CHAPTER-2

Experimental Methods
2.1 INSTRUMENTAL METHODS

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. Mass Spectrometry
8. Elemental Analyses
9. Job’s Method

2.1.1 INFRARED SPECTROSCOPY

The term “infra red” covers the range of the electromagnetic spectrum between 0.78 and 1000 μm. In the context of infra red spectroscopy, wavelength is measured in “wavenumbers”, which have the unit’s cm⁻¹.

wavenumber = 1 / wavelength in centimeters
It is useful to divide the infrared range into three regions; \textit{near}, \textit{mid} and \textit{far} infrared;

<table>
<thead>
<tr>
<th>Region</th>
<th>Wavelength range (\textmu m)</th>
<th>Wavenumber 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>
</tr>
</tbody>
</table>

**Theory of infrared absorption**

IR radiation does not have enough energy to induce electronic transitions. Absorption of IR is restricted to compounds with small energy differences in the possible vibrational and rotational states.

For a molecule to absorb IR, 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 (electromagnetic radiation consists of an oscillating electrical field and an oscillating magnetic field, perpendicular to each other) 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 change in the amplitude of 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 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.

**Molecular rotations**

Rotational levels are quantized, and absorption of IR by gases yields line spectra. However, in liquids or solids, these lines broaden into a continuum due to molecular collisions and other interactions.

**Molecular vibrations**

The positions of atoms in a molecule are not fixed; they are subject to a number of different vibrations. Vibrations fall into the two main categories of *stretching* and *bending*.

**Stretching:** Change in inter-atomic distance along bond axis

- Symmetric
- Asymmetric
**Bending**: Change in angle between two bonds. There are four types of bend:

- Rocking: In-plane Rocking
- Scissoring: In-plane Scissoring
- Wagging: Out-of-plane Wagging
- Twisting: Out-of-plane Twisting

**Vibrational coupling**

In addition to the vibrations mentioned above, interaction between vibrations can occur (coupling) if the vibrating bonds are joined to a single central atom. Vibrational coupling is influenced by a number of factors viz., strong coupling of stretching vibrations occurs when there is a common atom between the two vibrating bonds, coupling of bending vibrations occurs when there is a common bond between vibrating groups, coupling between a stretching vibration and a bending vibration occurs if the stretching bond is one side of an angle varied by bending vibration, coupling is greatest when the coupled groups have approximately equal energies, no coupling is seen between groups separated by two or more bonds.
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 the dilute solution. 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 band is found in the range 3310-3350 cm\(^{-1}\) (low intensity) in aliphatic, secondary amines and near 3490 cm\(^{-1}\) which shows much higher intensity in heterocyclic secondary amines such as pyrazole and imidazole.

b) 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. In primary aromatic amines there is one band in the region 1250-1340 cm\(^{-1}\) but in secondary amines two
bands have been found in the regions 1280-1350 cm\(^{-1}\) and 1230-1280 cm\(^{-1}\).

c) **C=N Stretching Frequency**

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

d) **N–N Stretching Frequency**

A strong band appearing in the region around 1000 cm\(^{-1}\) may reasonably be assigned\(^3\) to \(\nu\) (N–N) vibrations.

e) **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.
f) M–X Stretching Frequency

Metal-halogen stretching bands appear\(^2\) in the region of 500-750 cm\(^{-1}\) for M–F, 200-400 cm\(^{-1}\) for M–Cl, 200-300 cm\(^{-1}\) for M–Br and 100-200 cm\(^{-1}\) for M–I.

g) M–O Stretching Frequency

Metal-oxygen stretching frequency has been reported to appear in different region 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 in the 1230-1260, 1020-1080 and 870-890 cm\(^{-1}\) regions assigned\(^2\) to \(v\) (N–O) vibrations.

2.1.2 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

\(^1\)H- NMR Spectroscopy

Nuclear Magnetic Resonance (NMR) Spectroscopy is a powerful and theoretically complex analytical tool where experiments are performed on the nuclei of atoms. NMR spectroscopy is based on the measurement of electromagnetic radiations in the radio-frequency region of roughly 4 to 900 MHz. In contrast to ultraviolet, visible and infrared absorption, nuclei of atoms rather than outer electrons are involved in the absorption process. Nuclear magnetic resonance spectroscopy is one of the most powerful tools available to
the chemist and biochemist for elucidating the structure of chemical species. There are two types of spectrometers:

a. Continuous-Wave (CW).

b. Pulsed, or Fourier transform (FT-NMR)

All early studies were carried out with Continuous-Wave instruments. Fourier transform spectrometers were available commercially around 1970. In both types of instruments, the sample is positioned in a powerful magnetic field of strength of several teslas. The only nuclei that exhibit the NMR phenomenon are those for which spin quantum number \( I \) is greater than 0, the spin quantum number \( I \) is associated with the mass number and atomic number of the nuclei as follows:

<table>
<thead>
<tr>
<th>Mass number</th>
<th>Atomic number</th>
<th>Spin quantum number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Odd</td>
<td>Odd or Even</td>
<td>1/2, 3/2, 5/2.............</td>
</tr>
<tr>
<td>Even</td>
<td>Even</td>
<td>0</td>
</tr>
<tr>
<td>Even</td>
<td>Odd</td>
<td>1, 2, 3...............</td>
</tr>
</tbody>
</table>

The nucleus of \(^1\text{H}\) proton, has \( I = 1/2 \), whereas \(^{12}\text{C}\) and \(^{16}\text{O}\) have \( I = 0 \) and are therefore nonmagnetic. Nuclei for which, \( I = 1/2 \), include \(^1\text{H}, ^{13}\text{C}, ^{19}\text{F}\) and \(^{31}\text{P}\), while \(^2\text{H}\) and \(^{14}\text{N}\) have \( I = 1 \).
Nuclei of isotopes which possess an odd number of protons and odd number of neutrons or both exhibits 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 $0, 1, 2, 3, \ldots$ 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 charged nucleus generates a magnetic field that is analogous to the field produced when electricity flows through a coil of wire. The resultant magnetic moment, $\mu$, is oriented along the axis of spin and is proportional to the angular momentum $p$. Thus,

$$\mu = \gamma p$$

Where, $\gamma$ is gyromagnetic ratio.

Under the influence of the external magnetic field, a magnetic nucleus can take up different orientation with respect to that field, the number of possible orientation is given by $(2I+1)$, so that for nuclei with spin quantum number $1/2$, ($^1$H, $^{13}$C, $^{19}$F, etc.) only two orientations are allowed.
If a proton is precessing in the aligned orientation, it can absorb energy and pass into the opposed orientation, subsequently it can loose this extra energy and relax back into the aligned position. If the precessed nuclei are irradiated with a beam of radiofrequency energy of the proper frequency, the lower energy nuclei will absorb this energy and move to a higher energy state. If the precessing frequency is the same as the frequency of the radio-frequency beam, the nucleus and the radio-frequency beam are said to be in resonance, hence the term Nuclear Magnetic Resonance.

NMR spectra can be recorded by either holding the magnetic field constant or scanning the radio-frequency or by keeping the radio-frequency constant and varying the magnetic field. The higher the operating frequency, the better will be the resolution, and thus easier the interpretation.

$^{13}$C-NMR spectroscopy

Carbon-13 has a nuclear spin ($I = \frac{1}{2}$) and makes up 1.1% of naturally occurring carbon to make carbon nuclear magnetic resonance spectroscopy ($^{13}$C NMR) a useful technique. Since carbon is the element central to organic chemistry, $^{13}$C NMR plays an important role in determining the structure of unknown organic molecules and the study of organic reactions. In particular, the $^{13}$C NMR spectrum of an organic compound provides information concerning:

- the number of different types of carbon atoms present in the molecule
The major differences between $^{13}$C NMR and $^1$H NMR spectra are:

- No integration of carbon spectra
- Wide range (0-200 ppm) of resonances for common carbon atoms

$^{13}$C chemical shifts span slightly over 200 ppm in contrast to the typical 8 to 9 ppm range in the $^1$H NMR, thus considerably more structural information is generally available from $^{13}$C chemical shift data. Another very important difference between $^1$H and $^{13}$C NMR spectroscopy is that diamagnetic effects are dominant in the shielding of hydrogen nucleus, whereas paramagnetic effects are dominant contributors to the shielding of the $^{13}$C nucleus. Long range shielding effects that are important in the $^1$H NMR are less important in $^{13}$C NMR. As a result, $^{13}$C chemical shifts generally do not parallel $^1$H chemical shifts. Since the spin number for $^{13}$C is the same as for $^1$H, i.e; 1/2, the same rules apply for predicting the multiplicity of the absorption.

A $^{13}$C NMR spectrum consists of discrete, sharp lines corresponding to each non-equivalent carbon atom. These resonances are typically in the range 0 to 220 ppm with the TMS reference peak at 0 ppm. The main feature of $^{13}$C NMR
is its ability to give information concerning the chemical environment of carbon atoms. This helps to identify any functional groups present as well as giving clues towards the solution of the structure. 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 as "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.

### 2.1.3 ELECTRON SPIN RESONANCE SPECTROSCOPY

Electron paramagnetic resonance spectroscopy is a branch of absorption spectroscopy in which radiation of microwave frequency is absorbed by molecules possessing electron with unpaired spins. Gorter demonstrated$^{4,5}$ 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. The degeneracy of a paramagnetic ion is lifted in a strong static magnetic field 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 system includes elements containing 3d, 4d, 5d, 5f, 6d etc., electrons, atoms having an odd number of electrons like hydrogen, molecules containing odd number of electrons such as NO₂, NO etc., and free radicals which possess an unpaired electron like methyl, diphenylipecryl hydrazide, 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 later 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 neighboring, similar ions. The local field at any given site will depend on the arrangements of the neighbors 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. Thus 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 results 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 $E = h\nu = \frac{g\beta}{|B + B_N|}$ 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 super hyperfine structure. The effect
was first observed by Owens and Stevens in ammonium hexa chloroiridate and subsequently for a number of transition metal ions in various hosts.

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. \( d_{xy}, d_{yz}, d_{zx}, d_{x^2-y^2} \) and \( d_{x^2-z^2} \) 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 \( d_{zx} \)) and \( e_g \) (\( d_{x^2-z^2} \) 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 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 vectorically 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

\[ L = \sum m_l = 0, 1, 2, 3, 4, 5, 6. \]

\[ S, P, D, F, G, H, I \]

The total spin angular momentum \( S = \sum s_i \) where \( s_i \) is the value of spin angular momentum of the angular momentum of the individual electrons. The total spin angular momentum \( S \) 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 \( ^3P \) 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:

\[ d^1 d^9 : ^2D \]

\[ d^2 d^8 : ^3F, ^3P, ^1G, ^1D, ^1S \]
d^5 d^7 : 4F, 4P, 2H, 2G, 2F, 2D(2), 2P

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

d^5 : 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 ½) possible values of J representing state, arising from term splitting are 2, 1 and 0 and 4 ½, 3 ½, 2 ½, and 1 ½. Each state is 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 \( \text{Oh} \) as well as tetrahedral \( \text{Td} \) 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.

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 moment 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:

$$B/H = 1 + 4\pi(I/H) = 1 + 4\pi K$$

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 ($\chi_g$) 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:
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 thereby 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 on 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:

$$\chi_g = \frac{\Delta W}{W} \cdot \frac{W_{std}}{\Delta W_{std}} \cdot \chi_{std}$$
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Where \( \chi_g = \) Gram Susceptibility

\( \Delta W = \) Change in weight of the unknown sample with magnet on and off.

\( W = \) Weight of the known sample

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

\( W_{\text{std}} = \) Weight of standard sample.

\( \chi_{\text{std}} = \) Gram susceptibility of the standard sample.

2.1.6 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 (Ω), the units of \( \kappa \) are Ω\(^{-1}\) cm\(^{-1}\) or S cm\(^{-1}\) (Siemens per cm).
Molar Conductivity

If the conductivity $\kappa$ is in $\Omega^{-1} \text{cm}^{-1}$ and the concentration $C$ is in mol cm$^{-3}$, then the molar conductivity $\Lambda$ is in $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ 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 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 and 140-220 ohm$^{-1}$ cm$^2$ mol$^{-1}$ in methyl cyanide$^9$$^{11}$.

2.1.7 MASS SPECTROMETRY

In mass spectrometry, a substance is bombarded with an electron beam having sufficient energy to fragment the molecule. The positive fragments which are produced (cations and radical cations) are accelerated in a vacuum through a magnetic field and are sorted on the basis of mass-to-charge ratio. Since the bulk of the ions produced in the mass spectrometer carry a unit positive charge,
the value m/e is equivalent to the molecular weight of the fragment. The analysis of mass spectroscopy information involves the re-assembling of fragments, working backwards to generate the original molecule.

A very low concentration of sample molecules is allowed to leak into the ionization chamber (which is under a very high vacuum) where they are bombarded by a high-energy electron beam. The molecules fragment and the positive ions produced are accelerated through a charged array into an analyzing tube. The path of the charged molecules is bent by an applied magnetic field. Ions having low mass (low momentum) will be deflected most by this field and will collide with the walls of the analyzer. Likewise, high momentum ions will not be deflected enough and will also collide with the analyzer wall. Ions having the proper mass-to-charge ratio, however, will follow the path of the analyzer, exit through the slit and collide with the collector. This generates an electric current, which is then amplified and detected. By varying the strength of the magnetic field, the mass-to-charge ratio which is analyzed can be continuously varied.

The output of the mass spectrometer shows a plot of relative intensity vs the mass-to-charge ratio (m/e). The most intense peak in the spectrum is termed the base peak and all others are reported relative to it's intensity. The peaks themselves are typically very sharp, and are often simply represented as vertical
lines. The process of fragmentation follows simple and predictable chemical pathways and the ions, which are formed, will reflect the most stable cations and radical cations, which that molecule can form. The highest molecular weight peak observed in a spectrum will typically represent the parent molecule, minus an electron, and is termed the molecular ion (M^+). Generally, small peaks are also observed above the calculated molecular weight due to the natural isotopic abundance of ^13C, ^2H, etc. Many molecules with especially labile protons do not display molecular ions, an example of this is alcohols, where the highest molecular weight peak occurs at m/e one less than the molecular ion (M-1). Fragments can be identified by their mass-to-charge ratio, but it is often more informative to identify them by the mass which has been lost. That is, loss of a methyl group will generate a peak at M-15; loss of an ethyl, M-29, etc.

2.1.8 ELEMENTAL ANALYSES

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. Chloride was analyzed by conventional method^12. For the metal estimation^13, 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 chloride 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 silver nitrate solution. The precipitate was then dried and weighed.

2.1.9 JOB'S METHOD

Job's method of continuous variation is commonly used procedure for determining the composition of the complexes in solution. Job's method, as commonly practiced, is carried out in batch modes by mixing aliquots of two equimolar stock solutions of the metal and the ligand. These solutions are prepared in a manner such that the total analytical concentration of the metal and ligand is maintained constant, while the ligand: metal ratio varies from flask to flask, that is:

\[ C_M + C_L = k \]

Where \( C_M \) and \( C_L \) are analytical concentration of the metal and the ligand, respectively and \( k \) is the constant. The absorbance is plotted as a function of mole fraction (\( X \)) of the ligand or metal in the flasks.

Where, \( X = X_L \) or \( X_M \)

\[ X_L = C_L / (C_M + C_L) \]

\( X_L \) is the mole fraction of the ligand and \( X_M \) is the mole fraction of the metal.
The resulting curves, called as Job's plot, yield a maximum (or a minimum) the position of which indicates the metal: ligand ratio of the complex in solution. For example a maximum corresponding to 0.5 on the mole ratio fraction of the ligand scale suggest a complex of 1:1 composition, while a maxima at 0.67 and 0.75 indicate complexes of 2:1 and 3:1 stiochiometry, respectively.
REFERENCES


