CHAPTER I

GENERAL INTRODUCTION
A. HISTORICAL INTRODUCTION

The studies in field of coordination chemistry originated, when Disbach in 1704 prepared a new type of compound named prussain blue. The rapid activity in this era began in 1798 when Tasaert\(^1\) obtained orange crystalline hexamine cobalt(III) chloride. At the end of nineteenth century numerous compounds of this type containing metals such as Co, Pt, Fe etc. with amines were prepared.

The most successful attempt to explain the structure of these compounds was made by Alfred Werner\(^2\) in the year 1893. He gave the idea of primary and secondary valencies.

A little latter Lowry\(^3\) and Sidgwick\(^4,5\) explained the idea of Werner by electronic theory of valency.

The theory proposed by Sidgwick, although explains the structure of these compounds, however, it fails to explain the excess negative charge on the metal atom or ion which arises due to electron donation.

Recently, based on wave mechanical concept, four important theories were proposed, which can be applied to study the structure, stability and general properties of compounds. These are:

i. Valence bond theory,
ii. crystal field theory,
iii. ligand field theory and
iv. molecular orbital theory.

B. CHARACTERISATION OF COORDINATION COMPOUNDS

There are several physico-chemical methods, which have been used in order to explain the properties as well as the structure of coordination compounds. The present investigation is concerned with the structural characterisation of coordination compounds by following well known techniques -

1. Elemental analysis
2. Molar conductance
3. Infrared absorption spectrophotometry
4. Magnetic susceptibility
5. Visible absorption spectrophotometry and
6. Thermogravimetric analysis.

1. Elemental analysis:

The molecular formula of the coordination compounds can be deduced from elemental analysis. The metal is estimated by well known standard methods. The percentage of carbon, hydrogen and nitrogen have been estimated microanalytically.

2. Molar conductance:

When an electric current is passed through an electrolytic solution, the electrolyte gets ionised into
its ionic species. These ions are responsible for conductivity of solution. According to electrolytic theory, the conductance of solution depends upon the number of ions (concentration of electrolyte), charge on ions and their relative velocities in solution.

In general the specific conductance of complexes measured in conductivity water or nitrobenzene at a molar concentration $10^{-3}$ or $10^{-4}$. From this the molar conductance is determined.

The molar conductance measured for the complex provides the idea that the complex is either electrolyte or non-electrolyte, and if it is electrolyte then the number of ions present outside the coordination sphere (charge type).

The approximate molar conductance range and the charge type of complexes are reported$^6$.

3. Infrared absorption spectrophotometry

Infrared spectrophotometry is concerned with the molecular vibrations. Each bond in a molecule have its own vibrational frequency, when the radiation of same frequency strikes the molecule, it absorbs some of energy so that amplitude of vibrations increased. The intensity of resulting absorption band is proportional to the square of change in dipole moment$^7$. 
Consider a three atom system, it may undergo two types of fundamental vibrations. a. stretching vibrations, b. bending vibrations.

In stretching vibrations atoms vibrate along the bond axis. The two types of stretching vibrations are observed a. symmetric stretching vibrations and b. assymmetric stretching vibrations.

In bending vibrations atoms vibrate perpendicular to the bond axis. The four types of bending vibrations are assigned which are - a. scissoring, b. rocking, c. twisting and d. wagging.

The bending vibrations are observed at lower frequencies than stretching vibrations, since more energy is required for stretching of bond than the bending.

The infrared spectra recorded for amine complexes are however complicated. For these complexes following six fundamental vibrations are expected viz. symmetric and antisymmetric NH stretching, NH-symmetric deformation, NH-degenerate deformation, NH-rocking and M-N stretching.

The N-H stretching bands in free diamines appears around 3320, 3260 and 3165 cm\(^{-1}\), these bands show negative shift of 50-90 cm\(^{-1}\) on complexation. It has been difficult to assign M-N stretching vibrations empirically. Since several ligand vibrations also appear in this frequency region. The remaining three bending vibrations were
assigned by Nakagawa and Mizushima.\textsuperscript{11}

In heterocyclic compounds, however the position and intensity of aromatic ring vibrations depends upon the nature of ring and type of substitution. The absorption band is observed in region 1600-1350 cm\textsuperscript{-1}.

The three bands at about 1590, 1490 and 1400 cm\textsuperscript{-1} were observed in five membered rings, while four bands at about 1605, 1575, 1480 and 1430 cm\textsuperscript{-1} were observed for six membered rings. In case of imidazole complexes these bands are observed near 1550, 1492 and 1451 cm\textsuperscript{-1}.\textsuperscript{12}

In general lattice water shows absorption in 3550-3200 cm\textsuperscript{-1} region which is assigned to asymmetric and symmetric O-H stretching vibration and at 1630-1600 cm\textsuperscript{-1} (H-O-H bending)\textsuperscript{13} while coordinated water shows three bands wagging, rocking and M-O stretching vibrations. Admas and Lock\textsuperscript{14} have shown these vibrations appear near 600, 460 cm\textsuperscript{-1} and 390 cm\textsuperscript{-1} respectively.

4. Magnetic susceptibility measurement:

Measurement of magnetic susceptibility has contributed much of our understanding of coordination chemistry, as well as characterisation of these compounds, particularly in regard of oxidation states, stereochemistry of central atom and their bond types.

Magnetic properties in compounds arise from both the electrons and the nucleus. However magnetic properties
associated with electrons alone is of particular interest. We may consider an electron as a negatively charged sphere, spinning on its axis, and travelling in closed path about nucleus which gives rise to spin moment and orbital moment respectively. The two important groups of magnetism associated with the complexes are - a. diamagnetism, b. paramagnetism.

a. Diamagnetism:

It arises from interaction of applied magnetic field with the field induced in completed shells of electrons. The induced field opposes the applied field, hence the sample tend to move away from applied field. Thus diamagnetic susceptibility is a negative quantity.

b. Paramagnetism:

The paramagnetic substances placed in an applied field are attracted by the applied field, thus produces positive magnetic susceptibility which is independent of magnitude of the applied field and dependent upon the temperature.

The magnetic moment expressed in Bohr magneton can be calculated by equation -

$$\mu_{\text{eff}} = 2.84 \sqrt{X'_{m} \times T}$$

where $X'_{m}$ is the molar susceptibility and $T$ is absolute temperature.
In case of cobalt(III) and nickel(II) complexes the observed magnetic susceptibility for different structures are quite different, thus the magnetic measurements are helpful for deciding the ligand field arrangement; but for copper(II) complexes the magnetic susceptibility observed for different geometry is nearly same thus the stereochemistry of copper(II) complexes can not be predicted by magnetic data alone.

The theoretical and observed magnetic moments for the complexes of first row transition elements have been reported\(^{15}\).

5. Visible absorption spectra:

The most of the complexes of transition metals are coloured, thus shows absorption of radiation in visible region of electromagnetic radiation. The study of visible absorption spectra gives us knowledge of electronic structure and bonding in complexes.

Cobalt(III) ion has a \(d^7\) electronic configuration, which in octahedral or square-planar ligand field may give rise to spin-free \(t_2g^5e_g^2\) or spin-paired \(t_2g^6e_g^1\) configuration, depending on the strength of the crystal field, while in tetrahedral complexes it has ground state configuration \(e_g^4t_2g^3\).

The spectra of most of cobalt(III) octahedral complexes consists of a band near infrared region at 8.50 kK
which is assigned to the transition $^4T_{1g} \rightarrow ^4T_{2g}$ and a band in visible region near 20.00 K K which is identified for the transition $^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$\textsuperscript{16}.

In octahedral complexes of nickel a series of calculations done have shown that there may be three or four absorption bands, which are related to one another and to the ligand field stabilisation energy by following equations\textsuperscript{17} and these bands are assigned for transitions\textsuperscript{18,19} as

$$^3A_{2g}(F) \rightarrow ^3T_{2g}(F) \hspace{1cm} \tilde{v}_1 = 10 \text{ Dq}$$

$$^3A_{2g}(F) \rightarrow ^3T_{1g}(F) \hspace{1cm} \tilde{v}_2 = 9/5 \text{ (10 Dq)}$$

and

$$^3A_{2g}(F) \rightarrow ^3T_{1g}(P) \hspace{1cm} \tilde{v}_3 = 17000 + 6/5 \text{ (10 Dq)}$$

where $\tilde{v}$ represents the frequency of absorption band in cm$^{-1}$.

The copper(II) ion has ground state $t_{2g}^6 e_g^3$ configuration, and the excited state for square planar complexes has $t_{2g}^5 e_g^4$ configuration, for copper(II) complexes only one band in 22.20 - 12.50 K K region is observed, depending on the ligand field around the central metal ion, which is assignable to $t_{2g} \rightarrow e_g$ transition\textsuperscript{20}.

6. Thermogravimetric analysis:

The thermogravimetric analysis is concerned with the change in weight of sample being heated as a function of
temperature or time. The curve so produced is termed "thermogram" or "pyrolysis curve".

Solids which undergo two general type of reactions can be studied by thermogravimetry viz.

\[ \text{Reactant(s)} \rightarrow \text{product(s)} + \text{gas} \]
\[ \text{Reactant(s)} + \text{gas} \rightarrow \text{product(s)} \]

The first process involve the loss in mass, while in second process there is an increase in weight of substance with temperature. The processes in which association or dissociation with temperature is not observed can not be studied by thermogravimetric analysis.

In thermogravimetric analysis, the mass is monitored as the temperature is increased, when $\Delta G$ for the process becomes zero or negative, the reaction starts, which is indicated by deviation of mass from initial plateau, when the reaction stops a new plateau is observed. The nature of curve so obtained depends upon many factors such as rate of heating, heat of reaction, furnace atmosphere, amount of sample, nature of sample, particle size and packing of sample.

When the thermogravimetry is used in association with other physico-chemical techniques, as in present investigation such as magnetism, electronic and infrared spectrophotometry, its field of application becomes almost limitless, it provides a clear geometry for the complexes.