(CH_3)_2\) show spectral changes which correspond to pseudo-first order conditions, the observed rate constants did not depend on the concentrations of cobalt(II) complex and increased linearly with increase in dioxygen concentration (Fig.45 & 46). Linear plots of \(k_{obs}\) versus \([O_2]\) obtained determine the values of both rate constants, \(k_{on}\) and \(k_{off}\) from the slope and intercept, respectively of the straight line. Since the intercepts of these plots are close to 0, and therefore fail to yield precise values for \(k_{off}\). This clearly indicates that oxygenated complex is the predominant species in the reaction mixture \(k_{on}[O_2] \gg k_{off}\). The rate law which holds good is 249 as follows:

\[
\begin{align*}
    k_{obs} &= k_1[O_2] + k_1 \\
    \frac{\text{d}[\text{CoL}]}{\text{dt}} &= k_{obs}[\text{CoL}]
\end{align*}
\]

\(\text{CoL + O}_2 \rightleftharpoons \text{CoL}[O_2]\)
Similar observations were obtained for dioxygen binding in the temperature range from -75 to -40 °C in acetone solvent system for various cobalt complexes. At low temperature, the reactions are slower and autoxidation is retarded whereas in our experimental conditions there may be partial autoxidation due to high temperature. But autoxidation reaction does not interfere with the dioxygen binding process under large excess of O₂ with respect to cobalt(II) complex. Experimental data fitted to a single exponential equation. On the basis of kinetic data, results and discussion, the following mechanisms have been proposed (Scheme 8, 9) (Scheme 9 has been proposed for partial autoxidation).

\[
k_{\text{obs}} = k_{\text{on}}[O_2] + k_{\text{off}}
\]
Figure 45

\[ \log(A - A_i) \]

\[ [O_2] = \text{mol} \cdot \text{dm}^{-3} \]

- 3 \times 10^{-3}
- 1 \times 10^{-3}

Time (sec.)

Figure 46

\[ k_{\text{obs}} (s^{-1}) \]

\[ [O_2]/10^{-3} \text{ mol} \cdot \text{dm}^{-3} \]
Scheme 8
Scheme 9
Table 13. Analytical data of the complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>$[\alpha]$</th>
<th>M.P.</th>
<th>Found (Calcd.)</th>
<th>C</th>
<th>H</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(TPP)Co(Trp)]</td>
<td>11.3</td>
<td>108±3</td>
<td></td>
<td>75.43</td>
<td>4.56</td>
<td>9.59</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(75.44)</td>
<td>(4.57)</td>
<td>(9.60)</td>
<td></td>
</tr>
<tr>
<td>[(TPP)Ni(Trp)]</td>
<td>12.5</td>
<td>92±3</td>
<td></td>
<td>75.42</td>
<td>4.56</td>
<td>9.59</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(75.43)</td>
<td>(4.57)</td>
<td>(9.60)</td>
<td></td>
</tr>
<tr>
<td>[(TPP)Cu(Trp)]</td>
<td>11.0</td>
<td>110±4</td>
<td></td>
<td>75.08</td>
<td>4.54</td>
<td>9.55</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(75.09)</td>
<td>(4.55)</td>
<td>(9.56)</td>
<td></td>
</tr>
<tr>
<td>[(TPP)Zn(Trp)]</td>
<td>12.1</td>
<td>88±5</td>
<td></td>
<td>74.88</td>
<td>4.53</td>
<td>9.52</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(74.89)</td>
<td>(4.54)</td>
<td>(9.53)</td>
<td></td>
</tr>
<tr>
<td>[{(TPP)Co(Trp$^*$)}$_2$Sn(CH$_3$)$_2$]</td>
<td>9.4</td>
<td>80±5</td>
<td></td>
<td>70.73</td>
<td>4.62</td>
<td>8.83</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(70.74)</td>
<td>(4.63)</td>
<td>(8.84)</td>
<td></td>
</tr>
<tr>
<td>[{(TPP)Zn(Trp$^*$)}$_2$Sn(CH$_3$)$_2$]</td>
<td>9.3</td>
<td>60±5</td>
<td></td>
<td>70.25</td>
<td>4.59</td>
<td>8.77</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(70.26)</td>
<td>(4.60)</td>
<td>(8.78)</td>
<td></td>
</tr>
</tbody>
</table>

* deprotonated
<table>
<thead>
<tr>
<th>Complex</th>
<th>ν(C-O)</th>
<th>ν(C=C-O)</th>
<th>ν(M-O)</th>
<th>ν(M-N)</th>
<th>ν(Sn-O)</th>
<th>ν(Sn-C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(TPP)Co(Tri)]</td>
<td>1352</td>
<td>1593</td>
<td>490</td>
<td>356</td>
<td>470</td>
<td>525</td>
</tr>
<tr>
<td>[(TPP)Ni(Tri)]</td>
<td>1351</td>
<td>1590</td>
<td>480</td>
<td>385</td>
<td>465</td>
<td>508</td>
</tr>
<tr>
<td>[(TPP)Cu(Tri)]</td>
<td>1352</td>
<td>1592</td>
<td>495</td>
<td>390</td>
<td>462</td>
<td>543</td>
</tr>
<tr>
<td>[(TPP)Zn(Tri)]</td>
<td>1353</td>
<td>1591</td>
<td>480</td>
<td>376</td>
<td>464</td>
<td>540</td>
</tr>
<tr>
<td>[(TPP)Co(Tri)]₂Sn(CH₃)₂</td>
<td>1320</td>
<td>1618</td>
<td>490</td>
<td>357</td>
<td>472</td>
<td>521</td>
</tr>
<tr>
<td>[(TPP)Zn(Tri)]₂Sn(CH₃)₂</td>
<td>1322</td>
<td>1620</td>
<td>480</td>
<td>375</td>
<td>473</td>
<td>530</td>
</tr>
</tbody>
</table>
Table -15- $^1$H NMR assignments of the [{(TPP)Zn(Trp)}$_2$Sn(CH$_3$)$_2$] complex and correlations with 2D COSY NMR spectra (ppm)

<table>
<thead>
<tr>
<th>Protons</th>
<th>$^1$H NMR</th>
<th>COSY correlations</th>
</tr>
</thead>
<tbody>
<tr>
<td>-CH$_3$</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>-CH$_2$-</td>
<td>3.3,3.7</td>
<td>3.5,3.9</td>
</tr>
<tr>
<td>-CH-</td>
<td>5.3-5.5</td>
<td>5.3-5.5</td>
</tr>
<tr>
<td>-NH-C=C-</td>
<td>7.1,7.3</td>
<td>7.0, 7.1</td>
</tr>
<tr>
<td>-CH=C-</td>
<td>7.2</td>
<td>7.3</td>
</tr>
<tr>
<td>(Pyrrole protons)</td>
<td>7.5-7.6</td>
<td>7.4-7.6</td>
</tr>
<tr>
<td></td>
<td>7.95-7.96</td>
<td>7.94-7.96</td>
</tr>
<tr>
<td>-NH$_2$</td>
<td>5.3, 5.4</td>
<td>5.3, 5.4</td>
</tr>
<tr>
<td>-Ph</td>
<td>7.3-8.0</td>
<td>7.3-7.7</td>
</tr>
<tr>
<td>Carbons</td>
<td>$^{13}$C NMR</td>
<td></td>
</tr>
<tr>
<td>----------------------</td>
<td>---------------</td>
<td></td>
</tr>
<tr>
<td>-CH$_3$</td>
<td>7.1-7.8</td>
<td></td>
</tr>
<tr>
<td>Phenyl carbons</td>
<td>118.1-130.9</td>
<td></td>
</tr>
<tr>
<td>-COO</td>
<td>170.2</td>
<td></td>
</tr>
<tr>
<td>-CH$_2$-</td>
<td>54.3</td>
<td></td>
</tr>
<tr>
<td>-CH$_2$-</td>
<td>38.2</td>
<td></td>
</tr>
<tr>
<td>Ar-C=</td>
<td>108.6</td>
<td></td>
</tr>
<tr>
<td>NH-CH=</td>
<td>111.2</td>
<td></td>
</tr>
<tr>
<td>Pyrrole C $\alpha$</td>
<td>132.7</td>
<td></td>
</tr>
<tr>
<td>Pyrrole C $\beta$</td>
<td>145.1</td>
<td></td>
</tr>
</tbody>
</table>
CHAPTER - VI

Synthesis and characterization of novel chiral organotin complexes.
CHAPTER-VI

Experimental

L-tryptophan, l-valine (sisco research lab.), l-leucine (loba chemie), dibutyl, dimethyl and triphenyltin chlorides (fluka chemical) and 1,10-phenanthroline (BDH) were used as such. The IR spectra (200-4000 cm⁻¹) were recorded on a Carl-Ziess Specord M-80 spectrophotometer in nujol mulls. Microanalysis were obtained on a Carl-Erba Analyzer Model 1106. UV/Vis spectra were run on Systronic 119 spectrophotometer. The NMR spectra were recorded in CDCl₃ on an amx-500. The optical rotation of the complexes were recorded on ASI, India polarimeter.

Synthesis of the complex [C₄H₆N₃O₂Sn]

To a solution of l-tryptophan (0.204 g, 1 mmol) in hot dry methanol (25 mL) was added a solution of 1,10-phenanthroline (0.198 g, 1 mmol) in the same solvent. The resultant mixture was refluxed for 20 h after adding a solution of triphenyltin chloride (0.398 g, 1 mmol) in hot methanol. The mixture was allowed to stand overnight in refrigeration. The solid product obtained was isolated by filtration, washed with ether and dried in vacuo. (Fig. 47)

Synthesis of the complex [C₃H₇N₄O₂SnCl]

To a hot methanolic solution (25 mL) of l-tryptophan (0.204 g, 1 mmol) was
added 1,10-phenanthroline (0.198 g, 1 mmol) in the same solvent (20 mL). A solution of dibutyltin dichloride (0.303 g, 1 mmol) in methanol (10 mL) was added to above mixture. The resulting solution was refluxed for ca. 24 h. A white colour crystalline solid was obtained which was washed thoroughly with ether and dried in vacuo.

**Synthesis of the complex \([\text{C}^{25}\text{H}_{25}\text{N}_4\text{O}_2\text{SnCl}]\)**

The solution of l-tryptophan (0.204 g, 1 mmol) in methanol (25 mL) and 1,10-phenanthroline (0.198 g, 1 mmol) in methanol (10 mL) were taken together. A solution of dimethyltin dichloride (0.219 g, 1 mmol) in methanol (10 mL) was added to the above mixture. The resulting mixture was refluxed for ca. 24 h. The precipitate obtained was filtered off, washed with ether twice and dried in vacuo.

**Synthesis of the complex \([\text{C}_{35}\text{H}_{35}\text{N}_3\text{O}_2\text{Sn}]\)**

The complex was prepared by adding a solution of l-leucine (0.131 g, 1 mmol) in methanol (20 mL) and two/three drops of dimethylamine to the solution of 1,10-phenanthroline (0.198 g, 1 mmol) in methanol. The above mixture was refluxed for ca. 1 h and to this mixture a solution of triphenyltin chloride in hot methanol (20 mL) was added. The solution was refluxed for ca. 30 h. On refrigeration coloured crystalline product was isolated. The crystals were washed with ether and
dried in vacuo.

**Synthesis of the complex \([C_{26}H_{38}N_3O_2SnCl]\)**

L-leucine (0.131 g, 1 mmol) in methanol (20 mL) and two/three drops of dimethyl amine was added to the methanolic solution (10 mL) of 1,10-phenanthroline (0.198 g, 1 mmol). The solution was refluxed for ca. 2 h. To the above solution, dibutyltin dichloride (0.303 g, 1 mmol) in methanol (10 mL) was added in equimolar ratio. The resulting mixture was then refluxed for ca. 32 h. The crystalline product was obtained after keeping the solution in refrigeration for 24 h. The crystals were washed with ether and dried in vacuo.

**Synthesis of the complex \([C_{20}H_{26}N_3O_2SnCl]\)**

L-leucine (0.131 g, 1 mmol) in dry methanol (25 mL) was heated and two/three drops of dimethyl amine were added to the solution. A solution of 1,10-phenanthroline (0.198 g, 1 mmol) in methanol (10 mL) was refluxed with the above solution for ca. 2 h. To the resulting solution, dimethyltin dichloride (0.219 g, 1 mmol) in dry methanol (10 mL) was added and again refluxed for ca. 38 h. The precipitate obtained was filtered off in vacuum, washed with ether and dried in vacuo.

**Synthesis of the complex \([C_{19}H_{24}N_3O_2SnCl]\)**

L-valine (0.117 g, 1 mmol) in methanol (25 mL) with two/three drops of
dimethyl amine was refluxed with 1,10-phenanthroline (0.198 g, 1 mmol) in methanol (10 mL) for ca. 2 h. To the above solution, dimethyl tin dichloride (0.219 g, 1 mmol) in methanol (10 mL) was added and refluxed for ca. 34 h. A white amorphous product obtained was filtered, washed with ether and dried in vacuo. (Table 17)

Fig. 47
Results and Discussion

The complexes were characterized by IR, UV, $^1$H, $^{13}$C, $^{119}$Sn NMR spectroscopy. The l-amino acids exhibit ν(OH) band of the carboxylate group at ca. 3200 cm$^{-1}$. However, the IR spectrum of [C$_{41}$H$_{34}$N$_3$O$_2$Sn] does not show this band indicating the deprotonation of the carboxylic group. This is further supported by appearance of a new medium intensity band in far IR at 460 cm$^{-1}$ attributed to (Sn-O) stretching vibration indicating the coordination of metal through oxygen. No splitting has been observed in the band at ca. 1650 cm$^{-1}$ due to (COO)$_{\text{asym}}$ and (COO)$_{\text{sym}}$ which clearly indicates the monodentate nature of the carboxylate group. ν(C=N) band appears in 1582-1589 cm$^{-1}$ range in all the complexes. The vibrational bands attributed to C-H out of plane bending modes, appearing at 740 and 855 cm$^{-1}$ in the spectrum of free 1,10-phenanthroline are shifted to lower frequency at 725 and 808 cm$^{-1}$ respectively. The electronic spectra of the complex [C$_{41}$H$_{34}$N$_3$O$_2$Sn] was recorded in DMSO. Two prominent peaks observed at 220 and 264 nm in UV region are assigned to π to π* transition due to MLCT. (Table 18)

NMR Spectra

The $^1$H NMR was recorded in CDCl$_3$ on an amx-500 instrument. A doublet was observed in the high field at 3.3, 3.4 ppm due to -CH$_2$ protons of tryptophan in the complex [C$_{41}$H$_{34}$N$_3$O$_2$Sn]. A sharp signal was
observed at 9.1 ppm due to the tryptophan group (-CH-NH-) proton. The phenyl proton signals appear in the range of 7-8 ppm. Proton signals due to 1,10-phenanthroline appear at 7.5-8.5 ppm (Table-19).

Since -COOH proton signal is absent in $^1$H NMR spectra, it confirms the coordination through carbonyl group which is further supported by Sn-O peak in the far IR spectrum. $^{251}$ Our $^1$H NMR data for all other amino acids and organotin derivatives are quite comparable with the results reported earlier. $^{252,253}$

$^{12}$C NMR spectra of the complex $[C_4H_3N_2O_2Sn]$ recorded in CDCl$_3$, exhibit the carboxylic carbon signal at 4.17 ppm (showing upfield shift than the free amino acid) attributed to the monodentate nature of the carboxylic group. The bands due to phenyl carbon attached to tin are observed at 126-128 ppm. The carbons of 1,10-phenanthroline (heterocyclic carbons) are observed at 126, 136 and 145 ppm respectively. On the basis of spectral evidences, it may be inferred that the carboxylic acid of the l-amino acid is behaving as monodentate in these complexes and the complexes are octahedral in shape with a coordination number six around the tin atom.

$^{119}$Sn NMR spectrum of all the complexes have been run in DMSO d$_6$. $^{119}$Sn chemical shift at -280.931 ppm (Fig. 48) indicates that tin is in octahedral environment in the complex $[C_4H_3N_2O_2Sn]$ while the value of tin in the complex $[C_3H_3N_4O_2SnCl]$ is in lower field -260.9 ppm also
indicates the six coordinate geometry around the tin atom. The slightly higher value for the triphenyl complex in comparison to other alkyltin complex may be accounted for the increased polarizability of the phenyl groups and chelate effects. Our results are fully consistent with the six coordinated geometry as reported by Smith et. al. (Table 20).

Fig. 48
<table>
<thead>
<tr>
<th>Complex</th>
<th>M.P.</th>
<th>Yield</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>[%]</th>
<th>[α]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{41}H_{34}N_3O_2Sn$</td>
<td>190-193</td>
<td>72</td>
<td>68.39</td>
<td>4.72</td>
<td>5.82</td>
<td>11+1 in</td>
<td>DMSO</td>
</tr>
<tr>
<td>$C_{31}H_{37}N_4O_2SnCl$</td>
<td>195-198</td>
<td>80</td>
<td>57.08</td>
<td>5.68</td>
<td>8.59</td>
<td>13+1 in</td>
<td>MeOH</td>
</tr>
<tr>
<td>$C_{25}H_{25}N_4O_2SnCl$</td>
<td>230-233</td>
<td>75</td>
<td>52.86</td>
<td>4.39</td>
<td>9.86</td>
<td>12+1 in</td>
<td>MeOH</td>
</tr>
<tr>
<td>$C_{36}H_{35}N_3O_2Sn$</td>
<td>231-233</td>
<td>78</td>
<td>65.46</td>
<td>5.30</td>
<td>6.36</td>
<td>20+1 in</td>
<td>CHCl$_3$</td>
</tr>
<tr>
<td>$C_{26}H_{38}N_3O_2SnCl$</td>
<td>210-212</td>
<td>75</td>
<td>53.95</td>
<td>6.56</td>
<td>7.25</td>
<td>5+1 in</td>
<td>CHCl$_3$</td>
</tr>
<tr>
<td>$C_{20}H_{26}N_3O_2SnCl$</td>
<td>286-289</td>
<td>76</td>
<td>48.55</td>
<td>5.26</td>
<td>8.49</td>
<td>10+1 in</td>
<td>MeOH</td>
</tr>
<tr>
<td>$C_{19}H_{24}N_3O_2SnCl$</td>
<td>335-338</td>
<td>74</td>
<td>47.46</td>
<td>4.99</td>
<td>8.74</td>
<td>12+1 in</td>
<td>CHCl$_3$</td>
</tr>
<tr>
<td>Complex</td>
<td>vC=\text{N}</td>
<td>vCO</td>
<td>vSn-O</td>
<td>vSn-Cl</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------------</td>
<td>-------------</td>
<td>-----</td>
<td>-------</td>
<td>--------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C_{41}H_{34}N_{3}O_{2}Sn</td>
<td>1589</td>
<td>1650</td>
<td>460</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C_{31}H_{37}N_{4}O_{2}SnCl</td>
<td>1584</td>
<td>1630</td>
<td>450</td>
<td>321</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C_{23}H_{23}N_{4}O_{2}SnCl</td>
<td>1586</td>
<td>1620</td>
<td>430</td>
<td>320</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C_{36}H_{35}N_{3}O_{2}Sn</td>
<td>1582</td>
<td>1640</td>
<td>440</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C_{26}H_{38}N_{3}O_{2}SnCl</td>
<td>1586</td>
<td>1620</td>
<td>450</td>
<td>325</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C_{20}H_{24}N_{3}O_{2}SnCl</td>
<td>1585</td>
<td>1630</td>
<td>430</td>
<td>321</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C_{19}H_{24}N_{3}O_{2}SnCl</td>
<td>1583</td>
<td>1640</td>
<td>420</td>
<td>320</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 19: $^1$H NMR data of the complexes (ppm):

<table>
<thead>
<tr>
<th>Complex</th>
<th>NH (1H, s)</th>
<th>-C=CH-N- (1H, d)</th>
<th>Aryl (4H, b)</th>
<th>-CH$_2$ (2H, d)</th>
<th>-CH- (1H, m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$<em>{41}$H$</em>{34}$N$_3$O$_2$Sn</td>
<td>9.1</td>
<td>7.2</td>
<td>7.3-7.4</td>
<td>2.9, 3.0</td>
<td>3.3-3.6</td>
</tr>
<tr>
<td>C$<em>{31}$H$</em>{37}$N$_4$O$_2$SnCl</td>
<td>9.1</td>
<td>7.1</td>
<td>7.3-7.4</td>
<td>2.8, 2.9</td>
<td>3.4-3.5</td>
</tr>
<tr>
<td>C$<em>{25}$H$</em>{25}$N$_4$O$_2$SnCl</td>
<td>9.1</td>
<td>7.1</td>
<td>7.2-7.3</td>
<td>2.7, 2.8</td>
<td>3.3-3.4</td>
</tr>
<tr>
<td>C$<em>{36}$H$</em>{35}$N$_3$O$_2$Sn</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>C$<em>{26}$H$</em>{38}$N$_3$O$_2$SnCl</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3.3-3.5</td>
</tr>
<tr>
<td>C$<em>{20}$H$</em>{24}$N$_3$O$_2$SnCl</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3.3-3.6</td>
</tr>
<tr>
<td>C$<em>{19}$H$</em>{24}$N$_3$O$_2$SnCl</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Complex</td>
<td>-NH$_2$ (2H,m)</td>
<td>-Ph (15H,m)</td>
<td>-CH$_3$ (6H,s)</td>
<td>CH$_3$-CH-CH$_3$ (1H,m)</td>
<td></td>
</tr>
<tr>
<td>------------------</td>
<td>----------------</td>
<td>-------------</td>
<td>---------------</td>
<td>------------------------</td>
<td></td>
</tr>
<tr>
<td>C$<em>{41}$H$</em>{34}$N$_3$O$_2$Sn</td>
<td>6.9-7.0</td>
<td>7.9-8.0</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>C$<em>{31}$H$</em>{37}$N$_4$O$_2$SnCl</td>
<td>6.8-6.9</td>
<td>-</td>
<td>0.42-0.45</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>C$<em>{25}$H$</em>{29}$N$_4$O$_2$SnCl</td>
<td>6.8-7.0</td>
<td>-</td>
<td>0.44</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>C$<em>{36}$H$</em>{35}$N$_3$O$_2$Sn</td>
<td>6.9-7.1</td>
<td>7.2-7.9</td>
<td>-</td>
<td>1.3-1.4</td>
<td></td>
</tr>
<tr>
<td>C$<em>{26}$H$</em>{38}$N$_3$O$_2$SnCl</td>
<td>6.8-7.1</td>
<td>-</td>
<td>0.42-0.43</td>
<td>1.3-1.4</td>
<td></td>
</tr>
<tr>
<td>C$<em>{20}$H$</em>{24}$N$_3$O$_2$SnCl</td>
<td>6.9-7.0</td>
<td>-</td>
<td>0.43</td>
<td>1.2-1.3</td>
<td></td>
</tr>
<tr>
<td>C$<em>{15}$H$</em>{24}$N$_3$O$_2$SnCl</td>
<td>6.8-7.1</td>
<td>-</td>
<td>0.42</td>
<td>1.2-1.4</td>
<td></td>
</tr>
<tr>
<td>Complex</td>
<td>( H^1 )</td>
<td>( H^2 )</td>
<td>( H^3 )</td>
<td>( H^4 )</td>
<td>( H^5 )</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
</tr>
<tr>
<td>( C_{41}H_{34}N_3O_2Sn )</td>
<td>8.5</td>
<td>7.5</td>
<td>8.0</td>
<td>7.8</td>
<td>7.8</td>
</tr>
<tr>
<td>( C_{31}H_{37}N_4O_2SnCl )</td>
<td>8.4</td>
<td>7.4</td>
<td>7.9</td>
<td>7.8</td>
<td>7.8</td>
</tr>
<tr>
<td>( C_{25}H_{23}N_4O_2SnCl )</td>
<td>8.3</td>
<td>7.7</td>
<td>7.8</td>
<td>7.7</td>
<td>7.7</td>
</tr>
<tr>
<td>( C_{36}H_{35}N_3O_2Sn )</td>
<td>8.2</td>
<td>7.6</td>
<td>7.8</td>
<td>7.5</td>
<td>7.5</td>
</tr>
<tr>
<td>( C_{26}H_{38}N_3O_2SnCl )</td>
<td>8.2</td>
<td>7.6</td>
<td>7.8</td>
<td>7.5</td>
<td>7.5</td>
</tr>
<tr>
<td>( C_{20}H_{24}N_3O_2SnCl )</td>
<td>8.2</td>
<td>7.6</td>
<td>7.8</td>
<td>7.5</td>
<td>7.5</td>
</tr>
</tbody>
</table>
Table 20 - $^{13}$C NMR data of the complexes:

<table>
<thead>
<tr>
<th>Complex</th>
<th>C&lt;sup&gt;1&lt;/sup&gt;</th>
<th>C&lt;sup&gt;2&lt;/sup&gt;</th>
<th>C&lt;sup&gt;3&lt;/sup&gt;</th>
<th>C&lt;sup&gt;4&lt;/sup&gt;</th>
<th>C&lt;sup&gt;5&lt;/sup&gt;</th>
<th>C&lt;sup&gt;6&lt;/sup&gt;</th>
<th>C&lt;sup&gt;7&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{41}H_{34}N_3O_2Sn$</td>
<td>149.9</td>
<td>145.4</td>
<td>136.6</td>
<td>144.4</td>
<td>126.7</td>
<td>127.8</td>
<td>144.1</td>
</tr>
<tr>
<td>$C_{31}H_{37}N_4O_2SnCl$</td>
<td>149.8</td>
<td>145.2</td>
<td>136.4</td>
<td>143.3</td>
<td>126.6</td>
<td>127.7</td>
<td>143.0</td>
</tr>
<tr>
<td>$C_{25}H_{25}N_4O_2SnCl$</td>
<td>149.1</td>
<td>146.0</td>
<td>136.1</td>
<td>145.0</td>
<td>126.7</td>
<td>127.7</td>
<td>144.2</td>
</tr>
<tr>
<td>$C_{36}H_{35}N_3O_2Sn$</td>
<td>146.1</td>
<td>143.0</td>
<td>134.7</td>
<td>140.3</td>
<td>122.9</td>
<td>125.5</td>
<td>142.7</td>
</tr>
<tr>
<td>$C_{26}H_{38}N_3O_2SnCl$</td>
<td>146.4</td>
<td>142.6</td>
<td>134.3</td>
<td>140.4</td>
<td>123.0</td>
<td>125.6</td>
<td>142.7</td>
</tr>
<tr>
<td>$C_{20}H_{24}N_3O_2SnCl$</td>
<td>146.8</td>
<td>142.8</td>
<td>134.3</td>
<td>140.6</td>
<td>122.0</td>
<td>126.0</td>
<td>142.8</td>
</tr>
<tr>
<td>$C_{19}H_{24}N_3O_2SnCl$</td>
<td>145.1</td>
<td>151.5</td>
<td>132.7</td>
<td>141.7</td>
<td>121.9</td>
<td>125.5</td>
<td>143.0</td>
</tr>
<tr>
<td>Complex</td>
<td>C⁸</td>
<td>C⁹</td>
<td>C¹⁰</td>
<td>C¹¹</td>
<td>C¹²</td>
<td>C¹³</td>
<td>C¹⁴</td>
</tr>
<tr>
<td>------------------</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>C₄₁H₃₄N₃O₂Sn</td>
<td>136.3</td>
<td>145.4</td>
<td>149.0</td>
<td>147.0</td>
<td>148.1</td>
<td>128.4</td>
<td>128.4</td>
</tr>
</tbody>
</table>
Table 20- Contd.

<table>
<thead>
<tr>
<th>Complex</th>
<th>C^{15}</th>
<th>C^{16}</th>
<th>C^{17}</th>
<th>C^{18}</th>
<th>C^{19}</th>
<th>C^{20}</th>
<th>C^{21}</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{41}H_{34}N_{3}O_{2}Sn</td>
<td>128.4</td>
<td>128.4</td>
<td>128.4</td>
<td>128.4</td>
<td>128.1</td>
<td>128.1</td>
<td>128.1</td>
</tr>
<tr>
<td>C_{31}H_{37}N_{4}O_{2}SnCl</td>
<td>25.3</td>
<td>13.5</td>
<td>13.5</td>
<td>25.3</td>
<td>25.7</td>
<td>27.1</td>
<td>148.5</td>
</tr>
<tr>
<td>C_{25}H_{25}N_{4}O_{2}SnCl</td>
<td>146.1</td>
<td>40.1</td>
<td>38.2</td>
<td>108.1</td>
<td>112.0</td>
<td>118.7</td>
<td>124.3</td>
</tr>
<tr>
<td>C_{36}H_{35}N_{3}O_{2}Sn</td>
<td>128.3</td>
<td>128.3</td>
<td>128.3</td>
<td>128.3</td>
<td>128.1</td>
<td>128.1</td>
<td>128.1</td>
</tr>
<tr>
<td>C_{26}H_{36}N_{3}O_{2}SnCl</td>
<td>25.3</td>
<td>13.5</td>
<td>13.5</td>
<td>25.3</td>
<td>25.7</td>
<td>27.1</td>
<td>147.2</td>
</tr>
<tr>
<td>C_{20}H_{24}N_{3}O_{2}SnCl</td>
<td>145.1</td>
<td>45.1</td>
<td>38.7</td>
<td>25.1</td>
<td>24.2</td>
<td>24.2</td>
<td>-</td>
</tr>
<tr>
<td>C_{19}H_{24}N_{3}O_{2}SnCl</td>
<td>146.7</td>
<td>43.7</td>
<td>25.2</td>
<td>24.9</td>
<td>24.9</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

\[\text{132}\]
<table>
<thead>
<tr>
<th>Complex</th>
<th>C&lt;sup&gt;22&lt;/sup&gt;</th>
<th>C&lt;sup&gt;23&lt;/sup&gt;</th>
<th>C&lt;sup&gt;24&lt;/sup&gt;</th>
<th>C&lt;sup&gt;25&lt;/sup&gt;</th>
<th>C&lt;sup&gt;26&lt;/sup&gt;</th>
<th>C&lt;sup&gt;27&lt;/sup&gt;</th>
<th>C&lt;sup&gt;28&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>C&lt;sub&gt;41&lt;/sub&gt;H&lt;sub&gt;50&lt;/sub&gt;N&lt;sub&gt;4&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;SnCl</td>
<td>128.1</td>
<td>128.1</td>
<td>128.1</td>
<td>128.1</td>
<td>128.1</td>
<td>128.1</td>
<td>128.1</td>
</tr>
<tr>
<td>C&lt;sub&gt;31&lt;/sub&gt;H&lt;sub&gt;42&lt;/sub&gt;N&lt;sub&gt;4&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;SnCl</td>
<td>41.3</td>
<td>41.3</td>
<td>41.3</td>
<td>41.3</td>
<td>41.3</td>
<td>41.3</td>
<td>41.3</td>
</tr>
<tr>
<td>C&lt;sub&gt;22&lt;/sub&gt;H&lt;sub&gt;43&lt;/sub&gt;N&lt;sub&gt;4&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;SnCl</td>
<td>123.0</td>
<td>123.0</td>
<td>123.0</td>
<td>123.0</td>
<td>123.0</td>
<td>123.0</td>
<td>123.0</td>
</tr>
<tr>
<td>C&lt;sub&gt;36&lt;/sub&gt;H&lt;sub&gt;43&lt;/sub&gt;N&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;Sn</td>
<td>128.1</td>
<td>128.1</td>
<td>128.1</td>
<td>128.1</td>
<td>128.1</td>
<td>128.1</td>
<td>128.1</td>
</tr>
<tr>
<td>C&lt;sub&gt;20&lt;/sub&gt;H&lt;sub&gt;43&lt;/sub&gt;N&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;SnCl</td>
<td>40.3</td>
<td>40.3</td>
<td>40.3</td>
<td>40.3</td>
<td>40.3</td>
<td>40.3</td>
<td>40.3</td>
</tr>
<tr>
<td>C&lt;sub&gt;19&lt;/sub&gt;H&lt;sub&gt;42&lt;/sub&gt;N&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;SnCl</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 20- Contd.

<table>
<thead>
<tr>
<th>Complex</th>
<th>C⁹⁹</th>
<th>C¹⁰⁰</th>
<th>C¹³¹</th>
<th>C¹³²</th>
<th>C¹³³</th>
<th>C¹³⁴</th>
<th>C¹³⁵</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₄₁H₄₄N₃O₂Sn</td>
<td>127.6</td>
<td>127.6</td>
<td>170.9</td>
<td>54.4</td>
<td>39.4</td>
<td>108.7</td>
<td>111.4</td>
</tr>
<tr>
<td>C₃₁H₃₈⁴N₄O₂SnCl</td>
<td>121.3</td>
<td>124.9</td>
<td>118.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C₂₅H₂₃N₄O₂SnCl</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C₃₆H₃₅N₃O₂Sn</td>
<td>127.5</td>
<td>127.5</td>
<td>165.7</td>
<td>56.4</td>
<td>29.0</td>
<td>25.9</td>
<td>24.2</td>
</tr>
<tr>
<td>C₂₆H₃₄N₃O₂SnCl</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C₂₀H₂₄N₃O₂SnCl</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C₁₉H₂₄N₃O₂SnCl</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 20 contd. - $^1^3$C and $^{1^1^9}$Sn NMR data of the complexes:

<table>
<thead>
<tr>
<th>Complex</th>
<th>$^C^{36}$</th>
<th>$^C^{37}$</th>
<th>$^C^{38}$</th>
<th>$^C^{39}$</th>
<th>$^C^{40}$</th>
<th>$^C^{41}$</th>
<th>$^{1^1^9}$Sn $\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{4^1}H_{3^4}N_3O_2Sn$</td>
<td>118.2</td>
<td>124.3</td>
<td>123.4</td>
<td>121.0</td>
<td>124.3</td>
<td>118.4</td>
<td>-280.9</td>
</tr>
<tr>
<td>$C_{3^1}H_{3^7}N_4O_2SnCl$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-260.9</td>
</tr>
<tr>
<td>$C_{2^5}H_{2^5}N_4O_2SnCl$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-257.7</td>
</tr>
<tr>
<td>$C_{3^6}H_{3^5}N_3O_2Sn$</td>
<td>24.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-278.9</td>
</tr>
<tr>
<td>$C_{2^6}H_{3^8}N_3O_2SnCl$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-263.6</td>
</tr>
<tr>
<td>$C_{2^0}H_{2^4}N_3O_2SnCl$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-258.2</td>
</tr>
<tr>
<td>$C_{1^9}H_{2^4}N_3O_2SnCl$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-250.9</td>
</tr>
</tbody>
</table>
REFERENCES
References


36. F. Agbossou, J. F. Carpentier and A. Mortreux, Chem. Rev., 95, 2485


38. R. Vijyalakshmi, M. Kanthimathi, V. Subramanian and B. U. Nair
   Biochimica et Biophysica Acta, 1475, 157 (2000)


   122, 1 (2000).

43. S. J. Gregson, P. W. Howard, T. C. Jenkins, L. R. Kelland and D. E. Thurston,

   (1994).


46. H. Kurosaki, R. K. Sharma, S. Aoki, T. Inoue, Y. Okamoto, Y. Sugiura, M.


49. D. T. Breslin, C. Yu, D. Ly and G. B. Schuster, Biochemistry, 36, 10463
   (1997).


76. L. H. Yin, P. Cheng, S. P. Yan, X. Q. Fu, J. Li, P. D. Liao and Z. H. Jiang,


102. M. J. Bloemink and J. Reedijk, In Metal Ions in Biological Systems: A.


113. Y. Akawara, Main Group Metal Chemistry, 17, 225 (1994).


139. M. S. Lah, M. M. Dixon, K. A. Pattridge, W. C. Stallings, J. A. Fee and
156. L. A. Lipscomb, F. X. Zhou, S. R. Presnell, R. J. Woo, M. E. Peek, R. R.


1047 (2000).


232. M. T. Barton, N. M. Rowley, P. R. Ashton, C. J. Jones, N. Spencer, M. S.
154


233. J. Wojaczynski, L. Latos-Grazynski, P. J. Chmielewski, P. V. Calcar and


Co., Amsterdam), 1968.

238. A. M. Pyle, J. P. Rehmann, R. Meshoyrer, C. V. Kumar, N. J. Turro and

239. K. A. Meadows, F. Liu, J. Sou, B. P. Hudson and D. R. McMillin,

(1993).

241. S. Bhattcharya, N. Seth, V. G. Gupta, H. Noth, K. Polborn, M. Thoman and


245. T. Ikeue, Y. Ongo, T. Saiton, M. Nakamura, H. Fujii and M. Yokoyama,


