CHAPTER 2
Experimental Methods
Various physico-chemical methods are available for the study of coordination compounds. A brief description of the techniques employed for the investigation of the newly synthesized compounds in the present work are described given below:

1. Infra-red Spectroscopy
2. Nuclear Magnetic Resonance Spectroscopy
4. Magnetic Susceptibility Measurements
5. Molar Conductance Measurements.
6. Elemental analysis

**INFRA-RED SPECTROSCOPY**

Infrared absorption spectra are commonly obtained by placing the sample in one beam of a double beam infrared spectrophotometer measuring the relative intensity of transmitted light and therefore the absorbed light energy versus wave number when the infrared light of the same frequency is incident on the molecule, energy is absorbed and amplitude of that vibration is measured. When the molecule reverse from the excited state to the original ground state, the absorbed energy is released as heat. The occurrence or non-occurrence of an infrared radiation is governed by the following selection rules.

(i). In order for a molecule to absorb infrared radiation as vibrational excitation energy, there must be a change in the dipole moment of the molecule as it vibrates.

(ii). In 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 state $V_0$ to $V_1$ the frequency corresponding to its energy is called the fundamental frequency.

The frequency of certain groups of atoms is called group frequency. These frequencies 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 infrared radiation is usually said to have wavelength lying between 0.8 $\mu$ to 1000 $\mu$. The wave number i.e. the number of waves per centimeter is used to characterize the radiation.
The characteristic group frequencies relevant to the present work have been described in
the following few paragraphs.

Savoie and Giguere have taken the IR spectrum of chlorosulphuric acid for the first
time in all three states upto 60°C. Chackalackal and coworkers have recorded the IR spectra
of HSO₃Cl monomer as well as in the associated form. They have assigned the frequencies
observed in the IR spectra of the monomer as the characteristic SO₂ rocking, S-Cl stretching,
S-O-H stretching, SO₂ symmetric stretching, SO₂ asymmetric stretching and OH stretching
vibrations. Later it was mentioned that the SO₃Cl anion which has the C₃v symmetry is
expected to show six modes of vibration as the symmetric SO₃ stretching ν₁ (A) and asym-
metric SO₃ stretching ν₄ (E), a symmetric SO₃ bending ν₃ (A) and asymmetric SO₃ bending
ν₅ (E), a S-Cl stretching ν₂ (A) and S-Cl wagging ν₆ (E). It has been confirmed from the study
of few alkali and alkaline earth metal chlorosulphates that the positions of these bands are
not much altered except that the symmetric SO₃ stretching ν₁ (A) vibration undergoes a
positive shift if there is an increased interaction between metal ion and SO₃Cl⁻ group.

The frequency observed in the IR spectra of different organic molecules are given below:

**Pyridine Ring Vibrations**

The vibration spectra of pyridine exhibit three important ring vibrations, viz. 16b
(out-of-plane ring deformation), 6a and 8a (in-plane ring deformation) occur at 403, 601 and
1578 cm⁻¹ respectively. It has been found that all the three bands undergo positive shifts on
coordination of pyridine to metal ions and the magnitude of the shift depends on the
stereochemistries of the complexes and on the metal atoms. It has been suggested that the
band at 601 cm⁻¹ is more sensitive to the stereochemistry of the complexes such that in
tetrahedral, polymeric octahedral and octahedral complexes, it appears at 642, 631 and 625
cm⁻¹ respectively. In few complexes, the doubling of the above mentioned pyridine bands
have also been reported which has been suggested to be due to some interaction between
different pyridine molecules either within a single molecule or between different molecules
of the unit cell.
Triphenylphosphine

The triphenylphosphine moiety shows strong bands in 500-1480 cm\(^{-1}\) region. The two strong bands, one at 742 cm\(^{-1}\) and another at 695 cm\(^{-1}\) are characteristic of a mono substituted benzene ring\(^6\). However, bands in the region 1092-1118 cm\(^{-1}\) may, reasonably, be assigned to \(\nu (P-C)\) modes\(^7\). A strong band at ca. 500 cm\(^{-1}\) is a diagnostic feature of the triphenylphosphine. The strong bands in the region 1430-1480 cm\(^{-1}\) are associated to benzene ring. The coordination of triphenylphosphine may be inferred by positive shift in \(\nu (P-C)\) mode and appearance of a new band at ca. 270 cm\(^{-1}\) assignable to M-P stretching vibration.\(^8,9\)

Pyridine N-oxide

The free pyridine N-oxide shows\(^10\) strong absorption at 1243 cm\(^{-1}\) characteristic of the N-O stretching frequency. It has been found that the frequency of the N-O band undergoes a negative shift (~25 cm\(^{-1}\)) in pyridine N-oxide complexes indicating coordination through oxygen of the N-O group.\(^11,11\) The band of medium intensity observed in the 360-390 cm\(^{-1}\) region may be due to metal-ligand (M-O) stretching vibration\(^12\).

Methyl cyanide

The methyl cyanide molecule which belongs to the point group \(C_\infty\) shows eight normal modes of vibrations\(^13\) of which four belong to the degenerate (E) modes. It has been indicated that this molecule can coordinate through nitrogen\(^14-17\) as well as via the triple bond\(^18\). The position of the characteristic vibrations are affected when methyl cyanide undergoes coordination to the metal ions. However, the nitrile frequency (\(C\equiv N, 2255\) cm\(^{-1}\)) shifts towards higher wave number (~35 cm\(^{-1}\)) if CH\(_3\)CN coordinates through the nitrogen atom.

N-H Stretching And Bending Frequency

The N-H stretching vibration occur in the region 3300-3500 cm\(^{-1}\) in dilute solution\(^19,20\). The N-H stretching band shifts to lower value in the solid state due to extensive hydrogen bonding. Primary amines in dilute solutions, in non-polar solvents give two absorption bands in the above mentioned region, the first of which due to symmetric stretching is usually found near 3400 cm\(^{-1}\) and second which corresponds to asymmetrical modes is found near 3500 cm\(^{-1}\). Secondary amines show only a single weak band in the 3350-3310 cm\(^{-1}\) region. Aliphatic primary amines (neat) absorb at 3400-3330 cm\(^{-1}\) and at 3330-3250 cm\(^{-1}\). Aromatic primary
amines absorb at slightly higher frequencies. However, the N-H bending frequency of primary amine occurs in the region 1650-1590 cm\(^{-1}\) while secondary amine appears in the region 1650-1550 cm\(^{-1}\).

C-N Stretching Frequency

The C-N stretching frequency of aliphatic primary, secondary and tertiary amine appear as medium to weak absorptions in the region 1250-1020 cm\(^{-1}\) whereas aromatic amines display strong C-N stretching absorption in 1342-1266 cm\(^{-1}\) region\(^{19,20}\).

M-N Stretching Frequency

The metal-nitrogen (M-N) stretching frequency is of particular interest since it provide direct information regarding coordination. It appears in the low frequency region. The M-N stretching frequency depends on the following factors:

1. Mass of the metal and ligand,
2. Oxidation number of metal ion,
3. Coordination of metal ion,
4. Geometry of complex,
5. Basicity of ligand molecule,
6. Bridging or non-bridging anions, and
7. Ligand field stabilizing energy.

M-O Stretching Frequency

Metal-oxygen stretching frequency has been reported to appear in different region for different metal complexes. The \(v (M-O)\) band is usually broad and strong as contrast to \(v M-N\) is usually sharp and strong.

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

The nuclei of certain isotopes possess a mechanical spin or angular momentum. The total angular momentum depends on the nuclear spin or spin quantum number \(I\) which may have the values \(0, \frac{1}{2}, \frac{3}{2}, \ldots\) (depending on the particular nucleus). The NMR spectroscopy is most often concerned with nuclei having \(I = \frac{1}{2}\), examples of which include \(^{1}H, ^{31}P\) and \(^{19}F\).
For a nucleus with $I = \frac{1}{2}$ there are two values for the nuclear spin angular momentum quantum number $m$, viz., $+\frac{1}{2}$ and $-\frac{1}{2}$ which in the absence of a magnetic field are degenerate. In presence of magnetic field however, this degeneracy is destroyed such that the positive value of $m$ corresponds to the lower energy state and the negative value to higher, separated by $\Delta E$. A nucleus with a magnetic moment can be visualized as bar magnet which spins on its axis. The magnetic moment interacts with the external field when the nucleus is placed in it and produces torque. This torque interacts with the angular momentum and causes magnetic moment to precess about the applied field vector, $H_0$. The angular frequency $\omega$, of the precession is referred to as Larmor frequency whose magnitude is determined by the expression given below:

$$\omega = \gamma H_0$$

The quantity $\gamma$ (radians gauss$^{-1}$ sec$^{-1}$) referred to as the magnetogyric ratio, is a constant for a given nucleus.

In an NMR experiment one applies strong homogeneous magnetic field causing the nuclei to precess. Radiation of energy comparable to $\Delta E$ is then imposed with a radio frequency transmitter is equal to the Larmor frequency the two are said to be in 'resonance' and the energy can be transferred to and from the source and the sample and NMR signal is obtained when a nucleus is excited from the low energy to the high energy state. The Larmor frequency is generally matched with a fixed radio frequency by varying the field strength $H_0$.

The magnitude of the field seen at the nucleus; $H_N$ is different from the applied field $H_0$ due to shielding by electrons and is given by the relation.

$$H_N = H_0 (1 - \sigma)$$

where $\sigma$ is a constant representing the shielding of the nucleus by the electrons. An accurate measurement of $H_N$ and $H_0$ is very difficult. Instead a reference material is employed and the difference in the field strength $H_R$ at which the sample nucleus absorbs and $H_N$ at which the nucleus in the reference compound absorbs is measured. The chemical shift $\delta$ which is independent of the field strength is defined as

$$\delta = \frac{\Delta \nu \times 10^6}{\text{fixed frequency of the probe}}$$
where $\Delta \nu$ is the difference in the absorption frequencies of the sample and reference in cps, 
the fixed frequency or the oscillator frequency is characteristic of the instrument. A 60 Mc 
instrument has an oscillator frequency of $60 \times 10^6$ cps. The factor $\delta$ is a dimensionless 
quantity expressed in parts per million (ppm).

ULTRA-VIOLET AND VISIBLE (LIGAND FIELDS) 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$_{z^2}$ 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$_{zx}$) 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 orbitals is reversed the e going below and t going above the 
original degenerate level when a molecule absorbs radiation its energy equal in magnitude 
to $h \nu$ and expressed by the relation,

$$E = h \nu$$

or $E = h c/\lambda$

where $h$ is Planck’s constant $\nu$ and $\lambda$ are the frequency and wavelength of the radiation 
respectively and $c$ is the velocity of 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 add upto zero. 
The total orbital angular momentum of an incomplete d shell electron is obtained by adding 
L value of the individual electrons, which are treated as a vector with the component ml in 
the direction of the applied field. Thus
The total spin angular momentum $S = \sum S_i$, 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 $^3P$ and similarly if $S = 1\frac{1}{2}$ and $L=3$, the term will be $^4F$.

In general the terms arising from a $d^n$ configurations are as follows:

- $d^1 d^9 : 2D$
- $d^2 d^8 : 3F, 3P, 1G, 1D, 1S$
- $d^3 d^7 : 4F, 4P, 2H, 2G, 2F, 2D(2), 2F$
- $d^4 d^6 : 5D, 5H, 5G, 5F(2), 3D, 3P(2), 1I, 1G(2), 1F, 1D(2), 1S(2)$

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 the resultant angular momentum denoted by the quantum number $J$ which may have quantized positive values from $|L+S|$ up to $|L-S|$. For example in 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 whose case spin-orbit interactions are large and electrons repulsion parameters decrease. 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, a D state splits into two and F state into three and a G state into four states are tabulated below. This holds for an octahedral 'Oh' as well as tetrahedral 'Td' symmetry.

<table>
<thead>
<tr>
<th>Term Symbol</th>
<th>State</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>A_1</td>
</tr>
<tr>
<td>P</td>
<td>T_1</td>
</tr>
<tr>
<td>D</td>
<td>E + T_2</td>
</tr>
<tr>
<td>F</td>
<td>A_2 + T_1 + T_2</td>
</tr>
<tr>
<td>G</td>
<td>A_2 + E + T_1 + T_2</td>
</tr>
</tbody>
</table>

Transition from the ground state to the excited state occur according to 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 of that for this ion in a tetrahedral field.

Sometimes due to transfer of charge from ligand to metal or metal to ligands, bands appear in the ultraviolet region of the spectrum. Such spectra are known as 'charge transfer spectra' or redox spectra. For 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.

**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. Most compounds of the transition ele-
ments 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 magnetisation. The ratio \( B/H \) is called the magnetic permeability of the material and is given by

\[
\frac{B}{H} = 1 + 4\pi \left( \frac{I}{H} \right)
\]

\[
= 1 + 4\pi K
\]

where \( K \) is called the magnetic susceptibility per unit volume or volume susceptibility. \( \frac{B}{H} \) 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 the sample. Thus the volume susceptibility of a vacuum is by definition zero since in vacuum \( \frac{B}{H} = 1 \)

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

\[
\mu_{\text{eff}} = 2.84 \left( \chi_m^{\text{corr}} \cdot T \right) \mu_B \cdot \text{M}
\]

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 (B.M.). The magnetic moment of a single electron is given by
\[ \mu_s ( \text{in B.M.}) = g \, (S \, (S+1))^{1/2} \]

where \( S \) is the spin quantum number and \( g \) is the gyromagnetic ratio.

For Mn\(^{2+}\) and Fe\(^{3+}\) and other ions whose ground states are \( S \) states there is no orbital angular momentum. In general however, the transition metal ions 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

\[ \mu_{s+L} = g \, (4S \, (S+1) + L \, (L+1))^{1/2} \]

in which \( L \) represents the orbital angular momentum quantum number for the ion.

The spin magnetic moment is insensitive to environment of metal ion, the orbital magnetic moment is not. In order for an electron to have an orbital angular momentum and consequently 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 \( A_{1g} \) and \( E_g \) terms, 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 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:

\[ \chi_g = \frac{\Delta W}{W} \cdot \frac{W_{\text{Std}}}{\Delta W_{\text{Std}}} \chi_{\text{Std}} \]
where

\[
\chi_g = \text{Gram susceptibility}
\]

\[
\Delta W = \text{Change in weight of the unknown sample with magnet on and off}
\]

\[
W = \text{Weight of the known sample}
\]

\[
W_{\text{Std}} = \text{Weight of standard sample}
\]

\[
\Delta W_{\text{Std}} = \text{Change in weight of standard sample with magnets on and off}
\]

\[
\chi_{\text{Std}} = \text{Gram susceptibility of standard sample.}
\]

**CONDUCTANCE MEASUREMENTS**

The conductivity measurement is one of the simplest and easily available technique, used for characterization of compounds. It gives direct information regarding whether a given compound is ionic or covalent. For this purpose the measurement of molar conductance \( \Lambda_m \) which is related to the conductance value in the following manner:

\[
\Lambda_m = \frac{\text{Cell Constant} \times \text{Conductance}}{\text{Concentration of solute expressed in moles cm}^{-3}}
\]

The solution of \( 10^{-3} \) M strength were used for the conductance measurement. Molar conductance values of different types of electrolytes in few solvents are given below:

A 1:1 electrolyte may have a value of 75-95 \( \text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1} \) in CH\(_3\)NO\(_2\), 50-75 \( \text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1} \) in DMSO, 72-90 \( \text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1} \) in DMF and 100-160 \( \text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1} \) in CH\(_3\)CN\(^{21-23}\). Similarly a solution of 2:1 electrolyte may have value of 150-180 \( \text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1} \) in CH\(_3\)NO\(_2\), 130-170 \( \text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1} \) in DMF and 140-220 \( \text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1} \) in CH\(_3\)CN\(^{21-23}\).

**Apparatus**

The special cell used for conductivity measurements in the present work is the same as was designed\(^{24}\) by solomons as shown in Fig. 1. It consists of a tube approximately 10 cm long containing the electrodes and joining two 100 ml conical flasks. The electrodes were made from platinum foil (1 cm\(^2\)) and was firmly fixed on the tube so that no displacement could occur. The conical flasks were fitted with a socket (B-14 standard joint) and were capped (B-14 standard joint) to exclude all moisture from the cell.
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 with a Thomas and Coleman analyser, Carlo Erba 1106. Sulphur and chlorine were analysed by conventional methods\textsuperscript{25}. For the metal estimation,\textsuperscript{26} a known amount of complex was decomposed with a mixture of nitric-, perchloric- and sulphuric acids in a beaker. It was then dissolved in water and made up to a known volume so as to titrate it with standard EDTA. Metal tellurium and tin were analysed by established methods\textsuperscript{26,27}. 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 dried and weighed.
REFERENCES