CHAPTER-1
1.1 General Introduction and Theories of Coordination Compounds:

Twenty first century has been predicted as an era of science where specialization and generalization of knowledge will work together complementing one another. There will be great need of coordination among the various streams of the subjects and even within the various branches of the subject itself. Coordination chemistry has come out as a branch of modern inorganic chemistry which has justified its position at the crossroads of the various off-shoots of chemistry.

Coordination chemistry has been given a remarkable significance among the many branches of chemistry. Transition metals play a central role in the formation of a large number of coordination compounds.\(^1\)\(^-\)\(^6\) The coordination chemistry as a most potential branch of modern inorganic chemistry has widened its scope in the latter half of the present century. In the modern era coordination chemistry forms an integral part of several interdisciplinary researches. Over recent years, there has been considerable progress in our understanding on the reactivity of the coordinated ligands with transition and non-transition metal ions.

The word ‘complex’ employed by Albert acquired a new meaning and significance with the enunciation of coordination theory by Alfred Werner.\(^7\) This theory became the basis of understanding the existence of complex compounds, their structures and stereochemistry. Werner did not give any substantial theoretical background and this was the reason why this theory was not popularly accepted upto 1916.
Later on, Lowry and Sidgwick explained the Werners idea with the electronic theory of valency.\textsuperscript{8,9}

None of the above theories could explain satisfactorily the bonding in complexes. Later many theories came forward which can be applied practically to all types of complexes for their structure, stability and general properties.

Following theories have been applied to explain the nature of Metal-ligand bond.

(1) Valence bond theory.
(2) Crystal field theory.
(3) Ligand field theory.
(4) Molecular orbital theory.

**Valence Bond Theory:**

This theory was proposed by L. Pauling (1930).\textsuperscript{11} It was concentrated on the stereochemistry and magnetic properties of the central atom in a complex. This theory was not able enough to interprete the electronic spectra, thermodynamic or kinetic properties of complexes. Most structures can be understood on the basis of repulsion between pairs of electrons or the use of hybridised orbitals. The main weaknesses of the valence bond theory as applied to complexes were:

(1) Its failure to consider the existence of excited states and spectra of the complexes.
(2) Though specifying the number of unpaired electrons, it provides no further
explanation for magnetic behaviour. In brief this theory offers only qualitative
interpretation of stereochemical and allied properties and bond type.

Crystal Field Theory:

Crystal field theory was initiated by Bethe\textsuperscript{12} in 1929, and in the following
years it was applied to transition metal complexes by Penny and Schlapp\textsuperscript{13} and by
Vanvlec\textsuperscript{14} (1930). It was however more than two decades later, that the theory came to
be popularly accepted by coordination chemists. This was mainly due to the
contribution of Hartmann and Orgel and was popularised as ligand field theory by the
work of Ballhausen, Orgel, Nyholm, Figgis and Jorgensen, in the later years\textsuperscript{15-20} The
essential assumption of CFT is that the ligands which are treated merely as point
charges or point dipoles, produce a negative field around the central metal ion. Thus
the five “d” orbitals which were originally degenerate and equal in energy in a free
transition metal ion, become differentiated in the presence of electrostatic field. This
gives sets of orbitals higher and lower in energy depending upon the crystal field
grouping around central metal ion. This advantage of CFT lie in its capability of
explaining magnetic, spectral, thermodynamic, kinetic and spectrochemical properties
of the complexes based on splitting of d-orbitals. Since the CFT lays total emphasis
on the metal orbitals and does not consider ligand orbitals at all, it fails to explain; (I)
Intra ligand, metal to ligand and ligand to metal charge transfer bands associated with the ligand orbitals, (ii) Bonding existing in a large number of complexes, (iii) Covalency in metal ligand bonding (iv) Relative strength of various ligands.

**Ligand Field Theory:**

Electrostatic crystal field theory does not take into consideration the orbital overlap, hence a modified theory was developed. It is an extension of the electrostatic approach but also allows some covalent interaction between the orbitals on the metal and the ligand. Many evidences based on electron spin resonance, nuclear magnetic resonance and d-d absorption bands lead to the above conclusions. Three types of interactions are possible, the $\sigma$-overlap, $\pi$- overlap, or the $d\pi$-$p\pi$ overlap of orbitals, involving orbitals of metal and "p" orbitals of the ligands. The ligand field theory has been successfully used to interpret or predict, the most favourable coordination number, stereochemistry reaction paths for substitution reactions, magnetic and thermodynamic properties of the complexes.

The three important parameters of interelectronic interactions such as, the spin orbit coupling constant $\lambda$, and the two Racah parameters B and C are taken into consideration for the orbital overlap.

Many chemists have used this theory with remarkable success to interpret the properties of complexes. $^{15,16,19,23-25}$
Molecular Orbital Theory:

The more pragmatic method of molecular orbitals was originally conceived by Hund\textsuperscript{21} and Mulliken\textsuperscript{22} (1931). The molecular orbital theory envisages the group orbitals of various metal orbitals with the ligand group orbitals of similar symmetry giving rise to pairs of bonding and antibonding molecular orbitals. Some orbitals fail to interact due to unfavourable symmetrical considerations, resulting in non-bonding orbitals. According to this theory, the ligand electrons are accommodated in the bonding molecular orbitals and 'd' orbitals are accommodated in the non-bonding and an antibonding molecular orbitals. This corresponds to the splitting of 'd' orbitals as in the crystal field theory but the significant difference between the two approaches is that metal orbitals are not pure and the extent of overlap determines covalency. Thus it may be concluded that CFT and VBT are special cases of two extremes i.e. zero covalency and 100% covalency.

Molecular orbital theory, inspite of its utility, suffers from the limitation that the calculations involved are rather tedious and lengthy. Therefore, a via media, LFT or ACFT has been evolved which is essentially based on crystal field treatment but at the same time it also takes into consideration a moderate amount of overlapping of orbitals by adjusting various parameters in a suitable manner. A number of evidences based on electron spin resonance (ESR), nuclear magnetic resonance (NMR), nuclear
quadrupole resonance (NQR) and d-d absorption bands leads the conclusion mentioned above.

Studies in the field of coordination chemistry in solid state and solution have engaged the attention of workers. Solid state comprises preparation of solid complexes, their elemental analysis, spectral analysis, viz. infrared, ultraviolet-visible, electron-spin resonance, nuclear magnetic resonance, mossbaur, X-ray etc. Solution study comprises thermodynamic and kinetic aspects. Kinetic studies deal with rate mechanism of chemical reaction while thermodynamic studies mainly includes the stabilities of complex species formed in solution, under variety of conditions. There are several electometric techniques viz. pH-metry, Polarography, Amperometry, Voltametry, Conductometry, Electrophoresis, Chromatography etc., which are being frequently employed for discovering the physico-chemical phenomena of active chemical species.\textsuperscript{26-35}

1.2: Physico-chemical methods in the characterization of complexes:

The characterization of a coordination compound normally involves the identification as well as structural determinations. Among various physico-chemical techniques the elemental analysis, magnetic susceptibility, thermal and conductance help in deciding the molecular formulae of the complexes; while the sophisticated spectral methods help to establish the actual site of bonding of ligands to metal and also the stereochemistry of the complexes. The present investigation is concerned with
the structural characterization of coordination compounds with the help of following well known techniques.

1. Elemental analysis
2. Molar conductance
3. Magnetic susceptibility
4. Infrared absorption spectrophotometry
5. Electronic spectroscopy
   (UV-Visible absorption spectrophotometry)
6. Electron spin resonance spectroscopy
7. Thermogravimetric analysis.

1.21 **Elemental analysis**: The molecular formula of the coordination compound can be deduced from elemental analysis. For the determination of the metal contents, the complex was decomposed by heating with concentrated nitric acid and the contents were estimated by well known standard analytical methods. The percentage of C, H and N have been estimated microanalytically at Central Drug Research Institute (CDRI), Lucknow.

1.22 **Molar Conductance**: The electrical conductivity measurements have been used to determine the charged type of the complex molecules. In most cases molar conductance and not the equivalent conductance of charged complex falls in a predictable range, at a given concentration.

   As a result of the passage of electric current, an electrolyte gets decomposed into ions. These ions in solution are responsible for the conductance. The standard
unit of conductance which is the specific conductance i.e. reciprocal of specific resistance. A molar conductance may be defined as the conducting power of all the ions produced by one gram mole of an electrolyte in a given solution and it can be expressed by the following relation.

\[ \lambda = 1000 \, \text{k/C} \]

Where \( \lambda \) is molar conductance, \( k \) is specific conductance and \( C \) is the concentration in gram mole per litre.

In context with the coordination compounds, the determination of molar conductance value is quite meaningful as it assists in deciding whether a negative group is inside or outside the coordination sphere. Most ions, with the exception of those having long chains (H\(^+\), OH\(^-\)) and some complex ions have ionic conductance of about 60 ohm\(^{-1}\) cm\(^2\) mol\(^{-1}\) at 25°C in water. As a first approximation, one should expect the contribution of an ion I\(^{n-}\) to the molar conductivity to be about 60 mhos (s) and accordingly for uni-univalent salt, MA type 120 ohm\(^{-1}\) cm\(^2\) while for a unibivalent electrolyte, MA\(_2\) or M\(_2\)A will be about 240 ohm\(^{-1}\) cm\(^2\). The approximate values of the conductance varies with the change in size of ion, temperature, dielectric constant, relative velocity of ion and viscosity of the solvent.\(^{36-41}\)

**1.23 Magnetic Susceptibility:**\(^{42-47}\) The measurement of magnetic susceptibility has been of great value in characterization of transition metal complexes. The susceptibility measured for a given substance will consist of contributions, from
paramagnetic and diamagnetic susceptibilities, the former being much greater. Paramagnetic substances placed in an homogenous magnetic field are attracted by the field. The diamagnetism arises from the interaction of the applied magnetic field with the field induced in the closed shells of electrons. The field must necessarily oppose the applied field. The effect of this interaction is to cause the diamagnetic substance to move away from the applied field in order to diminish the interaction. Hence the diamagnetic susceptibility is a negative quantity. The diamagnetic effect does not exist in the absence of magenatic field but is present in all substances placed in a magnetic field. All compounds have this property to some extent and are usually independent of field strength and temperature. Its numerical value is less than unity.

Paramagnetism is caused by the presence of unpaired electrons in molecules. When such a field is placed in an external homogeneous field, it is attracted by the magnetic field with a force proportional to field strength.

In practice the gram susceptibility is measured and this is then converted into molar susceptibility. One obtains the effective moment by the following equation:

\[ \mu_{\text{eff}} = 2.84 \sqrt{x_M T} \text{ B.M.} \]

1.24 Infrared Absorption Spectroscopy: The most fundamental information that may be obtained from infra red spectra, is the knowledge of interatomic force in terms of force constant within a molecule. This gives important information about electronic structure and bonding in molecule. Absorption of infrared radiation in the
frequency range of 10000-200 cm$^{-1}$ by the inorganic molecules is used for their molecular vibration. These vibration comprise the motions of the atomic masses in the material about centers of vibrations. Electromagnetic radiation can induce transition among the vibrational energy levels only when the dipole moment changes either in magnitude or in the direction of the molecule and a vibrational spectrum can then be expected. The two important modes of vibration for a molecule are possible: stretching and bending vibrations. The former requires more energy. In stretching vibrations atoms vibrate along the bond axis. The two types of stretching vibration are observed (a) symmetric stretching vibrations and (b) asymmetric stretching vibrations.

In bending vibrations, atoms vibrate perpendicular to the bond axis. The four types of bending vibrations are types of bending vibration are assigned which are - (a) Scissoring (b) Rocking (c) Twisting and (d) Wagging.

From the observation of infrared spectra of a number of compounds having a common group, it has been found that a particular group absorbs a narrow range of frequency called the group frequency. The observation of a particular band is strong evidence for the presence of a specific group. Sometimes the band may be weak and difficult to observe or it may be masked by a strong neighbouring band. There are certain limitations for the concept of group vibration as it rests on the assumption that the vibrations of the particular group are relatively independent of the molecule. But in some systems it is not possible to isolate the group frequencies, because of the
frequency coupling. The symmetry of the molecule affects its vibrational mode. It has been observed that the molecule having more symmetrical structures exhibits fewer distinct vibrational modes. Hence, sufficient caution is necessary for the assignment of bands of the various groups. Moreover, the physical state and temperature also affect the frequencies in some substances.

Thus, infrared spectroscopy provides one of the useful technique for determining the mode of coordination of the ligand with the metal ion. This is often used as a technique to provide fingerprints for identification which is a function of the constituent atoms, bond lengths and bond angles. As a result of coordination of a metal ion with a ligand, the following changes take place usually in the infrared spectra.

(i) Appearance of new bands and splitting of degenerated modes due to lowering of the symmetry,

(ii) Shifting of the frequency bands and

(iii) Increase in the intensity of the spectra. The coordination of the ligand with metal, lowers its symmetry which results in splitting of forbidden vibration. The stronger the metal-ligand bond, larger will be the splitting of the degenerated mode. The shift in frequency, the magnitude of splitting and the intensity of newly permitted bands are useful as a measure of the effect of coordination.

In the infrared spectra of complexes formed by Schiff bases, the most important is the azomethine vibrational frequency, because it changes on complexation. It may either increase or decrease depending upon various factors such as coordination, extent
of pi-bonding, presence or absence of substituents in the adjacent position and also on the type of the compound being studied. This vibration in free Schiff bases usually occurs in the region 1640-1470 cm\(^{-1}\) and on coordination a negative shift is theoretically expected. But in some complexes it may also be found that the extent of pi-bonding between ligand and metal ion is so large that the effect of coordination is not seen in the shifting of the frequency to lower wave number but rather to high wave number although the azomethine group is involved in coordination. Various other bands due to stretching vibrations of aromatic rings, C-H, N-H, M-O, M-N and deformation vibrations of CH, NH or OH are also observed in the spectra.

1.25 Visible Absorption Spectrophotometry: When a molecule absorbs visible or ultraviolet radiation, an electron in the molecule undergoes a transition from a lower to a higher energy level. The study of electronic absorption spectra of transition metal complexes helps in understanding the electronic structure and bonding. Absorption in the visible region of the spectrum is dependent on the electronic structure of the molecule. Since the complexes are coloured, they usually give absorption bands in the visible region of the spectrum depending upon the number of ‘d’ electrons.

In metal complexes three main types of spectra are obtained:

(1) Ligand Spectra: Organic molecules frequently acts as ligands in transition metal complexes and they exhibit characteristic spectra. On complexation, the ligand spectral bands are shifted to a lower wave number. The magnitude of the shift is a measure of
the oxidation state of the metal atom. These intra ligand transitions usually occur in ultraviolet region.

**II) Charge Transfer Spectra**: Transition involving transfer of an electron from ligand to metal or vice-versa, is known as charge transfer transition and certain ligands show distinct charge transfer bands of high intensity. This phenomenon can not be explained by crystal field theory and represent the tendency of ligands to reduce the metal ion or vice-versa.

**III) d-d or Ligand Field Spectra**: This occurs in the near infrared, visible and ultraviolet region (10000-30000 cm\(^{-1}\) or 1000-333nm). Lower frequencies are not easily accessible at experimental level and the higher frequencies though accessible, are over-shadowed by the charge transfer and the intra ligand transitions. This has limited the study of d-d transitions only in the visible region of spectrum. These transitions are considered to be totally within the metal ion in the crystal field theory model, though some ligand contribution is included in ligand field theory or adjusted crystal field theory models. Molecular orbital theory treats these transitions as arising due to the excitation of the electron from the t\(_{2g}\) level to the e\(_{g}\) levels belonging largely to the metal itself. These d-d electronic transitions are weak because of the reason that the transitions of the same quantum shall be forbidden.

**SELECTION RULES FOR ELECTRONIC TRANSITION**:

Quantum mechanics imposes restrictions on electronic transition in terms of selection rules that arise from the properties of the wave function.
(I) **Spin selection rule**: Transition in which the spin multiplicity changes are not allowed that is $\Delta S=0$. The transition $S^2 - S^1 P^1$ is allowed only if the spin of the two electrons in $S^1 P^1$ State is $+1/2$ and $-1/2$ (singlet state); the transition to the triple state $(3p)$ is forbidden.

(II) **Laporte’s ‘orbital’ selection rule**: Any electronic transition is allowed only if $\Delta l=\pm 1$. Thus only the transition between an even state (g) and uneven state (u) are permitted, i.e. $g\longleftrightarrow u$ but $g\longleftrightarrow u$ and $u\longleftrightarrow u$.

The d-d transitions are ‘Laporte forbidden; since the change is $l=0$. The strictness of the selection rule is slightly violated or diluted because of the slight mixing (d-p mixing) or coupling of the orbitals or states in some cases resulting slightly enhanced intensity of the observed bands. Mixing of this kind occurs in complexes which do not possess a centre of symmetry. Thus Laporte allowed transitions are very intense, whilst Laporte forbidden transitions vary from weak intensity (if the complex is non-centrosymmetric) to very weak if it is centro symmetric.

From the number, position and intensity of the bands in the spectrum, it is possible to obtain information on the symmetry around the central metal ion, relative orders of energy levels, 10 Dq and other parameters. In addition to this, when the ligand also absorbs the visible region, the change in absorption bands indicate the complex formation.
1.26 Electron Spin Resonance Spectroscopy (E.S.R.)\textsuperscript{57-62}

It is also known as electron paramagnetic resonance (E.P.R.) spectroscopy. In the E.S.R. technique, one examines the energy absorbed from a microwave radiation by a paramagnetic system (molecules possessing electrons with unpaired spins) $m_s=\pm \frac{1}{2}$ when a steady magnetic field is applied at right angle to the direction of H- vector of the microwave radiation.

In EPR, a transition between the two different electron spin energy states occurs upon absorption of a quantum of radiation in the $r_f$ or microwave region. The energy $E$ of transition is given by the following equation.

$$E=\hbar \gamma = g\beta_H$$

When an unpaired electron comes in vicinity of a nucleus with a spin I, an interaction takes place which causes the absorption signal to be split into $2I+1$ components (due to nuclear spin- electron spin coupling). The energies of the levels are given by the following expression:

$$E = g\beta_H m_s + A m_m m_I$$

Where $A$ is reflected as the hyperfine coupling constant. This was first observed by Zavoyskiy and later by Cummerow and Halliday. It has now become one of the most important tools for the study of paramagnetic substance because ESR-spectrum is extremely sensitive to surrounding of the paramagnetic ion in the system. It provides information about the symmetry of surrounding, the nature and strength of
bonding, extent of delocalization of unpaired electrons, relative energies of various filled and unfilled molecular orbitals in the bonding scheme in both solid and solution.

1.27 Thermogravimetric Analysis:⁶³-⁷₀

The change in weight of a sample followed during continuous increase in temperature, is thermogravimetry. It provides to the analyst, a quantitative measurement of any weight change associated with a transition. The curves are characteristic for a given compound or system because of the unique sequence of physico-chemical reactions occurring at definite temperature ranges and rates. The study of T vs Δw gives information about the kinetics of decomposition, order of reaction, energy of activation and rate of reaction. For complexes containing water molecules, it has been possible to differentiate between lattice and coordinated water. It also helps in deciding the dehydration and decomposition temperature. The data may be employed to know the stabilities of metal complexes. The TGA and DTA are also very useful in characterizing the highly stable, heat resistant and explosive compounds.

The way and steps of thermal degradation reflects some significant information about the mechanism of formation of the compound.
1.3 SIGNIFICANCE:

The complexes of metals viz, Co, Ni, Cu etc., occur in traces in animal and plant bodies. These elements even in traces play a significant role in physiological and metabolic processes of living beings. It is well known that majority of 3d-transition elements have registered their importance in many biochemical phenomena, that is why they have been considered as life essential elements, though they are present in micro or ultramicro amounts.

In biological systems these metallic cations are incapable of independent existence. The metal ions cannot enter the cell by themselves. They are however carried by the chelating agents, which are sufficiently lipid soluble. The use of chelating agents depend upon the formation of stable and soluble metal chelates with metal ions. In course of biocirculation the metal ions compete to bind the chelating biological sites and thus some times help in dislodging the bound metals/bio-organic species in the form of soluble chelates. Hence chelating agents must be of low toxicity and unmetabolizable so as to persist unchanged in the biological systems in order to perform their scaverning functions. They must also be capable of penetrating into the metal storage sites. Further chelates should be much less toxic than the free metal ions.\textsuperscript{70-72}

The application of coordination compounds appear distinctly increased in past three decades. In recent years coordination compound are being used in the field of medicine, biology, industry and agriculture. However the most important application of
these, is in the areas of catalysis, electrochemistry, dyes and pigments, photography, extractive metallurgy, geochemistry, nuclear fuel cycle and radiopharmacy, analytical chemistry, biomedical and therapy.\textsuperscript{73,74}

It is a remarkable fact that certain physical and chemical properties of 2-amino pyridine, furan and ethyl-methyl ketone and their derivatives, have aroused interest regarding biochemistry and pharmacology of these substances. Several derivatives of these compounds after suitable structural modifications, are being used as drugs.

2-Furfuraldehyde have found a variety of applications in agriculture as insecticide, fungicide, germicide and in rubber industry as vaccanisation accelerators. 2-Amino pyridine is used in manufacturing the pharmaceuticals, especially in antihistaminic drugs, while ethyl-methyl ketone have the activity on central nervous system.

Coordination chemistry can find a use in medicine in a number of ways. Coordination compounds can be used in the treatment, management or diagnosis of disease. Complex can be formed in the body to handle dysfunction due to metal poisoning. Specifically four principal areas may be for the use of metal chelation therapy:

1. The use of coordination compounds or metal based drugs to treat disease,
2. The use of chelating or complexing agents to treat metabolic dysfunction,
3. The use of complexing, chelating or sequestering agents to remove heavy metal poisons from the body,
4. The use of coordination complexes to transport metals to specific sites in the body to aid in imaging.\textsuperscript{74}

The application of Schiff bases and metal chelates in the field of industry, agriculture and medicine are well known. The aldehydes and amines selected for present studies viz. 2-furfuraldehyde, salicylaldehyde, ethyl-methyl ketone, 2-aminopyridine, 2-amino phenol and N-phenyl thiourea are known for their biological potential. Hence present studies have been taken up with a view to workout and visualize the coordination chemistry of the titled systems.
REFERENCES


