PHYSICO-CHEMICAL STUDIES OF METAL COMPLEXES OF MACROCYCLIC LIGANDS

ABSTRACT

THESIS SUBMITTED FOR THE AWARD OF THE DEGREE OF

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BY

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DEPARTMENT OF CHEMISTRY
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ABSTRACT

The work embodied in present thesis is the description of an efficient synthetic procedure for obtaining 18-membered decaaza \([N_{10}]\) and 26-membered dodecaaza \([N_{12}]\) macrocyclic ligands. The results of the studies for the reactivity of these macrocycles towards members of 3d transition metal ions viz. \(Cr^{3+}\), \(Fe^{3+}\), \(Co^{2+}\), \(Ni^{2+}\), \(Cu^{2+}\) as well as towards group 12 metal ions, \(Zn^{2+}\), \(Cd^{2+}\) and \(Hg^{2+}\) have also been discussed. The products of these reactions have been thoroughly characterized using usual physico-chemical and spectroscopic studies.

Chapter 1 is a brief survey of literature describing the various known macrocyclic compounds, their coordination chemistry and the possible uses in different fields of science including medicines etc.

In Chapter 2 the synthetic procedure and characterization of 18-membered unsymmetrical dinucleating \([N_{10}]\) macrocycle namely, \([2,8,11,17]\)tetramethyl \([3,5,7,12,14,16]\)hexaphenyl \([1,3,5,7,9,10,12,14,16,18]\)decaazaoctadeca \([2,8,11,17]\)tetaene dihydroperchlorate and 26-membered unsymmetrical dinucleating \([N_{12}]\) macrocycle namely, \([2,12,15,25]\)tetramethyl \([3,11,16,24]\)tetraphenyl \([1,3,5,9,11,13,14,16,18,22,24,26]\)dodecaazahexacosa \([2,12,15,25]\)tetraene dihydroperchlorate symbolized as \(L^1.2\text{HClO}_4\) and \(L^2.2\text{HClO}_4\) respectively, have been discussed. The present macrocyclic ligands have been characterized by using the various available physico-chemical and spectroscopic techniques like FAB-mass, IR, \(^1\)HNMR and electronic spectra.
The ligands have been obtained by employing a two step one pot procedure using N-acetylaniline (C₆H₅NHCOCH₃) to generate a reactive intermediate containing C= N bonds. The intermediate is formed from condensation reaction between hydrazine hydrate (N₂H₄)aq. and C₆H₅NHCOCH₃ in methanol in presence of HClO₄ which has been monitored by recording UV-visible spectrum at different intervals. The disappearance of band at 320 nm characteristic of n → π* transition of (—CO—NH) group with a concomitant appearance of strong band at ~390 nm characteristic of π → π* transition of the C≡N bonds indicate the completion of the condensation process. It is then reacted with HCHO and aniline or 1,3-diaminopropane (capping agent) which has produced yellow colored solid products. These yellow colored solid compounds have been identified as the dihydroperchlorate salt of the ligand i.e. L₁²HClO₄ and L².2HClO₄. The FAB-mass, IR, ¹H-NMR and electronic spectral data of the products are consistent with the formation of the macrocyclic ligands through a mechanism involving the capping of the reactive intermediate at C≡N bonds. The spectroscopic data further confirmed the presence of unsymmetrical aza groups i.e. imine (C≡N) as well as amine groups in the molecular unit of the macrocycles. The IR spectra of the macrocyclic ligands showed strong absorption bands at ~1600 cm⁻¹ and ~ 1000 cm⁻¹ characteristic of ν(C≡N) and ν(N—N) stretching vibrations respectively. However, the spectrum did not show any band at ~1700 cm⁻¹ for the ν(C=O) bond stretching frequencies. The appearance of bands for ν(C≡N) and
\( \nu(N-N) \) stretching frequencies and disappearance of fundamental vibrations due to \( \nu(C==O) \) bond stretching frequencies indicate the cyclization process. The spectrum also contained frequencies characteristic of the fundamental vibrations (\( \nu_1, \nu_2, \nu_3 \)) of the counter ClO_4^- ion. The non-electrolytic nature of the macrocyclic ligands ie. \( L^1.2\text{HClO}_4 \) and \( L^2.2\text{HClO}_4 \) in Dimethyl sulfoxide, DMSO, which is a strong ionizing solvent, suggests the presence of a strong cation-anion interaction between the macrocyclic cation \([L.2\text{H}]^{2+}\) and the counter ClO_4^- ion in the solid state as well as in solutions.

Chapter 3 is the description of the reactivity and ligating capability of the macrocyclic ligands towards the metal chlorides MCl_3 (M = Cr or Fe) and MCl_2 (M= Co, Ni, Cu, Zn, Cd or Hg) as well as their derivative complexes \([M(\text{Ph}_3\text{P})_2 \text{Cl}_2]\) (M = Co, Ni, Zn, Cd or Hg). These reactions produce stable solid complexes which have been characterized employing analytical data, conductometric measurements, magnetic susceptibility studies and electronic (ligand field), IR, and EPR spectral studies. In view of the present physico-chemical and spectroscopic data, it is, reasonable, to suggest that the complexes formed are compatible with the stoichiometries \( M_2\text{LCl}_4(\text{ClO}_4)_2 \) (M = Fe or Cr; L=\( L^1 \) or \( L^2 \)) and \( M_2\text{LCl}_2(\text{ClO}_4)_2 \) (M = Co, Ni, Cu, Zn, Cd, or Hg; L = \( L^1 \) or \( L^2 \)). IR data of the complexes show the presence of the characteristic \( \nu(C==N) \) and \( \nu(C-N) \) stretching frequencies of the ligand moieties as well as that of the M—N bond stretching frequencies, henceforth,
confirm the encapsulation of metal ions in the macrocyclic cavities through chelation via unsymmetrical aza groups of imine as well as amine functions. The present macrocyclic ligands are, therefore, examples of dinucleating macrocycles possessing un-symmetrical aza groups in the molecular unit.

The magnetic susceptibility and ligand field spectral data of metal complexes have indicated the probable stereochemistries around the encapsulated metal ions. The encapsulated metal ions usually attain a hexa coordination environment with some distortion. In Cr$^{3+}$ complexes a trigonally distorted octahedral geometry is indicated. However, for Cu$^{2+}$ complexes, tetragonally distorted octahedral geometry has been evidenced. The diamagnetic nature and absence of a signal in EPR spectra of the Cu$^{2+}$ complexes reveal that the unpaired spins at each Cu$^{2+}$ ion get coupled giving a considerable Cu—Cu interaction in the present bimetallic complexes. The observed Magnetic moments and Ligand field transitions for Co$^{2+}$ complexes are consistent with a low-spin five coordinate square-pyramidal geometry. However, Ni$^{2+}$ complexes attain a trigonal-bipyramidal coordination environment around the metal ion. It has been found that the reactions of the macrocyclic ligands with the precursors [M(PPh$_3$)$_2$Cl$_2$] (M = Co, Ni, Zn, Cd or Hg) follow the ligand substitution reaction and are accompanied with a complete liberation of the ancillary PPh$_3$ ligand giving products which do not contain any coordinated PPh$_3$ in the coordination sphere.
This indicates that the macrocyclic effect for encapsulating metal ions is a more pronounced effect in comparison with the π-acidity i.e. ($M_{(dn)} \leftarrow \text{Ph}_3\text{P}_{(dn)}$) back bonding of PPh$_3$ towards the metal ions.

The Mössbauer spectra of complexes Fe$_2$L$^1$Cl$_4$(ClO$_4$)$_2$ (II) and Fe$_2$L$^2$Cl$_4$(ClO$_4$)$_2$ (IX), have been recorded in order to get an insight of the s-electron density as well as presence of anisotropy around the Fe$^{3+}$ nucleus in these complexes. The observed quadrupole splitting in the resonance peak has indicated that an electric field gradient is developed around the Fe$^{3+}$ ion resulting in a distortion from the perfect spherical octahedral symmetry of ligand coordination to the metal ion. Moreover, the magnitude of distortion is more in Fe$_2$L$^1$Cl$_4$(ClO$_4$)$_2$ (II) as compared to that observed for Fe$_2$L$^2$Cl$_4$(ClO$_4$)$_2$ (IX). The observed magnitude of isomer shift (δ) for both the complexes indicates that the s-electron density around the Fe$^{3+}$ ion is more than that in the source. This is probably, because of a decrease in screening effect of the d-electron density in Fe$^{3+}$ ion by an enhanced π-accepting power of the ligand which is due to the presence of un-saturation in the macrocyclic ligand. The Mössbaur data, therefore, support an un-saturation in the ligand moiety which is due to the presence of imine C=\text{N} linkages in the present macrocyclic ligands L$^1$ and L$^2$.

In chapter 4 the electrical and electrochemical investigations on some of the encapsulated metal complexes have been discussed. The conductometric data of the compounds have been analysed employing
modified Onsagar limiting equation according to the Fuoss and Edelson method. The thermodynamic parameters like first ionic association constant ($K_1$), free energy change ($\Delta G$) and limiting equivalent ionic conductance of the cation ($\lambda_{0+}$) have been evaluated on the basis of the conductometric data of the complexes $\text{Cr}_2\text{L}^1\text{Cl}_4(\text{ClO}_4)_2$ (I), $\text{Fe}_2\text{L}^1\text{Cl}_4(\text{ClO}_4)_2$ (II), $\text{Ni}_2\text{L}^1\text{Cl}_2(\text{ClO}_4)_2$ (IV), $\text{Cu}_2\text{L}^1\text{Cl}_2(\text{ClO}_4)_2$ (V), $\text{Cr}_2\text{L}^2\text{Cl}_4(\text{ClO}_4)_2$ (VIII), $\text{Fe}_2\text{L}^2\text{Cl}_4(\text{ClO}_4)_2$ (IX), $\text{Co}_2\text{L}^2\text{Cl}_2(\text{ClO}_4)_2$ (X), $\text{Ni}_2\text{L}^2\text{Cl}_2(\text{ClO}_4)_2$ (XI) and $\text{Cu}_2\text{L}^2\text{Cl}_2(\text{ClO}_4)_2$ (XII). It has been found that the magnitudes of $K_1$ and the corresponding $\Delta G$ for complexes with $\text{L}^1.2\text{HClO}_4$ are in the order $\text{Ni}^{2+} > \text{Cu}^{2+}$ and $\text{Cr}^{3+} > \text{Fe}^{3+}$ metals ions. However, for complexes with $\text{L}^2.2\text{HClO}_4$ the order is $\text{Ni}^{2+} > \text{Co}^{2+} > \text{Cu}^{2+}$ and $\text{Fe}^{3+} > \text{Cr}^{3+}$. These data further indicate that the macrocyclic cavity is more flexible for $\text{L}^2$ relative to that of $\text{L}^1$.

The cyclic voltammetric studies of the complexes have been carried out to analyse the electrochemical redox behaviour of the complexes in solution. The mechanism of various redox processes have also been proposed and discussed in chapter 4. The voltammetric studies were carried out for 1 mM solution of the complexes in DMSO using Pt vs. Ag/AgCl electrode at room temperature at scan rates of 0.1, 0.2, and 0.3 VVs$^{-1}$. The cyclic voltammogram (CV) of $\text{Cr}_2\text{L}^1\text{Cl}_4(\text{ClO}_4)_2$ (I) is compatible with a one step irreversible reduction process represented by the following scheme:
[Cr{$^{III}$}L{$^{I}$}Cr{$^{III}$}] $\overset{+2e}{\rightarrow}$ [Cr{$^{II}$}L{$^{I}$}Cr{$^{III}$}] $\overset{-1.1V}{\rightarrow}$ Cr$^{0}$ + [Cr{$^{IV}$}L{$^{I}$}]

The corresponding Cr$^{3+}$ complex with L$^{2}$HClO$_{4}$, Cr$^{2+}$L$^{2}$Cl$_{4}$(ClO$_{4}$)$_{2}$ (VIII), however follows one electron successive irreversible reduction steps given by the following scheme:

[Cr{$^{III}$}L{$^{2}$}Cr{$^{III}$}] $\overset{+e}{\rightarrow}$ [Cr{$^{II}$}L{$^{2}$}Cr{$^{III}$}] $\overset{+e}{\rightarrow}$ [Cr{$^{II}$}L{$^{2}$}Cr{$^{II}$}]

$\overset{-0.9V}{\rightarrow}$ $\overset{-1.1V}{\rightarrow}$

The CV of complex Fe$_{2}$L$^{I}$Cl$_{4}$(ClO$_{4}$)$_{2}$ (II) exhibits stepwise one electron redox-processes given by the following scheme:

[Fe{$^{III}$}L{$^{I}$}Fe{$^{III}$}] $\overset{+e}{\rightarrow}$ [Fe{$^{II}$}L{$^{I}$}Fe{$^{III}$}] $\overset{E_{\text{red( irr)}}}{\rightarrow}$ -0.35 V

[Fe$^{II}$L$^{I}$Fe$^{III}$] $\overset{-e}{\leftrightarrow}$ [Fe$^{II}$L$^{I}$Fe$^{II}$] $\overset{\overline{E_{1/2}}}{\rightarrow}$ -0.987 V

[Fe$^{II}$L$^{I}$Fe$^{II}$] $\overset{+e}{\rightarrow}$ [Fe$^{I}$L$^{I}$Fe$^{II}$] $\overset{E_{1/2}}{\rightarrow}$ -1.14 V

[Fe$^{I}$L$^{I}$Fe$^{II}$] $\overset{-e}{\rightarrow}$ [Fe$^{I}$L$^{I}$Fe$^{I}$] $\overset{E_{1/2}}{\rightarrow}$ -1.41 V

However, for Fe$_{2}$L$^{2}$Cl$_{4}$(ClO$_{4}$)$_{2}$ (IX) the CV shows two electron quasi-reversible redox processes as following:

[Fe{$^{III}$}L$^{2}$Fe{$^{III}$}] $\overset{+2e}{\rightarrow}$ [Fe{$^{II}$}L$^{2}$Fe{$^{II}$}] $\overset{E_{1/2}}{\rightarrow}$ -0.937 V

[Fe$^{II}$L$^{2}$Fe$^{II}$] $\overset{-2e}{\rightarrow}$ [Fe$^{II}$L$^{2}$Fe$^{I}$] $\overset{E_{1/2}}{\rightarrow}$ -1.34 V
The electrochemical processes of Co$_2$L^1Cl$_2$(ClO$_4$)$_2$ (III) are compatible with the following Scheme:

\[
\begin{align*}
[\text{Co}^{II}L^1\text{Co}^{II}]^+ & \xrightleftharpoons[+2e]{-0.4 \text{ V}} [\text{Co}^{I}L^1\text{Co}^{I}] \\
[\text{Co}^{I}L^1\text{Co}^{I}] & \xrightarrow{-2e/2e} [\text{Co}^{II}L^1\text{Co}^{II}] \\
[\text{Co}^{I}L^1\text{Co}^{I}] & \rightarrow \text{Co}^0 + [\text{Co}^{II}L^1] \\
\end{align*}
\]

The electrochemical redox behaviour of Ni$_2$L^1Cl$_2$(ClO$_4$)$_2$ (IV) is represented by the following Scheme:

\[
\begin{align*}
[\text{Ni}^{II}L^1\text{Ni}^{II}]^+ & \xrightarrow{+2e/-0.85 \text{ V}} [\text{Ni}^{I}L^1\text{Ni}^{I}] \\
[\text{Ni}^{I}L^1\text{Ni}^{I}] & \xrightarrow{+2e/-1.15 \text{ V}} [\text{Ni}^0 + L^1] \\
[\text{Ni}^{II}L^1\text{Ni}^{II}] & \xrightarrow{-2e} [\text{Ni}^{I}L^1\text{Ni}^{I}] \\
\end{align*}
\]

\[E_{1/2} = -1.17 \text{ to } -1.22 \text{ V (}\Delta E = 250 - 350 \text{ mV)}\]

The electrochemical process of Ni$_2$L^2Cl$_2$(ClO$_4$)$_2$ (XI) is different from that observed for the corresponding Ni$^{2+}$ complex with L$^1$ i.e. (IV) and may be shown by the following Scheme:

\[
\begin{align*}
[\text{Ni}^0L^2\text{Ni}]^+ & \xrightarrow{+2e/-1.0 \text{ V}} [\text{Ni}^{I}L^2\text{Ni}^{I}] \\
[\text{Ni}^{I}L^2\text{Ni}] & \xrightarrow{+2e/-1.6 \text{ V}} 2\text{Ni}^0 + L^2 \\
[\text{Ni}^{II}L^2\text{Ni}]^+ & \xrightarrow{-2e/-0.2 \text{ V}} [\text{Ni}^{III}L^2\text{Ni}^{III}] \\
\end{align*}
\]

\[E_{\text{red}} = -1.0 \text{ V} \quad E_{\text{red}} = -1.6 \text{ V} \quad E_{\text{oxd}} = -0.2 \text{ V}\]

The CV of the complex Cu$_2$L$^1$Cl$_2$(ClO$_4$)$_2$ (V) shows a single quasi-reversible wave consistent with a one step redox process involving two
electron redox mechanism, while the corresponding Cu₂L²Cl₂(ClO₄)₂ (XII) exhibits only irreversible redox processes shown by the following scheme:

\[
\begin{align*}
[Cu^{II}L^{I}Cu^{II}] & \xrightarrow{+2e} [Cu^{I}L^{I}Cu^{I}] \\
& \xleftarrow{-2e} \nonumber
\end{align*}
\]

and

\[
\begin{align*}
[Cu^{II}L^{II}Cu^{II}] & \xrightarrow{+e} [Cu^{II}L^{II}Cu^{II}] \\
& \xrightarrow{-0.225 \text{ V}} [Cu^{I}L^{II}Cu^{I}] \\
[Cu^{I}L^{II}Cu^{I}] & \xrightarrow{+2e} 2Cu + L \\
& \xleftarrow{-1.05 \text{ V}} \nonumber
\end{align*}
\]

\[
\begin{align*}
[Cu^{II}L^{II}Cu^{II}]^+ & \xrightarrow{\text{decomposition}} 2Cu^{2+} + L^2 \\
& \xrightarrow{+0.675 \text{ V}} \nonumber
\end{align*}
\]

\[
\begin{align*}
\text{Cu}^{2+} & \xrightarrow{+2e} \text{Cu} \\
& \xleftarrow{-0.15 \text{ V}} \nonumber
\end{align*}
\]

The present electrochemical data indicate that the newly synthesized macrocylces, L¹.2HClO₄ and L².2HClO₄ possess flexible cavities capable to accommodate the higher (+3) as well as the lower (+1) oxidation states of the transition metal ions.
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Dedicated
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My Parents
Certificate

Certified that the work embodied in this thesis entitled "Physico-Chemical Studies of Metal Complexes of Macrocyclic Ligands" is the result of original research carried out under my supervision by Ms. Raazia Arif and is suitable for submission for the award of Ph.D. degree of Aligarh Muslim University, Aligarh, India.

(Prof. Zafar Ahhad Siddiqi)
Ph.D. AvH Fellow (Germany)
Member, N.Y.A.Sc. (U.S.A)
Member, A.A.A.Sc. (U.S.A)
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I am extremely thankful to my mother and father who had been a constant source of inspiration in the pursuance of my education.

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In the end I must express my thanks to Mr. Mohd. Kalamuddin, who prepared the computerized text of the thesis and the Non-teaching staff of the Department specially of the Seminar Library who cheerfully solved my problems whenever I approached them.

(Raazia Arif)
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**Part-A** Synthesis and Characterization of complexes of [L\(^1\).2HClO\(_4\)] and [L\(^2\).2HClO\(_4\)] with 3d-metal ions: Encapsulation of Cr\(^{3+}\), Fe\(^{3+}\), Co\(^{2+}\), Ni\(^{2+}\) or Cu\(^{2+}\) ions.

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confirm the encapsulation of metal ions in the macrocyclic cavities through chelation via unsymmetrical aza groups of imine as well as amine functions. The present macrocyclic ligands are, therefore, examples of dinucleating macrocycles possessing un-symmetrical aza groups in the molecular unit.

The magnetic susceptibility and ligand field spectral data of metal complexes have indicated the probable stereochemistries around the encapsulated metal ions. The encapsulated metal ions usually attain a hexa coordination environment with some distortion. In Cr\(^{3+}\) complexes a trigonally distorted octahedral geometry is indicated. However, for Cu\(^{2+}\) complexes, tetragonally distorted octahedral geometry has been evidenced. The diamagnetic nature and absence of a signal in EPR spectra of the Cu\(^{2+}\) complexes reveal that the unpaired spins at each Cu\(^{2+}\) ion get coupled giving a considerable Cu—Cu interaction in the present bimetallic complexes. The observed Magnetic moments and Ligand field transitions for Co\(^{2+}\) complexes are consistent with a low-spin five coordinate square-pyramidal geometry. However, Ni\(^{2+}\) complexes attain a trigonal–bipyramidal coordination environment around the metal ion. It has been found that the reactions of the macrocyclic ligands with the precursors \([M(PPh_3)_2Cl_2]\) (M = Co, Ni, Zn, Cd or Hg) follow the ligand substitution reaction and are accompanied with a complete liberation of the ancillary PPh\(_3\) ligand giving products which do not contain any coordinated PPh\(_3\) in the coordination sphere.
This indicates that the macrocyclic effect for encapsulating metal ions is a more pronounced effect in comparison with the $\pi$- acidity i.e. $(M_{(d\pi)} \leftarrow \text{Ph}_3P_{(d\pi)})$ back bonding of PPh$_3$ towards the metal ions.

The Mössbauer spectra of complexes Fe$_2$L$_1$Cl$_4$(ClO$_4$)$_2$ (II) and Fe$_2$L$_2$Cl$_4$(ClO$_4$)$_2$ (IX), have been recorded in order to get an insight of the s-electron density as well as presence of an-isotropy around the Fe$^{3+}$ nucleus in these complexes. The observed quadrupole splitting in the resonance peak has indicated that an electric field gradient is developed around the Fe$^{3+}$ ion resulting in a distortion from the perfect spherical octahedral symmetry of ligand coordination to the metal ion. Moreover, the magnitude of distortion is more in Fe$_2$L$_1$Cl$_4$(ClO$_4$)$_2$ (II) as compared to that observed for Fe$_2$L$_2$Cl$_4$(ClO$_4$)$_2$ (IX). The observed magnitude of isomer shift ($\delta$) for both the complexes indicates that the s-electron density around the Fe$^{3+}$ ion is more than that in the source. This is probably, because of a decrease in screening effect of the d-electron density in Fe$^{3+}$ ion by an enhanced $\pi$-accepting power of the ligand which is due to the presence of un-saturation in the macrocyclic ligand. The Mössbaur data, therefore, support an un-saturation in the ligand moiety which is due to the presence of imine C$\equiv$N linkages in the present macrocyclic ligands L$^1$ and L$^2$.

In chapter 4 the electrical and electrochemical investigations on some of the encapsulated metal complexes have been discussed. The conductometric data of the compounds have been analysed employing
modified Onsagar limiting equation according to the Fuoss and Edelson method. The thermodynamic parameters like first ionic association constant \( K_1 \), free energy change \( \Delta G \) and limiting equivalent ionic conductance of the cation \( \lambda_{a+} \) have been evaluated on the basis of the conductometric data of the complexes \( \text{Cr}_2\text{L}^1\text{Cl}_4(\text{ClO}_4)_2 \) (I), \( \text{Fe}_2\text{L}^1\text{Cl}_4(\text{ClO}_4)_2 \) (II), \( \text{Ni}_2\text{L}^1\text{Cl}_2(\text{ClO}_4)_2 \) (IV), \( \text{Cu}_2\text{L}^1\text{Cl}_2(\text{ClO}_4)_2 \) (V), \( \text{Cr}_2\text{L}^2\text{Cl}_4(\text{ClO}_4)_2 \) (VIII), \( \text{Fe}_2\text{L}^2\text{Cl}_4(\text{ClO}_4)_2 \) (IX), \( \text{Co}_2\text{L}^2\text{Cl}_2(\text{ClO}_4)_2 \) (X), \( \text{Ni}_2\text{L}^2\text{Cl}_2(\text{ClO}_4)_2 \) (XI) and \( \text{Cu}_2\text{L}^2\text{Cl}_2(\text{ClO}_4)_2 \) (XII). It has been found that the magnitudes of \( K_1 \) and the corresponding \( \Delta G \) for complexes with \( \text{L}^1.2\text{HClO}_4 \) are in the order \( \text{Ni}^{2+} \gg \text{Cu}^{2+} \) and \( \text{Cr}^{3+} \gg \text{Fe}^{3+} \) metals ions. However, for complexes with \( \text{L}^2.2\text{HClO}_4 \) the order is \( \text{Ni}^{2+} \gg \text{Co}^{2+} \gg \text{Cu}^{2+} \) and \( \text{Fe}^{3+} \gg \text{Cr}^{3+} \). These data further indicate that the macrocyclic cavity is more flexible for \( \text{L}^2 \) relative to that of \( \text{L}^1 \).

The cyclic voltametric studies of the complexes have been carried out to analyse the electrochemical redox behaviour of the complexes in solution. The mechanism of various redox processes have also been proposed and discussed in chapter 4. The voltametric studies were carried out for 1 mM solution of the complexes in DMSO using Pt vs. Ag/AgCl electrode at room temperature at scan rates of 0.1, 0.2, and 0.3 \( \text{Vs}^{-1} \). The cyclic voltammogram (CV) of \( \text{Cr}_2\text{L}^1\text{Cl}_4(\text{ClO}_4)_2 \) (I) is compatible with a one step irreversible reduction process represented by the following scheme:
\[ [\text{Cr}^{III}L^1\text{Cr}^{III}] \xrightarrow{+2e} [\text{Cr}^{II}L^1\text{Cr}^{II}] \xrightarrow{-0.725V} \text{Cr}^0 + [\text{Cr}^{IV}L^1] \]

The corresponding Cr\(^{3+}\) complex with L\(^2\).2HClO\(_4\), \(\text{Cr}_2\text{L}^2\text{Cl}_4(\text{ClO}_4)_2\) (VIII), however follows one electron successive irreversible reduction steps given by the following scheme:

\[ [\text{Cr}^{III}L^2\text{Cr}^{III}] \xrightarrow{+e} [\text{Cr}^{II}L^2\text{Cr}^{III}] \xrightarrow{-0.9V} [\text{Cr}^{II}L^2\text{Cr}^{II}] \]

The CV of complex \(\text{Fe}_2\text{L}^1\text{Cl}_4(\text{ClO}_4)_2\) (II) exhibits stepwise one electron redox-processes given by the following scheme:

\[ [\text{Fe}^{III}L^1\text{Fe}^{III}] \xrightarrow{+e} [\text{Fe}^{II}L^1\text{Fe}^{III}] \quad E_{\text{red( irr)}} = -0.35 \text{ V} \]

\[ [\text{Fe}^{II}L^1\text{Fe}^{III}] \xrightarrow{-e} [\text{Fe}^{I}L^1\text{Fe}^{II}] \quad E_{1/2} = -0.987 \text{ V} \]

\[ [\text{Fe}^{II}L^1\text{Fe}^{II}] \xrightarrow{-e} [\text{Fe}^{I}L^1\text{Fe}^{II}] \quad E_{1/2} = -1.14 \text{ V} \]

\[ [\text{Fe}^{I}L^1\text{Fe}^{II}] \xrightarrow{-e} [\text{Fe}^{II}L^1\text{Fe}^{II}] \quad E_{1/2} = -1.41 \text{ V} \]

However, for \(\text{Fe}_2\text{L}^2\text{Cl}_4(\text{ClO}_4)_2\) (IX) the CV shows two electron quasi-reversible redox processes as following:

\[ [\text{Fe}^{III}L^2\text{Fe}^{III}] \xrightarrow{+2e} [\text{Fe}^{II}L^2\text{Fe}^{II}] \quad E_{1/2} = -0.937 \text{ V} \]

\[ [\text{Fe}^{II}L^2\text{Fe}^{II}] \xrightarrow{+2e} [\text{Fe}^{I}L^2\text{Fe}^{II}] \quad E_{1/2} = -1.34 \text{ V} \]
The electrochemical processes of Co$_2$L$^1$Cl$_2$(ClO$_4$)$_2$ (III) are compatible with the following Scheme:

\[
\begin{align*}
[\text{Co}^{II}\text{L}^1\text{Co}^{II}] & \xrightarrow{+2e} [\text{Co}^I\text{L}^1\text{Co}^I] \quad E_{\text{red}}^0 = -0.4 \text{ V} \\
[\text{Co}^I\text{L}^1\text{Co}^I] & \xrightarrow{-2e \rightarrow +2e} [\text{Co}^{II}\text{L}^1\text{Co}^{II}] \quad E_{1/2}^0 = -1.075 \text{ V} \\
[\text{Co}^I\text{L}^1\text{Co}^I] & \rightarrow \text{Co}^0 + [\text{Co}^{II}\text{L}^1] \quad E_{\text{oxd}}^0 = +0.2 \text{ V}
\end{align*}
\]

The electrochemical redox behaviour of Ni$_2$L$^1$Cl$_2$(ClO$_4$)$_2$ (IV) is represented by the following Scheme:

\[
\begin{align*}
[\text{Ni}^{II}\text{L}^1\text{Ni}^{II}]^+ & \xrightarrow{+2e} -0.85 \text{ V} [\text{Ni}^{II}\text{L}^1\text{Ni}^{II}] \xrightarrow{+2e} -1.15 \text{ V} \quad \text{Ni}^0 + \text{L}^1 \\
[\text{Ni}^{II}\text{L}^1\text{Ni}^{II}] & \xrightarrow{+2e} -2e^- \quad [\text{Ni}^{II}\text{L}^1\text{Ni}^{II}] \quad E_{1/2}^0 = -1.17 \text{ to } -1.22 \text{ V} \ (\Delta E = 250 \text{ to } 350 \text{ mV})
\end{align*}
\]

The electrochemical process of Ni$_2$L$^2$Cl$_2$(ClO$_4$)$_2$ (XI) is different from that observed for the corresponding Ni$^{2+}$ complex with L$^1$ i.e. (IV) and may be shown by the following Scheme:

\[
\begin{align*}
[\text{Ni}^{II}\text{L}^2\text{Ni}^{II}]^+ & \xrightarrow{+2e} -1.0 \text{ V} [\text{Ni}^{II}\text{L}^2\text{Ni}^{II}] \quad E_{\text{red}}^0 = -1.0 \text{ V} \\
[\text{Ni}^{II}\text{L}^2\text{Ni}^I] & \xrightarrow{+2e} -1.6 \text{ V} \quad 2\text{Ni}^0 + \text{L}^2 \quad E_{\text{red}}^0 = -1.6 \text{ V} \\
[\text{Ni}^{II}\text{L}^2\text{Ni}^{II}] & \xrightarrow{-2e} -0.2 \text{ V} \quad [\text{Ni}^{III}\text{L}^2\text{Ni}^{III}] \quad E_{\text{oxd}}^0 = -0.2 \text{ V}
\end{align*}
\]

The CV of the complex Cu$_2$L$^1$Cl$_2$(ClO$_4$)$_2$ (V) shows a single quasi-reversible wave consistent with a one step redox process involving two
electron redox mechanism, while the corresponding \( \text{Cu}_2L^2\text{Cl}_2(\text{ClO}_4)_2 \) \((\text{XII})\) exhibits only irreversible redox processes shown by the following scheme:

\[
\begin{align*}
\text{[Cu}^\text{II}L^\text{I}Cu^\text{II}] & \xrightleftharpoons{+2e\,-2e}{-0.225V} \text{[Cu}^\text{I}L^\text{I}Cu^\text{I}] \\
\text{[Cu}^\text{II}L^2\text{Cu}^\text{II}] & \xrightarrow{+2e\,-1.05V} 2\text{Cu} + L \\
\text{[Cu}^\text{II}L^2\text{Cu}^\text{I}] & \xrightarrow{\text{decomposition} +0.675V} 2\text{Cu}^2+ + L^2 \\
\text{Cu}^2+ & \xrightarrow{+2e\,-0.15V} \text{Cu}
\end{align*}
\]

The present electrochemical data indicate that the newly synthesized macrocycles, \( L^1.2\text{HClO}_4 \) and \( L^2.2\text{HClO}_4 \) possess flexible cavities capable to accommodate the higher (+3) as well as the lower (+1) oxidation states of the transition metal ions.
CHAPTER-1

REVIEW
The coordination chemistry of multidentate ligands has been a field of intensive investigations amongst inorganic chemists over the past so many decades. Metal ions binding with multidentate polyaza, mixed aza-oxa or aza-thia macrocycles have attracted the attention of inorganic and bio-chemists during the last 2-3 decades as these ligand systems serve as models for bio-molecules. There is no dearth of literature on the structural, synthetic or functional aspects of macrocyclic chemistry. Naturally occurring macrocyclic complexes like vitamin B₁₂, metalloporphyrins, chlorophyll and the industrially important metal phthalocynine have been studied for many years. Synthetic ring complexes which copy various aspects of the naturally occurring complicated macrocyclic ring systems are known. Study of such compounds find an analogy with the natural systems and were the main goal of early stage research. Although, the results obtained do not always closely parallel those obtained in the nature. The biochemical role of metal ions in the natural system is better understood through these synthetic models. The first documented macrocycle possessing a sub heterocyclic ring (Fig.1.1-1) was synthesized in 1886 by Baeyer via the condensation of pyrrole and acetone in presence of a mineral acid.
Vorlender\textsuperscript{8} in 1894 prepared a dimeric ethylene succinate (Fig. 1.1-II) from a diacid.

The widespread interest in examining the chemistry of such molecules is basically due to their unique and exciting properties to serve as receptors for metal ions as well as molecular cations, neutral molecules or molecular ions of widely differing physical and chemical properties which upon complexation can drastically alter their properties. Some of these macrocycles possess several desirable\textsuperscript{9} properties such as selective substrate recognition, stable complex formation, transport capabilities and catalysis etc. An intriguing feature of macrocyclic chemistry is that the design and synthesis of macrocycles with varying ring size and donor sites exhibiting specific properties can be achieved with relative ease. Over the last many years an extensive series of macrocyclic ligands have been prepared.
These macrocyclic ligands have been subdivided\textsuperscript{9} into various categories as below:

1. Coronands\textsuperscript{10,11} (Fig.1.2-I, II) are macrocyclic species which contain various heteroatoms as binding sites.

2. Crown ethers\textsuperscript{12} (Fig.1.2-III, IV) are macrocyclic polyethers.

3. Macrocyclic polycarbonyls are cyclic ligands containing carbonyl functionalities like macrocyclic oligoketones\textsuperscript{13} (Fig.1.2-V), polylactones\textsuperscript{14} and polylactams\textsuperscript{15} (Fig. 1.2-VI, VII).

4. Spherands\textsuperscript{16} (Fig.1.2-VIII) and hemispherands\textsuperscript{17} (Fig.1.2-IX) are macrocyclic ligands which consist of arrangements of phenyl groups.

5. Calixarenes\textsuperscript{18} (Fig.1.2-X), from Greek meaning chalice and arene (incorporation of aromatic rings), are macrocyclic phenol-formaldehyde condensation products.

6. Catenands\textsuperscript{19} (Fig.1.2-XI) are two separate but interlocked macrocyclic ligands.

7. Cryptands\textsuperscript{20,21} (Fig.1.2-XII, XIII) are macropoly-cyclic receptor molecules which provide a cavity for inclusion of a variety of substrates.

8. Sepulchrates\textsuperscript{22} (Fig.1.2-XIV) are polyaza macrobicycles analogous to the cryptands.
9. Speleands\textsuperscript{23} (Fig.1.2-XV) are hollow, macropolycyclic molecules formed by the combination of polar binding units with rigid shaping groups.

10. Cyclidenes\textsuperscript{24} (Fig.1.2-XVI) are bicyclic macrocycles, which coordinate one metal ion and contain a protected ‘void’ about the axial site of the metal ion.
IUPAC nomenclature to these compounds is cumbersome and not illustrative. Simple but unequivocally defined notations have been suggested for certain types of macrocycles. However, most of these compounds are represented by their structural formulae which give a clear picture.

The synthesis and application of macrocyclic moieties involving aza (N), oxa (O), phospha (P), and sulfa (S) ligating atoms as well as mixed biting sites (heteroatoms) have been a subject of considerable interest in recent years. The coordination chemistry of these macrocyclic systems, particularly those containing nitrogen donor atoms is expanding rapidly. The enormous work done by countless researchers with thousands of papers, hundreds of reviews and numerous patents about the coordination chemistry of macrocyclic ligands can not be
confined to a few pages. The field of coordination chemistry of polyaza macrocycles has undergone spectacular growth after independent reports in early 1960s by Curtis and Busch.

In general, macrocycles are organic heterocyclic compounds containing 10 to 30 atoms in a ring. They have an internal hydrophilic cavity formed by donor atoms and external hydrophobic frame work made up of chains. These macrocyles usually possess 4 to 10 donor atoms connected via 2 or 3 carbon atoms which are capable of interacting with a variety of species. The designing of new macrocyclic complexes is a current domain of research in view of their use as models for investigating binding sites in metaloprotiens in biological systems, as therapeutic reagents in chelate therapy and as cyclic antibiotics that owe their antibiotic actions to specific metal complexation. The specific types of macrocyclic metal complexes have been designed to act as models to study the magnetic exchange phenomena and in catalysis.

Besides these, there are a number of important biological processes such as photosynthesis and dioxygen transport in which macrocyclic complexes are involved. Many macrocyclic ligands have been prepared by conventional organic synthesis as well as employing in-situ procedures involving cyclization in the presence of metal ions. It was later found that the presence of metal ion enhance the cyclization process, increasing the yield of the cyclic products. The
metal ion plays an important role in directing the steric course of the reaction and this effect is termed as "metal template effect"\textsuperscript{45}. The metal is said to act as a template and such reactions have been termed as metal assisted template synthesis.

Curtis demonstrated the template potential of metal ions in the formation of isomeric tetraaza macrocyclic complexes by treating $[\text{Ni(en)}_3](\text{ClO}_4)_2$ with acetone (Fig. 1.3). Thompson and Busch\textsuperscript{26} have described the deliberate synthesis of a macrocycle (Fig. 1.4) using this procedure.

![Fig. 1.3](image1.png)

Schiff base condensation between a carbonyl compound and an organic amine in presence of a metal ion to yield an imine linkage has
led to the synthesis of many aza macrocycle complexes\textsuperscript{46,47} as illustrated by (Fig.1.5).

\begin{center}
\begin{tikzpicture}
\node at (0,0) {\includegraphics[width=\textwidth]{fig15.png}};
\end{tikzpicture}
\end{center}

Fig. 1.5

The crown polyethers are examples of macrocycles which have been prepared mainly by direct synthesis\textsuperscript{12,48,49} (Fig. 1.6). Mixed oxathia crowns are obtained from reaction of oligo(ethylene glycol) dichloride with dithiols\textsuperscript{50-52} (Fig. 1.7).

\begin{center}
\begin{tikzpicture}
\node at (0,0) {\includegraphics[width=\textwidth]{fig16.png}};
\end{tikzpicture}
\end{center}

Fig. 1.6

\begin{center}
\begin{tikzpicture}
\node at (0,0) {\includegraphics[width=\textwidth]{fig17.png}};
\end{tikzpicture}
\end{center}

Fig. 1.7
Ether-ester and ether-ester-amide macrocycles are derived from acid chlorides and oligo(ethylene glycols) or ethylenediamine\textsuperscript{53,54} (Fig. 1.8).

\[ \text{HX} \quad \text{O or NH} \]

\[ \text{Fig. 1.8} \]

Polythia macrocycles are obtained by reaction of an appropriate polythiane with a dibromoalkane. In some cases the reactions are metal template assisted\textsuperscript{55,56} (Fig. 1.9 and 1.10).

\[ \text{Fig. 1.9} \]

\[ \text{Fig. 1.10} \]
The phosphorus macrocycles are made via template condensation of coordinated polyphosphine ligands and a dibromoalkane\(^5\) (Fig. 1.11).

Template assisted single-stage ring closure methods are also reported\(^6\) (Fig. 1.12). The arsenic donor macrocycles are synthesized by reacting lithiated polyarsenes with a dichloroalkane\(^7\) (Fig 1.13).
Macropolycycles are, generally, made by progressive construction of the framework through a series of reaction of the appropriate reactants\textsuperscript{19-21,60-63}.

The above described synthetic methods have been extensively employed as easy approach to prepare various macropolycyclic ligands. There is still a need in several areas for a rational approach towards ligand design for selective complexation of metal ion in solution\textsuperscript{64}. A major determinant of the metal ion specificity is expected to be the nature of the metal binding residues. Metal binding studies have shown the importance of ligand field stabilization and hard-soft acid-base effects\textsuperscript{65} in determining metal ion specificity.

The diimine Schiff base macrocycles obtained by the condensation of one molecule each of dicarbonyl and diamine precursors have been termed “1+1” macrocycles and the tetraamine macrocycles obtained by the condensation of two molecules of the diamine moiety have been termed “2+2” macrocycles as a consequence of the number of heads and lateral units present\textsuperscript{66-71}. The formation of “1+1” macrocycle via intramolecular mechanism or “2+2” macrocycle via bimolecular mechanism during the synthesis of Schiff base macrocycle depends on following factors:

(1) The insufficient chain length to span the two carbonyl groups in the diamine will block the formation\textsuperscript{72} of “1+1” macrocycle.
(2) A “2+2” condensation may occur if the template ion is large with respect to the cavity size of the “1+1” ring.

(3) The electronic nature of the metal ion vis a vis the requirement of a preferred geometry of the complex.

(4) The conformation of the “1+1” acyclic chelate.

Synthesis of multidentate macrocyclic ligands by the metal template method has been recognized not only as offering high yields but also as selective routs to new ligands and their complexes. Most of early work featured the use of transition metal ions as the templating agent in the template synthesis of quadridentate macrocycles. The directional influence of orthogonal d-orbital was regarded as instrumental in guiding the synthetic pathway. This technique has been extended by using organo-transition metal derivatives to generate tridentate cyclononane complexes. The template potential of a metal ion in the formation of a macrocycle depends on the preference of the cations for stereochemistries in which the bonding d-orbitals are in orthogonal arrangements. This is exemplified by the observation that neither Cu$^{2+}$ nor Ni$^{2+}$ acts as template for the pentadentate “1+1” macrocycles (Fig.1.14, I-III) derived from the Schiff base condensation of 2,6-diacetylpyridine with triethylenetetraamine, N,N'-bis-(3-aminopropyl)ethylenediamine, or N,N'-bis(2-aminoethyl)-1,3-propanediamine, respectively. However, Mg$^{2+}$, Mn$^{2+}$, Fe$^{2+}$, Fe$^{3+}$, Co$^{2+}$, Zn$^{2+}$, Cd$^{2+}$, and
Hg$^{2+}$ serve as effective templates leading to the formation of 7-coordinate complexes (Fig 1.14-I, II) for condensation reactions between these reagents. The reactions using the metal ion Mg$^{2+}$, Mn$^{2+}$, Fe$^{3+}$, Fe$^{2+}$, Co$^{2+}$, Zn$^{2+}$, Cd$^{2+}$ and Hg$^{2+}$, have produced complexes with pentagonal bipyramidal geometries, while complexes with 6-coordinate pentagonal pyramidal geometries have been isolated using Co$^{2+}$, Cd$^{2+}$ and Hg$^{2+}$ metal ion$^{82-91}$. The synthesis of macrocyclic complexes by the metal template method has been further extended by the use of s- and p- block cations as template devices to synthesize penta- and hexa-dentate Schiff base macrocycles$^{92-97}$ and a range of tetraimine Schiff base macrocycles$^{66,67}$.

The size of metal ion and that of the anion are important to the template process because the balance between the size of the cation and anion will determine the degree of dissociation of the metal salt in the reaction medium$^{98}$. In the synthetic pathway of macropolycycles, the size of cation used as template has proved to be of importance. The compatibility between the radius of the templating cation and “hole” of the macrocycle contributes to the effectiveness of the synthetic pathway and to the geometry of the resulting complexes, as for example, cation of radii less than 0.80Å do not produce complexes of the type shown in (Fig.1.14-III).
Fenton and coworkers\textsuperscript{93,94,96,99,100} demonstrated cation-cavity "best fit" in the formation of Schiff base macrocycles by synthesizing oxaaza macrocycles using alkaline earth cations as templating devices. The smaller metal ion like Mg\textsuperscript{2+} favour the formation of "1+1" macrocycle as shown in (Fig. 1.15-I) while the large metal ions like Sr\textsuperscript{2+}, Ba\textsuperscript{2+} or Pb\textsuperscript{2+} etc. favour the formation of "2+2" macrocycle as shown in (Fig. 1.15-II). It has been reported\textsuperscript{93,94} that amongst alkaline earth cations only magnesium ion generates the pentadentate "1+1" macrocycle (Fig. 1.15-I) and this metal ion is ineffective in generating the hexadentate "1+1" macrocycle, which is contrary to that observed for large alkaline earth cations (Fig. 1.15-III).
Fig. 1.15
The alkaline earth metal ions also act\textsuperscript{66} as efficient templating agents for the Schiff base condensation of appropriate diamines with dicarbonyl precursors producing a fair yield of the complexes.

A mechanism consisting of a sequence of nucleophilic additions (followed by deamination) of NH\textsubscript{2} groups at the coordinated \textgreater C=N, centers was proposed. The results demonstrate the facility and reversibility of amine exchange (transamination) and its importance in the metal ion template synthesis of macrocyclic schiff-base ligands. The excess of free diamines or the free metal ion used in template procedure may suppress the yield of formation of the derived macrocycle. The sequence of reactions involving ring closure by transamination with a concomitant ring contraction and reduction in ligand denticity and subsequent ring expansion in the presence of larger metal ions has been illustrated in (Fig. 1.16). Thus it has been described\textsuperscript{101} that when the metal ion is too small for the macrocyclic cavity, ring contraction takes place by transamination with a concomittant reduction in ligand denticity and ring size. The complex of the ring-contracted macrocycle under goes ring expansion in the presence of larger metal ions.
Lindoy and co-workers have developed strategies for new macrocyclic ligand systems which are able to recognise particular transition and post transition metal ions. They have prepared\textsuperscript{102-104} and studied the discrimination of metal ions by ligand and by following the occurrence of “structural dislocation” along a series of closely related (Fig. 1.17–I, II) mixed donor ligand system\textsuperscript{105-109}.

![Fig. 1.17](image)

The coordination complexes of a wide variety of schiff-base ligands have been extensively studied and reviewed\textsuperscript{110-116}. The current interest lies in the synthesis of multi-dentate ligands because of their ability to form mono- and bis-species yielding complexes with different features. The metal derivatives of these ligands have drawn substantial attention from the researchers for their biological activities\textsuperscript{117-124}. 

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The molecules of life such as amino acids have been exploited for the synthesis of schiff base ligands and their transition metal complexes\textsuperscript{125-134}.

The idea that two metal atoms in close proximity could react in a cooperative manner with substrate molecules gave rise to binuclear system\textsuperscript{135}. A major role in building of binuclear complexes has been played by tertiary diphosphines, Bis(diphenylphosphino)methane (dppm) being particularly efficient for this purpose\textsuperscript{136}. Substitution of one of the donor atoms in the dppm skeleton for a softer (As) or harder (N) centre has been introduced to create hetero binuclear complexes of the platinum group metals\textsuperscript{137-141}. Such ligand systems studied by Balch have led to the synthesis of Pt–Rh complexes having two bridging ligands\textsuperscript{142}. A large number of transition metal-gold multimetallic complexes have been prepared containing transition metals V, Cr, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Pt and Ag\textsuperscript{143-145}. On the other hand, the synthesis and characterization of Pd–Au cluster compound have been reported\textsuperscript{146} because Pd is a catalytically important metal and Au-Pd heterogenous catalysts are known and commercially used for oxidation catalysis\textsuperscript{147}. Cu\textsuperscript{2+} complexes with various ligands derived from oxalates, oxamidates, oxamates [CuL] are known to act as paramagnetic ligands towards other metal ions\textsuperscript{148}. In particular it has been found that strong anti-ferromagnetic coupling is operative when CuL is bound to metal ions (Cu\textsuperscript{2+}, Ni\textsuperscript{2+} or Mn\textsuperscript{2+}) in a pseudo-octahedral (square planer in case
of copper) environment\textsuperscript{144-152}. Kahn and co-workers\textsuperscript{153, 154} have found that CuL can form ferromagnetic chains with Ni\textsuperscript{2+} and Mn\textsuperscript{2+} and that these chains can order magnetically at sufficiently low temperature. Fabretti\textsuperscript{155} has used CuL as a paramagnetic ligand which forms a trinuclear complex with Ni\textsuperscript{2+}. The peculiarity of this compound is that the central octahedrally coordinated Ni\textsuperscript{2+} ion has two water molecules with Cis-configuration.

The crystal and molecular structure of a very interesting binuclear compound, \textit{bis[\textmu-3,5-bis(2'Pyridyl)PyrazolateN'N:N'N"]} - \textit{bis[dimethanol nickel(II)] dichloro-dihydrate} has been reported\textsuperscript{156}. Two methanol molecules have been shown to be bonded to each Ni\textsuperscript{2+} rendering an octahedral environment. Binucleating macrocycles were obtained by Pilkington and Robson\textsuperscript{157} by 2+2 condensation of 2,6-diformyl-4-methyl phenol and 1,3-diaminopropane. The design and synthesis of binuclear macrocyclic transition metal complexes remains an important objective because of their use as potential catalysts. The neighbour metal ions in such binuclear macrocycle complexes may influence mutually on the electronic, magnetic and electro chemical properties of such closely spaced paramagnetic centers. Binucleating ligands with dissimilar coordination sites have been of particular interest because such macrocyclic complexes are thermodynamically stable and kinetically retarded with regard to metal dissociation and metal substitution relative to metal complexes of acyclic ligand.
Bis(macrocyclic) complexes incorporating two metal ions have also attracted attentions because they act as multi-electron redox agents or catalysts and therefore, may be regarded as models for polynuclear metalloenzymes. Furthermore, they can exhibit interesting physical properties due to the metal-metal interactions, consequently, some of these complexes are reported to be used as biomimetic multinuclear models which may provide an insight into the actual structure of the metalloenzyme or the mechanism of the catalysis. Bis(macrocyclic) diiron\textsuperscript{158} and dinickel\textsuperscript{159} compounds have been synthesized, in which the diiron complex contains a conjugated bridge between two metal in macrocycles. M.P. Suh and co-workers\textsuperscript{160} have synthesized bis(macrocyclic) Ni\textsuperscript{2+} and Ni\textsuperscript{+} complexes (Fig. 1.18) by template condensation reaction of formaldehyde and primary diamines.

![Diagram](image)

Fenton has reviewed\textsuperscript{161} this class of compounds emphasizing their relevance to bioinorganic model system. Some polyaza macro cyclic complexes have been modified and the reactions of Ni\textsuperscript{2+} and Fe\textsuperscript{2+}
complexes of 1,4,8,11-Tetraazacyclotetradecane with H₂O₂ and O₂ respectively, were reported\textsuperscript{162,163} to produce corresponding complexes of unsaturated (Fig. 1.19) bis(macro cyclic) ligands.

P. Comba and co-workers\textsuperscript{164} have also reported some bis macrocyclic octaaminedicopper(II) complexes which do not exhibit any coupling in their EPR spectra, irrespective of the size of the bridge, which is in contrast to the observation with other (CH₂) linked bis macrocyclic dicopper(II) complexes.

Tetraaza macrocycles usually coordinate with the N₄ donor set approximately coplanar for squareplanar or trans-octahedral arrangements. The more flexible macrocycles can also coordinate in ‘folded’ arrangements, usually to accommodate an additional chelate ligand in an octahedral arrangement and planar folded interconversions are facile. In planer coordination, some degree of tetrahedral distortion of the donor set is common and this can become substantial for larger ring sizes (Fig. 1.20).
In some instances the macrocycle configuration orients all Nitrogen lone pairs to the same side of the macrocycle, resulting in coordination geometry with metal ion displaced from the N₄ plane (Fig. 1.21) usually with square pyramidal coordination geometry.

![Diagram of coordinated 1,4,8,11-tetraazacyclotetradecane](image)

**Fig. 1.21**: Configuration of coordinated 1,4,8,11-tetraazacyclotetradecane. The + indicates that the NH group is above the plain of the (flattened) macrocycle; the – indicates that it is below.

*Pentaaza and higher polyaza macrocycles have begun to appear more frequently particularly in view of the potential of the larger macrocycles for binding more then one metal ion. The ligands derived*
from Schiff base condensations, particularly 2,6-diacetyl- and diformyl-pyridine\textsuperscript{165,166} (Fig. 1.22) are included in this category. Schiff-base condensation of pyrrole\textsuperscript{167} and dipyrrromethane\textsuperscript{168} moieties have also resulted in macrocycles capable of binuclear coordination as in the octaaza bis(dipyrrromethane) macroring (Fig. 1.23).

![Fig. 1.22](image)

![Fig. 1.23](image)

The polyaza analogs of the crown ethers are also capable of binuclear metal ion coordination as evidenced by the dicopper(II) complex of [24]N\textsubscript{8}\textsuperscript{169}. The incorporation of two copper(II) ions in polyaza macrocycles holds promise for the design of models for binuclear copper proteins. For example, the dicopper(II) complex of the hexaaza macrocycle (Fig. 1.24) has been found to exhibit features distinctly related to superoxide dismutase\textsuperscript{170,171}. The synthesis of pyridine analog to the spherands has also been reported as shown for ligand\textsuperscript{172,173} (Fig. 1.25).
A variety of Macrocyclic complexes which have adjacent nitrogen atoms as in cyclic hydrazines, hydrazones or diazines are reported to be formed by condensations of hydrazine, substituted hydrazines or hydrazones with appropriate carbonyl compounds. The reactions parallel in diversity those of amines, but are often more facile since the reacting NH₂ group is generally not coordinated and the electrophile is thus not in competition with the metal ion. The resulting macrocycles may be capable of coordination isomerism, since either of the adjacent Nitrogen atoms can act as donor atom. Condensation of monocarbonyl compound with a dihydrazone initially yields a macrocycle with a tetraaza six-membered chelate ring, as shown in figures (Fig. 1.26-I) and (Fig. 1.27-I). However this can isomerize to give a triaza five membered chelate ring as shown in (Fig. 1.28-I) where cyclization is by a reaction subsequent to the hydrazone / carbonyl condensation¹⁷⁴ or for the isomeric pair of compounds (Fig. 1.27 – II, III).
Compounds with triaza (Fig. 1.29) and tetraaza (Fig. 1.26-II) seven
membered chelate ring have also been prepared\textsuperscript{175}. Tetrade

dentate and
pentadentate aza macrocycles are formed by condensation of 2,6-diacetylpyridine with hydrazine (Fig. 1.30) or with dihydrazines\textsuperscript{174} (Fig. 1.31).

![Fig. 1.29](image1.png)  ![Fig. 1.30](image2.png)  ![Fig. 1.31](image3.png)

Goedken and Peng\textsuperscript{176} reported the synthesis of 14-membered octaaza macrocyclic complexes utilizing the template condensation reaction of butane, 2,3-dionedihydrazines and formaldehyde. A few other workers have also templated the synthesis of several macrocyclic ligands derived from hydrazine precursors\textsuperscript{177,178}. However, most of the reports concern with mononuclear complexes.

The chemistry of Binucleating macrocycles with flexible cavities capable to incorporate (encapsulate) two or more metal ions has attracted the attention of researchers working in this area. There are several reviews\textsuperscript{179} on this subject, emphasizing the use of such binuclear metal complexes to serve as models for biological systems as well as formation of dioxygen complexes\textsuperscript{180}, catalytic oxidation of organic substrates\textsuperscript{181} or the hydrolysis of capped
monoribonucleotides\textsuperscript{182}. In these reports conclusions have been drawn that the analogous mononuclear complexes are least effective in these processes and especially the catalytic activity of binuclear complexes is clearly higher. Furthermore, better models can be generated for specific enzymes and metal complexes of Binucleating macrocyclic ligands which can be potentially useful as general models to understand the reactivity changes caused by the proximity of both metal centers. In view of these reports, one can conclude that the investigations on the coordination chemistry of macrocyclic moieties with big cavities, capable to encapsulate two or more metal ions, are presently on the anvil and new reports are appearing in literature.
REFERENCES:


Synthesis and Characterization of 18-Membered Unsymmetrical Dinucleating \([N_{10}]\) Macrocycle i.e. \([L^1\cdot2\text{HClO}_4]\) and 26-Membered Unsymmetrical Dinucleating \([N_{12}]\) Macrocycle i.e. \([L^2\cdot2\text{HClO}_4]\)
INTRODUCTION

The survey of literature regarding the synthetic methods reported for a wide variety of macrocyclic ligands, their reactivity towards metal ions as well as their utility to serve as models for biological systems has been reviewed in chapter-1.

There has been considerable interest in the chemistry of binucleating macrocyles capable of incorporating two metal centers and the topic has been the subject of several recent reviews\(^1\).

This interest has arisen due to the occurrence of binuclear metal centers in enzymes such as red kidney bean purple acid phosphatase\(^2\) and urease\(^3\). Metal complexes of some binucleating hexaaza macrocycles form host-guest complexes with a range of anions such as maleate, pyrophosphate and triphosphate\(^4\). In addition they can display catalytic activity in the hydrolysis of phosphate derivatives\(^5\) and peptidase\(^6\).

Binuclear centers containing transition elements such as iron and copper are common among metallo-proteins\(^7\). These centers often function by binding and activating substrates. The individual metal ions found at the binuclear center, however, may have quite distinct role in the over all function. As for example, the active sites in erythrocyte super oxide dismutase (SOD), bind one metal ion to the substrate while the presence of other metal ion is responsible for maintaining the...
structural integrity of the active sites. In such cases, it is often found that the binuclear site of the metalloenzyme situates its metal ions in chemically distinct environments. Four distinct environments can be readily identified in respect of metal ions binding which are:

1. Symmetric, i.e. identical donor atoms bound to each metal in similar geometries.

2. Donor asymmetry i.e. different types of donor atoms bound to each metal.

3. Geometrical asymmetry i.e. inequivalent geometrical spatial arrangement of the donor atoms about each metal.

4. Coordination number asymmetry i.e. an unequal number of donor atoms coordinated to each metal.

All these possibilities can be illustrated diagrammatically as shown in (fig. 2.1).

Fig. 2.1: Classification of metal coordination environments found in metalloproteins containing multinuclear metal centers. M is general transition metal and W, X, Y and Z represent hetrotom donors (e.g. N, O, S, etc.).
The individual metals of binuclear centers have been found to possess donor asymmetry in, for example, cobalt-based methionine aminopeptidase, bovine SOD, and the trizinc enzyme phospholipase C. Geometric asymmetry of metalloprotein binuclear sites has been reported for the B2 protein active iron site of ribonucleotide reductase and certain adducts of the dicopper site of hemocyanin. There are several examples of binuclear metalloproteins where coordination number asymmetry is known or proposed. These include some copper-containing tyrosinases, hemerythrin, uterroferrin and the hydroxylase component of soluble methane mono-oxygenase. The asymmetric nature of a number of homodinuclear or heterodinuclear transition metal-derived metallobiosites where the individual metal ions are capable to have quite distinct roles in the functioning of the metalloenzyme concerned have led to search for carefully designed unsymmetric dinucleating ligands. Such ligands can result in dinuclear complexes capable of acting as models for the metallobiosites. It is also possible that any combination of these types of asymmetry may occur in a single binuclear enzyme. Coordination asymmetry in metalloenzymes presents the possibility of “open” coordination sites for direct interaction of one metal center with substrate. It is becoming apparent that coordination number asymmetry exists in a number of metalloproteins and may be responsible for imparting unique reactivity. However, the effects that geometric or coordination
number asymmetry have on the physical properties and function of binuclear sites are much less studied. The reason for this appears to stem from a lack of suitable model systems. Complexes having geometric\textsuperscript{25(a,b)} or coordination number asymmetry\textsuperscript{25(c,d)} are reported to be formed but are rare. The rational design of ligands that can induce coordination number asymmetry in binuclear complexes is a desirable target for developing a more complete description of spectroscopic and chemical reactivity properties related to metalloenzyme systems.

Dinucleating macrocyclic ligands with dissimilar coordination sites are of particular importance because hetero-dinuclear complexes derived from such macrocycles are thermodynamically stable and kinetically retarded with regard to metal dissociation and metal substitution\textsuperscript{26,27} relative to metal complexes of acyclic ligands. Macrocyclic ligands can provide a well-defined environment for the bound metal ions and influence their physico-chemical properties\textsuperscript{28}.

The polyaza macrocycles of the type (3k)-ane[N\textsubscript{k}] have been shown to produce bimetallic complexes\textsuperscript{29} when K>6. However, for (4k)-ane[N\textsubscript{6}] type where K\geq6 giving a (24)-ane[N\textsubscript{6}] as for example, [1,5,9,13,17,21]hexaaazacyclotetracosane macrocyclic tends to encapsulate\textsuperscript{30} only one metal ion in its cavity. Template reaction utilizing the “2:2” condensation of a diamine with 2,6 diformly-4-methyl phenol was the first one pot reaction giving a dinuclear complex\textsuperscript{31}. Later on, attempts to obtain macrocycles with different lateral chains...
through stepwise cyclization using two dissimilar alkyldiamines by template procedure were also successful\textsuperscript{32}. Most of the earlier efforts concentrated for isolating symmetrical macrocycles primarily because of their ease of synthesis\textsuperscript{33}. There are reports\textsuperscript{34} of large macrocycles with two or more cavities but possessing only identical biting sites (symmetrical macrocycles) to encapsulate the metal ions. However, there are relatively less reports\textsuperscript{35}, regarding metal ion encapsulation in large unsymmetrical macrocycles containing more than one type of metal binding sites. The unsymmetrical macrocycles so far reported\textsuperscript{32,36}, usually involved heteroatomic centers like N\textsubscript{2}O\textsubscript{2}, N\textsubscript{2}O\textsubscript{4}, N\textsubscript{4}O\textsubscript{2}. Polyazamacrocycles [N\textsubscript{k}] (where k ≤ 8) with different environments for the aza groups are known\textsuperscript{36}. However, to our knowledge, big macrocycles with K > 8 having unsymmetrical aza groups capable to encapsulate more than one metal ion are scarce\textsuperscript{35,37}. A route to obtain unsymmetrical [N\textsubscript{6}] macrocycle has recently been developed\textsuperscript{37} which utilizes multi-step procedure incorporating a suitable precursor generated in-situ by an N-acetylated amine, N-acetylpropane 1,3-diamine in presence of suitable metal ions. A few metal ion free polyaza macrocycles containing endocylic substitution in the rings have been reported\textsuperscript{38} from this laboratory.

A one pot synthetic procedure utilizing N-acetylaniline to generate an intermediate capping agent for cyclizing the appropriate diamines in the absence of any metal ion (non-template procedure) to
obtain metal ions free unsymmetrical polyaza macrocycles has recently been exploited in this laboratory\textsuperscript{39,40}.

In this chapter the synthesis and characterization of 18-
membered unsymmetrical \([N_{10}]\) dinucleating macrocycle, \([2,8,11,17]\)
tetramethyl \([3,5,7,12,14,16]\)hexaphenyl \([1,3,5,7,9,10,12,14,16,18]\)decaaazaoctadeca \([2,8,11,17]\)tetraene dihydroperchlorate i.e. 
\([L^1.2\text{HClO}_4]\) and 26-membered unsymmetrical \([N_{12}]\) dinucleating macrocycle, 
\([2,12,15,25]\)tetramethyl \([3,11,16,24]\)tetraphenyl \([1,3,5,9,11,13,14,16,18,22,24,26]\)dodecaazahexacosa \([2,12,15,25]\) tetraene dihydro-
perchlorate i.e. \([L^2.2\text{HClO}_4]\) have been described. The schemes for the formation of the these macrocycles have also been proposed on the basis of their physico-chemical and spectroschopic data like FAB–mass, IR, UV-visible, NMR etc.
EXPERIMENTAL

Reagents used:

Ethyl acetate (S.D. Fine, India), Aniline (Qualigens, India), 1,3-diaminopropane (E.Merck, Germany), Hydrazine hydrate (BDH, India), Perchloric acid (70%) (Merck, India), and Formaldehyde (37-41%) (Merck, India) were used as received. Solvents were purified and dried before their use by reported method.

Physical Measurements:

IR spectra were recorded as KBr discs on a Perkin Elmer model spectrum GX and $^1$ H NMR spectra of samples in $d_6$-DMSO on a Bruker DRX 300 spectrometer using TMS as internal reference. Electronic spectra and conductivities of $10^{-3}$M solution in DMSO were recorded on a Cintra-5GBS UV-visible spectrophotometer and Systronics-305 Conductivity Bridge respectively. FAB mass spectra of the ligands were recorded in m-nitrobenzyl alcohol (NBA) matrix using Jeol/SX-102 spectrometer. Results of microanalysis were obtained from analytical laboratory of RSIC, Central Drug Research Institute, Lucknow, India.
Synthesis of $[2,8,11,17]\text{tetramethyl } [3,5,7,12,14,16]\text{hexaphenyl } [1,3,5,7,9,10,12,14,16,18]\text{decaazaoctadeca } [2,8,11,17]\text{tetraene dihydroperchlorate i.e. } [L^1.2\text{HClO}_4]$:

Hydrazine hydrate (6.05 ml, 0.099 mol) was mixed with 30 ml of methanol in a two necked round bottomed flask placed on a constant temperature bath. Perchloric acid (10 ml, 0.099 mol) was added drop wise with continuous stirring maintaining the temperature of the reaction mixture at room temperature. N-acetylaniline (94 ml, 0.199 mol) was dropped slowly through a dropping funnel with continuous stirring and the reaction mixture was further stirred for 18 hours. Reaction was monitored by recording UV-visible spectrum of the reaction mixture at intervals which indicated formation of a species having C=N bonds. The disappearance of a band at 320 nm, characteristic of the $n \rightarrow \pi^*$ transition of (−CO−NH−) group of N-acetylaniline with a concomitant appearance of a new band at 385 nm is indicative of the formation of new species in the solution. The band at 385 nm is characteristic of the $n \rightarrow \pi^*$ transition reported for the C=N bond in the molecule. This reasonably indicates that the condensation process generated an intermediate species containing C=N bond in the molecular unit. Formaldehyde (20.3 ml, 0.299 mol) was added drop wise with continuous stirring over a period of one hour, which produced slight milkiness in the solution. It was again stirred overnight at room temperature.

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Aniline (9.1 ml, 0.099 mol) and formaldehyde (20.3 ml, 0.299 mol) taken in separate dropping funnels were dropped in the reaction mixture at a slow dropping rate which gave an exothermic reaction. The temperature of the reaction mixture was maintained at room temperature which was again stirred continuously over-night. This has afforded a yellow coloured solid product. The product was filtered off, washed with methanol and dried under vacuum, (yield = 27.82 g or 29%, mp = 128-130°C). The solid was soluble in 1,4-dioxane and dimethyl sulfoxide. The recrystallization of the compound has produced only amorphous solids.

Table-2.1: Analytical and Molar conductance ($\Lambda_m$) data of [L^2HC[04]:

<table>
<thead>
<tr>
<th></th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
<th>$\Lambda_m$ (cm$^2$ ohm$^{-1}$ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Observed</td>
<td>59.61</td>
<td>5.16</td>
<td>14.48</td>
<td>17.0</td>
</tr>
<tr>
<td>Calcd. For [C$<em>{48}$H$</em>{52}$ N$_{16}$Cl$_2$O$_8$]</td>
<td>59.62</td>
<td>5.17</td>
<td>14.49</td>
<td></td>
</tr>
</tbody>
</table>

UV-visible spectrum: $\lambda_{max} = 385$ nm ($\varepsilon = 1507$ lit mol$^{-1}$ cm$^{-1}$)

T.6458
Physico-chemical and spectroscopic data of [2,8,11,17]tetramethyl [3,5,7,12,14,16]hexaphenyl [1,3,5,7,9,10,12,14,16, 18]decazaoctadeca [2,8,11,17]tetraene dihydroperchlorate i.e. [L^2.HClO_4]:

Table 2.2: Important frequencies (cm\(^{-1}\)) observed in IR spectra of the ligand and their assignments:

<table>
<thead>
<tr>
<th>Assignments</th>
<th>(v(N-N))</th>
<th>(v(C=N))</th>
<th>(v(C-N))</th>
<th>(v_1)</th>
<th>(v_2)</th>
<th>(v_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band position</td>
<td>933 (s) 987 (s)</td>
<td>1613 (vs)</td>
<td>1245 (s)</td>
<td>1348 (s)</td>
<td>1172 (m)</td>
<td>1075 (s)</td>
</tr>
</tbody>
</table>

\(s=\)strong, \(vs=\)very strong, \(m=\)medium, \(w=\)weak

Table 2.3: Ion abundance for ligand and its fragmentation* peaks observed in FAB-mass spectrum of [L^2.HClO_4]:

<table>
<thead>
<tr>
<th>(m/z)</th>
<th>Assignments</th>
<th>%Abundance</th>
<th>(m/z)</th>
<th>Assignments</th>
<th>%Abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>766</td>
<td>([L^1]^*)</td>
<td>62</td>
<td>212</td>
<td>([(C_6H_5NHCH_2)_2]^*)</td>
<td>60</td>
</tr>
<tr>
<td>1100</td>
<td>([L^1.HClO_4+Bq\cdot2H]^+)</td>
<td>58</td>
<td>154</td>
<td>([(C_6H_5)^2]^+)</td>
<td>70</td>
</tr>
<tr>
<td>1055</td>
<td>([L^1+Rn]^+)</td>
<td>52</td>
<td>120</td>
<td>([(C_6H_5NHCH_2N)]^+)</td>
<td>80</td>
</tr>
<tr>
<td>383</td>
<td>(\frac{1}{2}[L^1]^+)</td>
<td>30</td>
<td>106</td>
<td>([(C_6H_5NHCH_2)]^+)</td>
<td>100</td>
</tr>
<tr>
<td>308</td>
<td>([(C_6H_5)_3]^+)</td>
<td>20</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*\(\text{NBA} (m-\text{Nitrobenzyl alcohol}) \text{ was used as the matrix for FAB recording which give its peaks at} \ [m/z = 136, 137, 154, 289, 307].\)

Table 2.4: Positions of resonance peaks \(\delta \) (ppm) observed in \(^1\text{HNMR of [L^1.HClO_4]}\) and their assignments:

<table>
<thead>
<tr>
<th>Assignments</th>
<th>(H_3C-N&lt;)</th>
<th>(H_3C-N^\ominus)</th>
<th>(H_2C-C=N)</th>
<th>(H_2C-C^\ominus)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak Positions</td>
<td>6.64 ((10H))</td>
<td>7.14 ((20H))</td>
<td>4.17 ((12H))</td>
<td>2.50 ((8H))</td>
</tr>
</tbody>
</table>

It was synthesized in the same manner as described above for L^1.2HClO_4. In a two necked round bottomed flask hydrazine hydrate (6.05 ml, 0.099 mol) taken in methanol (30 cm^3), was stirred at room temperature. Perchloric acid (10 ml, 0.099 mol) was added drop wise with continuous stirring and then N-acetylaniline (94 ml, 0.199 mol) was added slowly through a dropping funnel with continuous stirring. Like [L^1.2HClO_4], the reaction was monitored periodically by recording the UV-visible spectrum of the reaction mixture which indicated formation of a species having C=N bonds. The disappearance of a band at 320 nm, characteristic^35 of n → π^* transition of (–CO–NH–) group of N-acetylaniline with a concomitant appearance of a new band at 398 nm indicates the formation of the intermediate species containing C=N bond in the molecular unit. Formaldehyde (20.3 ml, 0.299 mol) was added drop-wise to the reaction mixture which was again stirred over night at room temperature. 1,3-diaminopropane (8.4 ml, 0.099 mol) and formaldehyde (20.3 ml, 0.299 mol) taken in two separate dropping funnels fitted with the reaction flask, were dropped simultaneously to the reaction mixture at a slow dropping rate which gave an exothermic reaction. The temperature of the reaction mixture was maintained at room temperature and again stirred continuously for
two days. This produced an oily yellow coloured mass. Methanol (200 ml) was added in this and the reaction mixture was again stirred for 8 hours which afforded a light yellow coloured solid product. The product was filtered off, washed with methanol and dried under vacuum (Yield = 12.85 g or 14%, m.p. = 280°C (dec.). The solid was soluble in 1,4-dioxane and dimethyl sulphoxide. Here too, recrystallization of the solid provided only amorphous compound.

Table-2.5: Analytical and Molar Conductance ($A_m$) data of $[L^2\cdot 2HClO_4]$:

<table>
<thead>
<tr>
<th></th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
<th>$A_m$ (cm$^2$ohm$^{-1}$mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Observed</td>
<td>54.30</td>
<td>6.02</td>
<td>18.10</td>
<td>11.0</td>
</tr>
<tr>
<td>Calcd. For</td>
<td>54.31</td>
<td>6.03</td>
<td>18.10</td>
<td></td>
</tr>
</tbody>
</table>

UV-visible spectrum: $\lambda_{\text{max}} = 398\text{nm}$ ($\varepsilon = 1490 \text{ lit mol}^{-1}\text{cm}^{-1}$).
Physico-chemical and spectroscopic data of \([2,12,15,25]\)tetramethyl [3,11,16,24]tetrphenyl [1,3,5,9,11,13,14,16,18,22,24,26] dodecaazahexacosa [2,12,15,25]tetraene dihydroperchlorate i.e. \([L^2.2HClO_4]\):

Table-2.6: Important frequencies (cm\(^{-1}\)) observed in IR spectra of the ligand and their assignments:

<table>
<thead>
<tr>
<th>Assignments</th>
<th>Aliphatic</th>
<th>Aromatic</th>
<th>Cl(_2)O_4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band Positions</td>
<td>933(_s)</td>
<td>1613(_s)</td>
<td>3397(_s)</td>
</tr>
<tr>
<td></td>
<td>989(_m)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| s = strong, m = medium, w = weak

Table-2.7: Ion abundance for ligand and its fragmentation* peaks observed in FAB-mass spectrum of \([L^2.2HClO_4]\):

<table>
<thead>
<tr>
<th>m/z</th>
<th>Assignments</th>
<th>%Abundance</th>
<th>m/z</th>
<th>Assignments</th>
<th>%Abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>728</td>
<td>([L^2]^+)</td>
<td>70</td>
<td>419</td>
<td>([\frac{1}{2}L^2.NCNCH_3]^+)</td>
<td>25</td>
</tr>
<tr>
<td>1232</td>
<td>([L^2.2HClO_4+Pz-3H]^+)</td>
<td>66</td>
<td>364</td>
<td>(\frac{1}{2}L^2]^+)</td>
<td>35</td>
</tr>
<tr>
<td>1035</td>
<td>([L^2+Pz]^+)</td>
<td>64</td>
<td>212</td>
<td>([(C_6H_5NHCH_2)_2]^+)</td>
<td>68</td>
</tr>
<tr>
<td>713</td>
<td>([L^2.CH_3]^+)</td>
<td>40</td>
<td>154</td>
<td>([(C_6H_5)_2]^+)</td>
<td>50</td>
</tr>
<tr>
<td>651</td>
<td>([L^2.-C_6H_5]^+)</td>
<td>20</td>
<td>120</td>
<td>([C_6H_5NHCH_2.N]^+)</td>
<td>95</td>
</tr>
<tr>
<td>448</td>
<td>([\frac{1}{2}L^2+C_6H_5N_3]^+)</td>
<td>22</td>
<td>118</td>
<td>([C_6H_5NC.CH_3]^+)</td>
<td>80</td>
</tr>
<tr>
<td>441</td>
<td>([\frac{1}{2}L^2+C_6H_5]^+)</td>
<td>20</td>
<td>106</td>
<td>([C_6H_5NHCH_2]^+)</td>
<td>100</td>
</tr>
</tbody>
</table>

*\(\text{NBA} (m\text{-nitrobenzyl alcohol})\) was used as the matrix for FAB recording which give its peaks at \([m/z = 136,137,154,289,307]\).

*\(\text{Pz} = \text{NBA (307)}\)

Table-2.8: Position of Resonance peaks δ (in ppm) observed in \(^1H\)-NMR of \([L^2.2HClO_4]\) and their assignments:

<table>
<thead>
<tr>
<th>Assignments</th>
<th>CH(_2)</th>
<th>H(_2)C-N(&lt;)</th>
<th>H(_3)C-C=N</th>
<th>H(_3)C-(\text{O}^N)</th>
<th>NH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak Position</td>
<td>2.8</td>
<td>7.0</td>
<td>4.01</td>
<td>2.49</td>
<td>5.8</td>
</tr>
<tr>
<td></td>
<td>(12H)</td>
<td>(20H)</td>
<td>(12H)</td>
<td>(8H)</td>
<td>(4H)</td>
</tr>
</tbody>
</table>

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RESULTS AND DISCUSSION

Formation of L\(^1\).2HClO\(_4\):

Condensation reaction of N-acetylaniline with hydrazine hydrate takes place in 2:1 mol ratio in presence of HClO\(_4\) in methanol, producing an intermediate species which contains C=N bonds. The reaction was monitored by periodically recording the UV-visible spectrum of the reaction mixture which indicated formation of a species having C=N bonds. The disappearance of a band at 320 nm, characteristic\(^{35}\) of the \(n \rightarrow \pi^*\) transition of (-CO-NH-) group of N-acetylanilnine with a concomitant appearance of a new band at 385 nm, is indicative of the formation of new species in the solution. The band at 385 nm is characteristic of the \(\pi \rightarrow \pi^*\) transition reported\(^{42}\) for the C=N bond in the molecule. This reasonably indicates that the condensation process generated an intermediate species containing C=N bonds in the molecular unit. Further reaction of the intermediate (in-situ) with a capping agent i.e. mixture of HCHO and aniline (2:1 mol ratio) induces the cyclization process giving a fairly air stable yellow coloured amorphous solid product reasonably, via a 2:2 cyclization process. Analytical data (Table-2.1) of the solid product L\(^1\).2HClO\(_4\) are consistent with the molecular formula \(C_{48}H_{50}N_{10}.2HClO_4\) \([C_{48}H_{52}N_{10}Cl_2O_8]\). The FAB mass spectrum of solid exhibited the
molecular ion peak \([L^1]^+ \text{ (m/z = 766)}\), along with various relevant peaks generated from the thermal fragmentation process (Table-2.3). The appearance of fragments like \([L^1\cdot2\text{HClO}_4+\text{Bq-2H}]^+ \text{ (m/z=1100)}, [L^1+\text{Rn}]^+ \text{ (m/z=1055)}, \) (NBA=metanitro benzyl alcohol having its own fragmentations at m/z=136 (Bq), 137, 154, 289 (Rn), 307) along with other fragments like \(1/2[L^1]^+ \text{ (m/z=383)}, [(\text{C}_6\text{H}_5\text{H})_3]^+ \text{ (m/z=308)}, [(\text{C}_6\text{H}_5\text{NHCH})_2]^+ \text{ (m/z=212)}, [(\text{C}_6\text{H}_5\text{H})_2]^+ \text{ (m/z=154)}, [\text{C}_6\text{H}_5\text{NHCH}_2\text{N}]^+ \text{ (m/z= 120) and [C}_6\text{H}_5\text{NHCH}_2]^+ \text{ (m/z=106})\) in good percent abundance is consistent with the presence of these substituents / groups in the framework of the macrocyclic moiety. The important bands observed in the IR spectrum of the compound are summarized in (Table-2.2). The observed important bands are characteristic of \(\nu(\text{N–N}), \nu(\text{C–N}), \nu(\text{C–N}) \text{ aliphatic}, \nu(\text{C–N}) \text{ aromatic}, \nu(\text{C–C}) \text{ and } \nu(\text{C–H}) \) fundamental stretching vibrations. The spectrum does not show the strong broad band in the region 1700-1750 cm\(^{-1}\) reported\(^{37}\) for \(\nu(\text{C=O}) \) stretching vibration of the N-acetylaniline. However, there is appearance of new strong absorption band at around 1600 cm\(^{-1}\) characteristic\(^{37}\) of \(\nu(\text{C=N}) \) stretching vibration. The spectrum also contains a band of strong intensity at \(\sim1000 \text{ cm}^{-1}\) indicating the presence of \(\text{N–N} \) bond in the molecular unit. The disappearance of fundamental vibrations due to \(\text{C=O} \) bond stretching frequency with the concomitant appearance of sharp bands for \(\text{C=N} \) and \(\text{N–N} \) bond frequencies indicates the cyclization process giving the final product which contains the \(\text{C=N} \) as
well as N—N bonds. Additional frequencies, characteristic of \( \nu(C—N) \) stretching vibration along with the vibrations of \( \text{C}_6\text{H}_5, \text{CH}_3, \) and \( \text{C—C} \) bands also appeared at their appropriate positions. The spectrum also contained frequencies characteristic of the fundamental vibrations \( (\nu_1, \nu_2, \nu_3) \) of the counter \( \text{ClO}_4^- \) ion, at the reported positions. The observed splitting of the band in the region \( (1050-1130) \text{ cm}^{-1} \) for characteristic \( \nu_2 \) stretching vibration of perchlorate group is indicative of a lowering of the \( \text{ClO}_4^- \) symmetry from perfect \( T_d \) symmetry observed for the free anion to a reduced \( (C_3v \text{ or } C_2v) \) symmetry. The reduction in symmetry is observed when \( \text{ClO}_4^- \) group is involved in bonding either through one oxygen or two oxygen atoms effecting \( C_3v \text{ or } C_2v \) symmetry, respectively of the perchlorate group. The ligand behaved as a non-electrolyte \( ^{44} \) (Table 2.1) in dimethyl sulfoxide, an ionising high dielectric constant \( (\varepsilon=46) \) solvent, supporting the presence of a strong cation-anion interaction between the \([\text{L.2H}]^{2+}\) and the counter \( \text{ClO}_4^- \) ion in the solution. It is reasonable to suggest that the \( \text{ClO}_4^- \) ion is encapsulated in the cavity of the present macrocyclic ligand. There are few reports in the literature \(^{30} \) indicating that protonated form of polyaza macrocycles having large cavities as in \([1,4,7,10,13,16]\text{hexaazacyclooctadecane}
\[1,5,9,13,17,\ 21]\text{hexaazacyclooctatetracosane and}[1,5,9,13,17,21,25,29]\text{octazacyclodotriacontan} \) form stable complexes with various organic as
well as inorganic anions such as succinate, Cl\(^-\), NO\(_3\)\(^-\) and complex anions. This has also been confirmed from the IR data of L\(^1\)2HClO\(_4\) where too, encapsulation of the counter ClO\(_4\)\(^-\) ion has been evidenced from observed splitting of \(\nu_2\) vibration mode (Table-2.2) into a doublet at 1075 cm\(^{-1}\) and 1118 cm\(^{-1}\). The encapsulation of ClO\(_4\)\(^-\) ions in the macrocyclic cavities can be illustrated as in Fig. 2.2. The \(^1\)H-NMR spectrum of L\(^1\)2HClO\(_4\) (Table-2.4) recorded in d\(_6\)-DMSO showed signals characteristic of the protons from H\(_3\)C\(=\)N\(^<\) (6.68, 10H); H\(_2\)C\(=\)N\(\equiv\)N (7.18, 20H), H\(_3\)C\(=\)N\(^<\) (4.18, 12H); H\(_2\)C\(\equiv\)N \(\equiv\)N (2.58, 8H). The UV-visible spectrum of the ligand showed band at 385 nm assignable\(^{40}\) to the excitation from the filled \(\pi\) bonded electron of C\(=\)N (HOMO) to an empty antibonding \(\pi^*\) orbital (LUMO) i.e. \(\pi \rightarrow \pi^*\) transition of the polyaza moiety. In view of the strong support from physico-chemical and spectroscopic data, the whole process of the formation of the macrocyclic ligand salt [2,8,11,17]tetramethyl [3,5,7,12,14,16]hexaphenyl [1,3,5,7,9,10,12,14,16,18]decaazaoctadeca [2,8,11,17]tetraene dihydroperchlorate i.e. L\(^1\)2HClO\(_4\) can be considered as involving 2:2 cyclization in accordance with the scheme-1 shown in (Fig. 2.2). First step (step 1) of the scheme shows the formation of the intermediate species while step 2 indicates the capping mechanism involving cyclization process resulting in the macrocyclic moiety.
Scheme -1

1st Step

\[ \text{HCN} + \text{H}_2\text{N}-\text{NH}_2 \xrightarrow{\text{HClO}_4} \left[ \text{C}_6\text{H}_5-N-\text{C}=\text{N}-\text{N}=\text{C}-\text{N}-\text{C}_6\text{H}_5 \right] \cdot \text{HClO}_4 - 2\text{H}_2\text{O} \]

2nd Step

\[ \left[ \text{C}_6\text{H}_5-N-\text{C}=\text{N}-\text{N}=\text{C}-\text{N}-\text{C}_6\text{H}_5 \right] \cdot \text{HClO}_4 + \text{C}_6\text{H}_5\text{NH}_2 + 2\text{HCHO} \]

Fig. 2.2: Scheme showing the mechanism for the formation of \( \text{L}^1.2\text{HClO}_4 \)
Formation of $\text{L}^2\cdot\text{2HClO}_4$:

The in-situ capping reaction of the intermediate species formed in the solution by condensation of N-acetylaniline and hydrazine hydrate with 1,3-diaminopropane and formaldehyde (1:2 mol ratio) follows the same reaction path resulting in $\text{L}^2\cdot\text{2HClO}_4$ as a stable light yellow coloured solid compound similar to that discussed for the formation of macrocyclic ligand $\text{L}^1\cdot\text{2HClO}_4$. Here too, the course of the reaction has been monitored by recording the UV-visible spectra of the reaction mixture at regular intervals which indicates formation of a species having C=N bonds. The disappearance of a band at 320 nm characteristic$^{35}$ of the $n \rightarrow \pi^*$ transition of (-CO-NH-) group of N-acetylaniline with a concomitant appearance of a new band at 398 nm is indicative of the formation of new species in the solution. The band at 398 nm is characteristic of the $\pi \rightarrow \pi^*$ transition reported$^{42}$ for the C=N bond in the molecule. This reasonably indicates that the condensation process generates an intermediate species containing C=N bonds in the molecular unit. Further reaction of the intermediate (in-situ) with a capping agent i.e. mixture of HCHO and 1,3-diaminopropane (2:1 mol ratio) induces the cyclization process giving a fairly air stable, light yellow coloured amorphous solid product, reasonably, via a 2:2 cyclization process. Analytical data (Table 2.5) of the solid product $\text{L}^2\cdot\text{2HClO}_4$ are consistent with the molecular formula $\text{C}_{42}\text{H}_{58}\text{N}_{12}\text{Cl}_2\text{O}_8$. The FAB-mass spectrum of solid
exhibited the molecular ion peak \([L^2]^+ (m/z=728)\), along with various relevant peaks generated from the thermal fragmentation process (Table 2.7). The appearance of fragments like \([L^2\cdot2\text{HClO}_4+\text{Pz}-3\text{H}]^+ (m/z=1232)\), \([L^2+ \text{Pz}]^+ (m/z=1035)\), (NBA= metanitro benzyl alcohol having its own fragmentations at \(m/z = 136, 137, 154, 289, 307\) (Pz)), \([L^2\cdot\text{CH}_3]^+ (m/z=713)\), \([L^2\cdot\text{C}_6\text{H}_5]^+ (m/z=651)\), \([\frac{1}{2}L^2+\text{C}_3\text{H}_6\text{N}_3]^+ (m/z=448)\), \([\frac{1}{2}L^2+\text{C}_6\text{H}_5]^+ (m/z=441)\), \([\frac{1}{2}L^2\cdot\text{NCNCH}_3]^+ (m/z=419)\), \(\frac{1}{2}[L^2]^+ (m/z=364)\), \([(\text{C}_6\text{H}_5\text{NHCH}_2)_{2}]^+ (m/z=212)\), \([(\text{C}_6\text{H}_5)_{2}]^+ (m/z=154)\), \([\text{C}_6\text{H}_5\text{NHCH}_2\text{N}]^+ (m/z=120)\), \([\text{C}_6\text{H}_5\text{NC.CH}_3]^+ (m/z=118)\), \([\text{C}_6\text{H}_5\text{NHCH}_2]^+ (m/z=106)\), in good percent abundance are consistent with the presence of these substituents/groups in the frame work of the macrocyclic moiety. The important bands observed in the IR spectrum of the compound are summarized in (Table-2.6). The observed important bands are characteristic of \(v(\text{N—N}), v(\text{NH}), v(\text{C—N}), v(\text{C—C})\) and \(v(\text{C—H})\) fundamental stretching vibrations. The spectrum does not show the strong broad band in the region 1700-1750 cm\(^{-1}\) reported\(^{37}\) for \(v(\text{C=O})\) stretching vibration of the N-acetylaniline. However, there is appearance of new strong absorption band at around 1600 cm\(^{-1}\) characteristic\(^{37}\) of \(v(\text{C=\text{N}})\) stretching vibration. The spectrum also contains a band of strong intensity at \(\sim1000\) cm\(^{-1}\) indicating the presence of N—N bond in the molecular unit. The disappearance of fundamental vibrations due to \(\text{C=O}\) bond stretching frequency with the concomitant appearance of sharp bands for \(\text{C=\text{N}}\) and N—N bond
frequencies indicate the cyclization process giving the final product which contains the C=N as well as N=N bonds. Additional frequencies characteristic of ν(C−N) stretching vibration along with the vibration of C\textsubscript{6}H\textsubscript{5}, CH\textsubscript{3} and C−C bonds also appeared at their appropriate positions. The spectrum also contained frequencies characteristic of the fundamental vibrations (ν\textsubscript{1}, ν\textsubscript{2}, ν\textsubscript{3}) of the counter ClO\textsubscript{4}− ion, at the reported\textsuperscript{43} positions. The observed splitting of the band in the region (1050–1130) cm\textsuperscript{-1} characteristic of ν\textsubscript{2} stretching vibration of perchlorate group is indicative of a lowering of the ClO\textsubscript{4}− symmetry from perfect T\textsubscript{d} symmetry observed for the free anion to a reduced (C\textsubscript{3v} or C\textsubscript{2v}) symmetry. The reduction in symmetry is observed when ClO\textsubscript{4} group is bonded either through one oxygen or two oxygen atoms effecting C\textsubscript{3v} or C\textsubscript{2v} symmetry of the perchlorate group. The ligand behaved as a non electrolyte\textsuperscript{44} (Table-2.5) in dimethyl sulfoxide (DMSO), an ionizing high dielectric constant (ε=46) solvent, supporting the presence of a strong cation-anion interaction between the [L.2H]\textsuperscript{2+} and the counter ClO\textsubscript{4}− ion in the solution. It is reasonable to suggest that the ClO\textsubscript{4}− ion is encapsulated in the cavity of the macrocyclic ligand. This has also been confirmed with the IR data of [L\textsuperscript{2}.2ClO\textsubscript{4}]. The encapsulation of ClO\textsubscript{4}− ions in the macrocyclic cavities can be illustrated as in Fig. 2.3.

The \textsuperscript{1}H-NMR spectrum of L\textsuperscript{2}.2ClO\textsubscript{4} (Table-2.8) recorded in d\textsubscript{6}-
DMSO showed signals that are characteristic of the protons from NH (5.8δ, 4H), H$_3$C$\equiv$N (2.49δ, 8H); H$_5$C$\equiv$C=\(N\) (4.01δ, 12H); H$_5$C$_6$=\(N\) (7.0δ, 20H) and CH$_2$ (2.8δ, 12H).

The UV-visible spectrum of the ligand showed band at 398 nm assignable to the excitation from the filled π bonded electron of C=\(N\) (HOMO) to an empty antibonding π* orbital (LUMO) i.e. \(\pi \rightarrow \pi^*\) transition of the polyaza moiety. The formation of the macrocyclic ligand salt [2,12,15,25]tetramethyl [3,11,16,24]tetraphenyl[1,3,5,9,11,13,14,16,18,22,24,26] dodecaazahexacosa [2,12,15,25]tetraane dihydro-perchlorate i.e. [L$^2$HClO$_4$] can be considered as involving 2:2 cyclization in accordance with the scheme-2 shown in (Fig. 2.3). First step (step-1) of the scheme-2 shows the formation of intermediate species while step-2 indicates the capping mechanism involving cyclization process resulting in the macrocyclic moiety.
Scheme - 2

1st Step

\[ 2\text{C}_6\text{H}_5\text{NH}—\text{CO—CH}_3 + \text{H}_2\text{N—NH}_2 \xrightarrow{\text{HClO}_4} \text{[C}_6\text{H}_5—\text{N—C=N—N=C—N—C}_6\text{H}_5\cdot\text{HClO}_4 \]

\[-2\text{H}_2\text{O} \]

2nd Step

\[ \text{H}_3\text{N} (\text{CH}_2)_2\text{NH}_2 + 2\text{HCHO} \xrightarrow{} \text{[H}_2\text{C=N—(CH}_2)_3—\text{N=CH}_2] + 2\text{H}_2\text{O} \]

\[ \text{[C}_6\text{H}_5—\text{N—C=N—N=C—N—C}_6\text{H}_5\cdot\text{HClO}_4 + \text{[H}_2\text{C=N—(CH}_2)_3—\text{N=CH}_2] \]

Fig. 2.3: Scheme showing the mechanism for the formation of \( \text{L}_2\cdot\text{2HClO}_4 \)
REFERENCES:


7. For reviews on binuclear enzymes and models see:


CHAPTER 3

Reactivity of \([L^{1.2}HClO_4]\) and \([L^{2.2}HClO_4]\) towards Metal Salts and their Derivative Complexes
INTRODUCTION

It is well known\(^1\) that almost all type of metal ions have been complexed with macrocyclic ligands\(^1^-^6\). The coordination chemistry of macrocyclic molecules has been extended for the encapsulation of molecular cations\(^5\), neutral molecules\(^7\) as well as complex anions\(^8\). The chemistry of binucleating macrocycles which are capable to incorporate two metal centers has been the subject of recent investigations\(^9\). Binuclear compounds of polyaza macrocycles have been classified into four types:

(i) Compounds of large polydentate rings with two metal ions coordinated by different sets of donor atoms, often with a bridging ligand such as azide linking the metal ions\(^10\).

(ii) Compounds which have covalently bonded to two or more separate aza macrocycles.

(iii) Polynuclear macrocyclic compounds with units linked facially by a bridging group between the metal ions.

(iv) Cofacial dimers with some degree of metal-metal bonding.

Transition-metal complexes of binucleating ligands\(^11\) are of interest because they provide the opportunity to study the intramolecular binding, along with the magnetic exchange interactions and multi electron redox reactions as well as possible activation of small
substrate molecules between the metal centers. They may also serve as models for certain metalloproteins for which the biological function is related to the occurrence of the metal centers in pairs. Synthetic macrocyclic ligands having a cavity size large enough to encapsulate two metal ions provide a means whereby the interactions and structural relationships between the metal centers may conveniently be studied in the laboratory. The preparation of novel macrocycles 18-membered \([N_{10}]\), \([L^1\cdot 2\text{HClO}_4]\) and 26-membered \([N_{12}]\), \([L^2\cdot 2\text{HClO}_4]\) moieties with unsymmetrical aza groups (possessing amine as well as imine functions) have been described in chapter-2. The reactivities of these macrocyclic ligands towards transition metal ions and their derivative complexes have also been examined and the characterizations of the resulting final products have been discussed in this chapter.
PART-A

Synthesis and Characterization of Complexes $[L^1\cdot2\text{HClO}_4]$ and $[L^2\cdot2\text{HClO}_4]$ with 3d-Metal Ions: Encapsulation of $\text{Cr}^{3+}$, $\text{Fe}^{3+}$, $\text{Co}^{2+}$, $\text{Ni}^{2+}$ or $\text{Cu}^{2+}$ Ions
EXPERIMENTAL

Reagents used:

The metal salts CrCl$_3$.6H$_2$O (BDH, India), anhydrous FeCl$_3$ (Ranbaxy, India), CoCl$_2$. 6H$_2$O (BDH, India), NiCl$_2$.6H$_2$O (Merck, India), CuCl$_2$.2H$_2$O (E.Merck, India) and glacial acetic acid (BDH, India) were used as received. Anhydrous CoCl$_2$ was prepared by dehydration of CoCl$_2$.6H$_2$O by acetic anhydride according to the reported method$^{12}$. Solvents were dried before use by reported method$^{13}$ and the precursors $[\text{MPh}_3\text{P})_2\text{Cl}_2]$ (M=Co or Ni) were prepared according to the reported procedures$^{14,15}$. 

Physical measurements:

IR spectra were recorded as KBr discs on a Perkin-Elmer model spectrum GX. The X-band ESR spectra of polycrystalline samples were recorded on a JEOL-RE series Model JES-RE3X spectrometer calibrated with diphenylpicrylhydrazyl (dpph: $g = 2.0037$) at room temperature. Electronic spectra of solution in DMSO were recorded on a Cintra 5 GBS UV-Visible spectrophotometer and the reflectance spectra of solid samples diluted with MgO were obtained using Perkin-Elmer Model LAMBDA-19 spectrophotometer at room temperature. Conductivities of $10^{-3}$ M solution of compounds in DMSO were measured on Systronics-305 Conductivity Bridge and the magnetic susceptibilities were estimated using Farady balance calibrated with Hg[Co(NCS)$_4$] at room
temperature. Results of microanalyses were obtained from Micro
Analytical Laboratory of Central Drug Research Institute, Lucknow,
India.
PREPRATION OF PRECURSORS

Preparation$^{14}$ of Dichlorobis(triphenylphosphine) cobalt(II) [Co(Ph$_3$P)$_2$ Cl$_2$]:

It was prepared by slowly mixing hot absolute ethanolic solutions of anhydrous CoCl$_2$ (1.30 g, 10 mmol) and triphenyl phosphine (5.24 g, 20 mmol) with continuous stirring. The complex began to precipitate as dark blue before the mixing was complete. The hot solution was allowed to stand, filtered hot and washed with absolute ethanol and ethyl acetate and finally dried in vacuum. (m.pt-225$^0$C).

Preparation$^{15}$ of Dichlorobis(triphenylphosphine) Nickel(II) [Ni(Ph$_3$P)$_2$ Cl$_2$]:

NiCl$_2$.6H$_2$O (1.19 g, 5.0 mmol) dissolved in minimum volume of water, was diluted with glacial acetic acid (25 ml). Triphenylphosphine (2.62 g, 10.0 mmol) taken in 50ml glacial acetic acid was added slowly to the above solution while stirring. The olive green microcrystalline solid separated out of the mother liquor was filtered off, washed with glacial acetic acid and dried in vacuum (m.pt-234$^0$C).
PREPRATION OF METAL COMPLEXES

*Reaction of macrocyclic ligand, L\(^1\).2HClO\(_4\), with metal salts:*

**Reaction of L\(^1\).2HClO\(_4\) with CrCl\(_3\).6H\(_2\)O; Isolation of Cr\(_2\)L\(^1\)Cl\(_4\)(ClO\(_4\))\(_2\) (I):**

Methanolic solution of CrCl\(_3\).6H\(_2\)O (0.548 g, 2.06 mmol) was added drop wise to a magnetically stirred solution of L\(^1\).2HClO\(_4\) (1.0 g, 1.03 mmol) in 1,4-dioxane (30 cm\(^3\)). The reaction mixture was stirred for 2 days at room temperature which gave reddish-orange coloured precipitate. The precipitate was filtered off washed first with 1,4-dioxane and then methanol, dried under vacuum [(I), m.pt.-260\(^\circ\)C (dec.), yield- 0.480 g or 38%].

**Reaction of L\(^1\).2HClO\(_4\) with anhydrous FeCl\(_3\); isolation of Fe\(_2\)L\(^1\)Cl\(_4\)(ClO\(_4\))\(_2\) (II):**

The ligand (1.0 g, 1.03 mmol) was dissolved in 1,4-dioxane (30 cm\(^3\)) and to this a methanolic solution of anhydrous FeCl\(_3\) (0.334 g, 1.88 mmol) was added drop wise with stirring at room temperature. The colour of the reaction mixture changed to blackish brown, which gave dark coloured precipitate. The precipitate was filtered off, washed with 1,4-dioxane followed by methanol. The dark brown coloured solid obtained was dried in vacuum. [(II), m.pt-240\(^\circ\)C (dec.), yield-0.718 g or 57%].
Reaction of $L^{1.2}\text{HClO}_4$ with $\text{CoCl}_2.6\text{H}_2\text{O}$; Isolation of $\text{Co}_2L^1\text{Cl}_2(\text{ClO}_4)_2$ (III):

The ligand (1.0 g, 1.03 mmol) was dissolved in 1,4-Dioxane (30 cm$^3$) and to this a methanolic solution of $\text{CoCl}_2.6\text{H}_2\text{O}$ (0.49 g, 2.06 mmol) was added drop wise at room temperature. The colour of the reaction mixture changed to dark green. The reaction mixture was further stirred for ca 48 hours at room temperature which gave green coloured precipitate. It was filtered off, washed with 1,4-Dioxane and then methanol. The green coloured solid obtained was dried in vacuum. [(III), m.pt-280°C (dec.), yield - 0.369g or 31%].

Reaction of $L^1.2\text{HClO}_4$ with $\text{NiCl}_2.6\text{H}_2\text{O}$; Isolation of $\text{Ni}_2L^1\text{Cl}_2(\text{ClO}_4)_2$ (IV):

$\text{NiCl}_2.6\text{H}_2\text{O}$ (0.489 g, 2.06 mmol) solution in methanol (20 cm$^3$) was added drop wise to the ligand (1.0 g, 1.03 mmol) solution in 1,4-Dioxane (30 cm$^3$) while stirring at room temperature. The colour of the reaction mixture changed to dark yellow. The reaction mixture was stirred for ca 48 hours at room temperature. Brown coloured amorphous solid was obtained. It was filtered off and washed with 1,4-Dioxane followed by methanol. The solid was dried in vacuum. [(IV), m.pt-278°C (dec.), yield-0.584 g or 49%].
Reaction of $L^1 \cdot 2\text{HClO}_4$ with CuCl$_2 \cdot 2\text{H}_2\text{O}$; Isolation of Cu$_2$L$_2^1\text{Cl}_2(\text{ClO}_4)_2$ (V):

The ligand (1.0 g, 1.03 mmol) dissolved in 1,4-Dioxane (30 cm$^3$) was reacted with a methanolic solution of CuCl$_2 \cdot 2\text{H}_2\text{O}$ (0.351 g, 2.06 mmol) at room temperature. The reaction mixture was further stirred for ca 48 hours at room temperature. It was then filtered off and washed with 1,4-Dioxane and then methanol. The greenish brown coloured solid obtained was dried in vacuum. [(V), m.pt 270°C (dec.), yield 0.578 g or 48%].
Reaction of macrocyclic ligand, $L^{1.2}\text{HClO}_4$, with precursors:

Reaction of $L^{1.2}\text{HClO}_4$ with $[\text{Co(Ph}_3\text{P})_2\text{Cl}_2]$; Isolation of $\text{Co}_2L^{1}\text{Cl}_2(\text{ClO}_4)_2$ (VI):

The ligand, $L^{1.2}\text{HClO}_4$ (0.5 g, 0.515 mmol) was dissolved in 1,4-Dioxane (30 cm$^3$) and reacted with the solution of $[\text{Co(Ph}_3\text{P})_2\text{Cl}_2]$ (0.5g, 1.03mmol) in methanol (25 cm$^3$) with continuous stirring. It was further stirred over-night at room temperature. The resulting solid product was filtered off and washed with 1,4-Dioxane and then methanol. Green coloured amorphous solid was obtained which was dried in vacuum. [(VI), m.pt.-280°C (dec.), yiled-0.380 g or 32%].

The mother liquor was concentrated to 1/4$^{th}$ of its original volume which has afforded colourless needles [m.pt-71-73°C]. The melting point and spectroscopic data confirmed the colourless needles to be free triphenylphosphine, which were liberated out of the precursor during its reaction with the ligand.

Reaction of $L^{1.2}\text{HClO}_4$ with $[\text{Ni(Ph}_3\text{P})_2\text{Cl}_2]$; Isolation of $\text{Ni}_2L^{1}\text{Cl}_2(\text{ClO}_4)_2$ (VII):

The ligand, $L^{1.2}\text{HClO}_4$ (1.0 g, 1.03 mmol) was dissolved in 1,4-Dioxane (30 cm$^3$) and reacted with the solution of $[\text{Ni(Ph}_3\text{P})_2\text{Cl}_2]$ (1.0 g, 2.06 mmol) in methanol (25 cm$^3$) with continuous stirring. It was stirred for ca 48 hours at room temperature. The resulting solid product was filtered off and washed with 1,4-Dioxane and then
methanol. The product was dried in vacuum giving brown coloured amorphous solid [(VII), m.pt.-278°C (dec.), yield 0.438g or 37%]. Here too, the mother liquor after concentration to 1/4\textsuperscript{th} of its original volume afforded colourless needles, which through analytical and spectroscopic methods was identified as free tripphenylphosphine.

Reaction of macrocyclic ligand, $L^2$-2HClO$_4$, with Metal salts:

Reaction of $L^2$-2HClO$_4$ with CrCl$_3$·6H$_2$O; Isolation of Cr$_2$L$^2$Cl$_4$(ClO$_4$)$_2$ (VIII):

The ligand (1.0 g, 1.077 mmol) was dissolved in 1,4-Dioxane (30 cm$^3$) and CrCl$_3$·6H$_2$O (0.570 g, 2.14 mmol) in methanol (25 cm$^3$). The metal salt solution was added to the ligand solution with continuous stirring at room temperature. It was further stirred for ca 30 hours. Colour of the reaction mixture changed from light yellow to dark orange. The yellowish red precipitate formed was filtered off, washed with 1,4-Dioxane followed by methanol and was dried in vacuum. [(VIII), m.pt-298°C (dec.), yield-0.790 g or 62%].

Reaction of $L^2$-2HClO$_4$ with anhydrous FeCl$_3$; Isolation of Fe$_2$L$^2$Cl$_4$(ClO$_4$)$_2$ (IX):

The metal salt solution, FeCl$_3$ (0.347 g, 2.14 mmol) taken in methanol (25 cm$^3$) was reacted with the ligand (1.0 g, 1.07 mmol) solution in 1,4-Dioxane (30 cm$^3$) as described above. The reaction mixture was stirred for
ca 48 hours at room temperatures. By this time the colour of the reaction mixture changed from light yellow to black-brown and some solid was separated out of the solution. The solid product was filtered off and washed with 1,4-Dioxane and then with methanol. It was dried under vacuum giving dark brown coloured amorphous solid. [(IX), m.pt.-310°C (dec.), yield-0.425 g or 33%].

Reaction of $L^2\cdot 2\text{HClO}_4$ with $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$; Isolation of $\text{Co}_2L^2\text{Cl}_2(\text{ClO}_4)_2$ (X):

The ligand (1.0 g, 1.07 mmol) dissolved in 1,4-Dioxane (30 cm$^3$) was reacted with the solution of $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ (0.509 g, 2.14 mmol) in methanol (20 cm$^3$). The reaction mixture was stirred for ca 48 hours at room temperature and the colour of the reaction mixture became greenish-brown. The precipitate formed was filtered off and washed with 1,4-Dioxane and then with methanol. Brown coloured solid was obtained after it was dried under vacuum. [(X) m.pt. > 300 °C, yield-0.703 g or 58%].

Reaction of $L^2\cdot 2\text{HClO}_4$ with $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$; Isolation of $\text{Ni}_2L^2\text{Cl}_2(\text{ClO}_4)_2$ (XI):

The ligand (1.0 g, 1.07 mmol) was dissolved in 1,4-Dioxane (30 cm$^3$) and to this the methanolic solution of $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ (0.508 g, 2.14 mmol) was added with continuous stirring. The reaction mixture was stirred for ca 48 hours at room temperature. The colour of the reaction mixture became brownish-yellow and the solid product formed was filtered off and washed with 1,4-Dioxane followed by
methanol. The solid was dried in vacuum giving dark yellow amorphous solid. [(XI), (m.pt.-298 °C (dec), yield-0.601 g or 50%).

**Reaction of \( L^2 \cdot 2\text{HClO}_4 \) with \( \text{CuCl}_2 \cdot 2\text{H}_2\text{O} \); Isolation of \( \text{Cu}_2L^2\text{Cl}_2(\text{ClO}_4)_2 \) (XII):**

\( \text{CuCl}_2 \cdot 2\text{H}_2\text{O} \), (0.364 g, 2.14 mmol) dissolved in methanol (30 cm³) was added drop wise to the ligand (1.0 g, 1.07 mmol) solution in 1,4-Dioxane (30 cm³) while stirring. The reaction mixture was continuously stirred for ca 36 hours at room temperature. The colour of the solution changes to dark brown from initial light yellow colouration. The brown colour solid formed was filtered off and washed with 1,4-Dioxane followed by methanol. The solid was dried in vacuum. [(XII), m.pt.-290 °C (dec), yield-0.849 g or 75%).

**Reaction of macrocyclic ligand, \( L^2 \cdot 2\text{HClO}_4 \), with Precursors:**

**Reaction of \( L^2 \cdot 2\text{HClO}_4 \) with \([\text{Co(Ph}_3\text{P})_2\text{Cl}_2]\); Isolation of \( \text{Co}_2L^2\text{Cl}_2(\text{ClO}_4)_2 \) (XIII):**

The precursor \([\text{Co(Ph}_3\text{P})_2\text{Cl}_2]\) (1.0 g, 1.07 mmol) was dissolved in methanol (20 cm³) and was reacted with the ligand (0.5 g, 0.535 mmol) solution in 1,4-Dioxane (30 cm³) with continuous stirring at room temperature. The reaction mixture was magnetically stirred for ca 30 hrs at room temperature. The colour of the reaction mixture changed to dark brownish-green. The brown colour solid formed was filtered off
and washed with 1,4-Dioxane followed by methanol and finally dried in vacuum. [(XIII), m.pt>300°C, yield-0.314 g or 26%].

The mother liquor was concentrated to 1/4\textsuperscript{th} of its original volume and kept at 5°C, which afforded colourless crystalline solid. [m.pt-71-73°C], The melting point and spectroscopic data confirmed the latter to be free triphenylphosphine, liberated out of the precursor during the reaction with the macrocyclic ligand.

**Reaction of L\textsuperscript{2}.2HClO\textsubscript{4} with [Ni(Ph\textsubscript{3}P)\textsubscript{2}Cl\textsubscript{2}]; Isolation of Ni\textsubscript{2}L\textsuperscript{2}Cl\textsubscript{2}(ClO\textsubscript{4})\textsubscript{2} (XIV):**

The precursor [Ni(Ph\textsubscript{3}P)\textsubscript{2}Cl\textsubscript{2}] (1.0 g, 1.07 mmol) was dissolved in methanol (20 cm\textsuperscript{3}) and the solution was reacted with ligand (0.5 g, 0.535 mmol) dissolved in 1,4-Dioxane (30 cm\textsuperscript{3}) with continuous stirring. The reaction mixture was magnetically stirred for ca 30 hrs at room temperature. The colour of the reaction mixture changes to dark brownish-yellow. The dark yellow solid formed was filtered off and washed with 1,4-Dioxane followed by methanol and was dried in vacuum. [(XIV), m.pt-298°C (dec.), yield-0.501 g or 41%].

The mother liquor was concentrated to 1/4\textsuperscript{th} of its original volume and kept at 5°C in refrigerator which afforded colourless crystalline solid [m.pt.-71-73°C], identified as free triphenylphosphine as above.
RESULTS AND DISCUSSION

The dihydroperchlorate salts of the macrocycles [2,8,11,17]tetramethyl [3,5,7,12,14,16]hexaphenyl [1,3,5,7,9,10,12,14,16,18]decaazaoctadeca [2,8,11,17]tetraene i.e. \([L^2\cdot\text{HClO}_4]\) and [2,12,15,25]tetramethyl [3,11,16,24]tetraphenyl [1,3,5,9,11,13,14,16,18,22,24,26]dodecaazahehexacosa [2,12,15,25]tetraene i.e. \([L^2\cdot\text{HClO}_4]\) exhibited considerable reactivity towards metal salts as well as their derivative complexes at room temperature producing fairly air stable solid products.

These macrocyclic ligands were reacted with \(\text{MCl}_3\) (\(M = \text{Cr} \) or \(\text{Fe}\)), \(\text{MCl}_2\) (\(M = \text{Co}, \text{Ni}, \) or \(\text{Cu}\)) and the precursors \([\text{Co}(\text{Ph}_3\text{P})_2\text{Cl}_2]\) and \([\text{Ni}(\text{Ph}_3\text{P})_2\text{Cl}_2]\) in 1:2 (\(L:M\)) mole ratio in 1,4-dioxane-methanol mixture. Analytical data of the products obtained from these reactions with \(L^1\cdot\text{HClO}_4\) and \(L^2\cdot\text{HClO}_4\) have been summarized in Tables (3.1 and 3.2 respectively). The observed data are consistent with the molecular formulae \([M_2\text{C}_{48}\text{H}_{50}\text{N}_{10}\text{Cl}_{15}\text{O}_{8}]\) (\(M = \text{Cr} \) (I) or \(\text{Fe} \) (II)), \([M_2\text{C}_{48}\text{H}_{50}\text{N}_{10}\text{Cl}_{14}\text{O}_{8}]\) (\(M = \text{Co} \) (III), \(\text{Ni} \) (IV) or \(\text{Cu} \) (V)), \([M_2\text{C}_{42}\text{H}_{56}\text{N}_{12}\text{Cl}_{6}\text{O}_{8}]\) (\(M = \text{Cr} \) (VIII), \(\text{Fe} \) (IX)) and \([M_2\text{C}_{42}\text{H}_{56}\text{N}_{12}\text{Cl}_{4}\text{O}_{8}]\) (\(M = \text{Co} \) (X), \(\text{Ni} \) (XI) or \(\text{Cu} \) (XII)). The complexes formed are compatible with the stoichiometries \(M_2\text{LCl}_4(\text{ClO}_4)_2\) (\(M = \text{Cr} \) or \(\text{Fe} \); \(L = L^1\) or \(L^2\)) and \(M_2\text{LCl}_2(\text{ClO}_4)_2\) (\(M = \text{Co}, \text{Ni} \) or \(\text{Cu} \); \(L = L^1\) or \(L^2\)).

Reactions of the precursors \([M(\text{Ph}_3\text{P})_2\text{Cl}_2]\) (\(M = \text{Co} \) or \(\text{Ni}\)) with the macrocyclic ligands \(L^1\cdot\text{HClO}_4\) and \(L^2\cdot\text{HClO}_4\) are accompanied with a
complete liberation of the ancillary ligand, triphenylphosphine, from the precursors affording products with molecular formula \([M_2C_{48}H_{50}N_{10}Cl_4O_8]\) (M = Co (VI) or Ni (VII)) and \([M_2C_{42}H_{56}N_{12}Cl_4O_8]\) (M=Co (XIII) or Ni (XIV)), respectively. Analytical data of the products obtained here are identical to that obtained from the corresponding reactions of the macrocyclic ligands with metal chlorides, MCl₂ (M = Co or Ni). It is note-worthy that the reaction of the precursors \([MCl_2(Ph_3p)_2]\) (M = Co or Ni) with the present macrocycles are accompanied with total liberation of the PPh₃ supporting ligand from the precursors resulting in the final products which do not contain bonded Ph₃P in the molecular unit. The stoichiometry of the final product is \(M_2LCl_2(ClO_4)_2\), (Table -3.1, 3.2). The liberation of Ph₃P as free ligand is, reasonably, through a ligand displacement mechanism\(^{16}\) (Path) in which the macrocyclic ligands act as a strong \(\sigma\) donor chelating agent encapsulating metal ions as a consequence of the macrocyclic effect.

The information regarding the electrolytic behaviour of the present complexes in solutions have been obtained from molar conductivity \((\Lambda_m)\) data measured in DMSO which is a strong ionizing solvent \((\varepsilon=46)\)\(^{13}\). The observed magnitudes of \(\Lambda_m\) (Table-3.1 and 3.4) suggest that the complexes (III-VII), (X), (XII) and (XIII) behave as a 1:1 electrolyte\(^{17}\) whereas (I), (II), (VIII), (IX), (XI) and (XIV) exhibit pseudo 1:2 electrolytic nature in solution.
IR Spectra

IR spectra of all the complexes (I-XIV) exhibited fundamental vibrations characteristic of the coordinated macrocycle as well as that of the coordinated perchlorate counter anion (Table-3.3, 3.4). The position of \( v(N-N) \) stretching vibration is shifted to a higher wave number as compared to that observed for free macrocyclic ligands i.e. \( L^1.2\text{HClO}_4 \) and \( L^2.2\text{HClO}_4 \) (Table-2.2,2.6). The position of the characteristic \( v(C=\text{N}) \) stretching vibrations is, however, shifted to a lower wave number in the complexes with reference to that indicated in the IR spectra of the free \( L^1.2\text{HClO}_4 \) and \( L^2.2\text{HClO}_4 \). In addition, the band observed in 400 – 500 cm\(^{-1}\) region is assignable\(^{18}\) to the (M—N) bond stretching vibrations of the complexes which supports the encapsulation of the metal ions in the macrocyclic cavities. This chelation is through the lone pairs available at aza groups of the imine, \( C=\text{N} \) and/or amine, \( \text{NH} \) functions present in the macrocyclic moieties (Fig- 3.1 and 3.2). The observed splitting of the fundamental \( v_2 \) stretching vibration\(^{19}\) of the perchlorate anion in the 1000 – 1100 cm\(^{-1}\) region suggests a strong attachment of the counter Cl\(_4^-\) anion to the metal ions in the complexes too, similar to that found for the \([L.2\text{H}]^{2+}\) cation with Cl\(_4^-\) ion in the salt of macrocyclic ligands (vide supra chapter 2).
Magnetic susceptibility and ligand field spectra

Complexes with $L^1\cdot2\text{HClO}_4$:

The electronic spectra of all the metal complexes show an intense absorption band ($\epsilon \sim 10^3 \text{ Lmol}^{-1}\text{cm}^{-1}$) in U.V. region which is assignable to that arising$^{20}$ from the $\pi \rightarrow \pi^*$ transition of the imine ($\text{C} = \text{N}$) bond of the ligand moiety as well as to ligand → metal, ($L \rightarrow M$) charge transfer (CT) transitions (Table-3.5, 3.6). An overlapping of the ligand $\pi \rightarrow \pi^*$ and CT bands has been observed. The spectra also contained a few bands in the visible region due to $d-d$ transitions of the metal ions coordinated/encapsulated to the macrocyclic moieties.

The observed positions and nature of the $d-d$ bands (Table 3.5 and 3.6) due to ligand field effects of the macrocyclic ligands with the $d^n$ configuration of metal ions along with the corresponding magnetic moment ($\mu_{\text{eff}}$) of the individual complexes have been used to ascertain the probable coordination geometry around the metal ions as discussed below:

The magnetic moment for the complex (I) is 3.2 BM, ($\mu_{\text{eff}}$ per $\text{Cr}^{3+} = 1.6 \text{ BM}$) which is very low compared to the $\mu_{\text{so}}$ (spin only) value theoretically expected for three unpaired electrons$^{21}$ ($d^3$ configuration) ($\mu_{\text{so}} = 3.88 \text{ BM}$). The lowering of magnetic moment from theoretically expected$^{21}$ spin-only value is probably due to the presence of considerable extent of anti-ferromagnetic interaction in the present bimetallic complex i.e. $\text{Cr}_2L^1\text{Cl}_4(\text{ClO}_4)_2$. However, number and positions
of the absorption bands observed in the electronic spectra of the complex (I) suggest that it attains a trigonally distorted octahedral geometry\textsuperscript{22}. The ground electronic state for d\textsuperscript{3} system in octahedral geometry having a perfect O\textsubscript{h} symmetry is \(^4A\text{g}(F)\) and the allowed excited states are \(^4T\text{g}(F), \ ^4T\text{g}(P)\) and \(^4T\text{g}(P)\). This will give rise to three spin–allowed transitions i.e. \(^4T\text{g}(F) \leftarrow \ ^4A\text{g}(F), \ ^4T\text{g}(F) \leftarrow \ ^4A\text{g}(F)\) and \(^4T\text{g}(P) \leftarrow \ ^4A\text{g}(F)\) in the order of their increasing energy (Table 3.5). The highest energy transition i.e. \(^4T\text{g}(P) \leftarrow \ ^4A\text{g}(F)\) is a two electron excitation process henceforth, may not be observed. It is usually obscured by the strong charge transfer bands\textsuperscript{21} (Fig. 3.1(a)).

The observed magnetic moment for complex (II) is 4.72 BM, (\(\mu_{\text{eff}}\) per Fe\textsuperscript{3+}=2.36 BM), which is lower than that expected for theoretically estimated\textsuperscript{21} \(\mu_{s,o}\) value (5.92 BM) for five unpaired electrons (5upe) in d\textsuperscript{5} configuration of the metal ion. This reduction in magnetic moment is indicative of the presence of a strong anti-ferromagnetic interaction which has a greater probability in dinuclear complexes. Such type of interaction is not uncommon in Fe\textsuperscript{3+} complexes. The electronic spectra of this complex exhibited four broad absorption bands (Table-3.5) with a few spikes associated with these bands centered at 20,000; 19,267; 17,391; 16,474 cm\(^{-1}\). These bands are assigned to the d–d transition for high-spin Fe\textsuperscript{3+} (d\textsuperscript{5}) complexes\textsuperscript{23} having octahedral geometry. These bands arise due to the spin-forbidden transitions in the order of increasing energy, \(^4T\text{g}(G) \leftarrow \ ^6A\text{g}, \ ^4T\text{g}(G) \leftarrow \ ^6A\text{g},\)
\(^4A_{1g} \rightarrow ^4E_{g}(G) \leftarrow ^6A_{1g} \) and \(^4T_{2g}(D) \leftarrow ^6A_{1g}\) which gain intensity due to possible \(d_{\pi} - P_{\pi}\) mixing (Fig. 3.1(a)).

The electronic spectra of complex (III) and (VI) are identical and exhibit a broad band centered at 25,974 cm\(^{-1}\), characteristic of the \((L \rightarrow M), CT\) and \(\pi \rightarrow \pi^*\) transitions along with three well defined bands in the lower energy region \((14,598 - 20,746\) cm\(^{-1}\)) arising from \(d-d\) transitions. The latter bands are reasonably comparable, with those reported\(^{22}\) for five coordinate Co\(^{2+}\) complexes having approximate square pyramidal geometry. The bands observed in the \(d-d\) region of compounds (III) and (VI) are therefore assigned\(^{24}\) (Table 3.5) to the transitions \(a_1 \leftarrow e\), \(a_1 \leftarrow e\) and, \(b_1 \leftarrow a_1\) characteristic of low-spin square pyramidal Co\(^{2+}\) complexes. The present complexes are diamagnetic in nature. However, the mononuclear low-spin square pyramidal Co\(^{2+}\) complexes are reported\(^{24}\) to exhibit \(\mu_{\text{eff}}\) value of about 2.2 B.M. expected for one unpaired electron on the metal ion with considerable spin-orbit coupling contributions\(^{25}\). The mononuclear five coordinate Co\(^{2+}\) complexes of the type \([\text{CoL}_2X]^+\) (where \(L =\) Diphenyl (o-diphenyl arsinophenyl) phosphine or diphenyl (o-methyl selinophenyl) phosphine and \(X =\) Cl, Br or I) is reported to exhibit magnetic moments consistent with one unpaired electron on the \(d_{z^2}\) orbital of the metal ion and the ground electronic stat is \(^2A_{1}(G)\). Such complexes exhibit well defined absorption bands due to \(b_1 \leftarrow a_1\) and \(a_1 \leftarrow e\) excitations. The band due to \(a_1 \leftarrow e\) transition is sensitive to the
molecular symmetry and gets split into two components as a result of the removal of the degeneracy caused by the reduction of the $C_{4v}$ symmetry of the basal plane to a lower $C_3$ symmetry. In the present complexes also the bands at around 17,000 and 14,500 cm$^{-1}$ are apparently the split components of the $a_1 \leftrightarrow e$ transition indicating a distorted geometry around the metal ion (Fig. 3.1(b)).

The complexes (IV) and (VII) are diamagnetic in nature. The diamagnetic complexes for Ni$^{2+}$ ions are usually characteristic of a square-planar geometry. The electronic spectra of complexes (IV) and (VII) exhibited bands which do not correspond to the allowed $d-d$ transitions of Ni$^{2+}$ complexes in square-planar geometry. However, the positions of the bands are comparable to that reported$^{22}$ for diamagnetic Ni$^{2+}$ complexes having trigonal-bipyramidal environment of ligand. The ground state configuration of Ni$^{2+}$ ion in diamagnetic trigonal-bipyramidal geometry is $(e'')^4 (e')^4$ belonging to $^1A'_1$ term and the singlet excited states are $(e'')^4 (e')^3 (a'_1)$ and $(e'')^3 (e')^4 (a'_1)$ also designated as $'E'$ and $'E''$ respectively derived from the $^1D$ free-ion term. The spin-allowed transitions are therefore $'E' \leftrightarrow 'A'_1'$ and $'E'' \leftrightarrow 'A'_1'$ which however involve two electron excitations$^{22}$ and are expected to be weak in intensity. The absorption bands observed at 19,762 cm$^{-1}$ and in 17,000 – 18,000 cm$^{-1}$ region for the complexes (IV) and (VII) (Table-3.5) be assigned to the spin-allowed transitions $'E' \leftrightarrow 'A'_1'$ and $'E'' \leftrightarrow 'A'_1'$ respectively. The appearance of a doublet in 17,000 – 18,000
cm$^{-1}$ region is the split component of the $^1E' \rightarrow ^1A'_1$ excitation. The splitting of this band arises due to reduction in the molecular symmetry from the perfect $D_3h$ for regular trigonal–bipyramidal geometry to a $C_{3v}$ symmetry of a distorted trigonal–bipyramidal geometry around Ni$^{2+}$ ions in the complexes as shown in Fig. 3.1(b). The distortion is quite probable due to the presence of ligand's asymmetry in the complexes (IV) and (VII).

The electronic spectra of complex (V) showed a broad maxima in the region 17,000 – 22,000 cm$^{-1}$ which is resolvable into two absorption peaks centered at 17,513 and 21,321 cm$^{-1}$. The splitting of the d–d band is characteristic of the excitations from the ground electronic state in a tetragonally distorted octahedral geometry with d$^9$ configuration of Cu$^{2+}$ ions. The presence of John-Teller distortion in d$^9$ system causes tetragonality and results in splitting of the energy levels. The various allowed excitations are $^2E_g \leftrightarrow ^2B_{1g}$, $^2B_{2g} \leftrightarrow ^2B_{1g}$, $^2A_{1g} \leftrightarrow ^2B_{1g}$ in the decreasing order of their energies from $d_{xy}$, $d_z^2$ and $d_{xz}$, $d_{yz}$ pairs to the σ antibonding half filled $d_{x^2-y^2}$ level$^{22}$. These transitions are also designated as $^2B_{2g} \leftrightarrow ^2B_{1g}$, $^2A_{1g} \leftrightarrow ^2B_{1g}$ and $^2E_g \leftrightarrow ^2B_{1g}$ respectively. The precise order of the energy levels in a tetragonally distorted symmetry is rather uncertain as it depends on the degree of distortion from $O_h$ symmetry. For a weak to moderate extent of tetragonality, the sequence of energy levels is $^2B_{1g} < ^2B_{2g} < ^2A_{1g} < ^2E_g$. The bands observed at 17,513 and 21,321 cm$^{-1}$ in the spectrum of (V) are
assigned to the transitions $^2\text{Eg} \leftarrow ^2\text{B}_1\text{g}$ and $^2\text{B}_2\text{g} \leftarrow ^2\text{B}_1\text{g}$ or $d_{x^2-y^2} \leftarrow d_z^2$ and $d_{x^2-y^2} \leftarrow d_{xy,yz}$ transitions respectively (Table 3.5). The complex (V) is diamagnetic in nature and the epr spectrum of the polycrystalline sample does not show any signal (Isotropic or anisotropic). The observed diamagnetic nature and absence of a signal for the bimetallic complex (V) reveal that the unpaired spin at each Cu$^{2+}$ ion in the dinuclear complex Cu$_2$L$^1$Cl$_2$(ClO$_4$)$_2$ gets coupled giving a considerable Cu – Cu interaction in the bimetallic complexes as shown in Fig. 3.1(c).

**Complexes with L$^2$.2HClO$_4$:-**

The observed $\mu_{\text{eff}}$ value of complex (VIII) is 3.4 BM ($\mu_{\text{eff}}$ per Cr$^{3+}$ = 1.7 BM) which is also very low from that expected for 3 unpaired electrons$^{21}$ (3upe) in a $d^3$ (Cr$^{3+}$) system (c.f. $\mu_{\text{so}} = 3.88$) similar to that discussed for (I). The anti-ferromagnetic interactions$^{21}$ exist in many polynuclear Cr$^{3+}$ complexes lowering their magnetic moments. The electronic spectrum of complex (VIII) is nearly identical to that of the complex (I). Here too, the electronic spectrum showed three absorption bands (Table-3.6) assigned to the excitation from the ground state $^4\text{A}_2\text{g}(F)$ to the allowed excited states $^4\text{T}_2\text{g}(F), ^4\text{T}_1\text{g}(F)$ and $^4\text{T}_1\text{g}(P)$ i.e. $^4\text{T}_2\text{g}(F) \leftarrow ^4\text{A}_2\text{g}(F), ^4\text{T}_1\text{g}(F) \leftarrow ^4\text{A}_2\text{g}(F)$ and $^4\text{T}_1\text{g}(P) \leftarrow ^4\text{A}_2\text{g}(F)$ transitions in order of increasing energy in an octahedral environment$^{22}$. The highest energy transition i.e. $^4\text{T}_1\text{g}(P) \leftarrow ^4\text{A}_2\text{g}(F)$ is a two electron excitation process henceforth, may not be observed. It is usually obscured by the strong charge transfer bands$^{21}$ (Fig. 3.2(a)).
The observed magnetic moment ($\mu_{\text{eff}}$) for the complex (IX) is 4.68 BM or 2.34 BM per Fe atom which is considerably lower than the theoretically estimated values for five unpaired electrons in $d^5$ configuration of the metal ion. This reduction in magnetic moment is due to presence of a strong intramolecular as well as intermolecular anti-ferromagnetic interaction between the two encapsulated Fe$^{3+}$ centers in the macrocyclic cavity similar to that reported for various dinuclear Fe$^{3+}$ complexes which adopt a distorted octahedral geometry.

The electronic spectrum of the complex exhibited three absorption bands in the (d–d) region centered at 19,960; 19,083 and 17,513 cm$^{-1}$ which are assignable to that of a high spin Fe$^{3+}$ ($d^5$ system) in an octahedral environment of ligand. These bands are assigned to the transitions (Table 3.6) $^4T_1g(G) \leftarrow ^6A_1g$, $^4T_2g(G) \leftarrow ^6A_1g$, $^4A_1g$, $^4E_g(G) \leftarrow ^6A_1g$ respectively. In view of these data the encapsulation of Cr$^{3+}$ and Fe$^{3+}$ ions in the cavity may be represented as typified in Fig. 3.2(a).

The complex (X) and (XIII) are paramagnetic in nature such that the observed $\mu_{\text{eff}}$ values (Table-3.6) are $\sim$3.90 BM ($\mu_{\text{eff}}$ $\sim$ 1.90 BM per Co atom). This is comparable to that reported for Co$^{2+}$ complexes having a low-spin square-pyramidal geometry (c.f. $\mu_{\text{eff}} = 2.2 - 2.3$ BM). Their electronic spectra contained a well defined high energy band at 27,472 cm$^{-1}$ characteristic of the (M $\leftarrow$ L) CT band along with bands due to d–d transitions (Table-3.6) in the 16,000–22,000 cm$^{-1}$ region. The energy bands are comparable with that observed for complexes.
These bands are assignable to the transition reported for low-spin five coordinate Co\(^{2+}\) complexes having approximate square-pyramidal geometry (Fig. 3.2(b)). The bands are assigned to the transitions \(b_1 \leftrightarrow a_1, a_1 \leftrightarrow e\) and \(a_1 \leftrightarrow e\), respectively, similar to that discussed above for Co\(_2\)L\(^1\)Cl\(_2\)(ClO\(_4\))\(_2\) (III) and (VI).

The electronic spectra of Ni\(^{2+}\) complexes with L\(^2\).2HClO\(_4\), (XI) and (XIV) (Table 3.6) are almost identical to that for complexes with L\(^1\).2HClO\(_4\), (IV) and (VII). The positions of the bands are comparable to that reported for diamagnetic Ni\(^{2+}\) complexes having trigonal-bipyramidal environment of ligand (Table 3.2(b)) as already discussed above for complexes (IV) and (VII).

The bands observed at 17,513 and 21,645 cm\(^{-1}\) in the electronic spectrum of (XII) are assigned to the transitions \(^2\)E\(_g\) \(\leftrightarrow\) \(^2\)B\(_1g\) and \(^2\)B\(_2g\) \(\leftrightarrow\) \(^2\)B\(_1g\) (Table-3.6) respectively for a distorted octahedral geometry around Cu\(^{2+}\) ion. The complex (XII) is diamagnetic in nature similar to that found for complex (V) and the epr spectrum of the polycrystalline sample does not show any signal revealing that the unpaired spin at each Cu\(^{2+}\) ion gets coupled giving a considerable Cu – Cu interaction in the bimetallic complexes as shown in Fig. 3.2(c).
Table-3.1: Colour, melting points, analytical data and molar conductance of the complexes of L\(^2\)HClO\(_4\):

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Compounds</th>
<th>Colour</th>
<th>m.pt/ dec.(°C)</th>
<th>Analysis % Found (Calculated)</th>
<th>(\Lambda_m) **</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Cr(_2)L(^2)Cl(_2)(ClO(_4))(_2)</td>
<td>Orangeish red</td>
<td>260</td>
<td>47.54 (4.11) 11.54 (8.56) 17.56 (17.58)</td>
<td>73</td>
</tr>
<tr>
<td></td>
<td>Cr(_2)C(_4)H(_5)N(_2)Cl(_2)O(_8)</td>
<td>Red</td>
<td></td>
<td>(47.56) (11.56) (17.58)</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>Fe(_2)L(^2)Cl(_2)(ClO(_4))(_2)</td>
<td>Blackish brown</td>
<td>240</td>
<td>47.54 (4.09) 11.47 (9.14) 17.46 (17.47)</td>
<td>65</td>
</tr>
<tr>
<td></td>
<td>Fe(_2)C(_4)H(_5)N(_2)Cl(_2)O(_8)</td>
<td></td>
<td></td>
<td>(47.26) (11.48) (17.47)</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>CO(_2)L(^2)Cl(_2)(ClO(_4))(_2)</td>
<td>Green</td>
<td>280</td>
<td>49.90 (4.31) 12.11 (10.20) 12.29 (12.30)</td>
<td>52</td>
</tr>
<tr>
<td></td>
<td>CO(_2)C(_4)H(_5)N(_2)Cl(_2)O(_8)</td>
<td></td>
<td></td>
<td>(49.91) (12.13) (12.30)</td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td>Ni(_2)L(^2)Cl(_2)(ClO(_4))(_2)</td>
<td>Brown</td>
<td>278</td>
<td>49.93 (4.31) 12.10 (10.15) 12.31 (12.31)</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>Ni(_2)C(_4)H(_5)N(_2)Cl(_2)O(_8)</td>
<td></td>
<td></td>
<td>(49.94) (12.13) (12.31)</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>Cu(_2)L(^2)Cl(_2)(ClO(_4))(_2)</td>
<td>Greenish brown</td>
<td>270</td>
<td>49.50 (4.19) 12.01 (10.90) 12.19 (12.20)</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>Cu(_2)C(_4)H(_5)N(_2)Cl(_2)O(_8)</td>
<td></td>
<td></td>
<td>(49.52) (12.03) (12.20)</td>
<td></td>
</tr>
<tr>
<td>VI*</td>
<td>Co(_2)L(^2)Cl(_2)(ClO(_4))(_2)</td>
<td>Green</td>
<td>280</td>
<td>49.90 (4.31) 12.11 (10.20) 12.29 (12.30)</td>
<td>52</td>
</tr>
<tr>
<td></td>
<td>Co(_2)C(_4)H(_5)N(_2)Cl(_2)O(_8)</td>
<td></td>
<td></td>
<td>(49.91) (12.13) (12.30)</td>
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</tr>
<tr>
<td>VII*</td>
<td>Ni(_2)L(^2)Cl(_2)(ClO(_4))(_2)</td>
<td>Brown</td>
<td>278</td>
<td>49.93 (4.30) 12.10 (10.15) 12.31 (12.31)</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>Ni(_2)C(_4)H(_5)N(_2)Cl(_2)O(_8)</td>
<td></td>
<td></td>
<td>(49.94) (12.13) (12.31)</td>
<td></td>
</tr>
</tbody>
</table>

Calculated values in parentheses.
*Products obtained from reactions with precursors.
** \(\text{cm}^2 \text{ohm}^{-1} \text{mol}^{-1}\)

Table-3.2: Colour, melting points, analytical data and molar conductance of the complexes of L\(^2\)HClO\(_4\):

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Compounds</th>
<th>Colour</th>
<th>m.pt/ dec.(°C)</th>
<th>Analysis % Found (Calculated)</th>
<th>(\Lambda_m) **</th>
</tr>
</thead>
<tbody>
<tr>
<td>VIII</td>
<td>Cr(_2)L(^2)Cl(_2)(ClO(_4))(_2)</td>
<td>Orangeish red</td>
<td>298</td>
<td>42.95 (4.76) 14.30 (8.85) 18.13 (18.15)</td>
<td>73</td>
</tr>
<tr>
<td></td>
<td>Cr(_2)C(_4)H(_5)N(_2)Cl(_2)O(_8)</td>
<td>Red</td>
<td></td>
<td>(42.96) (14.32) (18.15)</td>
<td></td>
</tr>
<tr>
<td>IX</td>
<td>Fe(_2)L(^2)Cl(_2)(ClO(_4))(_2)</td>
<td>Dark brown</td>
<td>&gt;300</td>
<td>42.67 (4.73) 14.21 (9.44) 18.03 (18.04)</td>
<td>63</td>
</tr>
<tr>
<td></td>
<td>Fe(_2)C(_4)H(_5)N(_2)Cl(_2)O(_8)</td>
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<td></td>
<td>(42.68) (14.22) (18.04)</td>
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</tr>
<tr>
<td>X</td>
<td>CO(_2)L(^2)Cl(_2)(ClO(_4))(_2)</td>
<td>Brown</td>
<td>&gt;300</td>
<td>45.14 (5.01) 15.02 (10.54) 12.71 (12.72)</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>CO(_2)C(_4)H(_5)N(_2)Cl(_2)O(_8)</td>
<td></td>
<td></td>
<td>(45.16) (15.05) (12.72)</td>
<td></td>
</tr>
<tr>
<td>XI</td>
<td>Ni(_2)L(^2)Cl(_2)(ClO(_4))(_2)</td>
<td>Dark yellow</td>
<td>298</td>
<td>45.16 (5.02) 15.05 (10.51) 12.72 (12.73)</td>
<td>72</td>
</tr>
<tr>
<td></td>
<td>Ni(_2)C(_4)H(_5)N(_2)Cl(_2)O(_8)</td>
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<td></td>
<td>(45.18) (15.06) (12.73)</td>
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</tr>
<tr>
<td>XII</td>
<td>Co(_2)L(^2)Cl(_2)(ClO(_4))(_2)</td>
<td>Brown</td>
<td>290</td>
<td>44.76 (4.96) 14.91 (11.27) 12.61 (12.62)</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td>Co(_2)C(_4)H(_5)N(_2)Cl(_2)O(_8)</td>
<td></td>
<td></td>
<td>(44.78) (14.93) (12.62)</td>
<td></td>
</tr>
<tr>
<td>XIII*</td>
<td>CO(_2)L(^2)Cl(_2)(ClO(_4))(_2)</td>
<td>Brown</td>
<td>&gt;300</td>
<td>45.14 (5.01) 15.02 (10.54) 12.71 (12.72)</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>CO(_2)C(_4)H(_5)N(_2)Cl(_2)O(_8)</td>
<td></td>
<td></td>
<td>(45.16) (15.05) (12.72)</td>
<td></td>
</tr>
<tr>
<td>XIV*</td>
<td>Ni(_2)L(^2)Cl(_2)(ClO(_4))(_2)</td>
<td>Dark yellow</td>
<td>298</td>
<td>45.16 (5.02) 15.05 (10.51) 12.72 (12.73)</td>
<td>72</td>
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<tr>
<td></td>
<td>Ni(_2)C(_4)H(_5)N(_2)Cl(_2)O(_8)</td>
<td></td>
<td></td>
<td>(45.18) (15.06) (12.73)</td>
<td></td>
</tr>
</tbody>
</table>

Calculated values in parentheses.
*Products obtained from reactions with precursors.
** \(\text{cm}^2 \text{ohm}^{-1} \text{mol}^{-1}\)
**Table 3.3: Important frequencies (cm⁻¹) observed in the IR spectra of the complexes and their assignments for L₁.2HClO₄:**

<table>
<thead>
<tr>
<th>Comp.</th>
<th>v(N-N)</th>
<th>v(C=N)</th>
<th>Aliphatic</th>
<th>Aromatic</th>
<th>ClO₄</th>
<th>v₁</th>
<th>v₂</th>
<th>v₃</th>
<th>v(M-N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>979ₘ</td>
<td>1593ₖ</td>
<td>1245ₖ</td>
<td>1349ₖ</td>
<td>1174ₘ</td>
<td>1025ₘ</td>
<td>1009ₘ</td>
<td>610ₜ</td>
<td>418, 432</td>
</tr>
<tr>
<td>II</td>
<td>973ₘ</td>
<td>1595ₖ</td>
<td>1258ₖ</td>
<td>1349ₖ</td>
<td>1176ₘ</td>
<td>1028ₘ</td>
<td>1012ₘ</td>
<td>612ₜ</td>
<td>419, 430</td>
</tr>
<tr>
<td>III</td>
<td>982ₘ</td>
<td>1600ₙ</td>
<td>1260ₘ</td>
<td>1355ₙ</td>
<td>1175ₙ</td>
<td>1042ₘ</td>
<td>1026ₘ</td>
<td>620ₜ</td>
<td>416, 428</td>
</tr>
<tr>
<td>IV</td>
<td>986ₘ</td>
<td>1595ₙ</td>
<td>1248ₙ</td>
<td>1353ₙ</td>
<td>1172ₙ</td>
<td>1043ₘ</td>
<td>1031ₘ</td>
<td>622ₜ</td>
<td>418, 440</td>
</tr>
<tr>
<td>V</td>
<td>985ₘₚ</td>
<td>1592ₙ</td>
<td>1262ₙ</td>
<td>1343ₙ</td>
<td>1170ₙ</td>
<td>1062ₘ</td>
<td>1044ₘ</td>
<td>612ₜ</td>
<td>426, 438</td>
</tr>
<tr>
<td>VI*</td>
<td>982ₘ</td>
<td>1600ₙ</td>
<td>1259ₙ</td>
<td>1355ₙ</td>
<td>1175ₙ</td>
<td>1046ₘ</td>
<td>1036ₘ</td>
<td>620ₜ</td>
<td>412, 432</td>
</tr>
<tr>
<td>VII*</td>
<td>986ₘ</td>
<td>1595ₙ</td>
<td>1246ₙ</td>
<td>1353ₙ</td>
<td>1172ₙ</td>
<td>1045ₘ</td>
<td>1032ₘ</td>
<td>622ₜ</td>
<td>419, 433</td>
</tr>
</tbody>
</table>

m = medium, mb = medium broad, s = strong, w = weak

*Products obtained from reactions with precursors.

**Table 3.4: Important frequencies (cm⁻¹) observed in the IR spectra of the complexes and their assignments for L².2HClO₄:**

<table>
<thead>
<tr>
<th>Comp.</th>
<th>v(N-N)</th>
<th>v(C=N)</th>
<th>v(C-H)</th>
<th>v(N-H)</th>
<th>Aliphatic</th>
<th>Aromatic</th>
<th>ClO₄</th>
<th>v₁</th>
<th>v₂</th>
<th>v₃</th>
<th>v(M-N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VIII</td>
<td>988ₘ</td>
<td>1596ₙ</td>
<td>1519ₜ</td>
<td>3432ₜ</td>
<td>1243ₘ</td>
<td>1350ₘ</td>
<td>1175ₘ</td>
<td>1102ₙ</td>
<td>1082ₘ</td>
<td>611ₜ</td>
<td>419, 432</td>
</tr>
<tr>
<td>IX</td>
<td>981ₘ</td>
<td>1595ₙ</td>
<td>1520ₜ</td>
<td>3430ₙ</td>
<td>1255ₙ</td>
<td>1353ₙ</td>
<td>1174ₙ</td>
<td>1095ₙ</td>
<td>1073ₘ</td>
<td>640ₜ</td>
<td>417, 435</td>
</tr>
<tr>
<td>X</td>
<td>985ₘ</td>
<td>1597ₙ</td>
<td>1520ₙ</td>
<td>335ₙₘ</td>
<td>1241ₙ</td>
<td>1349ₙ</td>
<td>1171ₙ</td>
<td>1094ₙ</td>
<td>1071ₘ</td>
<td>622ₜ</td>
<td>414, 441</td>
</tr>
<tr>
<td>XI</td>
<td>983ₘ</td>
<td>159ₙₘ</td>
<td>1522ₙ</td>
<td>340ₙₘ</td>
<td>1238ₙ</td>
<td>1349ₙ</td>
<td>1173ₙ</td>
<td>1099ₙ</td>
<td>106ₙₘ</td>
<td>62ₙₜ</td>
<td>412, 44ₙ</td>
</tr>
<tr>
<td>XII</td>
<td>980ₘ</td>
<td>159ₙₘ</td>
<td>152ₙₘ</td>
<td>342ₙₘ</td>
<td>126ₙₘ</td>
<td>135ₙₘ</td>
<td>1170ₙ</td>
<td>109ₘₘ</td>
<td>107ₙₘ</td>
<td>62ₙₜ</td>
<td>42₂, 4ₙₘ</td>
</tr>
<tr>
<td>XIII*</td>
<td>98ₙₘ</td>
<td>159ₙₘ</td>
<td>152₂ₘ</td>
<td>3ₙₙₘₘ</td>
<td>1₂ₙₘₘ</td>
<td>1ₙₘₘₘ</td>
<td>1ₙₘₘₘ</td>
<td>1₀ₙₘₘ</td>
<td>1₀ₙₘₘ</td>
<td>ₙₘₘₘ</td>
<td>ₙₘₘₘ, ₙₘₘₘ</td>
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<tr>
<td>XIV*</td>
<td>9ₘₘₘₘ</td>
<td>1ₘₘₘₘ</td>
<td>1ₘₘₘₘ</td>
<td>ₘₘₘₘₘ</td>
<td>ₘₘₘₘₘₘ</td>
<td>ₘₘₘₘₘₘ</td>
<td>ₘₘₘₘₘₘ</td>
<td>ₘₘₘₘₘ</td>
<td>ₘₘₘₘₘ</td>
<td>ₘₘₘₘₘ</td>
<td>ₘₘₘₘₘ, ₘₘₘₘₘ</td>
</tr>
</tbody>
</table>

m = medium, s = strong, w = weak

*Products obtained from reactions with precursors.
<table>
<thead>
<tr>
<th>Compounds</th>
<th>$\mu_{\text{eff}}$ (BM)</th>
<th>$\nu$ (nm)</th>
<th>$\nu$ (cm$^{-1}$)</th>
<th>Band Assignments</th>
<th>$\epsilon^{**}$</th>
<th>$\epsilon$/atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>3.2</td>
<td>382</td>
<td>26,178</td>
<td>$\pi^* \leftarrow \pi + \text{CT}$</td>
<td>1523</td>
<td>761</td>
</tr>
<tr>
<td></td>
<td></td>
<td>506</td>
<td>19,762</td>
<td>$^4T_{2g}$ (F) $\leftarrow$ $^4A_{2g}$ (F)</td>
<td>2411</td>
<td>1205</td>
</tr>
<tr>
<td></td>
<td></td>
<td>571</td>
<td>17,513</td>
<td>$^4T_{2g}$ (F) $\leftarrow$ $^4A_{2g}$ (F)</td>
<td>2936</td>
<td>1468</td>
</tr>
<tr>
<td>II</td>
<td>4.72</td>
<td>380</td>
<td>26,315</td>
<td>$\pi^* \leftarrow \pi + \text{CT}$</td>
<td>2253</td>
<td>1126</td>
</tr>
<tr>
<td></td>
<td></td>
<td>500</td>
<td>20,000</td>
<td>$^4T_{1g}$ (G) $\leftarrow$ $^6A_{1g}$</td>
<td>2933</td>
<td>1466</td>
</tr>
<tr>
<td></td>
<td></td>
<td>519</td>
<td>19,267</td>
<td>$^4T_{2g}$ (G) $\leftarrow$ $^6A_{1g}$</td>
<td>2849</td>
<td>1424</td>
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<td>575</td>
<td>17,391</td>
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<td>5000</td>
<td>2500</td>
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<td>607</td>
<td>16,474</td>
<td>$^4T_{2g}$ (D) $\leftarrow$ $^6A_{1g}$</td>
<td>4036</td>
<td>2018</td>
</tr>
<tr>
<td>III</td>
<td>Diamagnetic</td>
<td>385</td>
<td>25,974</td>
<td>$\pi^* \leftarrow \pi + \text{CT}$</td>
<td>1752</td>
<td>876</td>
</tr>
<tr>
<td></td>
<td></td>
<td>482</td>
<td>20,746</td>
<td>$b_1 \leftarrow a_1$</td>
<td>2355</td>
<td>1177</td>
</tr>
<tr>
<td></td>
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<td>571</td>
<td>17,513</td>
<td>$a_1 \leftarrow e$</td>
<td>1390</td>
<td>695</td>
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<td>498</td>
<td>249</td>
</tr>
<tr>
<td>IV</td>
<td>Diamagnetic</td>
<td>395</td>
<td>25,316</td>
<td>$\pi^* \leftarrow \pi + \text{CT}$</td>
<td>1823</td>
<td>911</td>
</tr>
<tr>
<td></td>
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<td>506</td>
<td>19,762</td>
<td>$^3E' \leftarrow ^3A_1$</td>
<td>2363</td>
<td>1181</td>
</tr>
<tr>
<td></td>
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<td>562</td>
<td>17,793</td>
<td>$^3E'' \leftarrow ^3A_1$</td>
<td>2303</td>
<td>1151</td>
</tr>
<tr>
<td></td>
<td></td>
<td>571</td>
<td>17,513</td>
<td></td>
<td>2651</td>
<td>1325</td>
</tr>
<tr>
<td>V</td>
<td>Diamagnetic</td>
<td>380</td>
<td>26,315</td>
<td>$\pi^* \leftarrow \pi + \text{CT}$</td>
<td>1752</td>
<td>876</td>
</tr>
<tr>
<td></td>
<td></td>
<td>469</td>
<td>21,321</td>
<td>$^3B_{2g} \leftarrow ^3B_{1g}$</td>
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<td>786</td>
</tr>
<tr>
<td></td>
<td></td>
<td>571</td>
<td>17,513</td>
<td>$^3E_g \leftarrow ^3B_{1g}$</td>
<td>988</td>
<td>494</td>
</tr>
<tr>
<td>VI*</td>
<td>Diamagnetic</td>
<td>385</td>
<td>25,974</td>
<td>$\pi^* \leftarrow \pi + \text{CT}$</td>
<td>1751</td>
<td>875</td>
</tr>
<tr>
<td></td>
<td></td>
<td>482</td>
<td>20,746</td>
<td>$b_1 \leftarrow a_1$</td>
<td>2355</td>
<td>1177</td>
</tr>
<tr>
<td></td>
<td></td>
<td>571</td>
<td>17,513</td>
<td>$a_1 \leftarrow e$</td>
<td>1390</td>
<td>695</td>
</tr>
<tr>
<td></td>
<td></td>
<td>682</td>
<td>14,662</td>
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<td>502</td>
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<td>VII*</td>
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<td>25,252</td>
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<td>571</td>
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</tbody>
</table>

* Products obtained from reactions with precursors

** lit mol$^{-1}$ cm$^{-1}$
Table-3.6: $\mu_{\text{eff}}$(BM) and electronic spectral data of the compounds and their assignments for $L^2_2$HClO$_4$:

<table>
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<th>Compounds</th>
<th>$\mu_{\text{eff}}$(BM)</th>
<th>$\nu$(nm)</th>
<th>$\nu$(cm$^{-1}$)</th>
<th>Band Assignments</th>
<th>$\epsilon$**</th>
<th>$\epsilon$/atom</th>
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<tr>
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<td>1080</td>
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<td>$^4T_{2g}$ (F) $\leftrightarrow$ $^4A_{2g}$ (F)</td>
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<td>17,513</td>
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<td>$^1E' \leftrightarrow$ $^1A'$</td>
<td>3782</td>
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<td>$^1E'' \leftrightarrow$ $^1A'$</td>
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</tbody>
</table>

* Products obtained from reactions with precursors
** lit mol$^{-1}$ cm$^{-3}$
Fig. 3.1(a)

Fig. 3.1(b)
Fig. 3.1 (c)

$M = \text{Cu}^{2+}$

Fig. 3.2 (a)

$M = \text{Fe}^{3+}$ or $\text{Cr}^{3+}$
Fig. 3.2(b)

M = Co$^{2+}$ or Ni$^{2+}$

Fig. 3.2(c)

M = Cu$^{2+}$
PART-B

Synthesis and Characterization of Complexes [L\(^1\).2HClO\(_4\)] and [L\(^2\).2HClO\(_4\)] with Group 12 Metal Ions: Encapsulation of Zn\(^{2+}\), Cd\(^{2+}\) or Hg\(^{2+}\) Ions
EXPERIMENTAL

Reagents used:

The salt ZnCl₂, CdCl₂ 2½H₂O, HgCl₂ (All Merck, India) were commercially pure and used as received. Solvents were purified and dried before use.

PREPRATION OF PRECURSORS

Preparation of Dichlorobis(triphenylphosphine) Zinc(II) [Zn(Ph₃P)₂Cl₂]:

Anhydrous zinc chloride (1.0 g, 5.0 mmol) was dissolved in ether (50 cm³) and was reacted with triphenylphosphine (2.62 g, 10.0 mmol) dissolved in dry benzene (30 cm³) at room temperature. The reaction mixture was magnetically stirred and colourless shining crystalline solid product started coming out of the solution. The solid was filtered, washed with ether and dried in air [m.pt-295°C].

Preparation of Dichlorobis(triphenylphosphine) Cadmium(II) [Cd(Ph₃P)₂Cl₂]:

Triphenylphosphine (2.62 g, 10.0 mmol) dissolved in hot ethanol (100 cm³) and cadmium chloride (1.0 g, 5.0 mmol) dissolved in hot ethanol (50 cm³) were mixed together. After cooling, colourless crystals appeared which was filtered off, washed with ethanol and dried in air [m.pt-245°C].
**Preparation**\textsuperscript{29} of Dichlorobis(triphenylphosphine) Mercury(II) [Hg(Ph\textsubscript{3}P)\textsubscript{2}Cl\textsubscript{2}]:

Hot alcoholic solutions of mercuric chloride (1.0 g, 5.0 mmol) and triphenylphosphine (2.62 g, 10.0 mmol) were mixed with stirring. Colourless shining solid started coming out of the solution. Which was filtered, washed with alcohol and dried in air [m.pt.-273\textdegree{}C (dec.)].

**PREPRATION OF METAL COMPLEXES**

*Reaction of the macrocyclic ligand, L\textsuperscript{1.2HClO\textsubscript{4}} with metal salts:*

**Reaction of L\textsuperscript{1.2HClO\textsubscript{4}} with anhydrous ZnCl\textsubscript{2}; Isolation of Zn\textsubscript{2}L\textsuperscript{1}Cl\textsubscript{2}(ClO\textsubscript{4})\textsubscript{2} (XV):**

ZnCl\textsubscript{2} (0.280 g, 2.06 mmol) taken in methanol (25 cm\textsuperscript{3}) was added drop wise to the ligand (1.0 g, 1.03 mmol) solution with continuous stirring at room temperature. The reaction mixture was further stirred for about 48 hours at room temperature. The solid formed was filtered off and washed with 1,4-Dioxane and then methanol. The solid was dried in vacuum giving yellow coloured solid [m.pt.-280\textdegree{}C (dec.), yield-0.184 g or 15\%].

**Reaction of L\textsuperscript{1.2HClO\textsubscript{4}} with anhydrous CdCl\textsubscript{2}.2\textfrac{1}{2}H\textsubscript{2}O; Isolation of Cd\textsubscript{2}L\textsuperscript{1}Cl\textsubscript{2}(ClO\textsubscript{4})\textsubscript{2} (XVII):**

CdCl\textsubscript{2}.2\textfrac{1}{2}H\textsubscript{2}O (0.471 g, 2.06 mmol) taken in methanol (25 cm\textsuperscript{3}) was added drop wise to the ligand (1.0 g, 1.03 mmol) solution with continuous stirred for about 48 hours at room temperature. The reaction mixture was further stirred for about 48 hours at room temperature.
temperature. The solid formed was filtered off, washed with 1,4-Dioxane and then methanol, and dried in vacuum. Yellow coloured solid was obtained [m.pt-288°C, yield-0.287 g or 22%].

**Reaction of L¹.2HClO₄ with HgCl₂; Isolation of Hg₂L¹Cl₂(ClO₄)₂ (XIX):**

HgCl₂ (0.559 g, 2.06 mmol) taken in methanol (25 cm³), was added drop wise to the ligand (1.0 g, 1.03 mmol) solution with continuous stirring at room temperature. The reaction mixture was further stirred for about 48 hours at room temperature. The solid formed was filtered off, washed with 1,4-Dioxane and followed by methanol, dried in vacuum. Grey coloured solid was obtained [m.pt-310°C (dec.) yield-0.531 g or 36%].

**Reaction of the macrocyclic ligand, L¹.2HClO₄, with precursors:**

**Reaction of L¹.2HClO₄ with [Zn(Ph₃P)₂Cl₂]; Isolation of Zn₂L¹Cl₂(ClO₄)₂ (XVI):**

[Zn(Ph₃P)₂Cl₂] (0.67 g, 1.02 mmol) taken in methanol (25 cm³) was added drop wise to the ligand (0.5 g, 0.515 mmol) solution with continuous stirring at room temperature. The reaction mixture was further stirred for about 48 hours at room temperature. The solid formed was filtered off and washed with 1,4-Dioxane and then methanol, dried in vacuum. Yellow coloured solid was obtained [m.pt-280°C (dec.), yield-0.161 g or 27%]. The mother liquor was concentrated
to 1/4th of it's original volume and kept at 5°C which afforded colourless crystalline solid [m.pt-71-73°C]. The colourless solid was identified as free triphenylphosphine.

**Reaction of L^1.2HClO_4 with [Cd(Ph_3P_2)_2Cl_2]: Isolation of Cd_2L^1Cl_2(ClO_4)_2 (XVIII):**

The ligand (0.5 g, 0.515 mmol) solution in 1,4-Dioxane (30 cm³) was reacted with the precursor, [Cd(Ph_3P)_2Cl_2] (0.545 g, 1.02 mmol) taken in methanol (25 cm³) in an analogous manner as above. The reaction mixture was stirred additionally for ca 48 hours. Yellow coloured solid formed was filtered off, washed with 1,4-Dioxane followed by methanol and dried in vacuum. [m.pt-288°C (dec), yield-0.192 g or 29%]. Here too the mother liquor was concentrated to 1/4th of its original volume and kept at 5°C which gave crystalline solid that was identified as triphenylphosphine [m.pt.-71-73°C].

**Reaction of L^1.2HClO_4 with [Hg(Ph_3P_2)_2Cl_2]: Isolation of Hg_2L^1Cl_2(ClO_4)_2 (XX):**

The ligand (0.5 g, 0.515 mmol) taken in 1,4-Dioxane (30 cm³) and [Hg(Ph_3P)_2Cl_2](0.543 g, 1.02 mmol) solution in methanol (25 cm³) was reacted together as above at room temperature. The reaction mixture was stirred additionally for ca 48 hours. Grey coloured solid formed was filtered off, washed with 1,4-Dioxane followed by methanol and then dried in vacuum [m.pt-305°C (dec), yield-0.231 g or 31%]. Here too, the mother liquor has produced colourless crystalline solids as described above which was identified as free triphenylphosphine [m.pt.-71-73°C].
Reaction of macrocyclic ligand, \( L^2 \cdot 2\text{HClO}_4 \), with Metal salts:

Reaction of \( L^2 \cdot 2\text{HClO}_4 \) with \( \text{ZnCl}_2 \): Isolation of \( \text{Zn}_2L^2\text{Cl}_2(\text{ClO}_4)_2 \) (XXI):

The ligand (1.0 g, 1.07 mmol) was dissolved in 1,4-Dioxane (30 cm\(^3\)) and to this the methanolic (25 cm\(^3\)) solution of \( \text{ZnCl}_2 \) (0.291 g, 2.14 mmol) was added drop wise with continuous stirring. The reaction mixture was stirred ca 48 hours at room temperature which gave yellow coloured precipitate. The precipitate was filtered off and washed with 1,4-Dioxane followed by methanol. The yellow colour solid obtained, was dried in vacuum. [m.pt-278\(^0\)C (dec), yield 0.607 g or 45\%].

Reaction of \( L^2 \cdot 2\text{HClO}_4 \) with \( \text{CdCl}_2 \cdot 2\text{H}_2\text{O} \): Isolation of \( \text{Cd}_2L^2\text{Cl}_2(\text{ClO}_4)_2 \) (XXIII):

The metal salt \( \text{CdCl}_2 \cdot \text{H}_2\text{O} \) (0.431 g, 2.14 mmol) was dissolved in methanol (30 cm\(^3\)) and was added drop wise to the ligand (1.0 g, 1.07 mmol) solution in 1,4-Dioxane (35 cm\(^3\)). The reaction mixture was stirred ca 48 hours at room temperature. Here too, yellow coloured precipitate obtained, was filtered off and washed with 1,4-Dioxane followed by methanol and then dried in vacuum.[m.pt-240\(^0\)C (dec), yield- 0.126 g or 17\%].

Reaction of \( L^2 \cdot 2\text{HClO}_4 \) with \( \text{HgCl}_2 \): Isolation of \( \text{Hg}_2L^2\text{Cl}_2(\text{ClO}_4)_2 \) (XXV):

Methanolic solution of \( \text{HgCl}_2 \) (0.581 g, 2.14 mmol) was added drop wise to a magnetically stirred solution of the ligand (1.0 g, 1.07 mmol) in (30 cm\(^3\)) 1,4-Dioxane. The reaction mixture was stirred
at room temperature for ca 48 hours. Colour of the mother liquor became grayish and the precipitate obtained was filtered off and washed with 1,4-Dioxane and then methanol. The off white coloured solid obtained, was dried in vacuum [m.pt-140°C, yield 0.616 g or 41%].

Reaction of the macrocyclic ligand, \( L^2.2\text{HClO}_4 \), with precursors:

Reaction of \( L^2.2\text{HClO}_4 \) with \([\text{Zn(Ph}_3\text{P)}_2\text{Cl}_2]\): Isolation of \( \text{Zn}_2L^2\text{Cl}_2(\text{ClO}_4)_2 \) (XXII):

The ligand, \( L^2.2\text{HClO}_4 \) (0.5 g, 0.535 mmol) was dissolved in 1,4-Dioxane (30 cm\(^3\)) and to this the methanolic solution of \([\text{Zn(Ph}_3\text{P)}_2\text{Cl}_2] \) (0.706 g, 1.07 mmol) was added drop wise with continuous stirring. The reaction mixture was stirred ca 48 hours at room temperature. The yellow coloured precipitate obtained was filtered off and washed with 1,4-Dioxane followed by methanol. It was dried in vacuum. The product was yellow coloured solid [m.pt-275°C, yield 0.303 g or 45%]. The mother liquor was concentrated to 1/4\(^{th}\) of its original volume and kept at 5°C, which afforded colourless needles [m.pt-71-73°C]. The melting point and spectroscopic data confirmed the latter to be free triphenylphosphine, liberated out of the precursors during the reaction with ligand.

Reaction of \( L^2.2\text{HClO}_4 \) with \([\text{Cd(Ph}_3\text{P)}_2\text{Cl}_2]\): Isolation of \( \text{Cd}_2L^2\text{Cl}_2(\text{ClO}_4)_2 \) (XXIV):

The ligand (0.5 g, 0.535 mmol) was dissolved in 1,4-Dioxane (30 cm\(^3\)) and to this the methanolic (30 cm\(^3\)) solution of \([\text{Cd(Ph}_3\text{P)}_2\text{Cl}_2] \)
(0.572 g, 1.07 mmol) was added drop wise with continuous stirring. The reaction mixture was stirred for ca 48 hours at room temperature. The yellow coloured precipitate obtained was filtered off and washed with 1,4-Dioxane followed by methanol. The product was dried in vacuum. Here too, yellow coloured amorphous solid was obtained [m.pt-240°C (dec.) yield 0.124 g or 18%]. The mother liquor was concentrated to 1/4th of its original volume and kept at 5°C, which afforded colourless needles [m.pt.-71-73°C]. The melting point and spectroscopic data confirmed the latter to be free triphenylphosphine, liberated out of the precursor during the reaction with ligand.

**Reaction of L².2HClO₄ with [Hg(Ph₃P)₂Cl₂]: Isolation of Hg₂L²Cl₂(ClO₄)₂ (XXVI):**

Methanolic solution of [Hg(Ph₃P)₂Cl₂] (0.570 g, 1.07 mmol) was added drop wise to a magnetically stirred solution of ligand (0.5 g, 0.535 mmol) in 1,4-Dioxane (35 cm³). The reaction mixture was stirred at room temperature for ca 48 hours. The colour of the mother liquor became grayish and precipitate obtained in the reaction flask was filtered off and washed with 1,4-Dioxane followed by methanol. Off white amorphous solid obtained was dried in vacuum. [m.pt-144°C (dec.), yield-0.303 g or 40%]. The mother liquor was concentrated to 1/4th of its original volume and kept at 5°C which afforded colourles needles [m.pt-71-73°C]. The melting point and spectroscopic data
confirmed the latter to be free triphenylphosphine, liberated out of the precursor during the reaction with ligand.
RESULTS AND DISCUSSION

The dihydroperchlorate salts of the macrocycles [2,8,11,17]tetramethyl [3,5,7,12,14,16]hexaphenyl [1,3,5,7,9,10,12,14,16,18]decaazaoctadeca [2,8,11,17]tetraene i.e. [L\textsuperscript{2}HClO\textsubscript{4}] and [2,12,15,25]tetramethyl [3,11,16,24]tetraphenyl [1,3,5,9,11,13,14,16,18,22,24,26]dodecaazahexacosa [2,12,15,25]tetraene i.e. [L\textsuperscript{2}HClO\textsubscript{4}] have exhibited considerable reactivity with group 12 metal salts MCl\textsubscript{2} [M=Zn\textsuperscript{2+}, Cd\textsuperscript{2+} or Hg\textsuperscript{2+}] as well as towards their precursors [Zn(Ph\textsubscript{3}P)\textsubscript{2}Cl\textsubscript{2}], [Cd(Ph\textsubscript{3}P)\textsubscript{2}Cl\textsubscript{2}] and [Hg(Ph\textsubscript{3}P)\textsubscript{2}Cl\textsubscript{2}].

Analytical data of the products obtained from reactions of MCl\textsubscript{2} with L\textsuperscript{1}.2HClO\textsubscript{4} and L\textsuperscript{2}.2HClO\textsubscript{4} have been summarized in (Tables-3.7 and 3.8). The observed data are consistent with the molecular formulae [M\textsubscript{2}C\textsubscript{48}H\textsubscript{50}N\textsubscript{10}Cl\textsubscript{4}O\textsubscript{8}] (M=Zn (XV), Cd (XVII), Hg (XIX)) and [M\textsubscript{2}C\textsubscript{42}H\textsubscript{56}N\textsubscript{12}Cl\textsubscript{4}O\textsubscript{8}] (M=Zn (XXI), Cd (XXIII), Hg (XXV)) respectively, which are compatible with the stoichiometry M\textsubscript{2}LCl\textsubscript{2}(ClO\textsubscript{4})\textsubscript{2} (M= Zn, Cd or Hg; L=L\textsuperscript{1} or L\textsuperscript{2}).

Reactions of the precursors [M(Ph\textsubscript{3}P)\textsubscript{2}Cl\textsubscript{2}] (M= Zn, Cd or Hg) with the macrocyclic ligands L\textsuperscript{1}.2HClO\textsubscript{4} and L\textsuperscript{2}.2HClO\textsubscript{4} are accompanied with a complete liberation of the ancillary ligand, triphenylphosphine, from the precursors affording products with molecular formulae [M\textsubscript{2}C\textsubscript{48}H\textsubscript{50}N\textsubscript{10}Cl\textsubscript{4}O\textsubscript{8}] (M=Zn (XVI), Cd (XVIII), Hg (XX)) and [M\textsubscript{2}C\textsubscript{42}H\textsubscript{56}N\textsubscript{12}Cl\textsubscript{4}O\textsubscript{8}] (M=Zn (XXII), Cd (XXIV), Hg (XXVI)) respectively. IR spectroscopic data of the products (XVI, XVIII, XX,
which were obtained from reactions of the precursors with the macrocyclic ligands did not exhibit any bands characteristic of the presence of coordinated Ph₃P in the complexes. Moreover, equivalent amounts of Ph₃P were recovered from the mother liquor of each of these reaction mixtures (see experimental part). Furthermore, the analytical data of the products XVI, XVIII, or XX, and XXII, XXIV or XXVI obtained from reactions of the macrocyclic ligands L¹.2HClO₄ and L².2HClO₄ with the precursors are identical to that obtained from the corresponding reactions using metal chlorides (Table 3.7 and 3.8). The liberation of ancillary Ph₃P ligands is the consequence of the macrocyclic effect which appears to be more pronounced compared to π-acidity of Ph₃P towards metal ions.

The complexes (XV-XXVI) did not show solubility in usual organic solvents henceforth, their ionic behaviour and spectroscopic studies in solution could not be investigated.

The important bands observed in the IR spectrum of the compound are summarized in (Table-3.9 and 3.10). These bands are characteristic of ν(N—N), ν(C—N), ν(C=N), ν(C—C) and ν(C—H) fundamental stretching vibrations. The appearance of a strong absorption band at around 1600 cm⁻¹ is characteristic of ν(C=N) stretching vibration. There is a shift of ~20 cm⁻¹ to lower wave number in the position of ν(C=N), stretching vibration in the complex with reference to that indicated in the IR spectra of free ligand i.e.
L\textsuperscript{1}.2HClO\textsubscript{4} or L\textsuperscript{2}.2HClO\textsubscript{4}. A band of strong intensity at \( \sim 1000 \text{ cm}^{-1} \) is characteristic of the presence of \( N-N \) bond in the molecular unit. The \( \nu(N-N) \) stretching vibration is shifted to higher wave number as compared to that observed for free macrocyclic ligands i.e. L\textsuperscript{1}.2HClO\textsubscript{4} and L\textsuperscript{2}.2HClO\textsubscript{4}. Additional frequencies characteristic of \( \nu(C-N) \) and skeletal \( \nu(C-C) \) stretching vibrations also appeared at their appropriate positions. The two bands observed in 415 – 480 \text{ cm}^{-1} \) region are characteristic\textsuperscript{18} of \( \nu(M-N) \) stretching vibrations indicating the encapsulation of metal ion in the macrocyclic cavity. The IR spectrum showed the splitting of the \( \nu_2 \) stretching vibration\textsuperscript{19} of ClO\textsubscript{4}\textsuperscript{-} group in the region 1050 – 1080 \text{ cm}^{-1} \) suggesting that in solid state ClO\textsubscript{4}\textsuperscript{-} group is coordinated to the cation.
Table-3.7: Colour, melting points, analytical data and molar conductance of the complexes of L^4:2HClO₄:

<table>
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<th>S.No.</th>
<th>Compounds</th>
<th>Colour</th>
<th>m.pt./dec.°C</th>
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<td></td>
<td></td>
<td>C</td>
<td>H</td>
<td>N</td>
</tr>
<tr>
<td>XV</td>
<td>Zn₂L^4Cl₂(CIO₄)₂</td>
<td>Yellow</td>
<td>280</td>
<td>49.35</td>
<td>4.28</td>
<td>11.98</td>
</tr>
<tr>
<td></td>
<td>Zn₂C₁₂H₂₆N₁₂Cl₂O₈</td>
<td></td>
<td></td>
<td>(49.36)</td>
<td>(4.28)</td>
<td>(11.99)</td>
</tr>
<tr>
<td>XVI*</td>
<td>Zn₂L^4Cl₂(CIO₄)₂</td>
<td>Yellow</td>
<td>280</td>
<td>49.35</td>
<td>4.28</td>
<td>11.98</td>
</tr>
<tr>
<td></td>
<td>Zn₂C₁₂H₂₆N₁₂Cl₂O₈</td>
<td></td>
<td></td>
<td>(49.36)</td>
<td>(4.28)</td>
<td>(11.99)</td>
</tr>
<tr>
<td>XVII</td>
<td>Cd₂L^4Cl₂(CIO₄)₂</td>
<td>Light</td>
<td>288</td>
<td>45.69</td>
<td>3.89</td>
<td>11.09</td>
</tr>
<tr>
<td></td>
<td>Cd₂C₁₂H₂₆N₁₂Cl₂O₈</td>
<td>Yellow</td>
<td></td>
<td>(45.71)</td>
<td>(3.90)</td>
<td>(11.10)</td>
</tr>
<tr>
<td>XVIII*</td>
<td>Cd₂L^4Cl₂(CIO₄)₂</td>
<td>Light</td>
<td>288</td>
<td>45.69</td>
<td>3.89</td>
<td>11.09</td>
</tr>
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<td></td>
<td>Cd₂C₁₂H₂₆N₁₂Cl₂O₈</td>
<td>Yellow</td>
<td></td>
<td>(45.71)</td>
<td>(3.90)</td>
<td>(11.10)</td>
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<tr>
<td>XIX</td>
<td>Hg₂L^4Cl₂(CIO₄)₂</td>
<td>Gray</td>
<td>310</td>
<td>40.06</td>
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<td></td>
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<td>(40.07)</td>
<td>(3.47)</td>
<td>(9.74)</td>
</tr>
<tr>
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<td>Hg₂L^4Cl₂(CIO₄)₂</td>
<td>Gray</td>
<td>&gt;300</td>
<td>40.06</td>
<td>3.46</td>
<td>9.75</td>
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<td></td>
<td>Hg₂C₁₂H₂₆N₁₂Cl₂O₈</td>
<td></td>
<td></td>
<td>(40.07)</td>
<td>(3.47)</td>
<td>(9.74)</td>
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* Products obtained from reactions with precursors

Table -3.8: Colour, melting points, analytical data and molar conductance of the complexes of L^4:2HClO₄:

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<th>S.No.</th>
<th>Compounds</th>
<th>Colour</th>
<th>m.pt./dec.°C</th>
<th>Analysis %</th>
<th>Found</th>
<th>Calculated</th>
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<tr>
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<td></td>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
<td>N</td>
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<td>XXI</td>
<td>Zn₂L^4Cl₂(CIO₄)₂</td>
<td>Yellow</td>
<td>278</td>
<td>44.69</td>
<td>4.95</td>
<td>14.87</td>
</tr>
<tr>
<td></td>
<td>Zn₂C₁₂H₂₆N₁₂Cl₂O₈</td>
<td></td>
<td></td>
<td>(44.64)</td>
<td>(4.96)</td>
<td>(14.88)</td>
</tr>
<tr>
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<td>Zn₂L^4Cl₂(CIO₄)₂</td>
<td>Yellow</td>
<td>275</td>
<td>44.69</td>
<td>4.95</td>
<td>14.87</td>
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<tr>
<td></td>
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<td></td>
<td></td>
<td>(44.64)</td>
<td>(4.96)</td>
<td>(14.88)</td>
</tr>
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<td>(41.21)</td>
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<td>(13.73)</td>
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<td>242</td>
<td>41.20</td>
<td>4.4</td>
<td>13.72</td>
</tr>
<tr>
<td></td>
<td>Cd₂C₁₂H₂₆N₁₂Cl₂O₈</td>
<td></td>
<td></td>
<td>(41.21)</td>
<td>(4.5)</td>
<td>(13.73)</td>
</tr>
<tr>
<td>XXV</td>
<td>Hg₂L^4Cl₂(CIO₄)₂</td>
<td>Off White</td>
<td>140</td>
<td>36.01</td>
<td>4.01</td>
<td>12.01</td>
</tr>
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<td></td>
<td>Hg₂C₁₂H₂₆N₁₂Cl₂O₈</td>
<td></td>
<td></td>
<td>(36.02)</td>
<td>(4.01)</td>
<td>(12.01)</td>
</tr>
<tr>
<td>XXVI*</td>
<td>Hg₂L^4Cl₂(CIO₄)₂</td>
<td>Off White</td>
<td>146</td>
<td>36.01</td>
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<tr>
<td></td>
<td>Hg₂C₁₂H₂₆N₁₂Cl₂O₈</td>
<td></td>
<td></td>
<td>(36.02)</td>
<td>(4.01)</td>
<td>(12.01)</td>
</tr>
</tbody>
</table>

* Products obtained from reactions with precursors
Table-3.9: Important frequencies (cm⁻¹) observed in the IR spectra of the complexes and their assignments for L¹.2HClO₄:

<table>
<thead>
<tr>
<th>Comp.</th>
<th>v(N-N)</th>
<th>v(C=N)</th>
<th>v(C-H)</th>
<th>v(N-H)</th>
<th>Aliphatic v(C-N)</th>
<th>Aromatic v(C-N)</th>
<th>ClO₄</th>
<th>v(M-N)</th>
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<tr>
<td>XV</td>
<td>950&lt;sub&gt;m&lt;/sub&gt;</td>
<td>1603&lt;sub&gt;s&lt;/sub&gt;</td>
<td>1248&lt;sub&gt;m&lt;/sub&gt;</td>
<td>1334&lt;sub&gt;m&lt;/sub&gt;</td>
<td>1172&lt;sub&gt;m&lt;/sub&gt;</td>
<td>1074&lt;sub&gt;m&lt;/sub&gt;</td>
<td>618&lt;sub&gt;w&lt;/sub&gt;</td>
<td>425, 475</td>
</tr>
<tr>
<td>XVI*</td>
<td>950&lt;sub&gt;m&lt;/sub&gt;</td>
<td>1603&lt;sub&gt;s&lt;/sub&gt;</td>
<td>1250&lt;sub&gt;m&lt;/sub&gt;</td>
<td>1332&lt;sub&gt;m&lt;/sub&gt;</td>
<td>1172&lt;sub&gt;m&lt;/sub&gt;</td>
<td>1070&lt;sub&gt;m&lt;/sub&gt;</td>
<td>616&lt;sub&gt;w&lt;/sub&gt;</td>
<td>418, 476</td>
</tr>
<tr>
<td>XVII</td>
<td>952&lt;sub&gt;m&lt;/sub&gt;</td>
<td>1600&lt;sub&gt;s&lt;/sub&gt;</td>
<td>1256&lt;sub&gt;m&lt;/sub&gt;</td>
<td>1345&lt;sub&gt;s&lt;/sub&gt;</td>
<td>1174&lt;sub&gt;m&lt;/sub&gt;</td>
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<td>622&lt;sub&gt;w&lt;/sub&gt;</td>
<td>416, 448</td>
</tr>
<tr>
<td>XVIII*</td>
<td>952&lt;sub&gt;m&lt;/sub&gt;</td>
<td>1600&lt;sub&gt;s&lt;/sub&gt;</td>
<td>1256&lt;sub&gt;m&lt;/sub&gt;</td>
<td>1346&lt;sub&gt;s&lt;/sub&gt;</td>
<td>1174&lt;sub&gt;m&lt;/sub&gt;</td>
<td>1104&lt;sub&gt;s&lt;/sub&gt;</td>
<td>622&lt;sub&gt;w&lt;/sub&gt;</td>
<td>417, 445</td>
</tr>
<tr>
<td>XIX</td>
<td>964&lt;sub&gt;m&lt;/sub&gt;</td>
<td>1598&lt;sub&gt;s&lt;/sub&gt;</td>
<td>1258&lt;sub&gt;m&lt;/sub&gt;</td>
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<td>624&lt;sub&gt;w&lt;/sub&gt;</td>
<td>422, 456</td>
</tr>
<tr>
<td>XX*</td>
<td>964&lt;sub&gt;m&lt;/sub&gt;</td>
<td>1599&lt;sub&gt;s&lt;/sub&gt;</td>
<td>1258&lt;sub&gt;m&lt;/sub&gt;</td>
<td>1357&lt;sub&gt;s&lt;/sub&gt;</td>
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<td>1095&lt;sub&gt;w&lt;/sub&gt;</td>
<td>626&lt;sub&gt;w&lt;/sub&gt;</td>
<td>423, 460</td>
</tr>
</tbody>
</table>

m = medium, mb = medium broad, s = strong, w = weak
*Products obtained from reactions with precursors

Table-3.10: Important frequencies (cm⁻¹) observed in the IR spectra of the complexes and their assignment for L².2HClO₄:

<table>
<thead>
<tr>
<th>Comp.</th>
<th>v(N-N)</th>
<th>v(C=N)</th>
<th>v(C-H)</th>
<th>v(N-H)</th>
<th>Aliphatic v(C-N)</th>
<th>Aromatic v(C-N)</th>
<th>ClO₄</th>
<th>v(M-N)</th>
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<td>999&lt;sub&gt;m&lt;/sub&gt;</td>
<td>1609&lt;sub&gt;s&lt;/sub&gt;</td>
<td>1522&lt;sub&gt;w&lt;/sub&gt;</td>
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<td>1171&lt;sub&gt;m&lt;/sub&gt;</td>
<td>1072&lt;sub&gt;m&lt;/sub&gt;</td>
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<tr>
<td>XXII*</td>
<td>996&lt;sub&gt;s&lt;/sub&gt;</td>
<td>1609&lt;sub&gt;s&lt;/sub&gt;</td>
<td>1519&lt;sub&gt;m&lt;/sub&gt;</td>
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<td>1259&lt;sub&gt;s&lt;/sub&gt;</td>
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<td>1172&lt;sub&gt;m&lt;/sub&gt;</td>
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<td>988&lt;sub&gt;m&lt;/sub&gt;</td>
<td>1607&lt;sub&gt;s&lt;/sub&gt;</td>
<td>1511&lt;sub&gt;m&lt;/sub&gt;</td>
<td>333&lt;sub&gt;m&lt;/sub&gt;</td>
<td>1235&lt;sub&gt;s&lt;/sub&gt;</td>
<td>1326&lt;sub&gt;ab&lt;/sub&gt;</td>
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<tr>
<td>XXIV*</td>
<td>989&lt;sub&gt;m&lt;/sub&gt;</td>
<td>1607&lt;sub&gt;s&lt;/sub&gt;</td>
<td>1513&lt;sub&gt;s&lt;/sub&gt;</td>
<td>333&lt;sub&gt;s&lt;/sub&gt;</td>
<td>1238&lt;sub&gt;s&lt;/sub&gt;</td>
<td>1328&lt;sub&gt;ab&lt;/sub&gt;</td>
<td>1174&lt;sub&gt;m&lt;/sub&gt;</td>
<td>1092&lt;sub&gt;m&lt;/sub&gt;</td>
</tr>
<tr>
<td>XXV</td>
<td>987&lt;sub&gt;m&lt;/sub&gt;</td>
<td>1606&lt;sub&gt;s&lt;/sub&gt;</td>
<td>1525&lt;sub&gt;m&lt;/sub&gt;</td>
<td>335&lt;sub&gt;s&lt;/sub&gt;</td>
<td>1240&lt;sub&gt;s&lt;/sub&gt;</td>
<td>1356&lt;sub&gt;s&lt;/sub&gt;</td>
<td>1178&lt;sub&gt;m&lt;/sub&gt;</td>
<td>1062&lt;sub&gt;m&lt;/sub&gt;</td>
</tr>
<tr>
<td>XXVI*</td>
<td>989&lt;sub&gt;m&lt;/sub&gt;</td>
<td>1608&lt;sub&gt;s&lt;/sub&gt;</td>
<td>1527&lt;sub&gt;m&lt;/sub&gt;</td>
<td>3358&lt;sub&gt;m&lt;/sub&gt;</td>
<td>1242&lt;sub&gt;s&lt;/sub&gt;</td>
<td>1354&lt;sub&gt;mb&lt;/sub&gt;</td>
<td>1176&lt;sub&gt;m&lt;/sub&gt;</td>
<td>1079&lt;sub&gt;m&lt;/sub&gt;</td>
</tr>
</tbody>
</table>

* Products obtained from reactions with precursors
PART-C

$^{57}$Fe-Mössbauer Spectroscopic Investigations of Fe$^{3+}$ Complexes of L$^1$.2HClO$_4$ and L$^2$.2HClO$_4$
INTRODUCTON

Mössbauer spectroscopic technique has been shown to be a very useful method to identify the electronic configuration and stereochemical arrangement of ligands i.e. approximate symmetry around the Fe$^{2+}$ as well as Fe$^{3+}$ ions. There are numerous reports where application of this technique has been well illustrated for identification of iron complexes with a view to establish the molecular geometry vis-à-vis nature of the coordinated ligands$^{31}$. The application of the technique has been further elaborated for the study of biological molecules i.e. proteins containing two or more iron atoms in a cluster formation i.e. like Fe$_4$S$_4$, CoFe$_3$S$_4$, ZnFe$_3$S$_4$, CdFe$_3$S$_4$ and NiFe$_3$S$_4$ clusters e.g. Desulfo vibrio gigas ferredoxin II (Dg Fd (II))$^{32}$. The mössbauer technique has also been successfully used for the characterization of diiron complexes of bicyclopolyaza macrocycle$^{33}$. It has been shown that nature of axial ligand also plays an important role as it affects the magnitude of the isomer shift as well as quardrupole splitting in the complexes.

Mössbauer spectroscopy has been used as a key to unlock some basic physical, chemical and biological phenomenon, as a guide for finding new ways of solving applied scientific and technical problems. The continuing rapid growth in the number of publications on
Mössbauer spectroscopy and its various applications can be illustrated by simply comparing the size of the annual Mössbauer effect data indices.

In Mössbauer spectrum, we try to know the physics of the hyperfine interactions and the relevant parameters. Thereafter, the kind of chemically interesting information being reflected by isomer shifts and quadrupole splitting, particularly with respect to bonding and structural properties.

**Importance of Mössbauer effect**

In a short time after the discovery of Mössbauer effect in 1958\(^{34}\), it has become an important experimental tool for the investigation of hyperfine interactions in solids. Mössbauer spectroscopy has a number of advantages over other methods because it is more selective and it singles out a specific isotope such as \(^{57}\)Fe etc. Properties of the surrounding environment can be studied, although indirectly, via hyperfine interactions\(^{35}\). Mössbauer spectroscopy can be used as an analytical tool to determine the total amount of a given isotope, to check the inhomogeneity of the sample or to identify the various components it may contain\(^{36}\). The line width of \(^{57}\)Fe is \(4.5 \times 10^{-9}\) ev and the quality factor \(Q = \Delta E / E_y = 4.5 \times 10^{-9} / 14.4 \times 10^{-3}\) gives a high sensitivity of about 3 parts in \(10^{13}\). A few other isotopes known for their high selectivity are \(^{181}\)Ta (\(Q \approx 10^4\)) and \(^{62}\)Zn (\(Q \approx 2 \times 10^{15}\)) but they are
too difficult to perform experiments with. Thus, the Mössbauer resonance furnishes important information about the very small perturbations.

The limitations of the method are obvious, too. The number of useful isotopes is relatively small. In biological studies, in particular, the only nuclei of immediate significance are $^{57}$Fe and its radio active parent $^{57}$Co and the two iodine isotopes $^{127}$I and $^{129}$I. Other limitations are the fixed energy resolution determined by the nuclear life time and the fact that only immediate environment of the Mössbauer isotopes can be studied. A further serious restriction is that the system must be in the solid form.

**Hyperfine interaction in the Mössbauer effect**

In the Mössbauer effect, the line width of the nuclear transition is small and the resonant absorption is extremely sensitive to energy variation of the gamma radiation. Therefore the minute interaction between the nucleus and the orbital electrons which are not observed generally by other methods can easily be observed in the Mössbauer effect. It is thus the influence of the electronic environment on the nuclear gamma transition, both in emission and absorption, which determines the hyperfine structure of the Mössbauer radiation.

The principal interactions in the Mössbauer effect are:-

1. Nuclear Isomer-Shift
2. Nuclear Quadrupole Interaction

3. Nuclear Magnetic Hyperfine Interaction

4. Static and Dynamic Aspect of Lattice structure

**Isomer-Shift**

The nuclear electric charge is extended in space and is surrounded by the orbital electronic cloud. We know that the s-electrons are nearest to the nucleus. Therefore, the electrostatic interaction is different for point charges and extended charge distributions. A change in the s-electron density will result in an altered coulombic interaction that produces a shift of the nuclear energy levels. This effect could be called as the ‘electric monopole interaction’. The effect depends on the difference in the nuclear radii of the ground (R_{gd}) and isomeric excited (R_{ex}) states and is known as the ‘Isomer-Shift’.

The isomer shift in the nuclear level may be calculated by making some reasonable assumptions.

(i) The deviation is non-relativistic.

(ii) The electron charge density (\rho_e) over the nucleus is constant and thus only the s-electrons contribute to the interaction.

(iii) A perturbation treatment is used and it is assumed that the size of the nucleus does not affect the electron wave functions.
The energy of the gamma ray represents the different electrostatic energy of the nucleus in two different states of excitation, differing only in nuclear radius. The effect of the electric monopole interaction is to shift nucleus levels without lifting the spin degeneracy. The shifts are very small compared to the total energy of the gamma ray and generally of the order $10^{-12} E_\gamma$.

The expression for the change in the energy of the gamma ray due to the nuclear electrostatic interaction ($\delta E_{ex} - \delta E_{gd}$) is therefore, given by equation 3.1.

$$\delta E_{ex} - \delta E_{gd} = (2\pi Z e^2/5) |\psi(o)|^2 (R_{ex}^2 - R_{gd}^2) \quad \text{(3.1)}$$

$$\delta E = (2\pi Z e^2/5) |\psi(o)|^2 R^2 \quad \text{(Relative to point nucleus)}$$

if $E_s$ and $E_a$ are the energy difference for source and absorber respectively then

$$E_s = E_0 + \delta E_s = E_0 + (2\pi Z e^2/5) |\psi_s(o)|^2 [R_{ex}^2 - R_{gd}^2] \quad \text{(3.2)}$$

$$E_a = E_0 + \delta E_a = E_0 + (2\pi Z e^2/5) |\psi_a(o)|^2 [R_{ex}^2 - R_{gd}^2] \quad \text{(3.3)}$$

The isomer shift ($I S$) = $E_a - E_s$

$$I S = (2\pi Z e^2/5) \{|\psi_o(o)|^2 - |\psi_s(o)|^2\} [R_{ex}^2 - R_{gd}^2] \quad \text{(3.4)}$$

$$Or = (4\pi Z e^2/5) R^2 (\delta R / R) \{|\psi_o(o)|^2 - |\psi_s(o)|^2\} \quad \text{(3.5)}$$

\noindent nuclear \quad atomic

where \quad $R_{ex} - R_{gd} = \delta R$

and \quad $R_{ex}^2 - R_{gd}^2 = (R_{ex} - R_{gd}) (R_{ex} + R_{gd}) \approx \delta R (2R)$
The equation (3.5) consists of two factors, one is that of nuclear radius effect and the second being the electronic charge density at the nucleus. The latter is basically an atomic or chemical parameter since it is affected by the valence state of the atom. Therefore, to observe the Isomer-Shift it is must that

i) The mean square radius of the nuclear ground state must be different from that of the nuclear excited state.

ii) The chemical make up in the source and absorber must be different. For example two different valence states may be used as the electron density at the nucleus is different in source and absorber.

**Quadrupole interaction**

In the case of Isomer Shift the effect of the electrostatic interaction between nuclear and electronic charges is derived by assuming the nucleus to be spherical and the charge density to be uniformed. If these conditions are relaxed, other effects appear which are in fact higher order terms in the multipole expansion of the electrostatic interaction. These terms do not shift the nuclear levels, they split them, i.e., they lift all or part of their \((2I + 1)\) fold degeneracy (where \(I\) is the nuclear spin quantum number).

The second non vanishing term of the electrostatic interaction of a nucleus with its surrounding electronic charge is the quadrupole coupling. This is the result of the interaction of the nuclear quadrupole moment with the gradient of the electric field due to other charges in
the crystal etc. The nuclear quadrupole moment reflects the deviation of the nucleus from spherical symmetry. An oblate (flattened) nucleus has a negative quadrupole moment while a prolate (elongated) one has a positive moment. Nuclei whose spin is zero or $\frac{1}{2}$ are spherically symmetric and have a zero quadrupole moment. Thus the ground state of $^{57}\text{Fe}$ with $I = \frac{1}{2}$ can not exhibit nuclear quadrupole splitting. However the excited state has $I = \frac{3}{2}$ giving the quadrupole splitting of this energy level.

The macrocyclic $\text{Fe}^{2+}/\text{Fe}^{3+}$ complexes are well defined through various techniques and it is an established fact that their properties are due to various geometric arrangements of ligand surrounding metal ion. But such efforts using Mössbauer technique for the study of hyperfine field parameters are limited.

In this chapter $^{57}\text{Fe}$ - Mössbauer spectroscopic investigations on the newly synthesise dinuclear $\text{Fe}^{3+}$ complexes $\text{Fe}_2\text{L}^1\text{Cl}_4(\text{ClO}_4)_2$ (II) and $\text{Fe}_2\text{L}^2\text{Cl}_4(\text{ClO}_4)_2$ (IX) have been discussed to assertain the electronic as well as stereochemical environment around $\text{Fe}^{3+}$ ions ecapsulated in the present dinucleating unsymmetrical macrocycles $\text{L}^1.2\text{HClO}_4$ and $\text{L}^2.2\text{HClO}_4$. 


EXPERIMENTAL

DATA ACQUISITION

The Mössbauer velocity spectrometer may be fabricated conform to the available data acquisition and storage devices. Generally the constant velocity mode and the constant acceleration mode are used extensively to record the Mössbauer spectrum. In a constant velocity mode the data is recorded for a preset time and the velocity increment is made for the next data point. In this way the spectrum can be scanned to the accuracy. However, the long term instabilities in the pulse height selection system lead to the distorted line shapes which result in spurious shifts of the spectrum which may be very well interpreted as isomer shifts. However, this technique does involve elaborate data recording equipment. In the constant acceleration mode, source or absorber is made to pass through all the velocity intervals, required to obtain the spectrum in a short intervals time 50 ms. The process is repeated until the spectrum is obtained to the required statistical accuracy. This method necessitates the use of a multi channel analyzer of a data storage device like a small electronic computer.
METHOD

The Mössbauer data were taken with the $^{57}\text{Co}$ diffused into a copper matrix supplied by the Inter-University Consortium for Department of Atomic Energy Facilities (DAEF), Indore (MP), India.

The experiment was performed at room temperature $300^\circ\text{k}$ when the absorber was kept stationary and the source drive was moving with a constant velocity (10mm/sec). The data acquisition procedure is as described above. All the spectra were taken without an applied magnetic field. The spectrum was fitted with NORMOS program 1990 for its solution.

The velocity is calibrated with an $\alpha$ ion ($\text{Fe}_2\text{O}_3$) foil standard. The quadrupole splitting and isomer shift both are positive in each case. The line width, area, quadrupole splitting and isomer shift are shown in Table-3.11.
RESULTS AND DISCUSSION

The Mössbauer spectra of complexes Fe$_2$L$^1$Cl$_4$(ClO$_4$)$_2$ (II) and Fe$_2$L$^2$Cl$_4$(ClO$_4$)$_2$ (IX) were recorded at 300°K and are shown in fig-3.3(a) and fig-3.3(b). The Mössbauer parameters are summarized in Table-3.11. The present data are clearly suggestive of presence of high-spin +3 oxidation state of iron in these complexes. The magnitude of isomer shift ($\delta$) is comparable to that reported$^{31}$ for various high-spin Fe$^{3+}$ complexes having hexa coordination around the metal ion. The magnitude of isomer shift is moderately positive suggesting that the s-electron density is higher in the complexes compared to that in the source. The spectra show the presence of quadrupole splitting with $\Delta$Eq of $\geq 0.5$ mms$^{-1}$ even at room temperature suggesting the presence of a considerable electric field gradient around the Fe$^{3+}$ ion which is much higher in complex (II) compared to that in (IX). The electric field gradient becomes more effective$^{31}$ if the molecular geometry gets distorted from the perfect octahedral structure such that its symmetry is lower than spherical $O_h$ symmetry. It is interesting to note that the magnitude of the quadrupole splitting is lower ($\Delta$Eq$=0.483$ mms$^{-1}$) in the complex Fe$_2$L$^2$Cl$_4$(ClO$_4$)$_2$ with reference to that in the complex Fe$_2$L$^1$Cl$_4$(ClO$_4$)$_2$ ($\Delta$Eq$=0.667$ mms$^{-1}$) suggesting that the latter complex has a grossly distorted-octahedral geometry. This seems plausible in view of the probable molecular structure of the ligand [L$^1$.2HClO$_4$] (see chapter-2) which may apparently provide more asymmetric hexa
coordination biting sites to Fe$^{3+}$ ions compared to that possible for the ligand [L$^2$.2HClO$_4$]. It also appears from the spectra of complexes (II) and (IX) that the peaks lie to the positive side of zero velocity i.e. the quadrupole coupling constant (qcc) is positive. It further reflects that transition is taking place from higher energy state to lower energy state i.e. ($\pm 3/2 \rightarrow \pm 1/2$). Since the magnetic splitting does not appear in these complexes therefore it suggests that internal magnetic field is absent at the Mössbauer nucleus in each case and the states remain doubly degenerated, showing the presence of Kramer’s degeneracy. The observed magnitudes of isomer shift ($\delta$) for the present complexes (II) and (IX) are low while the quadrupole splitting parameter ($\Delta$Eq) is high compared to those reported$^{33}$ for a number of [N$_4$] macrocyclic complexes. The isomer shift, $\delta$, is inversely related to the amount of s-electron density at the nucleus$^{40}$. Ligand that are good $\sigma$ donors lead to increase the s-electron density at the iron nucleus and hence lower the $\delta$ value. Moreover, the d-electron density can also influence the s-electron density by screening the s electrons from the effect of the nuclear charge. It has been argued$^{33}$ that presence of unsaturation in the macrocyclic moiety due to the presence of imine (C= N) linkages lowers the d-electron density because of an enhanced $\pi$-accepting power of the imine bond. It may increases the s-electron density at the nucleus or in another words the $\delta$ value is shifted towards a lower value$^{41}$. The present macrocyclic ligands L$^1$.2HClO$_4$ and L$^2$.2HClO$_4$ are
unsymmetrical dinucleating ligands possessing imine, (C≡N) bonds which are here responsible for the observed low magnitude of the isomer shift (δ) for the complexes (II) and (IX).
Table-3.11: Line width, Area, Isomer shift (δ) and Quadrupole splitting (∆Eq) of Fe³⁺ encapsulated complexes of L¹.2HClO₄ and L².2HClO₄:

<table>
<thead>
<tr>
<th>S.N.</th>
<th>Compound</th>
<th>Line width (WID)</th>
<th>Error</th>
<th>Area line (ARE)</th>
<th>Error</th>
<th>ISO (δ)</th>
<th>Error</th>
<th>QUA (∆Eq)</th>
<th>Error</th>
<th>χ²</th>
</tr>
</thead>
<tbody>
<tr>
<td>II</td>
<td>Fe₂L¹Cl₄(ClO₄)₂</td>
<td>0.551618 ± 0.014921</td>
<td></td>
<td>0.037991 ± 0.000695</td>
<td></td>
<td>0.361410 ± 0.009775</td>
<td></td>
<td>0.667494 ± 0.013428</td>
<td></td>
<td>0.9905</td>
</tr>
<tr>
<td>IX</td>
<td>Fe₂L²Cl₄(ClO₄)₂</td>
<td>0.820244 ± 0.114853</td>
<td></td>
<td>0.004928 ± 0.000318</td>
<td></td>
<td>0.294404 ± 0.037944</td>
<td></td>
<td>0.483642 ± 0.070945</td>
<td></td>
<td>0.9446</td>
</tr>
</tbody>
</table>
Fig. 3.3 – a, b
REFERENCES:


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CHAPTER-4

Electrical and Electrochemical Investigations of the Bimetallic Complexes of the Macrocyclic Ligands
INTRODUCTION

The information concerning the ion selectivity and ionic associations in metal ion encapsulated macrocyclic ligands have been determined utilizing the electrical conducting behaviour of complexes in suitable solvents. These informations have been utilized to explore the application of these complexes to an ion-selective electrode (ISE)\(^1\). The ionic transport behaviour contained in a polymeric membrane of ISE was found to be largely dependent on the nature of both the selectivity and stability of these metal complexes on the metal ion or counter anion. The selectivity of these macrocyclic complexes is strongly affected by the solvent media, the stability of complexes and their interactions with a cation or counter anion\(^2\).

The ionic association constant of macrocyclic ligands have been determined after carrying out a conductometric studies\(^3,4\). Jenkins and Monk\(^5\) suggested that conductance measurement are also applicable for determining the formation constants of the complexes. Katayana and Tomomush\(^6,7\) studied the ion-pair formation constants of tris (ethylenediamine) cobalt(III) complexes with maleate and fumerate based on a continuous variation method for a conductometric determination. Conductometric studies for the ionic association constants of Co\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\) and Zn\(^{2+}\) perchlorates in methanol-ethylene glycol mixtures have been reported by Doe and Kitagawa\(^8\).
Koryta and Dvorak\(^9\) have introduced a method for the conductometric determination of dissociation constants of the transition metal complexes. The effective size of complex cation is the key factor amongst the various factors which can influence the extent to which ions associate in solution. This may be seen, for instance, by comparison of identical salts containing organic ions in non aqueous solvents, where the dissociation constants are found to increase with increasing size of the organic ions\(^5\).

In this chapter, conductometric measurements in non-aqueous system, dimethyl sulfoxide (DMSO) have been made and the data were treated by using a modified Onsagar limiting equation according to the Fuoss and Edelson method\(^10\). The thermodynamic ionic association constants of the encapsulated divalent and trivalent metal complexes of the present macrocycles \([L^1.2\text{HClO}_4]\) and \([L^2.2\text{HClO}_4]\) have been determined. The free energies of the first association reaction of these metal complexes in +2 as well as +3 oxidation states have also been calculated and discussed.

The technique of cyclic voltametry (CV) involves cycling the potential of an electrode, which is immersed in an unstirred solution, and measuring the resulting current. The effectiveness of CV results from its capability for rapidly observing redox behaviour over a wide potential range. Cyclic voltametry provides the technique to study an electro active species generated during the forward scan and then
probing its fate with the reverse scan and subsequent cycles, all in a matter of seconds or even less. The time scale of the experiment is adjustable over several orders of magnitude by changing the potential scan rate enabling some assessment of the rates of various reactions.

The important parameters of cyclic voltammogram are the magnitude of the anodic peak current \(i_p\) and the cathodic peak current \(i_{pc}\), the anodic peak potential \(E_{pa}\) and the cathodic peak potential \(E_{pc}\).

The formal reduction potential \(E^0_{\frac{1}{2}}\) for a reversive couple is centred between \(E_{pa}\) and \(E_{pc}\)

\[
E^0_{\frac{1}{2}} = \frac{E_{pa} + E_{pc}}{2} \quad \text{----(4.1)}
\]

The number of electrons transferred in the electrode reaction \(n\) for a reversible couple can be determined from the separation between the peak potentials, which at 25\(^\circ\)C is given by the following relationship:

\[
E_p = E_{pa} - E_{pc} = \frac{0.059}{n} \quad \text{----(4.2)}
\]

For a reversible redox couple the values of \(i_{pa}\) and \(i_{pc}\) should be of comparable magnitude i.e. \(i_{pa} / i_{pc} = 1\)

The peak current for a reversible system increases with \(V^{1/2}\) and is directly proportional to concentration. However, the ratio of peak
current can be significantly influenced by chemical reactions coupled to the electrode process. A faster or rapid scan rate allow less time for the chemical reaction to occur between the positive and negative scans. In fact, for sufficiently fast scan rates the effect of the chemical reaction becomes negligible and $i_{pc} / i_{pa}$ approaches unity.

Electrochemical irreversibility is caused by slow electron exchange of the redox species with the working electrode and is characterized by a separation of peak potentials greater than indicated by equation 2. The cyclic voltammetric investigations of the electrochemical behaviour of the macrocyclic complexes containing the metal ions $\text{Cr}^{3+}$, $\text{Fe}^{3+}$, $\text{Co}^{2+}$, $\text{Cu}^{2+}$ and $\text{Ni}^{2+}$ have been carried out and discussed in this chapter.
EXPERIMENTAL

Reagents used:-

Tetrabutylammoniumbromide (Fluka), HClO₄ (70%, BDH), AgNO₃ (Ranbaxy) were analytical grade and used as received. The metal complexes used in this experiment were as described in chapter-3. The solvent DMSO was dried and distilled according to the reported method\textsuperscript{11}. The tetrabutylammoniumperchlorate used for CV studies was prepared by titrating 1mM solution of tetrabutylammoniumbromide with standardized perchloric acid. The resulting solid at the end point was filtered, washed and dried in a desiccator. A 0.4 molar solution of the electrolyte has been used as supporting electrolyte in the CV measurement.

Physical Measurements:-

Conductivities were measured using Systronics-305 Conductivity Bridge at room temperature on a frequency of 1 KHz in DMSO solutions. The conductivity cell of the cell constant 1.00cm\textsuperscript{-1} (determined by using 1mM KCl as standard solutions) was used. The concentration ranges of the complexes studied were 10\textsuperscript{-3} to 10\textsuperscript{-4} mol/liter.

Cyclic voltametric measurements were recorded on a CH-instrument Electrochemical Analyzer. High purity DMSO was employed for the CV studies with 0.4 M tetrabutylammonium-perchlorate as supporting electrolyte. A three electrode configuration
used comprised of a Pt microcylinder working electrode, a Pt wire as auxiliary electrode and Ag/AgCl as the reference electrode. Experiments were carried out at room temperature.
RESULTS AND DISCUSSION

Conductivity Measurements:

Evaluation of $K_1$, First ionic association constant and thermodynamic parameters of $\text{Cr}_2L^1\text{Cl}_4(\text{ClO}_4)_2$ (I), $\text{Fe}_2L^1\text{Cl}_4(\text{ClO}_4)_2$ (II), $\text{Ni}_2L^2\text{Cl}_2(\text{ClO}_4)_2$ (IV), $\text{Cu}_2L^1\text{Cl}_2(\text{ClO}_4)_2$ (V), $\text{Cr}_2L^2\text{Cl}_4(\text{ClO}_4)_2$ (VIII), $\text{Fe}_2L^2\text{Cl}_4(\text{ClO}_4)_2$ (IX), $\text{Co}_2L^2\text{Cl}_2(\text{ClO}_4)_2$ (X), $\text{Ni}_2L^2\text{Cl}_2(\text{ClO}_4)_2$ (XI) and $\text{Cu}_2L^2\text{Cl}_2(\text{ClO}_4)_2$ (XII) from conductivity data:

Thermodynamic ionic association constant as well as the corresponding free energy ($\Delta G$) of the metal encapsulated macrocyclic complexes I, II, IV, VIII, IX, X, XI and XII in DMSO have also been estimated by carrying out the conductometric studies at room temperature. Conductometric data were treated according to modified Onsagar limiting equation employing Fuoss and Edelson method. The Onsagar limiting equation at low concentration range of the electrolyte is given by the relation\textsuperscript{10,12}.

$$\Lambda = \Lambda^0 - S C_0^{1/2} \quad \text{---------}(4.3)$$

Here, $\Lambda$ is the equivalent conductance at each appropriate concentration $C_0$ and $\Lambda^0$ is the limiting equivalent conductance and $S$ represents slope of the plot of $\Lambda$ vs. $C_0^{1/2}$. The consecutive association equilibria of the complexes in solution may be represented as following:


\[
A^{2+} + X^- \rightleftharpoons AX^+ \quad \text{------ (4.4)}
\]

and

\[
AX^+ + X^- \rightleftharpoons AX_2 \quad \text{------ (4.5)}
\]

Where \( A^{2+} \) indicates the complex cations \([\text{Cr}_2L^4\text{Cl}_4\text{(ClO}_4)^-]^+, \quad [\text{Fe}_2L^4\text{Cl}_4\text{(ClO}_4)^-]^+, \quad [\text{Ni}_2L^4\text{Cl}_4\text{(ClO}_4)^-]^+, \quad [\text{Cu}_2L^4\text{Cl}_4\text{(ClO}_4)^-]^+, \quad [\text{Cr}_2L^2\text{Cl}_4\text{(ClO}_4)^-]^+, \quad [\text{Fe}_2L^2\text{Cl}_4\text{(ClO}_4)^-]^+, \quad [\text{Co}_2L^2\text{Cl}_4\text{(ClO}_4)^-]^+, \quad [\text{Ni}_2L^2\text{Cl}_4\text{(ClO}_4)^-]^+ \) and \([\text{Cu}_2L^2\text{Cl}_4\text{(ClO}_4)^-]^+: \)

\( X^- \) is either \( \text{Cl}^- \) or \( \text{ClO}_4^- \). The corresponding ionic association constant \( K_1 \) and \( K_2 \) are given by

\[
K_1 = \frac{[AX^+]}{[A^{2+}][X^-]} \quad \text{and} \quad K_2 = \frac{[AX_2]}{[AX^+][X^-]} \quad \text{--- (4.6, 4.7)}
\]

Where \( f_{2+}, f_+, f \) and \( f^- \) are the activity coefficients of \( A^{2+}, AX_2 \) and \( X^- \) respectively. In general \(^{10} K_2 \ll K_1 \) and it's concentration is very low in comparison to \( K_1 \), henceforth, the ionic equilibrium represented by equation (4.7) is only considered. The onsalgar limiting law then becomes

\[
\Lambda F = \Lambda_0 - DK_1 / \Lambda_0 \quad \text{------ (4.8)}
\]

where \( D = C_0 f_{2+} \Lambda F (\Lambda F - \Lambda_0^0 / 2) \)

and

\[
F = [(1 - \delta C_0^{1/2})^{-1} + (\Lambda_0^0 - \Lambda_0^-)] / [1 + (\Lambda_0^0 - \Lambda_0^-) 2\Lambda_0^0]
\]

Here, \( F \) is a function which corrects the conductance ratio, \( \Lambda / \Lambda_0^0 \), for the effect of interionic forces on the mobility. The parameter \( \delta \) is the ratio
of the slope ($S$) and limiting equivalent conductance of the complex cations and $\lambda_0$-value for ClO$_4^-$ and NO$_3^-$ ions are 70.9 S cm$^2$ mol$^{-1}$ and 71.8 S cm$^2$ mol$^{-1}$ respectively. The ionic activity coefficient of $A^{2+}, f_{2+}$ has been estimated using the following modified Debye-Huckel equation:

$$-\log f_{2+} = 1.828\times (\varepsilon T)^{-3/2} Z_i^2 \cdot I^{1/2} \quad \text{---------(4.9)}$$

where $Z_i = 2$ (effective charge on the complex cation)

and $\varepsilon = \text{dielectric constant of the solvent DMSO (} \varepsilon = 46\text{)}$

$I = \text{Ionic strength (C}_0\text{)}$

The experimental equivalent conductivity data for each complex and the estimated several parameters like limiting equivalent conductance ($\lambda^0$), the activity coefficient ($f_{2+}$) and $D$ for the complexes-I, II, IV, V, VIII, IX, X, XI and XII measured in DMSO at 25 °C have been summarized in Table –4.1. The plots of $\lambda$ vs. $C_0^{1/2}$ and $AF$ vs. $D$ have been shown in Figures 4.1 –4.9.

The slope of the plot of $AF$ vs. $D$ has provided the magnitude of $(K_1/\lambda^0)$ which ultimately gives the magnitudes of first ionic association constant ($K_1$) according to equation (4.8) and the magnitudes are summarized in Table 4.2.
The limiting equivalent ionic conductance \( \lambda_{0+} \) of the cation of the macrocyclic metal complexes has been determined according to Kohlrausch law\(^{13} \) as

\[
\Lambda^0 = \lambda_{0+} + \lambda_{0-}.
\]  
\[\text{------------------(4.10)}\]

or

\[
(\lambda_{0+} = \Lambda^0 - \lambda_{0-})
\]

and the magnitude for each complex cation are tabulated in Table 4.2.

The free energy changes due to first ionic association reactions were also obtained using the thermodynamic relationship i.e.

\[
\Delta G = -RT\ln K_1.
\]  
\[\text{--------(4.11)}\]

and the magnitude is shown in Table 4.2.

It is apparent from Table-4.2 that the magnitude of first ion-association constant \((K_1)\) and the corresponding free energy change \((\Delta G)\) for complexes with \(L^1.2\text{HClO}_4\) macrocycle vary in the order \(\text{Ni}^{2+} > \text{Cu}^{2+}\) for divalent metal ions and \(\text{Cr}^{3+} > \text{Fe}^{3+}\) for trivalent metal ions. For complexes with \(L^2.2\text{HClO}_4\) macrocycle the order is \(\text{Ni}^{2+} > \text{Co}^{2+} > \text{Cu}^{2+}\) for divalent metal ions however, for trivalent metal ions the order is \(\text{Fe}^{3+} > \text{Cr}^{3+}\) which is reverse to that observed for corresponding complexes with \(L^1.2\text{HClO}_4\) macrocycle. This may be correlated to the flexibility of the macrocyclic cavity which apparently is more for \(L^2\) and therefore, stabilizes more efficiently the cations of smaller sizes.
magnitude of $K_1$ for all these complexes is usually lower than those reported\textsuperscript{14} for divalent metal complexes of $[N_6]$ polyaza macrocycle. This indicates that the extent of ionization small for the present complexes low producing a relatively low concentration of the free complex cation $[M_2LCl_2(ClO_4)]^+$ ($M = \text{Co}^{2+}, \text{Ni}^{2+}$ or $\text{Cu}^{2+}$) or $[M_2LCl_4(ClO_4)]^+$ ($M = \text{Fe}^{3+}$ or $\text{Cr}^{3+}$) and counter anion $\text{ClO}_4^-$ in solution. It is quite probable that the complex cations and the counter ion have a greater tendency for association to give the ion-pair formation in solution. Ion-pair formation in solution is reported\textsuperscript{15} to become significant at a concentration where plot of $\Lambda$ vs. $C_0^{1/2}$ deviates markedly from linearity. This is defined as limiting concentration for the individual complexes which has been obtained from the corresponding plots of $\Lambda$ vs. $C_0^{1/2}$. The limiting concentration for ion-pair formation for complexes with $L^1.2\text{HClO}_4$ macrocycle is in the range $20 \times 10^{-3} - 25 \times 10^{-3}$ mol L$^{-1}$ while for complexes with $L^2.2\text{HClO}_4$ macrocycle lies in the range $15 \times 10^{-3} - 22 \times 10^{-3}$ mol L$^{-1}$ (Table - 4.3). This further indicates that the tendency of ion–pair formation is more for complexes with $L^2.2\text{HClO}_4$ macrocycle compared to that for complexes with $L^1.2\text{HClO}_4$ macrocycle in solution.
Table- 4.1: Several Parameters of Metal Complexes in DMSO at Room Temperature:-

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Concentration (mol L⁻¹)</th>
<th>(A) ((\ell^2 \text{cm}^2 \text{mol}^{-1}))</th>
<th>(A^0) ((\ell^2 \text{cm}^2 \text{mol}^{-1}))</th>
<th>(f_{2+})</th>
<th>(F)</th>
<th>(D)</th>
</tr>
</thead>
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<td>I</td>
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<td></td>
<td>.8347</td>
<td>1.2344</td>
<td>0.7576</td>
</tr>
<tr>
<td></td>
<td>2.4 \times 10^{-4}</td>
<td>65</td>
<td></td>
<td>.8480</td>
<td>1.2020</td>
<td>0.6541</td>
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<tr>
<td></td>
<td>1 \times 10^{-4}</td>
<td>67</td>
<td></td>
<td>.9010</td>
<td>1.1195</td>
<td>0.2568</td>
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<tr>
<td></td>
<td>5 \times 10^{-5}</td>
<td>74</td>
<td></td>
<td>.9287</td>
<td>1.0806</td>
<td>0.1545</td>
</tr>
<tr>
<td>VIII</td>
<td>1 \times 10^{-3}</td>
<td>73</td>
<td>122</td>
<td>.7188</td>
<td>1.8715</td>
<td>7.4259</td>
</tr>
<tr>
<td></td>
<td>7 \times 10^{-4}</td>
<td>75</td>
<td></td>
<td>.7591</td>
<td>1.6571</td>
<td>4.1798</td>
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<tr>
<td>(5 \times 10^{-4})</td>
<td>79</td>
<td>.7923</td>
<td>1.5143</td>
<td>2.7786</td>
<td></td>
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</tr>
<tr>
<td>(3 \times 10^{-4})</td>
<td>81</td>
<td>.8347</td>
<td>1.3802</td>
<td>1.4222</td>
<td></td>
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<tr>
<td>(2.4 \times 10^{-4})</td>
<td>89</td>
<td>.8480</td>
<td>1.3234</td>
<td>1.3611</td>
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<td></td>
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<tr>
<td>(1 \times 10^{-4})</td>
<td>105</td>
<td>.9010</td>
<td>1.1752</td>
<td>0.6937</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(5 \times 10^{-5})</td>
<td>110</td>
<td>.9287</td>
<td>1.1182</td>
<td>0.3541</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**IX**

| \(1 \times 10^{-3}\) | 63 | 97 | .7188 | 1.6971 | 4.4894 |
| \(7 \times 10^{-4}\) | 64 | .7591 | 1.9172 | 4.8381 |
| \(5 \times 10^{-4}\) | 68 | .7923 | 1.3764 | 1.4325 |
| \(3 \times 10^{-4}\) | 75 | .8347 | 1.2962 | 1.1860 |
| \(2.4 \times 10^{-4}\) | 77 | .8480 | 1.2636 | 0.9663 |
| \(1 \times 10^{-4}\) | 85 | .9010 | 1.1511 | 0.4350 |
| \(5 \times 10^{-5}\) | 90 | .9287 | 1.1006 | 0.2325 |

**X**

| \(1 \times 10^{-3}\) | 50 | 98 | .7188 | 1.9882 | 3.6020 |
| \(7 \times 10^{-4}\) | 58 | .7591 | 1.7096 | 2.6428 |
| \(5 \times 10^{-4}\) | 64 | .7923 | 1.5400 | 1.9371 |
| \(3 \times 10^{-4}\) | 72 | .8347 | 1.3730 | 1.2344 |
| \(2.4 \times 10^{-4}\) | 75 | .8480 | 1.3285 | 1.0268 |
| \(1 \times 10^{-4}\) | 85 | .9010 | 1.1829 | 0.4669 |
| \(5 \times 10^{-5}\) | 100 | .9287 | 1.1082 | 0.0681 |

**XI**

| \(1 \times 10^{-3}\) | 72 | 94 | .7188 | 1.3178 | 3.2657 |
| \(7 \times 10^{-4}\) | 78 | .7591 | 1.2481 | 2.6051 |
| \(5 \times 10^{-4}\) | 79 | .7923 | 1.2042 | 1.8140 |
| \(3 \times 10^{-4}\) | 82 | .8347 | 1.1520 | 1.1227 |
| \(2.4 \times 10^{-4}\) | 82 | .8480 | 1.1386 | 0.8810 |
| \(1 \times 10^{-4}\) | 87 | .9010 | 1.0826 | 0.4005 |
| \(5 \times 10^{-5}\) | 94 | .9287 | 1.0511 | 0.2376 |

**XII**

| \(1 \times 10^{-3}\) | 46 | 76 | .7188 | 1.7115 | 2.3049 |
| \(7 \times 10^{-4}\) | 50 | .7591 | 1.5331 | 1.5740 |
| \(5 \times 10^{-4}\) | 53 | .7923 | 1.4168 | 1.1034 |
| \(3 \times 10^{-4}\) | 59 | .8347 | 1.2951 | 0.7350 |
| \(2.4 \times 10^{-4}\) | 61 | .8480 | 1.2624 | 0.6113 |
| \(1 \times 10^{-4}\) | 67 | .9010 | 1.1512 | 0.2719 |
| \(5 \times 10^{-5}\) | 74 | .9287 | 1.1006 | 0.1643 |
Table 4.2: Ionic Association Constant, Free Energy and Limiting Equivalent Conductance of Cations:

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$K_1$ (L mol$^{-1}$)</th>
<th>$-\Delta G$ (KJ mol$^{-1}$)</th>
<th>$\lambda_0^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>45.50</td>
<td>9.46</td>
<td>75.1</td>
</tr>
<tr>
<td>II</td>
<td>16.66</td>
<td>6.97</td>
<td>54.1</td>
</tr>
<tr>
<td>IV</td>
<td>453</td>
<td>15.16</td>
<td>12.1</td>
</tr>
<tr>
<td>V</td>
<td>434</td>
<td>15.04</td>
<td>3.1</td>
</tr>
<tr>
<td>VIII</td>
<td>206</td>
<td>13.20</td>
<td>51.1</td>
</tr>
<tr>
<td>IX</td>
<td>218</td>
<td>13.34</td>
<td>26.1</td>
</tr>
<tr>
<td>X</td>
<td>136</td>
<td>12.17</td>
<td>27.1</td>
</tr>
<tr>
<td>XI</td>
<td>183</td>
<td>12.91</td>
<td>23.1</td>
</tr>
<tr>
<td>XII</td>
<td>105</td>
<td>11.54</td>
<td>5.1</td>
</tr>
</tbody>
</table>

Table 4.3: Magnitude of Limiting Concentrations for the complexes:

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Complexes</th>
<th>Limiting concentration (mol L$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>$\text{Cr}_2\text{L}^1\text{Cl}_4(\text{ClO}_4)_2$</td>
<td>$25 \times 10^{-3}$</td>
</tr>
<tr>
<td>II</td>
<td>$\text{Fe}_2\text{L}^1\text{Cl}_4(\text{ClO}_4)_2$</td>
<td>$20 \times 10^{-3}$</td>
</tr>
<tr>
<td>IV</td>
<td>$\text{Ni}_2\text{L}^1\text{Cl}_2(\text{ClO}_4)_2$</td>
<td>$20 \times 10^{-3}$</td>
</tr>
<tr>
<td>V</td>
<td>$\text{Cu}_2\text{L}^1\text{Cl}_2(\text{ClO}_4)_2$</td>
<td>$20 \times 10^{-3}$</td>
</tr>
<tr>
<td>VIII</td>
<td>$\text{Cr}_2\text{L}^2\text{Cl}_4(\text{ClO}_4)_2$</td>
<td>$15 \times 10^{-3}$</td>
</tr>
<tr>
<td>IX</td>
<td>$\text{Fe}_2\text{L}^2\text{Cl}_4(\text{ClO}_4)_2$</td>
<td>$20 \times 10^{-3}$</td>
</tr>
<tr>
<td>X</td>
<td>$\text{Co}_2\text{L}^2\text{Cl}_2(\text{ClO}_4)_2$</td>
<td>$22 \times 10^{-3}$</td>
</tr>
<tr>
<td>XI</td>
<td>$\text{Ni}_2\text{L}^2\text{Cl}_2(\text{ClO}_4)_2$</td>
<td>$20 \times 10^{-3}$</td>
</tr>
<tr>
<td>XII</td>
<td>$\text{Cu}_2\text{L}^2\text{Cl}_2(\text{ClO}_4)_2$</td>
<td>$20 \times 10^{-3}$</td>
</tr>
</tbody>
</table>
Fig. 4.1(a): Plotting of $A$ vs. $C_0^{1/2}$ for $\text{Cr}_2\text{L}^1\text{Cl}_4(\text{ClO}_4)_2$

Fig. 4.1(b): Plotting of $\Delta F$ vs. $D$ for $\text{Cr}_2\text{L}^1\text{Cl}_4(\text{ClO}_4)_2$
Fig. 4.2(a): Plotting of $A$ vs. $C_0^{1/2}$ for Fe$_2$L$^1$Cl$_4$(ClO$_4$)$_2$.

Fig. 4.2(b) Plotting of $\Lambda F$ vs. $D$ for Fe$_2$L$^1$Cl$_4$(ClO$_4$)$_2$. 

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Fig. 4.3(a): Plotting of $\Lambda$ vs. $C_0^{1/3}$ for Cu$_2$L$_3$Cl$_6$(ClO$_4$)$_2$.

Fig. 4.3(b): Plotting of $\Lambda F$ vs. $D$ for Cu$_2$L$_3$Cl$_6$(ClO$_4$)$_2$.
Fig. 4.4(a): Plotting of $\Lambda$ vs. $C_0^{1/2}$ for Ni$_2$L$^1$Cl$_4$(ClO$_4$)$_2$

Fig. 4.4(b): Plotting of $\Delta F$ vs. $D$ for Ni$_2$L$^1$Cl$_2$(ClO$_4$)$_2$
Fig. 4.5 (a): Plotting of \(A\) vs. \(C_0^{1/2}\) for \(\text{Cr}_2\text{L}^2\text{Cl}_4(\text{ClO}_4)_2\)

Fig. 4.5 (b): Plotting of \(\Delta F\) vs. \(D\) for \([\text{Cr}_2\text{L}^2\text{Cl}_4(\text{ClO}_4)_2]\)
Fig. 4.6(a): Plotting of $\Lambda$ vs. $C_0^{1/2}$ for Fe$_2$L$^2$Cl$_4$(ClO$_4$)$_2$

Fig. 4.6(b): Plotting of $\Delta F$ vs. $D$ for Fe$_2$L$^2$Cl$_2$(ClO$_4$)$_2$
Fig. 4.7(a): Plotting of $A$ vs. $C_0^{1/2}$ for Co$_2$L$_2$Cl$_2$(ClO$_4$)$_2$.

Fig. 4.7(b): Plotting of $\Lambda F$ vs. $D$ for Co$_2$L$_2$Cl$_2$(ClO$_4$)$_2$.
Fig. 4.8(a): Plotting of $A$ vs. $C_0^{1/2}$ for $\text{Ni}_2\text{L}^2\text{Cl}_2(\text{ClO}_4)_2$

Fig. 4.8(b): Plotting of $\Delta F$ vs. $D$ for $\text{Ni}_2\text{L}^2\text{Cl}_2(\text{ClO}_4)_2$
Fig. 4.9(a): Plotting of $\Lambda$ vs. $C_0^{1/2}$ for $\text{Cu}_2L^2\text{Cl}_2(\text{ClO}_4)_2$

Fig. 4.9(b): Plotting of $\Lambda F$ vs. $D$ for $\text{Cu}_2L^2\text{Cl}_2(\text{ClO}_4)_2$
RESULT AND DISCUSSION

CYCLIC VOLTAMMETRY:

The electrochemical behaviour of the complexes

\( \text{Cr}_2\text{L}^1\text{Cl}_4\text{(ClO}_4\text{)}_2(I), \quad \text{Fe}_2\text{L}^1\text{Cl}_4\text{(ClO}_4\text{)}_2(\text{II}), \quad \text{Co}_2\text{L}^1\text{Cl}_2\text{(ClO}_4\text{)}_2(\text{III}), \)

\( \text{Ni}_2\text{L}^1\text{Cl}_2\text{(ClO}_4\text{)}_2(\text{IV}), \quad \text{Cu}_2\text{L}^1\text{Cl}_2\text{(ClO}_4\text{)}_2(\text{V}), \quad \text{Cr}_2\text{L}^2\text{Cl}_2\text{(ClO}_4\text{)}_2(\text{VIII}), \)

\( \text{Fe}_2\text{L}^2\text{Cl}_4\text{(ClO}_4\text{)}_2(\text{IX}), \quad \text{Ni}_2\text{L}^2\text{Cl}_2\text{(ClO}_4\text{)}_2(\text{XI}), \quad \text{Cu}_2\text{L}^2\text{Cl}_2\text{(ClO}_4\text{)}_2(\text{XII}), \)

has been studied employing cyclic voltammetry in DMSO in the potential range +1.6 to -1.6 at the three different scan rates i.e. 0.1, 0.2, 0.3 V s\(^{-1}\). The typical cyclic voltammograms generated through computer stimulation are given in Figures (4.10 – 4.18) and the magnitudes of reduction potentials (\(E^\theta_{\text{red}}\)), oxidation potential (\(E^\theta_{\text{oxid}}\)) as well as the half wave potential (\(E^\theta_{1/2}\)) for the formation of redox couple in solution have been summarized in Table 4.4.

The cyclic voltammogram (CV) of complex \( \text{Cr}_2\text{L}^1\text{Cl}_4\text{(ClO}_4\text{)}_2(\text{I}) \) recorded at the scan rate of 0.1 V s\(^{-1}\) (Fig. 4.10) exhibited a single irreversible cathodic wave at -1.1 V and the reverse sweep exhibited an irreversible anodic wave at +0.725 V suggesting one step irreversible reduction process followed by disproportionation reaction giving the formation of \( \text{Cr}^0 \) [Scheme -1]. The strong anodic peak at +0.725 V is characteristic of an electrochemically active species adsorbed at the surface of the electrode\(^{16}\). However, for the corresponding \( \text{Cr}^{3+} \) complex with \( \text{L}^2\cdot2\text{HClO}_4 \) macrocycle (VIII) the CV contained two irreversible cathodic wave at -0.9 V and -1.1 V (Fig. 4.11)
indicating the presence of two successive one electron irreversible reduction steps [Scheme –2] as shown below:

**Scheme –1:**

\[
[\text{Cr}^{III} L^1 \text{Cr}^{III}] + 2e^{-} \rightarrow [\text{Cr}^{II} L^1 \text{Cr}^{II}] \rightarrow \text{Cr}^{0} + [\text{Cr}^{IV} L^1]
\]

**Scheme –2:**

\[
[\text{Cr}^{III} L^2 \text{Cr}^{III}] + e^{-} \rightarrow [\text{Cr}^{II} L^2 \text{Cr}^{III}] \rightarrow [\text{Cr}^{II} L^2 \text{Cr}^{II}]
\]

The CV of complex Fe$_2$L$^1$Cl$_4$(ClO$_4$)$_2$ (II) exhibited cathodic waves at 
$-0.35$ V ($C_1$), $-0.975$ V ($C_2$), $-1.2$ V ($C_3$) and $-1.425$ V ($C_4$) (Fig. 4.12). However the reverse sweep contained only three anodic peaks at $-1.4$ V, 
$-1.28$ V and $1.0$ V. The cathodic peaks $C_2$, $C_3$ and $C_4$ may be coupled with anodic peaks at $-1.0$ V, $-1.28$ and $-1.4$V respectively to form quasi-reversible couples at $E^0_{1/2} = -0.987$ V, $-1.24$ V and $-1.41$ V respectively (Table 4.4) for the stepwise one electron redox-processes shown by Scheme –3.

**Scheme–3:**

\[
[\text{Fe}^{III} L^1 \text{Fe}^{III}] + e^{-} \rightarrow [\text{Fe}^{II} L^1 \text{Fe}^{III}] \quad E^0_{\text{red( irr)}} = -0.35 \text{ V}
\]

\[
[\text{Fe}^{II} L^1 \text{Fe}^{III}] \quad E^0_{1/2} = -0.987 \text{ V}
\]

\[
[\text{Fe}^{II} L^1 \text{Fe}^{II}] \quad E^0_{1/2} = -1.24 \text{ V}
\]

\[
[\text{Fe}^{I} L^1 \text{Fe}^{II}] \quad E^0_{1/2} = -1.41 \text{ V}
\]
However for Fe$_2$L$^2$Cl$_4$(ClO$_4$)$_2$ (IX) complex the CV shows only two cathodic waves at $-1.0$ V and $-1.5$ V and the reverse sweep shows two weak anodic peaks at $-1.187$ V and $-0.875$ V (Fig. 4.13) which may be coupled with the corresponding cathodic peaks to form quasi-reversible couples involving two electron redox processes as shown in Scheme-4.

**Scheme-4:**

\[
\begin{align*}
[\text{Fe}^{III}L^2\text{Fe}^{III}] & \xrightarrow{2e^-} [\text{Fe}^{II}L^2\text{Fe}^{II}] & E_{1/2}^0 &= -0.937 \text{ V} \\
[\text{Fe}^{II}L^2\text{Fe}^{II}] & \xrightarrow{2e^-} [\text{Fe}^{I}L^2\text{Fe}^{I}] & E_{1/2}^0 &= -1.34 \text{ V}
\end{align*}
\]

It has been reported$^{17}$ that mononuclear Fe$^{2+}$–Chelating complexes with imine ligands forming M–N bond show two quasi-reversible redox waves $E_{1/2}^0 \sim -0.5$ V and at $\sim -1.0$ V for the stepwise one electron redox processes Fe$^{III/II}$ and Fe$^{II/I}$ respectively. In the present bimetallic complexes with unsymmetrical macrocyclic ligand however the redox couples involving one electron electrochemical reaction Fe$^{III/II}$ and Fe$^{II/I}$ occur at a relatively more negative applied potentials. This observation is reasonable in view of the report$^{17}$ that for strong $\sigma$ donor ligands, the redox couples are generated at a lower applied potential (or higher negative potential) compared to simple acyclic $\sigma$ donor ligands.

The CV of complex Co$_2$L$^1$Cl$_2$(ClO$_4$)$_2$ (III) has an irreversible weak cathodic wave at $-0.4$ V and a relatively intense cathodic wave at $-1.15$ V (Fig. 4.14). The reverse sweep, however exhibits only one peak at $-1.0$ V which may be coupled with the second cathodic wave generate a quasi-
A reversible redox couple at $E^{0}_{1/2} = -1.075$ V ($\Delta E = 150$ mV). The first cathodic wave is due to a 2 electron single step reduction process of the bimetallic $[\text{Co}^{II}\text{L}^{1}\text{Co}^{II}]$ complex involving one electron reduction at each Co$^{2+}$ metal ion. There is a steep rise in the anodic current just after the applied potential of +0.2 V. This unusual steep rise in current suggests that an electrochemically active species $[\text{Co}^{II}\text{L}^{1}]$ is formed along with the deposition of metallic cobalt on the surface of the electrode. The overall electrochemical processes may be represented by the following scheme 5.

**Scheme 5:**

\[
\begin{align*}
[\text{Co}^{II}\text{L}^{1}\text{Co}^{II}] & \xrightarrow{+2e} [\text{Co}^{I}\text{L}^{1}\text{Co}^{I}] & E^0_{\text{red}} = -0.4 \text{ V} \\
[\text{Co}^{I}\text{L}^{1}\text{Co}^{I}] & \xrightarrow{-2e} [\text{Co}^{II}\text{L}^{1}\text{Co}^{II}] & E^0_{1/2} = -1.075 \text{ V} \\
[\text{Co}^{I}\text{L}^{1}\text{Co}^{I}] & \rightarrow \text{Co}^0 + [\text{Co}^{II}\text{L}^{1}] & E^0_{\text{oxd}} = +0.2 \text{ V}
\end{align*}
\]

The electrochemical redox behaviour of Ni$_2$L$^1$Cl$_2$(ClO$_4$)$_2$ (IV) has been studied at three different scan rates i.e. 0.1, 0.2 and 0.3 Vs$^{-1}$ (Fig. 4.15). The CV recorded at 0.1 Vs$^{-1}$ shows two cathodic waves at -1.15 V and -1.30 V of nearly equal intensity, however at a higher scan rate of 0.2 Vs$^{-1}$ the intensity of the first cathodic wave diminishes to give a shoulder like feature while the second cathodic wave becomes very intense with a slight shift in its position to a more negative applied potential (-1.35 V). The intensity of the latter is further increased with a further shift to -1.4 V while the first cathodic wave observed at -1.15 V disappears. There is appearance of a new cathodic wave at -0.85 V when the CV was recorded at even a higher scan rate of 0.3 Vs$^{-1}$. 

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The reverse sweep at all the three scan rates show a weak intensity anodic wave at an identical potential (-1.05 V). The second cathodic wave may be coupled with the anodic wave to generate a quasi-reversible redox couple at 

\[ E^{0}_{1/2} = -1.17 \text{ to } -1.22 \text{ V } (\Delta E = 250 - 350 \text{ mV}) \]

The electrochemical reaction may be represented by the following Scheme -6.

**Scheme -6:**

\[
\begin{align*}
[Ni^{II}_{II}L^{I}Ni^{II}]^+ & \xrightarrow{+2e} [Ni^{II}_{II}L^{I}Ni^{II}] \xrightarrow{-2e} Ni^{0} + L^{I} \\
[Ni^{II}_{II}L^{I}Ni^{II}] & \xrightarrow{+2e} [Ni^{II}_{II}L^{I}Ni^{III}] \quad E^{0}_{1/2} = -1.17 \text{ to } -1.22 \text{ V } \quad (\Delta E = 250 - 350 \text{ mV})
\end{align*}
\]

The Ni^{2+} complex with the L^{2}.2HClO_{4} macrocycle i.e. Ni_{2}L^{2}Cl_{2}(ClO_{4})_{2} (XI) shows two irreversible strong cathodic waves at -1.0 V and -1.6 V and the reverse sweep shows the irreversible anodic wave at -0.2 V (Fig. 4.16). The electrochemical process here appears to be different from that observed for the complex (IV) and are compatible with the following scheme -7.

**Scheme 7:**

\[
\begin{align*}
[Ni^{II}_{I}L^{II}Ni^{I}]^+ & \xrightarrow{-2e} [Ni^{II}_{I}L^{II}Ni^{I}] \quad E^{0}_{\text{red}} = -1.0 \text{ V} \\
[Ni^{II}_{I}L^{II}Ni^{I}] & \xrightarrow{+2e} 2Ni^{0} + L^{II} \quad E^{0}_{\text{red}} = -1.6 \text{ V} \\
[Ni^{III}_{II}L^{III}Ni^{III}]^+ & \xrightarrow{-2e} [Ni^{III}_{II}L^{III}Ni^{III}] \quad E^{0}_{\text{oxd}} = -0.2 \text{ V}
\end{align*}
\]

The electrochemical behaviour of Cu^{2+} complexes with L^{1}.2HClO_{4} and L^{2}.2HClO_{4} i.e. Cu_{2}L_{2}(ClO_{4})_{2} (L = L^{I} (V) or L^{II} (XII)) are different. The complex (V) exhibits formation of a quasi-reversible redox couple at
\[ E_{1/2}^0 = -0.112 \text{ V at scan rate } 0.2 \text{Vs}^{-1} \text{ or at } E_{1/2}^0 = -0.108 \text{ V at a scan rate of } 0.3 \text{Vs}^{-1} \text{ (Fig 4.17-a,b)}. \text{ This shows that the complex is reversibly reduced in a single step involving two electron redox process as shown below in a Scheme 8.}

**Scheme 8:**

\[
[Cu^{II}L^{I}Cu^{II}] \xrightleftharpoons{+2e} \xleftarrow{-2e} [Cu^{I}L^{I}Cu^{I}]
\]

It has been reported\(^{19}\) that the binuclear Cu\(^{2+}\) complexes with [N\(_4\)O\(_2\)] macrocycle show two quasi-reversible waves at \(E_{1/2}^0 = -0.375 \text{ V and } -0.824 \text{ V}\) consistent with the one electron successive redox steps reaction as observed in the present case.

However, the electrochemical behaviour of complex Cu\(_2L^2Cl_2(ClO_4)_2\) (XII) has been found entirely different from that observed for the corresponding complex with L\(^2\).HClO\(_4\) i.e. (V) stated above. The behaviour of complex (XII) is shown in (Fig. 4.18) which is typical of binuclear Cu\(^{II}\)Cu\(^{II}\) complexes reported in the literature\(^{16}\). Here, the CV shows three cathodic peaks at \(E_{\text{red}}^0\) values of \(-0.225, -0.875 \text{ and } -1.05 \text{ V}\), a very high intensity anodic wave at \(E_{\text{oxd}}^0 +0.675 \text{ V}\) and an anodic process with \(E_{\text{oxd}}^0\) values at \(-0.15\) V. The intense anodic peak at +0.675 V represents the formation of electrochemically active species adsorbed\(^{17}\) on the electrode. The first two cathodic waves suggests that the reduction of binuclear complex [Cu\(^{II}\)L\(^2\)Cu\(^{II}\)] occurs in two one electron reduction steps, such that the reduction at \(-1.05 \text{ V}\) is followed by a disproportionation\(^{18}\) process represented by the third cathodic
wave. However, the irreversible oxidation occurs in one step followed by decomposition to generate metallic copper. Considering all these processes the complete mechanism of the electrode processes may be described by scheme -9 as shown below:

**Scheme - 9:**

\[
[Cu^{II}L^{2}Cu^{II}] \xrightarrow{+e, \pm 0.225 \text{ V}} [Cu^{I}L^{2}Cu^{II}] \xrightarrow{+e, \pm 0.875 \text{ V}} [Cu^{I}L^{2}Cu^{I}]
\]

\[
[Cu^{I}L^{2}Cu^{I}] \xrightarrow{+2e, \pm 1.05 \text{ V}} 2Cu + L^{2}
\]

\[
[Cu^{III}L^{2}Cu^{III}]^{+} \xrightarrow{\text{decomposition, } +0.675 \text{ V}} 2Cu^{2+} + L^{2}
\]

\[
Cu^{2+} \xrightarrow{+2e, \pm 0.15 \text{ V}} Cu
\]

The present electrochemical data indicate that the newly synthesized macrocycles, \( L^{1}.2\text{HClO}_4 \) and \( L^{2}.2\text{HClO}_4 \) possess flexible cavities capable to accommodate the higher (+3) as well as the lower (+1) oxidation states of the transition metal ions.
Table - 4.4: Electrochemical data of complexes:

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Compounds</th>
<th>$E^e_{\text{red}}$ (Volts)</th>
<th>$E^e_{1/2}$ (Volts)</th>
<th>$E^e_{\text{oxd}}$ (Volts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>$\text{Cr}_2\text{L}^1\text{Cl}_4(\text{ClO}_4)_2$</td>
<td>$-1.1^{\text{a}_{\text{irr}}}$</td>
<td></td>
<td>$+0.725^{\text{a}_{\text{irr}}}$</td>
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<tr>
<td>II</td>
<td>$\text{Fe}_2\text{L}^1\text{Cl}_4(\text{ClO}_4)_2$</td>
<td>$-0.35^{\text{a}_{\text{irr}}}$</td>
<td>$-0.975^{\text{a}}$</td>
<td>$-0.987^{\text{qr}}$</td>
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<tr>
<td></td>
<td></td>
<td>$-1.2^{\text{a}}$</td>
<td>$-1.24^{\text{qr}}$</td>
<td>$-1.28^{\text{a}}$</td>
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<td></td>
<td></td>
<td>$-1.425^{\text{a}}$</td>
<td>$-1.41^{\text{qr}}$</td>
<td>$-1.4^{\text{a}}$</td>
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<td>III</td>
<td>$\text{Co}_2\text{L}^1\text{Cl}_2(\text{ClO}_4)_2$</td>
<td>$-0.4^{\text{a}_{\text{irr}}}$</td>
<td>$-1.15^{\text{a}}$</td>
<td>$-1.075^{\text{qr}}$</td>
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<tr>
<td>IV</td>
<td>$\text{Ni}_2\text{L}^1\text{Cl}_2(\text{ClO}_4)_2$</td>
<td>$-1.15^{\text{a}_{\text{irr}}}$</td>
<td>$-1.30^{\text{a}}$</td>
<td>$-1.17^{\text{qr}}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$-1.35^{\text{b}}$</td>
<td>$-1.2^{\text{qr}}$</td>
<td>$-1.05^{\text{b}}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$-1.4^{\text{c}}$</td>
<td>$-1.22^{\text{qr}}$</td>
<td>$-1.05^{\text{c}}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$-0.85^{\text{qr}}$</td>
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<td>V</td>
<td>$\text{Cu}_2\text{L}^1\text{Cl}_2(\text{ClO}_4)_2$</td>
<td>$-0.282^{\text{b}}$</td>
<td>$-0.112^{\text{b}_{\text{qr}}}$</td>
<td>$+0.058^{\text{b}}$</td>
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<td>$-0.291^{\text{c}}$</td>
<td>$-0.108^{\text{c}_{\text{qr}}}$</td>
<td>$+0.074^{\text{c}}$</td>
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<td>VIII</td>
<td>$\text{Cr}_2\text{L}^2\text{Cl}_4(\text{ClO}_4)_2$</td>
<td>$-0.9^{\text{a}_{\text{irr}}}$</td>
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<td></td>
<td>$-1.1^{\text{a}_{\text{irr}}}$</td>
<td></td>
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<tr>
<td>IX</td>
<td>$\text{Fe}_2\text{L}^2\text{Cl}_4(\text{ClO}_4)_2$</td>
<td>$-1.0^{\text{a}}$</td>
<td>$-0.937^{\text{a}_{\text{qr}}}$</td>
<td>$-0.875^{\text{a}}$</td>
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<td>$-1.5^{\text{a}}$</td>
<td>$-1.34^{\text{a}_{\text{qr}}}$</td>
<td>$-1.187^{\text{a}}$</td>
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<tr>
<td>XI</td>
<td>$\text{Ni}_2\text{L}^2\text{Cl}_2(\text{ClO}_4)_2$</td>
<td>$-1.0^{\text{a}_{\text{irr}}}$</td>
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<td>$-1.6^{\text{a}_{\text{irr}}}$</td>
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<td>XII</td>
<td>$\text{Cu}_2\text{L}^2\text{Cl}_2(\text{ClO}_4)_2$</td>
<td>$-0.225^{\text{a}_{\text{irr}}}$</td>
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<td>$+0.675^{\text{a}_{\text{irr}}}$</td>
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<tr>
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<td>$-0.875^{\text{a}_{\text{irr}}}$</td>
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<td>$-0.15^{\text{a}_{\text{irr}}}$</td>
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</table>

*a at 0.1 VS\(^{-1}\) scan rate, \(^{a}\) at 0.2 VS\(^{-1}\) scan rate, \(^{c}\) at 0.3 VS\(^{-1}\) scan rate,
irr = irreversible
qr = quasi-reversible
Fig. 4.10: Cyclic voltamogram of Cr$_2$L$^1$Cl$_4$(ClO$_4$)$_2$ (I) recorded at 0.1 Scan Rate

Fig. 4.11: Cyclic voltamogram of Cr$_2$L$^2$Cl$_4$(ClO$_4$)$_2$ (VIII) recorded at 0.1 Scan Rate
Fig. 4.12: Cyclic voltamogram of Fe₂LCl₄(ClO₄)₂ (II) recorded at 0.1 Scan Rate

Fig. 4.13: Cyclic voltamogram of Fe₂L²Cl₄(ClO₄)₂ (IX) recorded at 0.1 Scan Rate
Fig. 4.14: Cyclic voltamogram of Co₂L²⁻(ClO₄)₂ (III) recorded at 0.1 Scan Rate
Fig. 4.15: Cyclic voltamogram of Ni$_2$L$_2$Cl$_2$(ClO$_4$)$_2$ (IV) recorded at 0.1, 0.2, 0.3 Scan Rate

Fig. 4.16: Cyclic voltamogram of Ni$_2$L$_2$Cl$_2$(ClO$_4$)$_2$ (XI) recorded at 0.1 Scan Rate
Fig. 4.17(a): Cyclic voltamogram of Cu$_2$L$^1$Cl$_3$(ClO$_4$)$_2$ (V) recorded at 0.2 Scan Rate

Fig. 4.17(b): Cyclic voltamogram of Cu$_2$L$^1$Cl$_3$(ClO$_4$)$_2$ (V) recorded at 0.3 Scan Rate
Fig. 4.18: Cyclic voltamogram of Cu₂L²Cl₂(ClO₄)₂ (XII) recorded at 0.1 Scan Rate
REFERENCES:


