CHAPTER 2

PHYSICAL METHODS USED IN THE STUDY

1. MOLAR CONDUCTANCE
2. MOLECULAR WEIGHT
3. MAGNETIC SUSCEPTIBILITY
4. ELECTRONIC ABSORPTION SPECTROSCOPY
5. INFRA-RED ABSORPTION SPECTROSCOPY
The modern co-ordination chemists have placed considerable emphasis on physical methods in order to understand their chemistry as well as to characterise the co-ordination compounds. Several other inorganic problems have also been solved by employing modern physical methods. A brief description of some of these methods made use of in the present investigations (given below) would, therefore, not be out of place:

1. Molar conductance
2. Molecular weight
3. Magnetic susceptibility
4. Electronic absorption spectroscopy
5. Infrared absorption spectroscopy.

1. MOLAR CONDUCTANCE:

This property is based on the fact that when an electrolyte is dissolved in water, it immediately dissociates into ions bearing positive and negative charges. When an electromotive force is applied, the electrodes attract the ions of opposite sign (i.e., cations towards cathode and anions towards anode). They are immediately discharged on reaching the electrodes. These charged ions are responsible for the conductance and are free to move independently. The fraction of the total
electrolyte dissociated into ions depends on the concentration and the "degree of dissociation". The following equation has been derived for the calculation of the "degree of dissociation".

\[ \lambda = \frac{(1 - 1)}{(n - 1)} \]

where \( \lambda \) is degree of dissociation; \( n \) is the number of ions in which each molecule of the electrolyte splits, and '1' is the Van't Hoff factor.

Thus by calculating '1' degree of dissociation may be calculated.

The results of conductance measurements are generally expressed in terms of the equivalent conductance \( (\Lambda) \) or the molar conductance \( (\mu) \) of the solution, because in the case of electrolytes the specific conductance, i.e., inverse of the specific resistance depends upon concentration.

The molar and equivalent conductivity may be defined as the conductivity multiplied by the volume in ml. containing one gram molecule or one gram equivalent of the electrolyte and is expressed by the relation

\[ \mu \text{ or } \Lambda = \frac{1000 K}{C} \text{ ohm}^{-1} \text{ cm}^{2} \]

where, \( K \) is the specific conductivity, and \( C \) is the concentration of the solution in g. mole or g. equivalent per litre. Since
the g. mol: and g. equivalent for uni-univalent electrolytes
is the same, their molar and equivalent conductivities will
be identical. Details of molar conductance are given in
standard works.

The molar conductance$^{1,2}$ of a uni-univalent salt, $\text{MA}$, will
be about 100-120 ohm$^{-1}$ cm$^2$, but that of $\text{M}_2\text{A}$ or $\text{MA}_2$ will be
about 240-250 ohm$^{-1}$ cm$^2$ approximately. The salts or complexes
of the type $\text{M}_3\text{A}$ or $\text{MA}_3$ and $\text{M}_4\text{A}$ or $\text{MA}_4$ will be about 360-400
ohm$^{-1}$ cm$^2$ and 480-500 ohm$^{-1}$ cm$^2$ respectively, and for a
nonionic compound Petersen$^3$ found the value equal or less than
8.4 ohm$^{-1}$ cm$^2$.

Sometimes the apparent molar conductivity of a compound
is greater than the predicted one. The cause of this enhanced
molar conductance was supported by Werner and Miolati,$^4$ by the
fact that the reaction between the compound and water does
take place, giving rise to a greater number of ions than the
predicted one.

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1 Glastone, S.; Textbook of Physical Chemistry, Second
2 Grinberg, A.A.; An Introduction to the Chemistry of Complex
2. MOLECULAR WEIGHT:

Since the stability of a complex ion is often greatly affected by changes of temperature, the cryoscopic method is by far the most valuable one for determining molecular weight for the purpose of investigating complex ions, because it involves minimum departure from ordinary temperature. The relationship between the depression of freezing point and vapour pressure enables one to determine the molecular weight of the dissolved substances. The extent of freezing point depression depends on the concentration of the solute and the following equation holds good for ideal dilute solution:

\[ M = 1000 \frac{K_f \frac{W_2}{\Delta T_f}}{W_1} \]

where, \( M \) is molecular weight of the solute, \( W_2 \) g., dissolved in \( W_1 \) g. of the solvent. \( \Delta T_f \) is the observed depression of freezing point and \( K_f \) is called the cryoscopic constant or molal depression constant of freezing point. Details of the determining molecular weight by the cryoscopic method are given in standard works.

The determination of molecular weight may be employed to determine the type of electrolyte if the true molecular weight is known or the true molecular weight if the type of the electrolyte is known. The chief advantages of the determination of molecular weight is only to supplement other methods of investigations.
The above two methods will enable one to find out the type of the electrolyte and the molecular weight of the complex.

3. **Magnetic Susceptibility:**

The determination of magnetic susceptibility\(^5,6\) is widely used to establish the structure of complexes, in conjunction with electronic spectra. When a substance is placed in a magnetic field, a magnetic moment is generated in a direction opposite to the applied field, due to field induced motion of the electrons. As a result if the material is repelled by a nonuniform magnetic field it is said to be diamagnetic. This diamagnetic effect exists only in the presence of a magnetic field. The substances containing one or more unpaired electrons, however, have a permanent magnetic moment, which also exists without any magnetic field and arises from the net spin and orbital angular momenta of the unpaired electrons. Such substances are said to be paramagnetic. In all substances containing unpaired electrons, the paramagnetic effect is dominant over diamagnetic effect, because the magnitude of the paramagnetic effect is approximately two times greater than diamagnetic effect.

The experimental measurement of magnetic properties generally determines the magnetic susceptibility, but a quantity of great interest to a modern inorganic chemist is the magnetic moment.


The volume magnetic susceptibility, $\chi$, is given by the relation

$$\chi = \frac{I}{H}$$

where, 'I' represents the intensity of magnetization induced by the field strength, $H$, per unit volume of the substance.

Since the volume susceptibility is a dimensionless quantity, hence magnetic susceptibility is generally defined as weight susceptibility, $\chi_w$, which is given by

$$\chi_w = \chi / \text{density (d)}$$

The molar susceptibility, $\chi_M$, is defined as

$$\chi_M = \left( \frac{M}{d} \right) \chi$$

where, 'M' is the molecular weight and 'd' represents density.

The experimental measurement of magnetic susceptibility consists of para magnetic and diamagnetic susceptibility, and hence measured susceptibility is corrected as follows:

Corrected paramagnetic susceptibility = Measured susceptibility - Diamagnetic susceptibility

The diamagnetic susceptibility is a negative value. The effective magnetic moment, ($\mu_{\text{eff}}$), may be calculated using the following relation

$$\mu_{\text{eff}} = 2.84 \left( \chi_A - \frac{1}{T} \right)^\frac{1}{2} \text{ B.M.}$$
where, $T$ is the absolute temperature, $\chi_A'$ is the corrected molar susceptibility and $\mu_{\text{eff}}$ is the magnetic moment of the substance under study. The unit of magnetic moment is Bohr Magnetons (B.M.), and the above equation holds good only to those substances which obey Curie law

$$\chi_A' = C / T, \text{ where } C \text{ is a constant.}$$

The relation of the magnetic moment to the number of unpaired electrons per molecule, $\mu$ is given by the relation

$$\mu = \sqrt{n(n+2)} \text{ B.M.}$$

The applications of magnetic data are given in standard works, and need no mention.

In short the magnetic susceptibility measurements may be used to study the bond type and structures of complexes. It may also be used to determine the various types of bonding possible in complexes, number of unpaired electrons, orbital hybridization, degree of covalent character, and possible structure of the complexes.

4. **ELECTRONIC ABSORPTION SPECTROSCOPY:**

The study of electronic absorption spectroscopy is most widely accepted in the wave length range 200 nm to 800 nm of the electromagnetic spectrum which corresponds to ultra-violet and visible region. The study of electronic spectra has helped in understanding (i) the transition in electronic states of
the molecules. (ii) the relation between electronic vibrational and rotational spectra, and (iii) the structure of the co-ordination compounds. In the last two decades, remarkably large interest has been observed in the transitional metal complexes and electronic spectra\textsuperscript{7-10} has played an important role in elucidating the structure of these complexes. The transition metal complexes display a great range of colours of varying intensity. These colours are the consequence of the absorption of visible electromagnetic radiations. They also absorb radiation of ultra-violet region.

During the absorption of electromagnetic radiation by a molecule which gets excited from a lower energy states to a higher energy states, in order that absorption takes place, the frequency of radiation should be equal to the difference between the lower energy states and the higher energy states.

In an octahedral environment the spin allowed d-d transitions\textsuperscript{11} for a d\textsuperscript{7} ion cobalt (II) are \(4 \emptyset_2 \rightarrow 4 \emptyset_1 (F) \rightarrow 4 \emptyset_1 (F) \rightarrow 4 \emptyset_1 (F) \rightarrow 4 \emptyset_1 (F) \rightarrow 4 \emptyset_1 (F).

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While in the case of tetrahedral symmetry the spin allowed d-d transitions\textsuperscript{12} are \(4 \, A_2 \rightarrow 4 \, T_2\); \(4 \, A_2 \rightarrow 4 \, T_1 \, (F)\) and \(4 \, A_2 \rightarrow 4 \, T_1 \, (P)\) and they are represented by \(\gamma_1\), \(\gamma_2\) and \(\gamma_3\) respectively. The following relationships are used to calculate \(\Delta\) and \(\beta\):

\[
\begin{align*}
\gamma_1 &= \Delta \\
\gamma_2 &= 1.5 \Delta + 7.5 \, B' - Q \\
\gamma_3 &= 1.5 \Delta + 7.5 \, B' + Q
\end{align*}
\]

where, \(B'\) is the effective value of the Racah interelectronic repulsion term in the complex

\[
\beta = \frac{B' \, \text{complex}}{B \, \text{free ion}}
\]

or

\[
\beta = \frac{B \, \text{free ion} - B' \, \text{complex}}{B \, \text{free ion}} \times 100
\]

For a strong field \(d^6\) complexes Cobalt (III) the spin allowed d-d transitions are \(1 \, A_{1g} \rightarrow 1 \, T_{1g}\); and \(1 \, A_{1g} \rightarrow 1 \, T_{2g}\).

Shibata and Urbain\textsuperscript{13} noticed that in cobalt complexes, two bands are always present, one of which occurs in the visible while the other in the near ultraviolet region.

Tsuchida\textsuperscript{14} proposed that the first absorption band in visible zone is a consequence of electronic transitions within the inner


\textsuperscript{13} Shibata and Urbain; Compt. rend., 157: 593, 1914.

\textsuperscript{14} Tsuchida; Bull. Chem. Soc., Japan, 11: 785, 1936.

electron rings of the transition metal ion, which is the nucleus of the complex. The second band is due to the electrons linking the ligands with the central metal ion.

Kuroya and Tsuchida, after obtaining ample experimental facts, showed that a third band is also present in such complexes which contain at least two negative ligands in trans position. This third band was absent when the negative ligands are adjacent to each other.

Basolo and Shimura raised question as to the extent the presence of the third band with two negative ligands can be taken as absolute. In cis-configuration of the complexes it does appear that the absorption band in ultra-violet region occurs at shorter wave lengths than the trans-configuration of the complexes. It has been observed that the absorption intensity of the cis complexes is nearly twice as great as that of trans compounds.

5. INFRA-RED SPECTROSCOPY:

In recent years, infra-red spectroscopy has been used extensively by the chemists and has become a routine method of analysis in every chemical laboratory. One of the greatest applications of vibrational spectroscopy is the determination of the structure of a molecule.

The infra-red region of the spectrum extends from the visible (700 nm) until it overlaps the microwave region. The first one extends from 700 nm to 2,000 nm (2\(\mu\)). The region from 2\(\mu\) to 16\(\mu\) is known as infra-red region.

The most fundamental information that can be obtained from infra-red spectra is the knowledge of interatomic force in terms of force constant within a molecule, which gives important information about electronic structure and bonding in a molecule. The intensity of infra-red spectra is related with dipole moment and polarizability of the molecule.

In the typical spectrum of an amine complex\(^{18}\) which is of particular interest w.v.t. the present work there are present the N-H stretching vibrations around 330 cm\(^{-1}\), actually a doublet in primary amine; the inplane (scissoring) bending of N-H at 1610 cm\(^{-1}\), and the out of plane bending of NH\(_2\) at about 830 cm\(^{-1}\), which is broad for primary amines. The series of weak bands between 3140 and 2500 cm\(^{-1}\) and the bond at 2040 cm\(^{-1}\) are due to NH\(_3^+\) group.

Several papers\(^{19}\) have been published to assign the absorption bands in simple amine complexes. These spectra have been analysed in terms of M - NH\(_3\) group. Generally four regions have been assigned near 3300, 1600, 1300 and 625 cm\(^{-1}\) for N - H stretching; NH\(_3\) degenerate deformation; NH\(_3\) symmetric deformation; and - NH\(_3\)


rocking, respectively. These assignments have been supported by Deuteration\textsuperscript{20} studies.

The carbonyl group\textsuperscript{21} may be recognised, though its exact position is uncertain and depends upon its environment. Kelones show absorption bands between 1725 and 1690 cm\textsuperscript{-1}. If an amide group is attached it will show absorption bands between 1690 - 1600 cm\textsuperscript{-1}.

Duval and his co-workers\textsuperscript{22,23} have studied many complexes using infrared absorption measurements. He showed that nearly all hexacovalent cobalt amine complexes absorbed in three principal regions. The first region, being quite intense, extends between 800 - 850 cm\textsuperscript{-1}. The second region of prominent absorption is due to deformation vibration of the amine group near 1300 cm\textsuperscript{-1}, and the third one near 1500 - 1600 cm\textsuperscript{-1} which is generally less intense.

\begin{itemize}
  \item \textsuperscript{20} Mizushima, S.; Nakagawa, I.; and Quagliano, J.V.; J. Chem. Phys., 23: 1367, 1955.
  \item Duval, Duval and Lecomte; Compte. rend., 224: 1632, 1947.
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