CHAPTER II
INSTRUMENTAL METHODS
AND THEORY
There are several physico-chemical methods available for the characterization of coordination compounds. A brief description of the techniques used in the investigation of the newly synthesized macrocyclic 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

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 result is 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 within 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/wavelength in centimeters

$\nu = 1/\lambda$

It is useful to divide the infrared region into three sections; near, mid and far infrared;
<table>
<thead>
<tr>
<th>Region</th>
<th>Wavelength range(μm)</th>
<th>Wavelength range (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Near</td>
<td>0.78-2.5</td>
<td>12800-4000</td>
</tr>
<tr>
<td>Middle</td>
<td>2.5-50</td>
<td>4000-200</td>
</tr>
<tr>
<td>Far</td>
<td>50-1000</td>
<td>200-10</td>
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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 3300-3500 cm⁻¹ in 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 absorption bands in the above mentioned region, the first of which due to symmetric stretch is usually found near 3400 cm⁻¹ and second which corresponds to asymmetric stretch mode found near 3500 cm⁻¹. These bands are usually 125-150 cm⁻¹ apart. 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 3310-3350 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 in the general region of 2840-3000 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 showed\(^1\) 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 (\(v_{\text{asy, CH}_3}\)). The second arises from symmetric stretching (\(v_{\text{sym, CH}_3}\)) 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 positions.

c) **C–N Stretching Frequency**

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

d) **C=\(\text{N}\) Stretching Frequency**

Schiff’s bases (RCH=NR, imines), oximes, thiazoles, iminocarbonates etc. show the C=\(\text{N}\) stretching frequency in the 1471-1689 cm\(^{-1}\) region.\(^1,2\) Although the intensity of the C=\(\text{N}\) 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 assigned\(^3\) to \(v\) (N–N) vibrations.
f) **Sn–N Stretching Frequency**

A medium intensity band appearing in the region around 445-480 cm\(^{-1}\) may reasonably be assigned\(^4\) to \(\nu\) (Sn–N) vibrations.

g) **C–O Stretching Frequency**

The C–O stretching vibrations in phenols generally produce\(^5\) a strong band in the 1000–1260 cm\(^{-1}\) region of the spectrum. The C–O stretching mode is coupled with the adjacent C–C stretching vibration, thus it might better be described as an asymmetric C–C–O stretching vibration.

h) **O–H Stretching Frequency**

The O–H stretching frequency is observed\(^2,6\) 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) **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 exhibited\(^2\) the metal-nitrogen frequencies in the 300-450 cm\(^{-1}\) region.

j) **M–X Stretching Frequency**

Metal-halogen stretching bands appear\(^2\) 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.
k) 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 nitrato complexes lie in the range of 250-350 cm$^{-1}$. Furthermore unidentate nitrate group display bands around 1497, 1271 and 992 cm$^{-1}$ region assigned$^2$ to v (N–O) vibrations.

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

2. NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

$^1$H 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, $I = \frac{1}{2}n$, 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 $I = \frac{1}{2}$ include $^1$H, $^{19}$F, $^{13}$C, $^{31}$P and $^{15}$N, while $^2$H 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, $\mu$, 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 $^1$H NMR spectra in DMSO-d$_6$ using a Bruker AC 200E NMR
spectrometer with Me$_4$Si as an internal standard were obtained from Guru
Nanak Dev University, Amritsar and Indian Institute of Technology, Kanpur,
India.


\textbf{\(^{13}\text{C} \text{NMR Spectroscopy}\)}

\(^{13}\text{C}\) has a nuclear spin of \(\frac{1}{2}\) and can be observed by NMR at a frequency of 10.705 MHz at a field strength of 10 Kilogauss. The relative abundance of \(^{13}\text{C}\) is only 1.1\% (compared to \(^{12}\text{C}\)), the \(^{13}\text{C}\) resonance has only 1.6\% the sensitivity of \(^{1}\text{H}\) resonances and the relaxation time for \(^{13}\text{C}\) is longer than \(^{1}\text{H}\). \(^{13}\text{C}\) chemical shifts span slightly over 200 ppm in contrast to the typical 8 to 9 ppm range in the \(^{1}\text{H}\) NMR; thus considerably more structural information is generally available from \(^{13}\text{C}\) NMR chemical shift data. The second very important difference between \(^{1}\text{H}\) and \(^{13}\text{C}\) NMR spectroscopy is that diamagnetic effects are dominant in the shielding of the hydrogen nucleus, whereas paramagnetic effects are the dominant contributors to the shielding of the \(^{13}\text{C}\) nucleus. Long-range shielding effects that were important in the \(^{1}\text{H}\) NMR are less important in \(^{13}\text{C}\) NMR. As a result, \(^{13}\text{C}\) chemical shifts generally do not parallel \(^{1}\text{H}\) chemical shifts. Since the spin number for \(^{13}\text{C}\) is the same for \(^{1}\text{H}\), the same rule apply for predicting the multiplicity of this absorption. The coupling constants for \(^{13}\text{C}-^{1}\text{H}\) are large (100-250 Hz) and thus interpretation of the \(^{13}\text{C}\) spectra can be difficult because of the overlapping \(^{13}\text{C}-^{1}\text{H}\) multiplets. To simplify the spectrum, \(^{13}\text{C}\) NMR spectra are generally recorded under double resonance conditions in which the coupling of \(^{1}\text{H}\) to \(^{13}\text{C}\) is destroyed. Complete \(^{1}\text{H}\) coupling is accomplished by irradiating the \(^{1}\text{H}\) resonance region with a broad band width radio frequency radiation, termed “noise”. sufficient to cover the entire \(^{1}\text{H}\) resonance region. The \(^{13}\text{C}\) NMR spectra thus obtained contain only singlet resonances corresponding to its chemical shifts.
\textsuperscript{13}C NMR spectra were recorded in DMSO-d\textsubscript{6} using Jeol Eclipse-400 spectrophotometer from King Saud University, College of Sciences, Riyadh, Saudi Arabia (Kingdom of Saudi Arabia).

3. ELECTRON SPIN RESONANCE SPECTROSCOPY

In 1936, Gorter demonstrated\textsuperscript{7,8} 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\textsubscript{2}, NO etc. and free radicals which posses an unpaired electron like methyl, diphenyl,
picryl, hydazide 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 ions 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 $E = \hbar \nu = g\beta I/2B + B_N 1/2$ 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 hexachloroiridate and subsequently for a number of transition metal ions in various hosts.\textsuperscript{9,10,11}

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 $g_{\parallel}$ and $g_{\perp}$ values were calculated from these spectra.

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. $d_{xy}$, $d_{xz}$, $d_{yz}$, $d_{z^2}$ and $d_{e^2}$ are
degenerate. However, in coordination compounds due to the presence of ligands this degeneracy is lifted and d-orbitals split into two groups called $t_{2g}$ ($d_{xy}, d_{xz}$ and $d_{yz}$) 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 $hv$ and can be expressed by the relation:

$$E = hv$$

Or

$$E = hc/\lambda$$

where $h$ is Planck's constant, $v$ and $\lambda$ 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 $m_l$ in the direction of the applied field.
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 \( \tau \) 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 \(^3\text{P}\) and similarly if \( S = 1 \frac{1}{2} \), and \( L = 3 \), the term will be \(^4\text{F}\).

In general, the terms arising from a \( d^6 \) configuration are given below:

\[
\begin{align*}
d^1d^9 & : \quad ^2\text{D} \\
d^2d^8 & : \quad ^3\text{F}, \, ^3\text{P}, \, ^1\text{G}, \, ^1\text{D}, \, ^1\text{S} \\
d^3d^7 & : \quad ^4\text{F}, \, ^4\text{P}, \, ^2\text{H}, \, ^2\text{G}, \, ^2\text{F}, \, ^2\text{D}(2), \, ^2\text{P} \\
d^4d^6 & : \quad ^5\text{D}, \, ^3\text{H}, \, ^3\text{G}, \, ^3\text{F}(2), \, ^3\text{D}, \, ^2\text{P}(2), \, ^1\text{I}, \, ^1\text{G}(2), \, ^1\text{F}, \, ^1\text{D}(2), \, ^1\text{S}(2) \\
d^5 & : \quad ^4\text{S}, \, ^4\text{G}, \, ^4\text{F}, \, ^4\text{D}, \, ^4\text{P}, \, ^2\text{I}, \, ^2\text{H}, \, ^2\text{G}(2), \, ^2\text{F}(2), \, ^2\text{D}(3), \, ^2\text{P}, \, ^2\text{S}. 
\end{align*}
\]

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 \(^3\text{P} \) (\( L = 1, \, S = 1 \)), \(^4\text{F} \) (\( L = 3, \, S = 1 \frac{1}{2} \)) 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-orbit 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).

<table>
<thead>
<tr>
<th>S</th>
<th>--------</th>
<th>A₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>---------</td>
<td>T₁</td>
</tr>
<tr>
<td>D</td>
<td>---------</td>
<td>E + T₂</td>
</tr>
<tr>
<td>F</td>
<td>---------</td>
<td>A₂ + T₁ + T₂</td>
</tr>
<tr>
<td>G</td>
<td>---------</td>
<td>A₂ + E + T₁ + T₂</td>
</tr>
</tbody>
</table>
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 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-d₆ were recorded on a Pye-Unicam 8800 spectrophotometer at room temperature from the Instrumentation Center, Department of Chemistry, Aligarh Muslim University, Aligarh, India.

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

\[ \frac{B}{H} = I + 4\pi(I/H) = I + 4\pi \kappa \]

where \( \kappa \) 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 (\( \chi_g \)) is used instead of volume susceptibility. The \( \mu_{\text{eff}} \) value
can then be calculated from the gram susceptibility multiplied by the molecular
weight and corrected for diamagnetic value as

\[ \mu_{\text{eff}} = 2.84\sqrt{\frac{\chi_g^{\text{corr}}}{M}} \cdot T \cdot BM \]

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

\[ \mu_s = g \sqrt{S(S+1)} \text{ BM} \]

where \( S \) is the spin quantum number and \( g \) is the gyromagnetic ratio. For \( \text{Mn}^{2+} \), \( \text{Fe}^{3+} \) 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 \( \text{Co}^{2+} \) and \( \text{Ni}^{2+} \), 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.

$$X_g = \frac{\Delta W}{W} \cdot \frac{W_{std}}{\Delta W_{std}} \cdot X_{std}$$

where $X_g$ = Gram Susceptibility

$\Delta W$ = Change in weight of the unknown sample with magnets on and off.

$W$ = Weight of the known sample

$\Delta W_{std}$ = Change in weight of standard sample with magnets on and off.

$W_{std}$ = Weight of standard sample.

$X_{std}$ = Gram susceptibility of the standard sample.

The magnetic susceptibility measurements were carried out using Faraday balance at 300°K from Guru Nanak Dev University, Amritsar, India.
6. **CONDUCTIVITY**

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

\[ R = \rho \left[ \frac{l}{A} \right] \]

where \( l \) is the length of a sample of electrolyte and \( A \) is the cross sectional area.

The symbol \( \rho \) 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, \( \kappa \)

\[ \kappa = \frac{l}{\rho} = \frac{l}{RA} \]

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

**Molar Conductivity**

If the conductivity \( \kappa \) is in \( \Omega^{-1} \) cm\(^{-1}\) and the concentration \( C \) is in mol cm\(^{-3}\), then the molar conductivity \( \Lambda \) is in \( \Omega^{-1} \) cm\(^2\) mol\(^{-1}\) and is defined by

\[ \Lambda = \frac{\kappa}{C} \]

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 ohm\(^{-1}\) cm\(^2\) mol\(^{-1}\) in nitromethane, 50-75 ohm\(^{-1}\) cm\(^2\) mol\(^{-1}\) in dimethyl formamide, 50-100 ohm\(^{-1}\) cm\(^2\) mol\(^{-1}\) in dimethylsulfoxide and 100-160 ohm\(^{-1}\) cm\(^2\) mol\(^{-1}\) in methyl cyanide.

Similarly a solution of 2:1 electrolyte may have a value of 150-180 ohm\(^{-1}\) cm\(^2\)
mol$^{-1}$ in nitromethane, 130-170 ohm$^{-1}$ cm$^2$ mol$^{-1}$ in dimethylformamide, 100-200 ohm$^{-1}$ cm$^2$ mol$^{-1}$ in dimethylsulfoxide and 140-220 ohm$^{-1}$ cm$^2$ mol$^{-1}$ in methyl cyanide.$^{12-14}$

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

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. Chlorine was analyzed by conventional method.$^{15}$ For the metal estimation$^{16}$, 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 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.
REFERENCES