EXPERIMENTAL METHODS

Several Physico-chemical methods are available for the study of coordination compounds. The techniques used for the investigation of the structure of newly synthesized compounds described in the present work are as under:

1. Infra-red spectra
2. Ultra-violet and visible (ligand-field) spectra
3. Magnetic susceptibility
4. Molar conductance

It will, therefore, be quite appropriate to describe these technique in detail.

**Infrared spectra:**

Infrared spectroscopy is a very useful technique for ascertaining the coordination site and bonding in the complexes.

The infrared region extends from 25 \( \mu \) to 15 \( \mu \) (4000 to 667 cm\(^{-1}\)). The region from 0.8 \( \mu \) to 2.5 \( \mu \) (12,500 to 4000 cm\(^{-1}\)) called the near infrared region and that from
15/μ to 200/μ (667 to 50 cm\(^{-1}\)) is called the far infrared region. The compound whose spectrum is to be recorded may be solid, a liquid or a gas. The spectrum of a solid can be examined either in nujol or in Hexachlorbutadiene or KBr. The infrared frequencies are determined by the mechanical motion in the molecule while the intensities are related to electrical properties.

Various stretching and bending vibrations of a bond occur at certain quantized frequencies. When infrared light of the same frequency is incident on the molecule, energy is absorbed and the amplitude of that vibration is increased when the molecule reverts from the excited state to the original ground state, the absorbed energy is released as heat.

A non-linear molecule that contains \(n\) atoms has \(3n-6\) possible fundamental vibrational modes. Sometimes these vibrational modes are less than the expected number. Since the absorption of electromagnetic radiation in i.r. region is possible only when there is a change in the dipole moment of the molecule during the normal vibration if there is no such change, it will be "infra red inactive". The occurrence or non occurrence of an infra red radiation is governed by the following rules.
1) In order to a molecule to absorb infrared radiation as vibration excitation energy, there must be a change in the dipole moment of the molecule as it vibrates.

2) In absorption of radiation only transitions for which change in the vibrational energy level is \( V = \pm 1 \), can occur, since most of the transitions will occur from the state \( V_0 \) to \( V_1 \), the frequency corresponding to this energy is called the fundamental frequency.

While the complete normal coordinate analysis of a given molecule is necessary for prediction of all the bands in its I.R. spectrum, it is at times enough to consider the frequencies of certain group of atoms called "Group frequencies". These frequencies are characteristic of the groups, irrespective of the nature of molecule to which these groups are attached. The absence of any band in the appropriate region indicates the absence of that particular group in the molecule. Not all the vibrational frequencies however, are group frequencies. Each molecule undergoes vibrations which are characteristic of the molecule as a whole and are strongly dependent upon the geometrical arrangement in the space and the kind and masses of the molecule's constituent atoms. Such frequencies are called as fingerprint frequencies.
In addition to the group frequencies and fingerprint or characteristic frequencies, a spectrum of a substance shows overtone and combination absorption, which arise from multiples of fundamental frequencies. These absorptions are generally weaker than the fundamental frequencies. In the following paragraphs the characteristic frequencies which are required for the discussion of the compounds described in this work will be discussed.

**N-H Stretching:** The N-H Stretching vibrations occur in the region 3500 - 3300 cm$^{-1}$ in dilute solutions. The N-H stretching band shifts to lower value in the solid state due to extensive hydrogen bonding. Primary amines in dilute solutions, in nonpolar solvent give two absorption bands in the above mentioned region, the first of which due to symmetric stretch is usually found near 3500 cm$^{-1}$ and the second which corresponds to asymmetrical modes is found near 3400 cm$^{-1}$. These bands are usually 125-150 cm$^{-1}$ apart. Secondary amines show only a single N-H stretching in dilute solutions. The N-H band in pyrrole occurs at 3488 cm$^{-1}$ and the frequency range for substituted pyrroles has been found to be 3435-3400 cm$^{-1}$.

**N-H Deformation:** For the deformation frequencies of the NH$_2$ group in Primary amines four characteristic peaks
should appear, but the only definite assignment has been done in the case of scissoring vibrations, generally observed in the region 1650-1590 cm$^{-1}$. The lower frequency deformation vibrations of the NH$_2$ group have not been investigated in detail. The NH$_2$ twisting, wagging and torsional vibrations in methylamine have, however, been assigned to 1455, 780 and 265 cm$^{-1}$ respectively.

C-H Stretching Vibrations: The C-H stretching frequencies are found in the range 3100-3000 cm$^{-1}$. In aromatic compounds C-H absorption bands have been found in the region 3038 cm$^{-1}$. Many monosubstituted aromatic compounds show a characteristic triplet of this type at about 3058 cm$^{-1}$ in carbon tetrachloride solution, but there are some times more bands than this. In nearly all the cases, however, one band is stronger than others. Pyridine shows C-H absorption band in the range 3070-3020 cm$^{-1}$ which appears as a series of multiple absorptions under high resolution. The position and number of these bands vary with the substituents involved.

B-H Stretching Frequency: The BH$_2$ stretching absorption give rise to strong band in the region 2230-2460 cm$^{-1}$ and BH stretch appeared as a single peak at about 2470 cm$^{-1}$. 
C - H in Plane and out of plane Deformation: A number of characteristic absorption bands in the region 1250-1000 cm\(^{-1}\) are exhibited by most of the heterocyclic compounds and are attributed to C-H in plane deformation bands\(^7\). Bands appearing in the region 900-700 cm\(^{-2}\) have been attributed to the C-H out of plane deformation vibrations and the position of these bands depends on the number of free hydrogen atoms adjacent to one another\(^7\).

C = C and C = N Stretching: These frequencies occur from 1700-1575 cm\(^{-1}\). The C = N absorption in open-chain system or in non conjugated systems occurs within the range 1690-1640 cm\(^{-1}\) but in conjugated ring systems, both C = C and C = N stretching bands are present\(^7\). Therefore, the identification of C = N absorption is difficult due to interaction with C = C. Pyridine shows a C = N absorption band at 1580 cm\(^{-1}\).

C - N Stretching Frequency: The C - N stretching absorption gives rise to strong bands in the region 1350-1250 cm\(^{-1}\) in all the amines\(^7\). In aromatic primary amines there is one band in the region 1340-1250 cm\(^{-1}\) but in secondary amines two bands have been found in the region 1350-1280 cm\(^{-1}\) and 1280-1230 cm\(^{-1}\).
\textbf{M - N Stretching Frequency:} The M - N stretching frequency is of particular interest since it provides direct information regarding the coordinate bond. It appears in the low-frequency region. The M-N stretching frequency depends on the following factors:

i) Mass of the metal and ligand.

ii) Oxidation number of metal ion.

iii) Coordination number of metal ion.

iv) Geometry of the complex.

v) Basicity of the ligand molecule.

vi) Bridging or non-bridging anions.

vii) Ligand field stabilization energy.

\textbf{M - X Stretching Frequency:} The most widely investigated and probably the best understood aspect of the work on metal ligand vibration is that on metal-chlorine systems and to a lesser extent, metal-bromine and metal-iodine systems. Most of these frequencies lie below 400 cm$^{-1}$ region. Apart from the simple halide ions the commonest ligands are those in which the donor atom is carbon, nitrogen or oxygen. The vibrational frequencies associated with M-O, M-C and M-N bands cover large ranges which extend into the low frequency regions. Ligands involving non first row element
donor atoms (such as P, As, Sb, S, Se and Te) usually require low frequency measurements for location of the modes associated with metal ligand skeleton. The presence of the heavier atom in the ligand also gives rise to the low frequency ligand bands.

Metal-halogen stretching frequencies generally increase as the oxidation number of the metal increases. This might be expected on the grounds that, the greater the positive charge on the M ion, the nearer the negative X ion can approach and the more it will be polarized, thus leading to greater covalent character of the M-X bond. Lewis et al. have studied the complexes of the type $\left[\text{M(III)D}_2\text{Cl}_2\right]^+\text{ClO}_4^-$ and $\left[\text{M(III)D}_2\text{Cl}_2\right]^-$ $\text{M} = \text{Fe, Ru, Te, Os, Re}$; $\text{D} = \text{O-phenylene-bis dimethyl arsine}$. The infrared antisymmetric metal-chlorine stretching frequencies were observed at 373, 349 cm$^{-1}$; 340, 316 cm$^{-1}$; 343, 304 cm$^{-1}$; 322, 288 cm$^{-1}$; 325, 279 cm$^{-1}$ respectively, suggesting that the metal halogen stretching frequencies increase as the oxidation number of the metal increases.

Woodward and Taylor$^{82}$ have measured the totally symmetric stretching frequencies for $\text{InCl}_4^-$ (321 cm$^{-1}$); $\text{InCl}_5^2-$ (295 cm$^{-1}$); $\text{InCl}_5^3-$ (275 cm$^{-1}$), suggesting that for a given oxidation state of a metal, the metal halogen stretching
frequencies decrease as the coordination number of the metal ion increases.

It has been found that the metal halogen stretching frequencies depend on the mass \( M \), as the mass of the metal \( M \) increases the stretching frequencies will tend to decrease. In the complexes of the type \( \text{M(II)}D_2\text{Cl}_2/\text{M} = \text{Fe}, \text{Ru}, \text{Os} \), the Fe - Cl, Ru - Cl, Os - Cl stretching modes were observed at 349, 316, 288 cm\(^{-1}\) respectively, suggesting that there is a decrease in the M-Cl stretching frequency (cm\(^{-1}\)), on passing down the group. Similarly, for the \( \text{M(III)}D_2\text{Cl}_2/\text{ClO}_4^+ \) complex, the M-Cl stretching mode decreases in order Co-Cl (388 cm\(^{-1}\)), Rh-Cl(358 cm\(^{-1}\)) and Ir-Cl(335 cm\(^{-1}\))\(^7\). In the square planar Rh(I) and Ir(I) complexes, \( \text{Rh(Cl(PPh}_3)_2 \) and \( \text{Ir(Cl(PPh}_3)_2 \), Rh-Cl and Ir-Cl stretching modes were observed at 309 cm\(^{-1}\) and a pair at 317 cm\(^{-1}\) and 311 cm\(^{-1}\), respectively, suggesting that some bond strengthening might occur on passing from Rh to Ir, in these system\(^7\).

In the halogen bridged molecules of the type \( M_2X_6 \), in which the metal atoms have a square planar configuration, four stretching modes mainly associated with the bridging MX system and four mainly associated with the terminal M-X group are observed. The best known examples of ions of this type are the \( \text{Pt}_2X_6^{2-} \) and \( \text{Pd}_2X_6^{2-} \) systems, where \( X = \)
Cl, Br and I. Adams et al. have analysed the infrared spectra of such systems and on rough calculation, found that the M-Cl bridge bond stretching force constants ranged from 75-100% of those for the terminations. It has been suggested by Adams and Churchill that, in the square planar systems, the sharing of an edge results in little distortion of the metal-metal distance, whereas, if the two tetrahedra share an edge the metal atoms are brought more closely together which leads to electrostatic repulsion and a consequent lengthening of the bridge bonds.

Complexes of the type Rh$_2$X$_2$L$_4$, in which a square planar bridge is involved, have been investigated by Adams and Chandler. In these systems the spectra are not complicated by terminal Rh-Cl frequencies and the assignment is thus reasonably certain.

The complexes KCuCl$_3$, NH$_4$CuCl$_3$ and LiCuCl$_3$·2H$_2$O all contain the planar Cu$_2$Cl$_6$ ion. Adams and Lock have assigned the terminal bridging frequencies in these species and found that the two terminal modes lie very close together. In the complex Cu$_2$X$_4$ [Pyridine-1-oxide], the four halogens are all in terminal position, the copper atoms being bridged by the pyridine-1-oxide molecule. In this complex a single band at 315 cm$^{-1}$ with a shoulder at
325 cm\(^{-1}\) must be due to the terminal Cu-Cl stretching frequency. This strongly supports the assignments of the higher frequency band in \( \sqrt{\text{Cu}_2\text{Cl}_6} \) to the Cu-Cl terminal stretch 81.

**Ultraviolet and Visible (Ligand-field) Spectra:**

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 molecules from ground state to higher electronic state. While ultraviolet and visible spectra of organic molecules have been extensively studied, the application of ligand field spectra to coordination chemistry has come into fashion relatively recently. 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 ligand, 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 \( t_{2g} \) orbital goes below and the set of \( e_g \) orbital goes above the original level of the degenerate orbitals in an octahedral complex. In the case of tetrahedral complexes the position of the two sets of orbitals is reversed, the e set going below and the t set going above
the original degenerate level. When a molecule absorbs energy equal in magnitude to \( h\nu \) (where \( h \) is the Planck's constant and \( \nu \) is the frequency of radiation) which is sufficient to cause electronic transitions, the electrons are excited from the ground to the excited state.

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 configuration into groups of levels having lower degeneracies known as "term symbols".

The orbital angular momentum of electrons in a filled shell vectorially add up to zero. The total orbital angular momentum of an incomplete 'd' shell electrons is obtained by adding \( L \) values of the individuals electrons, which are treated as a vector with the component \( m_l \) in the direction of the applied field, thus

\[
L = \sum_i m_l_i = 0 \quad 1 \quad 2 \quad 3 \quad 4 \quad 5 \quad 6
\]

\[ S = \sum_i S_i \quad \text{where} \quad S_i \quad \text{is the value of spin angular momentum of the individual elec-} \]
trons. 'S' has a degeneracy equal to $2S + 1$, which is also known as "spin multiplicity". Thus a term is finally denoted as $^\Lambda L$. 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:

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

Coupling of $L$ and $S$ also occurs, because both $L$ and $S$ if non-zero, generate magnetic field and thus tend to orient their moment 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 $(L - S)$ eg
in case of \( ^3P \) \((L = 1, S = 1)\) and \( ^4F \) \((L = 3, S = 1\frac{3}{2})\) positive values of \( J \) representing states arising from term splitting are 2, 1 and 0 and 4\(\frac{1}{2}\), 2\(\frac{1}{2}\) and 1\(\frac{1}{2}\) respectively. Each state specified by \( J \) is \( 2J + 1 \) fold degenerate. The total number of states obtained from a term is called multiplet and each value of \( J \) associated with a given value of \( L \) is called a component. Spectral transitions due to spin orbit coupling in atoms 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 orbital interactions are relatively small, another scheme called "JJ coupling scheme" is used when spin orbital interactions are large and electron repulsion parameters decrease.

The spin angular momentum of an individual electron couples with its orbital momentum to give an individual \( J \) for that electrons. 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) Transition between states of different multiplicity are forbidden.

ii) Transitions involving the excitation of more than one electron are forbidden.

iii) In a molecule, which has a centre of symmetry,
transitions between two grade or two ungrade states are forbidden.

The ground term of a $d^n$ system is the one which has the highest spin multiplicity and the highest $L$ value. All the terms of a given system further split in the presence of a ligand field. Interelectronic repulsions within a configuration give the energies of the terms above the ground term. The energies are functions of two parameters related to the electronic repulsion. The two parameters may be chosen in either the way of Condon and shortly ($F_2$ and $F_4$) or in that of Racah ($B$ and $C$) for $d$ orbital electrons. For the first transition series ions the value of $C/B$ is around 4.0 and is about $1000 \text{ cm}^{-1}$. 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, $P$ state does not split, a $D$ state splits into two, $F$ state into three and a $G$ state into four states as tabulated below. This holds for an octahedral $O_h$ as well as for $T_d$ symmetry.

\[
\begin{align*}
S & \quad \rightarrow \quad A_1 \\
P & \quad \rightarrow \quad T_1 \\
D & \quad \rightarrow \quad E + T_2
\end{align*}
\]
In weak crystal fields the inter electronic repulsions are larger. The crystal field may however, be of comparable magnitude (medium strength) or it may be larger than the inter electronic repulsion.

Correlation diagram for free ion (weak field): Strong-field configuration from $d^1$ to $d^9$ for both octahedral and tetrahedral cases are available. In addition to the qualitative aspects of transition from weak to strong crystal fields it is necessary to have quantitative results available for the interpretation of spectra. The so called Tanabe-Sugano diagrams make it possible. In these diagrams the energies of the levels of a $d^n$ system as $E/B$ are plotted as the vertical coordinate and the crystal field strength in the form of $Dg/B$ as the horizontal coordinate. This diagram requires two parameters $B$ and $C$ for the interelectronic repulsions. It can be drawn only if the ratio $C/B$ is specified.

Transition from the ground state to the excited state occurs according to selection rules described earlier. The energy level order of the state 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 ligand, bands appear in the ultraviolet region of the spectrum. Such spectra are known as "charge transfer spectra". For metal complexes there are often possibilities that charge transfer spectra extend into the visible region to obscure d-d transitions. However, these should be clearly discerned from the ligand bands which might also occur in the same region.

**Magnetic Susceptibility:**

The most rewarding application of magneto-chemistry has been one which deals with the coordination compounds. This is because the more important aspects of magneto-chemistry are concerned with the effect arising from the incomplete shells of electrons, isolated from each other and these conditions are fulfilled by the complex compounds of the transition metals.

There are several kinds of magnetism in substances viz., paramagnetism, diamagnetism and ferromagnetism or antiferromagnetism. The magnetic effects arising from the
spin angular momentum and orbital angular momentum of the electrons give rise to paramagnetism. Most of the 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.

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 spin value, i.e., the contribution to the moment from only the electron spin effect, is given by the equation:

\[ \mu_s \text{ (in B.M)} = g \sqrt{S(S + 1)} \]

where \( S \) is the spin quantum number and \( g \) is the gyromagnetic ratio or g factor and \( \sqrt{S(S + 1)} \) is the value of the angular momentum of the electron. Thus \( g \) is the ratio of
the magnetic moment to the angular momentum. \( \mu_s \) is the spin magnetic moment of one electron in units of Bohr magnetons (1 B.M = e\hbar /4 mc).

When there is appreciable spin-orbit coupling in a molecule or ion which gives splitting of the ground state, that is, large compared to KT, \( \lambda \gg KT \); where \( \lambda \) is the spin orbit coupling constant \( J \), there will be an appreciable contribution to the moment from this coupling. The moment expected when spin orbit coupling is present is given by:

\[
\mu_{s,0} = g \sqrt{J(J+1)} \text{ B.M}
\]

where \( J \) is the total angular momentum of the ground state, given according to LS coupling, by \( \sqrt{L+S}, \sqrt{L+S} \rightarrow 1 \) \( \rightarrow \sqrt{L-S} \), if the shell is less than half filled with electrons, the ground state is \( \sqrt{L-S} \); and if it is more than half filled, it is \( \sqrt{L+S} \), for the gaseous atom, the g factor is given by the following formula:

\[
g = \frac{1 + J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}
\]

The value for the measured magnetic moments close to the spin only value are expected for the spin free six coordinate complexes: \( t_2g^3, t_2g^3e_1^1, t_2g^6e_2^2, t_2g^6e_3^3 \) and
for the spin paired complexes $t_2 g^6, t_2 g^6 e g^1$. For the first row transition metal ions in which quenching of the orbital contribution is expected to be complete, temperature independent paramagnetism accounts for the deviations of the measured moment, $\mu$, from the spin only moment, $\mu_s$. For those ions where spin-orbit coupling is appreciable the following equation shows the contribution of this effect to the measured moment

$$\mu = \mu_s \left[ \frac{(1-\alpha)\lambda}{\Delta} \right]$$

where $\alpha$ is a constant for a metal ion, $\lambda$ is the spin orbit coupling constant and $\Delta$ is the separation of the ground and excited states and can be obtained from the electronic spectra.

Generally the experimental effective magnetic moment of electron is higher than the spin magnetic moment of the electron. This is because the orbital motion of the electron also makes a contribution to the moment, if the orbital motion makes its full contribution to the magnetic moment then:

$$\mu_{S+L} = \sqrt{4S(S+1)+L(L+1)}$$
where $L$ is the orbital angular momentum quantum of the ions.

While 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 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.

Electrons in $d_y$ states cannot contribute to the orbital moment because the $d_{x^2-y^2}$ and $d_{z^2}$ orbitals cannot be transformed into one another by a rotation about any axis. However, all $dE$ states excepting $d^3$ and $d^6$ contribute to the orbital moment.

No orbital contributions are expected for octahedral high spin complexes of configuration: $d^3(d^3)$, $d^4(d^3d^2)$, $d^5(d^3d^2)$, $d^6(d^6d^2)$, $d^7(d^6d^2)$ while for $d^1(d^2)$, $d^2(d^2)$, $d^3(d^4d^2)$ and $d^4(d^5d^2)$ a non zero orbital moment contribution is possible. For low-spin complexes of octahedral symmetry and orbital moment contribution is seen for $d^4(d^4)$ and $d^5(d^5)$ and non for $d^6(d^6)$ and $d^7(d^6d^2)$.

In tetrahedral complexes due to term inversion it follows that where one does not expect orbital moment
contribution in $O_h$ symmetry one expects it in $T_d$ symmetry. For high-spin tetrahedral complexes no orbital moment contribution is, therefore, expected for $d^1\_1$, $d^2\_2$, $d^3\_3$, $d^4\_4$ while for $d^5\_5$ no orbital moment is expected. Low spin tetrahedral complexes for central ion of first transition series are not generally known.

An orbital moment contribution is expected for tetrahedral and octahedral complexes when the ground state is split. However, the terms splitting into a three-fold orbitally degenerate state $T$ will contribute but that splitting into a two-fold orbitally degenerate state $E$ will not contribute as it is non-magnetic. The one-fold orbitally degenerate state $A$ should give no orbital moment contribution.

Even when no splitting of the ground state appears in cases having no orbital moment contribution, an interaction with the higher states can appear due to spin-orbit coupling, giving an orbital moment transition metal series for the complexes, a decrease of the moment compared with the pure spin moment is expected, but in the second half of the series an increase should be seen. It has been found that for octahedral complexes there is appreciable orbital moment contribution and for tetrahedral complexes it is compara-
tively lesser.

The magnetic moments are not measured directly, therefore, one measures the magnetic susceptibility of a material from which it is possible to calculate the magnetic moment of the paramagnetic ion or atom.

If a substance is placed in a magnetic field of magnitude $H$, the flux $B$, with the substance is given by:

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

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

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

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 the sample. Thus the volume susceptibility of a vacuum is by definition zero since in vacuum it must be $B/H = 1$.

Conventionally instead of volume susceptibility, gram susceptibility ($\chi_g$) is used where magnetic suscepti-
bility is considered on weight basis. \( \chi_g \) when multiplied by the molecular weight of the complex and corrected for diamagnetic values give rise to \( \chi_M^{\text{corr}} \). The \( \mu \) value is calculated from the \( \chi_M^{\text{corr}} \) by the following expression:

\[
\mu_{\text{eff}} = 2.84 \sqrt{\chi_M^{\text{corr}} \cdot T \cdot \text{B.M.}}
\]

where 'T' is the absolute temperature at which the experiment is performed.

Magnetic susceptibility may or may not be dependent on the temperature as given by the Curie's law

\[
\chi_M^{\text{corr}} = \frac{C}{T}
\]

where 'T' is the absolute temperature and 'C' is a constant called Curie constant.

In general, however, deviations are found and \( \mu_{\text{eff}} \) value depends on temperature within a certain limit of temperature range \((20^\circ - 40^\circ\text{K})\). The dependence of \( \chi_M^{\text{corr}} \) upon T is given by

\[
\chi_M^{\text{corr}} = \frac{C}{T - \theta}
\]

This equation expresses what is known as the Curie-Weiss
law and $\theta$ is called the Weiss constant.

In some systems the deviation from the Curie law is due to interionic or intermolecular interaction. As a result of these interactions the orientations of the magnetic dipoles are influenced by the orientation of the neighbours. In such condition the magnetic moment at a given temperature is given by:

$$\mu_{\text{eff}} = 2.84 \sqrt{\chi_M^{\text{corr}}} \cdot (T - \theta)$$

Gouy magnetic balance is used for the measurement of magnetic susceptibility of the samples. In this method the sample was finally powdered and filled in the Gouy tube very carefully. The tube was suspended vertically between two poles of an electromagnet. The length of the tubes was adjusted in such a way that the lower end remained under the influence of the magnetic field. The weight of the tube containing sample was noted with the magnet on and off, the Gouy tube was calibrated with standard $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

The gram susceptibility was calculated by the following formula:

$$\chi_g = \frac{\Delta H \ln K}{W \ln K} \cdot \frac{W_{\text{std}}}{\Delta W_{\text{std}}} \cdot \chi_{\text{std}}.$$
\( \chi_g \) = gram susceptibility of unknown sample

\( \Delta W \ln K \) = change in weight of unknown sample with magnet on and off.

\( W \ln K \) = weight of unknown sample.

\( \Delta W \text{ std} \) = change in weight of standard sample with magnet on and off.

\( W \text{ std} \) = weight of the standard sample

\( \chi \text{ std} \) = gram susceptibility of the standard sample

\( \chi \text{ std} \approx 5.92 \times 10^{-6} \text{ for CuSO}_4 \) \text{ for unit } \text{ mmol}^{-1} \text{ L}^{-1} \text{ cm}^{-1} \)

\( \Delta W \) = corrected = \( \Delta W \text{(sample + tube)} - \Delta W \text{(empty tube)} \).

**Conductometry:**

Electrolytic conductivity is a measure of the ability of a solution to carry electric current. Solution of electrolyte conduct an electric current by the migration of ions under the influence of an electric field. Like the metal conductor they obey Ohm's law. Thus if two platinum electrodes are inserted into a solution of electrolyte and connected to a source of electricity, then the current \( I \) flowing through the electrolyte will vary inversely with the resistance \( R \) and directly with the applied potential
difference (E) this may be expressed as

\[ I = \frac{E}{R} \]  

(1)

where \( I \) is the current in amperes, \( R \) is the resistance in ohms and \( E \) is the applied potential difference in volts. The term conductance is defined as the case with which the current flows through the electrolytes. It can also be defined as the reciprocal of resistance.

\[ C = \frac{I}{R} \]  

(2)

The unit of conductance (C) is reciprocal ohm's or mhos.

The observed conductance \( C \) of a solution depends inversely on the distance \( l \) between two electrodes directly upon the area 'a', thus

\[ C = K \frac{a}{l} \]  

(3)

where 'K' is the specific conductance which is defined as the reciprocal of the resistance in ohm's of one cm. cube of liquid at a particular temperature. The unit of specific conductance is reciprocal ohm's or mhos.
The specific conductance is a suitable property for characterising metallic conductors, but it is not very good for electrolyte solution, because the specific conductance depends upon the concentration of solution as well, the electrical conductance of a solution depends upon the number of ions per unit volume of the solution and upon velocities with which these ions move under the influence of the applied electromotive force. As a solution of electrolyte is diluted, the specific conductance, $K$ in equation (3) will decrease, since the number of ions available to carry an electric current in each cubic cm solution will also decrease.

In order to express the ability of individual ions to conduct, a function called the equivalent conductance is employed. It may be derived from equation (3) where $(a)$ is the area of electrodes set one cm apart and are placed in an electrolyte solution containing one gm equivalent of the solute, if $C_s$ is the concentration of the solution in gm equivalent per litre then the volume of the solution in cubic centimeter per equivalent is equal to $1000/c\bar{s}$, then equation (3) becomes

$$\Lambda = \frac{1000 \, K}{C_s}$$

(4)
where \( \Lambda \) is the equivalent conductance of the electrolyte.

Generally, the electrolytes behave on dilution in two ways:

i) Electrolytes like NaOH and HCl have high value of conductivity even at low dilution and there is no rapid increase in their equivalent conductivity on dilution. Such electrolytes are called strong electrolytes. Mineral acids, alkali and alkaline earth hydroxides and most of other salts belong to this class.

ii) Electrolytes like acetic acid have a low value of equivalent conductivity at higher concentration and there is a rapid increase in their equivalent conductivity on dilution. Such electrolytes are termed weak electrolytes. Most of the organic acids and bases belong to this class.

The solution whose conductivity is to be determined is placed in a special type of cell known as conductivity cell. There are various type of conductivity cells. The cell is made up of pyrex glass and the electrode contains
platinum disc coated with finely divided platinum black welded to platinum wires and fused in two glass tubes. The glass tubes contain mercury and are firmly fixed in the ebonite cover of the cell so that the distance between the electrodes may not change during the experiment. Since the conductance changes with temperature, it is necessary to keep the conductivity cell containing the solution in a thermostat.

Generally, the measured conductances are different from the specific conductance as the electrodes are not exactly 1 sq. cm. in area and 1 cm apart. Therefore, the conductance will have to be multiplied by a certain factor in order to get the correct value of specific conductances.

\[
\text{specific conductance} = \frac{1}{a} \text{ conductance}. 
\]

The factor \(1/a\) is known as cell constant, the value of cell constant can be calculated from the following equation:

\[
\text{Cell constant} = \frac{\text{specific conductance}}{\text{measured conductance}} \quad (5)
\]

Once the cell constant has been determined, the molar conductance of an electrolyte solution can be easily obtained
by the following expression:

\[ \Lambda_M = 1000 \times \text{cell constant} \times \text{measured conductance} \]

concentration of solute expressed in mole cm

where \( \Lambda_M \) is the molar conductance of the solution.

Several studies of molar conductivities of different kinds of electrolytes in different solvents are now available and it is useful to compare \( \Lambda_M \) values of a given complex with that of the similar electrolyte. Conventionally solution of \( 10^{-3} M \) strength are used for the conductance measurement. Molar conductance value of different types of electrolytes in few solvents are given below:

A 1:1 electrolyte may have a value of 75-95 ohm\(^{-1}\) cm\(^2\) mole\(^{-2}\) in nitromethane, 50-75 ohm\(^{-1}\) cm\(^2\) mole\(^{-1}\) in DMSO and 70-90 ohm\(^{-1}\) cm\(^2\) mole\(^{-1}\) in DMF\(^{82-85}\).