

Chapter- 2

This chapter covers the basic principles, theories and techniques of various physico-chemical methods involved in characterization of the macrocycles.

2.1 INSTRUMENTAL METHODS AND THEORY

There are several physico-chemical methods available for the study of coordination compounds and a brief description of the techniques used in the investigation of the newly synthesized complexes described in the present work are given below:

- 1- Infrared Spectroscopy
- 2- Nuclear Magnetic Resonance Spectroscopy
- 3- Electron Paramagnetic Resonance Spectroscopy
- 4- Ultraviolet and Visible (Ligand Field) Spectroscopy
- 5- Magnetic Susceptibility Measurements
- 6- Molar Conductance Measurements
- 7- Elemental Analysis

2.1.1 INFRARED SPECTROSCOPY

When Infrared light is passed through a sample some of the frequencies are absorbed while other frequencies are transmitted through the sample without being absorbed. The plot of the percent absorbance or percent transmittance against frequency, results an infrared spectrum.

The IR radiation does not have enough energy to induce electronic transitions observed in UV spectroscopy. Absorption of IR radiation is restricted to the compounds with small energy differences in the possible vibrational and rotational states. For a molecule to absorb IR radiation, the vibrations or rotations with in a molecule must cause a net change in the dipole

moment of the molecule. The alternating electrical field of the radiation interacts with fluctuations in the dipole moment of the molecule. If the frequency of the radiation matches the vibrational frequency of the molecule then radiation will be absorbed, causing a net change in the amplitude of the molecular vibration.

In the absorption of the radiation, only transition for which change in the vibrational energy level is $\Delta V=1$ can occur, since most of the transition will occur from stable V_0 to V_1 the frequency corresponding to its energy is called the fundamental frequency.

The group frequency which are frequencies of certain groups are characteristic of the group irrespective of the nature of the molecule in which these groups are attached. The absence of any band in the approximate region indicates the absence of that particular group in the molecule.

The term "infrared" covers the range of electromagnetic spectrum between 0.78 and 1000 μm . In the context of infrared spectroscopy, wavelength is measured in "wavenumbers", which have the unit in cm^{-1}

Wave number = $1/\text{wavelength in centimeters}$

$$\nu = 1/\lambda$$

It is useful to divide the infrared region into three sections; near, mid and far infrared;

Region	Wavelength range(μm)	Wavelength range (cm^{-1})
Near	0.78-2.5	12800-4000
Middle	2.5-50	4000-200
Far	50-1000	200-10

Important Group Frequencies in the IR Spectra Pertinent to the Discussion of the Newly Synthesized Compounds.

a) N–H Stretching Frequency

The N–H Stretching vibrations occur in the region $3300\text{-}3500\text{ cm}^{-1}$ in the dilute solution.¹ The N–H stretching band shifts to lower value in the solid state due to the extensive hydrogen bonding. Primary amines in the dilute solutions, in non-polar solvents give two absorptions i.e. symmetric stretch found near 3400 cm^{-1} and asymmetric stretch mode found near 3500 cm^{-1} . Secondary amines show only a single N–H stretching band in dilute solutions. The intensity and frequency of N–H stretching vibrations of secondary amines are very sensitive to structural changes. The bands are found in the range $3310\text{-}3350\text{ cm}^{-1}$ (low intensity) in aliphatic, secondary amines and near 3490 cm^{-1} (much higher intensity) in heterocyclic secondary amines such as pyrazole and imidazole.

b) Methyl Group Frequency

Absorption arising from C–H stretching in the alkanes occurs generally in the region of $2840\text{-}3000\text{ cm}^{-1}$. The position of C–H stretching vibrations are among the most stable in the spectrum. An examination of a large number of saturated hydrocarbons containing methyl group showed¹ in all cases, two

distinct bands occurring at 2960 cm^{-1} and 2870 cm^{-1} . The first of these results from asymmetric stretching mode in which two C–H bonds of the methyl group are extending while the third one is contracting ($\nu_{\text{asy}}, \text{CH}_3$). The second arises from symmetric stretching ($\nu_{\text{sy}}, \text{CH}_3$) in which all three of the C–H bonds extend and contract in phase. The presence of several methyl groups in a molecule results in a strong absorption band at these vibrational modes.

c) C–N Stretching Frequency

The C–N stretching absorption gives rise to strong bands in the region $1250\text{-}1350\text{ cm}^{-1}$ in all the amines.^{1,2} In primary aromatic amines there is one band in the region $1250\text{-}1340\text{ cm}^{-1}$ but in secondary amines two bands have been found in the region $1280\text{-}1350\text{ cm}^{-1}$ and $1230\text{-}1280\text{ cm}^{-1}$.

d) C=N Stretching Frequency

Schiff's bases ($\text{RCH}=\text{NR}$, imines), oximes, thiazoles, iminocarbonates etc. show the C=N stretching frequency in the $1471\text{-}1689\text{ cm}^{-1}$ region.^{1,2} Although the intensity of the C=N stretch is variable, however it is usually more intense than the C=C stretch.

e) N–N Stretching Frequency

A strong band appearing in the region around 1000 cm^{-1} may reasonably be assigned³ to $\nu(\text{N–N})$ vibrations.

f) S–H Stretching Frequency

The S–H stretching vibrations in mercaptans are usually observed in the range $2500\text{-}2600\text{ cm}^{-1}$. The S–H absorption is not inherently strong and is often difficult to detect in dilute solution or in samples examined in very thin cells.

g) C–S Stretching Frequency

The C–S stretching frequency generally appears^{1,2} as a band of weak or moderate intensity in the range 570-720 cm^{-1} . There appears to be a progressive decrease in the frequency in the order, primary, secondary and tertiary C–S. In aromatic derivatives the C–S frequency is higher due to the presence of the intense C–H out of plane deformation band in this region. In phenyl, sulphonyl, halides the C–S vibration occurs between 706-715 cm^{-1} .

h) O–H Stretching Frequency

The O–H stretching frequency is observed^{2,4} nearly in the same range as N–H frequency (3400-3500 cm^{-1}). However, the observed absorption for N–H is normally narrower than for O–H. This is a useful means of distinguishing N–H and O–H stretching modes.

i) Amide Bands

Amide I Band: All amides show a carbonyl absorption band known as the amide I band.^{1, 4} Its position depends on the degree of hydrogen bonding and thus on the physical state of the compound. The C=O absorption (amide I band) of amides occurs at longer wave length than normal carbonyl absorption due to the resonance effect. Primary amides have a strong amide I band in the region of 1650 cm^{-1} when examined in the solid phase. When the amide is examined in dilute solution the absorption is observed at a higher frequency, near 1690 cm^{-1} . Simple open chain secondary amides absorb near at 1640 cm^{-1} when examined in solid state.

Amide II Band: Primary and secondary amides show a second strong band in the $1600\text{-}1500\text{ cm}^{-1}$ region which is absent from the spectra of tertiary amides and also from those of cyclic lactams under normal conditions. This band is generally referred to as the amide II band.

Primary amides show this second band very close to the main carbonyl absorption. Usually its intensity is about half to one-third that of the CO absorption and it lies on the low-frequency side in the range $1650\text{-}1620\text{ cm}^{-1}$ in case of solids.^{5,6} In some instances the two bands fall so close together in the spectrum of solid materials that only a single band appears. However, the two bands show frequency shifts in opposite directions following changes of state, thus the presence of both can be established in this way. Various workers in this field^{5,6} have reported that the band occurs in the $1620\text{-}1650\text{ cm}^{-1}$ region in the solid state, falling to $1590\text{-}1620\text{ cm}^{-1}$ in dilute solution.

All secondary amides show amide II absorption band in the region of 1550 cm^{-1} in case of solids. There are various views by different workers to explain this band in case of secondary amides. One commonly accepted explanation of this band is that it arises from the NH deformation mode and that it is therefore similar in origin to the amide II band of unsubstituted amides. However, this simple explanation is not entirely satisfactory for various reasons. The most popular of the alternative explanations offered has been the assignment of this band to a C–N stretching motion in which the C–N link has considerable double-bond character due to its resonance with the carbonyl group.⁵ This is supported to some extent by deuteration data and is

consistent with the results of X-ray work⁷, but has other defects, that it does not account for the absence of the band in tertiary amides, or for the polarization results.

Lenormant⁸ gave a third explanation and revived the two molecular state theory in a modified form. In this, both amide I and II bands are attributed to carbonyl vibrations. The first arises from the normal keto form and the second from a polar modification associated as a dimer. This theory has been seriously weakened by **Gierer's** observations⁹ that the amide II band persists in vapours when only unassociated molecules are present.

Frazer and Price¹⁰ have reconciled all these discordant views. Accordingly, they assigned the amide II band as a mixed vibration, which can best be described as an out-of-phase combination of OCN and NH vibrations in which the angular displacement of the hydrogen atom plays the greater part. This view, that mixed vibrations are involved has won almost general acceptance. Several groups of workers⁶ have found a frequency range of 1515-1570 cm^{-1} for materials examined in the solid state, a considerable proportion of which absorb near the mean value of 1540 cm^{-1} . In solution the amide II band shifts towards lower frequencies with in the range 1510-1650 cm^{-1} .

Amide III Band: This absorption band occurs in secondary amides^{10,11} in the region 1305-1200 cm^{-1} and is usually notably weaker than either of the amide I or II bands. It is almost certain due to a mixed vibration involving OCN and N-H modes, The amide III absorption in normal amides is sensitive to deuteration changes, indicating mixing but in thioamides it is essentially

unchanged and is then wholly attributable to a C–N mode. Changes of state result in marked shifts in normal amides, but are notably reduced in the thio-derivatives.

Amide IV and Amide VI Bands : Mizushima et al¹¹ identified the low frequency absorptions in secondary amides near 620 cm^{-1} and 600 cm^{-1} and termed them as amide IV and amide VI bands, respectively, they have their origins in skeletal modes and are of limited use for characterization purposes.

j) **Pyridine Ring Vibration**

The free pyridine molecule exhibits three important ring vibrations, i.e. 6a and 8a vibrations (in-plane ring deformations) appearing around 601 and 1578 cm^{-1} respectively^{12,13}, while the 16b vibration (out- of- plane ring deformation) is observed around 403 cm^{-1} . It has been indicated, that the positions of the two lower bands are very sensitive and undergo a positive shift after coordination. The magnitude of the positive shift is reported to be a function of the stereochemistry and the nature of the metal ions.

k) **(M–N)_{py} Stretching Frequency**

The involment of the pyridine nitrogen in coordination is confirmed by the appearance of a medium intensity band in the region $225\text{-}260\text{ cm}^{-1}$ corresponding^{12,13} to $\nu(\text{M–N})_{\text{py}}$.

l) **M–N Stretching Frequency**

The M–N stretching frequency is of particular interest since it provides direct information regarding the metal-nitrogen coordinate bond. Different amine complexes exhibited² the metal-nitrogen frequencies in the $300\text{-}450\text{ cm}^{-1}$ region.

m) **M–S Stretching Frequency**

The metal-sulfur stretching frequency is interesting, as it gives a direct evidence for coordination through the sulfur atom in metal mercapto complexes. It has been reported² that M–S appear in the region 325-390 cm^{-1} .

n) **M–X Stretching Frequency**

Metal-halogen stretching bands appear² in the region of 500-750 cm^{-1} for MF, 200-400 cm^{-1} for MCl, 200-300 cm^{-1} for MBr and 100-200 cm^{-1} for MI.

o) **M–O Stretching Frequency**

Metal-oxygen stretching frequency has been reported to appear in different regions for different metal complexes. The M–O stretching frequency of nitrate complexes lie in the range of 250-350 cm^{-1} . Furthermore unidentate nitrate group display bands around 1497, 1271 and 992 cm^{-1} region assigned² to ν (N–O) vibrations.

FTIR spectra (4000-200 cm^{-1}) were recorded as KBr or CsCl discs on a Perkin Elmer-621 spectrophotometer from Central Research Drug Institute, Lucknow, India.

2.1.2 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

¹H NMR Spectroscopy

Nuclei of isotopes which possess an odd number of protons, and odd number of neutrons or both exhibit mechanical spin phenomenon which are associated with angular momentum. This angular momentum is characterized by a nuclear spin quantum number, I such that, $I = 1/2n$, where n is an integral 0, 1, 2, 3, -----etc.

The nuclei with $I = 0$, do not possess spin angular momentum and do not exhibit magnetic resonance phenomena. The nuclei of ^{12}C and ^{16}O fall into this category. Nuclei for which $I = 1/2$ include ^1H , ^{19}F , ^{13}C , ^{31}P and ^{15}N , while ^2H and ^{14}N have $I = 1$.

Since atomic nuclei are associated with charge, a spinning nucleus generates a small electric current and has a finite magnetic field associated with it. The magnetic dipole, μ , of the nucleus varies with each element. When a spinning nucleus is placed in a magnetic field, the nuclear magnet, experiences a torque which tends to align it with the external field. For a nucleus with a spin of $1/2$, there are two allowed orientations of the nucleus, parallel to the field (low energy) and against the field (high energy). Since the parallel orientation is lower in energy, this state is slightly more populated than the anti-parallel, high energy state.

If the oriented nuclei are now irradiated with electromagnetic radiation of the proper frequency, the lower energy state will absorb a quantum of energy and spin-flip to the high energy state. When this spin transition occurs, the nuclei are said to be in resonance with the applied radiation, hence the name Nuclear Magnetic Resonance.

The amount of electromagnetic radiation necessary for resonance depends on both the strength of the external magnetic field and on the characteristic of the nucleus being examined. The nucleus of the proton, placed in 14,000 gauss field, undergoes resonance when irradiated with radiation in the 60 MHz, higher magnetic fields, such as those common in superconducting

magnets, require higher energy radiation and give a correspondingly higher resolution.

The ^1H NMR spectra in DMSO-d_6 using a Bruker AC 200E NMR spectrometer with Me_4Si as an internal standard were obtained from Guru Nanak Dev University, Amritsar and Indian Institute of Technology, Kanpur, India.

2.1.3 ELECTRON SPIN RESONANCE SPECTROSCOPY

In 1936, Gorter demonstrated^{14,15} that a paramagnetic salt when placed in a high frequency alternating magnetic field absorbs energy which is influenced by the application of a static magnetic field either parallel or perpendicular to the alternating magnetic field. Since then this phenomenon has become a technique of immense importance in science.

It is well known that a paramagnetic ion has a magnetic moment and therefore its ground state is degenerate. If this ion is placed in a strong static magnetic field the degeneracy is lifted and the energy levels undergo a Zeeman splitting. Application of an oscillating magnetic field of appropriate frequency will induce transitions between the Zeeman levels and the energy is absorbed from the electromagnetic field. If the static magnetic field is slowly varied, the absorption shows a series of maxima. The plot between the absorbed energy and the magnetic field is called the electron paramagnetic resonance spectrum.

A system of charges exhibit paramagnetism whenever it has a resultant angular momentum. Such paramagnetic systems includes elements containing 3d, 4d, 4f, 5d, 5f, 6d etc. electrons, atoms having an odd number of electrons

like hydrogen, molecules containing odd number of electrons such as NO_2 , NO etc. and free radicals which possess an unpaired electron like methyl, diphenyl picryl hydrazide free radical etc. are among the suitable reagents for EPR investigation. Splitting of energy levels in EPR occurs under the effect of two types of fields, namely the internal crystalline field and applied magnetic field. While studying a paramagnetic ion in a diamagnetic crystal lattice, two types of interactions are observed, i.e. interactions between the paramagnetic ions called dipolar interaction and the interactions between the paramagnetic ion and the diamagnetic neighbour called crystal field interaction. For small doping amount of paramagnetic ion in the diamagnetic host, the dipolar interaction will be negligibly small. The latter interaction of paramagnetic ion with diamagnetic ligands modifies the magnetic properties of the paramagnetic ions. According to crystal field theory, the ligand influences the magnetic ion through the electric field, which they produce at its site and their orbital motion gets modified. The crystal field interaction is affected by the outer electronic shells.

The dipole-dipole interaction arises from the influence of magnetic field of one paramagnetic ion on the dipole moments of the neighbouring, similar ions. The local field at any given site will depend on the arrangements of the neighbours and the direction of their dipole moments. Thus the resultant magnetic field on the paramagnetic ion will be the vector sum of the external field and the local field. This resultant field varies from site to site giving a random displacement of the resonance frequency of each ion and thus broadening the line widths.

Hyperfine interactions are mainly magnetic dipole interactions between the electronic magnetic moment and the nuclear magnetic moment of the paramagnetic ion. The quartet structure in the EPR of vanadyl ion is the result of hyperfine interactions. The origin of this can be understood simply by assuming that the nuclear moment produces a magnetic field B_N at the magnetic electrons and the modified resonance condition will be $E = h\nu = g\beta |B + B_N|$ where B_N takes up $2I+1$, where I is the nuclear spin. There may be an additional hyperfine structure also due to interaction between magnetic electrons and the surrounding nuclei called superhyperfine structure. The effect was first observed by Owens and Stevens in ammonium hexa chloroiridate¹⁶ and subsequently for a number of transition metal ions in various hosts.^{17, 18}

EPR spectra of all the copper complexes were recorded on a JEOL JES RE2X EPR spectrometer at room temperature from the Department of Physics, Aligarh Muslim University, Aligarh, India. The $g_{||} > g_{\perp}$ and G values were calculated from these spectra.

2.1.4 ULTRA-VIOLET AND VISIBLE (LIGAND FIELD) SPECTROSCOPY

Most of the compounds absorb light somewhere in the spectral region between 200 and 1000 nm. These transitions correspond to the excitation of electrons of the molecules from ground state to higher electronic states. In a transition metal all the five d-orbitals viz. d_{xy} , d_{yz} , d_{xz} , d_{z^2} and $d_{x^2-y^2}$ are degenerate. However, in coordination compounds due to the presence of

ligands this degeneracy is lifted and d-orbitals split into two groups called t_{2g} (d_{xy} , d_{yz} and d_{xz}) and e_g (d_{z^2} and $d_{x^2-y^2}$) in an octahedral complex and t and e in a tetrahedral complex. The set of t_{2g} orbitals goes below and the set of e_g orbitals goes above the original level of the degenerate orbitals in an octahedral complex. In case of the tetrahedral complexes the position of the two sets of the orbitals is reversed, the e going below and t going above the original degenerate level. When a molecule absorbs radiation, its energy is equal in magnitude to $h\nu$ and can be expressed by the relation:

$$E = h\nu$$

$$\text{or } E = hc/\lambda$$

Where h is Planck's constant, ν and λ are the frequency and wavelength of the radiation, respectively and c is the velocity of the light.

In order to interpret the spectra of transition metal complexes, the device of energy level diagram based upon 'Russell Saunder Scheme' must be introduced. This has the effect of splitting the highly degenerate configurations into groups of levels having lower degeneracies known as 'Term Symbols'.

The orbital angular momentum of electrons in a filled shell vectorially adds up to zero. The total orbital angular momentum of an incomplete d shell electron is observed by adding L value of the individual electrons, which are treated as a vector with a component ml in the direction of the applied field.

Thus

$$L = \sum_i m_{li} = 0, 1, 2, 3, 4, 5, 6,$$

S, P, D, F, G, H, I

The total spin angular momentum $S = \sum_i s_i$ where s_i is the value of spin angular momentum of the individual electrons. S has a degeneracy τ equal to $2S + 1$, which is also known as 'Spin Multiplicity'. Thus a term is finally denoted as $^{\tau}L$. For example, if $S = 1$ and $L = 1$, the term will be 3P and similarly if $S = 1\frac{1}{2}$, and $L = 3$, the term will be 4F .

In general the terms arising from a d^n configuration are as follows.

$$d^1 d^9 : \quad ^2D$$

$$d^2 d^8 : \quad ^3F, ^3P, ^1G, ^1D, ^1S$$

$$d^3 d^7 : \quad ^4F, ^4P, ^2H, ^2G, ^2F, ^2D(2), ^2P$$

$$d^4 d^6 : \quad ^5D, ^3H, ^3G, ^3F(2), ^3D, ^2P(2), ^1I, ^1G(2), ^1F, ^1D(2), ^1S(2)$$

$$d^5 : \quad ^4S, ^4G, ^4F, ^4D, ^4P, ^2I, ^2H, ^2G(2), ^2F(2), ^2D(3), ^2P, ^2S.$$

Coupling of L and S also occurs, because both L and S if non-zero, generate magnetic fields and thus tend to orient their moments with respect to each other in the direction where their interaction energy is least. This coupling is known as 'LS coupling' and gives rise to resultant angular momentum denoted by quantum number J which may have quantized positive values from $|L + S|$ up to $|L - S|$ e.g., in the case of 3P ($L = 1, S = 1$), 4F ($L = 3, S = 1\frac{1}{2}$) possible values of J representing state, arising from term splitting are 2, 1 and 0 and $4\frac{1}{2}, 3\frac{1}{2}, 2\frac{1}{2}$, and $1\frac{1}{2}$. Each state specified by J is $2J + 1$ fold degenerate. The total number of states obtained from a term is called the multiplet and each value of J associated with a given value of L is called component. Spectral transitions due to spin-orbit coupling in an atom or ion occurs between the

components of two different multiplets while LS coupling scheme is used for the elements having atomic number less than 30, in that case spin-orbital interactions are large and electrons repulsion parameters decreases. The spin-angular momentum of an individual electron couples with its orbital momentum to give an individual J for that electron. The individual J 's couple to produce a resultant J for the atom. The electronic transitions taking place in an atom or ion are governed by certain 'Selection Rules' which are as follows

1. Transitions between states of different multiplicity are forbidden.
2. Transitions involving the excitation of more than one electron are forbidden.
3. In a molecule, which has a centre of symmetry, transitions between two gerade or two ungerade states are forbidden.

It is possible to examine the effects of crystal field on a polyelectron configuration. The ligand field splitting due to cubic field can be obtained by considerations of group theory. It has been shown that an S state remains unchanged. P states does not split, and D state splits into two and F state into three and G state into four states as tabulated below: (Applicable for an octahedral 'Oh' as well as tetrahedral 'Td' symmetry).

S ----- A_1

P ----- T_1

D ----- $E + T_2$

F ----- $A_2 + T_1 + T_2$

G ----- $A_2 + E + T_1 + T_2$

Transitions from the ground state to the excited state occur according to the selection rules described earlier. The energy level order of the states arising from the splitting of a term state for a particular ion in an octahedral field is the reverse that of the ion in a tetrahedral field. However, due to transfer of charge from ligand to metal or metal to ligand, sometimes bands appear in the ultraviolet region of the spectrum. These spectra are known as 'Charge Transfer Spectra or 'Redox Spectra.' In metal complexes there are often possibilities that charge transfer spectra extend into the visible region to obscure d-d transition. However, these should be clearly discerned from the ligand bands, which might also occur in the same region.

The electronic Spectra of complexes in DMSO were recorded on a Pye-Unicam 8800 spectrophotometer at room temperature from the Aligarh Muslim University, Aligarh, India.

2.1.5 MAGNETIC SUSCEPTIBILITY MEASUREMENTS

The determination of magnetic moments of transition metal complexes have been found to provide ample information in assigning their structure. The main contribution to bulk magnetic properties arises from magnetic moment resulting from the motion of electrons. It is possible to calculate the magnetic moments of known compounds from the measured values of magnetic susceptibility.

There are several kinds of magnetism in substances viz. diamagnetism, paramagnetism and ferromagnetism or antiferromagnetism. Mostly compounds of the transition elements are paramagnetic. Diamagnetism is attributable to the closed shell electrons with an applied magnetic field. In the closed shell the

electron spin moment and orbital moment of the individual electrons balance one another so that there is no magnetic moment. Ferromagnetism and antiferromagnetism arise as a result of interaction between dipoles of neighbouring atoms.

If a substance is placed in a magnetic field H , the magnetic induction B with the substance is given by

$$B = H + 4\pi I$$

Where I is the intensity of magnetization. The ratio B/H is called magnetic permeability of the material and is given by

$$B/H = I + 4\pi(I/H) = I + 4\pi K$$

Where K is called the magnetic susceptibility per unit volume or volume susceptibility. B/H is the ratio of the density of lines of force within the substance to the density of such lines in the same region in the absence of sample. Thus the volume susceptibility of a vacuum is by definition zero since in vacuum $B/H = 1$.

When magnetic susceptibility is considered on the weight basis, the gram susceptibility (χ_g) is used instead of volume susceptibility. The μ_{eff} value can then be calculated from the gram susceptibility multiplied by the molecular weight and corrected for diamagnetic value as

$$\mu_{\text{eff}} = 2.84 \sqrt{\chi_M^{\text{corr}} \cdot T} \text{ BM}$$

where T is the absolute temperature at which the experiment is performed.

The magnetic properties of any individual atom or ion will result from some combination of these two properties that is the inherent spin moment of the electron and the orbital moment resulting from the motion of the electron around the nucleus. The magnetic moments are usually expressed in Bohr Magnetons (BM). The magnetic moment of a single electron is given by

$$\mu_s = g\sqrt{S(S+1)} BM$$

Where S is the spin quantum number and g is the gyromagnetic ratio. For Mn^{2+} , Fe^{3+} and other ions whose ground states are S states there is no orbital angular momentum. In general however, the transition metal ion in their ground state D or F being most common, do possess orbital angular momentum. For such ions, as Co^{2+} and Ni^{2+} , the magnetic moment is given by

$$\mu_{(S+L)} = g\sqrt{4S(S+1) + L(L+1)}$$

In which L represents the orbital angular momentum quantum number for the ion.

The spin magnetic moment is insensitive to the environment of metal ion. the orbital magnetic moment is not. In order for an electron to have an orbital angular momentum and there by an orbital magnetic moment with reference to a given axis, it must be possible to transform the orbital into a fully equivalent orbital by rotation about that axis. For octahedral complexes the orbital angular momentum is absent for A_{1g} , A_{2g} and E_g term. but can be present for T_{1g} and T_{2g} terms. Magnetic moments of the complex ions with A_{2g} and E_g ground terms may depart from the spin-only value by a small amount. The magnetic moments of the complexes possessing T ground terms usually

differ from the high spin value and vary with temperature. The magnetic moments of the complexes having a ${}^6A_{1g}$ ground term are very close to the spin-only value and are independent of the temperature.

For octahedral and tetrahedral complexes in which spin-orbit coupling causes a split in the ground state an orbital moment contribution is expected. Even no splitting of the ground state appears in cases having no orbital moment contribution, an interaction with higher states can appear due to spin-orbit coupling giving an orbital moment contribution.

Practically the magnetic moment value of the unknown complex is obtained by a Gouy Magnetic balance. Faraday method can also be applied for the magnetic susceptibility measurement of small quantity of solid samples.

The gram susceptibility is measured by the following formula.

$$\chi_g = \frac{\Delta W}{W} \cdot \frac{W_{std}}{\Delta W_{std}} \cdot \chi_{std}$$

Where χ_g = Gram Susceptibility

ΔW = Change in weight of the unknown sample with magnets on and off.

W = Weight of the known sample

ΔW_{std} = Change in weight of standard sample with magnets on and off.

W_{std} = Weight of standard sample.

χ_{std} = Gram susceptibility of the standard sample.

Magnetic susceptibility measurements were carried out using Faraday balance at 300°K from Guru Nanak Dev University, Amritsar, India.

2.1.6 CONDUCTIVITY

The resistance of a sample of an electrolytic solution is defined by

$$R = \rho [l/A]$$

Where l is the length of a sample of electrolyte and A is the cross sectional area. The symbol ρ is the proportionality constant and is a property of a solution. This property is called resistivity or specific resistance. The reciprocal of resistivity is called conductivity, κ

$$\kappa = l/\rho = l/RA$$

Since l is in cm, A is in cm^2 and R in ohms (Ω), the units of κ are $\Omega^{-1} \text{cm}^{-1}$ or S cm^{-1} (Siemens per cm)

Molar Conductivity

If the conductivity κ is in $\Omega^{-1} \text{cm}^{-1}$ and the concentration C is in mol cm^{-3} , then the molar conductivity Λ is in $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ and is defined by

$$\Lambda = \kappa/C$$

Where C is the concentration of solute in mol cm^{-3} .

Conventionally, solutions of 10^{-3} M concentration are used for the conductance measurement. Molar conductance values of different types of electrolytes in a few solvents are given below;

A 1:1 electrolyte may have a value of 70-95 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ in nitromethane, 50-75 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ in dimethyl formamide and 100-160 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ in methyl cyanide. Similarly a solution of 2:1 electrolyte may have a

value of 150-180 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ in nitromethane, 130-170 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ in dimethylformamide and 140-220 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ in methyl cyanide.^{19,21}

The electrical conductivities of 10^{-3} M solutions in DMSO were recorded on a Control Dynamics Conductivity Bridge equilibrated at $25^\circ \text{C} \pm 0.01^\circ \text{C}$.

2.1.7 ELEMENTAL ANALYSIS

The chemical analysis is quite helpful in fixing the stoichiometric composition of the ligand as well as its metal complexes. Carbon, hydrogen and nitrogen analyses were carried out on a Perkin Elmer-2400 analyzer from Central Drug Research Institute, Lucknow, India. Sulfur and Chlorine were analyzed by conventional method.²² For the metal estimation²³, a known amount of complex was decomposed with a mixture of nitric, perchloric and sulfuric acids in a beaker. It was then dissolved in water and made up to known volume so as to titrate it with standard EDTA. For sulphur and chlorine estimation, a known amount of the sample was decomposed in a platinum crucible and dissolved in water with a little concentrated nitric acid. The solution was then treated with either silver nitrate or Barium chloride solution. The precipitate was then dried and weighed.

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