CHAPTER II

THE PRINCIPLES UNDERLYING THE PHYSICOCHEMICAL

METHODS EMPLOYED FOR CHARACTERISING COMPLEXES
A complete study of coordination compounds involves, in addition to their synthesis, their characterisation using various physicochemical methods. Apart from such routine measurements as analysis, conductance, molecular weight and magnetic susceptibility, some modern spectroscopic techniques involving various regions of electromagnetic radiations are also used. This chapter outlines the principles underlying the different physicochemical methods used in the investigation.

I. **CONDUCTIVITY AND MOLECULAR WEIGHT MEASUREMENTS**

These two colligative properties were measured to provide information regarding the number of ions in solution and the degree of dissociation of the complex molecule.

The conductance is expressed in terms of molar conductance represented by \( \lambda \) and is found to increase with dilution and to reach a maximum value at infinite dilution, i.e. \( \lambda_\infty \). In addition to water, some nonaqueous solvents have also been employed for such measurements. The value of \( \lambda_\infty \) in these has been found to be less than 1 mhos for non-electrolytes, but falls between 27-29 mhos for 1:1; 40-44 mhos for 1:2 and above 50 mhos for 1:3 electrolytes. The corresponding values for molar conductances in water are well known and comparison has been made with these for interpreting the values obtained.
Molecular weights could be determined only of those complexes which were appreciably soluble in water. The cryoscopic method was used. In all cases the values found were less than the calculated ones, and a calculation of Van't Hoff factor 'i', showed that the complexes dissociate in solution.

II. INFRARED ABSORPTION SPECTROPHOTOMETRY

Infrared spectroscopy has provided physicists and chemists with an extremely elegant and powerful tool for the elucidation of the structure of complex molecules. The infrared absorption spectrum of a molecule is highly characteristic and often has been referred to as a molecular "fingerprint". Great importance is attached to infrared spectroscopy for even isomers (which have the same atoms and the same bonds but different arrangement) can be distinguished.

Infrared spectra originate from the different modes of vibration (namely stretching and deformation etc.) and in order that a vibration may result in the absorption of infrared energy, that vibration must cause a change in the dipole moment of the molecule. The two important vibrations which are mainly affected on coordination, are stretching and bending or deformation. The stretching vibrations, as these require more energy, occur at shorter wave lengths while the bending vibrations are located at longer wave length as these
require less energy.

In case of the metal complexes containing amine as ligands, the important vibrational frequencies which offer evidence for coordination are symmetric and asymmetric N-H stretching and deformation, C-H stretching and M-N stretching. In aromatic amine complexes, in addition to these, C-C and ring stretching modes are also important\textsuperscript{211}.

N-H stretching vibrations are located in the region 3450-3050 cm\textsuperscript{-1} and the position, intensity and the shape of these depend upon the structure of the parent molecule. Primary amines show a doublet, secondary amines a singlet and tertiary amines do not absorb in this region. Coordination causes a considerable negative shift in the position of these bands.

The N-H deformation vibrations may be observed either due to in-plane or out-of-plane modes. Although coordination shifts these bands to higher wave numbers the assignment of these is usually found to be difficult.

The frequencies of C-N stretching vibrations are considerably lowered on coordination and these are specifically seen between 1100-1000 cm\textsuperscript{-1} and 1340-1250 cm\textsuperscript{-1} for primary aliphatic and aromatic amines, respectively\textsuperscript{212}.

The amine complexes are also characterized by the M-N stretchings, which are dependent upon many factors viz.,
oxidation number of metal, masses of metal and ligands, coordination number of metal, stereochemistry of molecule and ligand field strength. Due to the heavy mass of the metal, these are usually observed in the far infrared region \(213\).

In the spectra of aromatic amines some very characteristic intense bands are located in the region 3100-3000 cm\(^{-1}\) and 1600-1300 cm\(^{-1}\). These are C-H and ring stretching vibrations, respectively. In addition to these, the out-of-plane bending vibrations which are coupled with adjacent hydrogens bending in phase are also seen in the spectra of heteroamines, their positions depending upon the particular pattern of hydrogen atoms in the ring. Coordination of aromatic amines to the metals usually causes a positive shift in the position of these bands.

In the present complexes another important absorption band is the metal-oxygen stretching vibration which occurs as a medium to weak band in the range 550-350 cm\(^{-1}\) depending upon the mass of metal and bond order. The presence of these bands in the spectra is an indication that the oxalate and water groups are coordinated.

III. MAGNETIC SUSCEPTIBILITY

The measurement of magnetic susceptibility is very useful in the study of coordination compounds as it provides
direct information about the bond types and geometries of the complexes. For convenience, the substances have been roughly divided into three classes namely paramagnetic, diamagnetic and ferromagnetic.

Paramagnetism is attributed to intrinsic molecular current which gives the molecule a permanent magnetic moment and hence, has a permeability (μ) which is a positive quantity while, diamagnetism is due to molecular currents induced by an external field which gives rise to a magnetic moment in a direction opposite to that of the field and hence to a negative value of permeability. Paramagnetism is caused by the presence of unpaired electrons in the substance, and is independent of the magnitude of applied magnetic field, but is dependent on temperature while diamagnetic susceptibility is independent both of magnetic field and temperature.

For many cases, the permanent magnetic moment is a combined function of spin and orbital motion of the electron. During the experimental determination of magnetic moment, the quantity that is actually measured is X_g or gram susceptibility. It is multiplied by molecular weight to give X_M or molar susceptibility. It is necessary to apply a correction to this quantity called the diamagnetic correction which results from the demagnetism of the molecule. The magnetic moment is now calculated by the expression
\[
\langle \text{eff} \rangle = 2.83 \sqrt{X_M \cdot T}
\]

Its value is directly related to the number of unpaired electrons and helps in deducing the structure of molecules.

Copper(II), which is a d\(^9\) system has one unpaired electron regardless of the geometry of the complex, and the magnetic moment falls in the range 1.79 - 2.02 B.M. In this case, therefore, magnetic moment alone, is not helpful in determining the structure.

In case of nickel(II), a d\(^8\) system, the four covalent square planar complexes are diamagnetic, while tetrahedral complexes are paramagnetic. Among octahedral complexes, outer and inner orbital types can be distinguished as former are paramagnetic and later diamagnetic, respectively. Which of these structures will be taken up by the complex depends upon the relative field strength of the ligands\(^{214}\).

Cobalt(II) is a d\(^7\) system, and the value of magnetic moment depends upon the shape of the complex molecule and ligand field strength. In the tetra-coordinated cases, the square planar and tetrahedral geometries are characterised by one or three unpaired electrons, respectively and the magnetic moments fall in the range 1.8 - 2.9 B.M. and 4.20 - 4.80 B.M. The six-coordinate complexes are always octahedral but among these, inner orbital or low spin and
outer orbital or high spin types are also possible and magnetic moments are a great help in determining bond type as the former contain one and the latter, three unpaired electrons²¹⁵.

IV. ELECTRONIC SPECTROSCOPY

As mentioned in chapter I, the degenerate 'd' orbitals of the metal, under the influence of a ligand field are broken down into two levels, thus permitting the transition of an electron in the molecule from a lower 'd' level to a higher one. These d-d transitions are the origin of the characteristic colours and the absorption spectra of transition metal complexes²¹⁶, and are dependent upon the field surrounding the metal ion, i.e. the geometrical shape of the complex ion.

Copper(II) has \((t_{2g})^6(e_g)^3\) ground state configuration and the corresponding excited state in a planar structure is \((t_{2g})^5(e_g)^4\). The excitation of the single electron from \(t_{2g}\) level is responsible for the single band which is usually found in the range 22.22 - 12.50 kK in all copper(II) complexes.

The ground state for nickel(II) is always composed of a spin triplet regardless of the nature of the crystal field surrounding it. The ligand field stabilisation
parameters favour an octahedral arrangement around the metal, and by using detailed calculation it has been shown that either three or four absorption bands are present in such complexes 217.

The first absorption band which is located in the region 8.00 - 11.00 kK is the \( v_1 \) band which is equal to \( 10D_q \) and the \( v_2 \) and \( v_3 \) transitions are observed in the ranges 15.00 - 19.50 kK and 25.00 - 30.00 kK. It is also found, that irrespective of the ligand used, the ratio \( v_2/v_1 \) is always around 1.60.

Cobalt(II) has different ground states under different fields. In a weak octahedral field it is \( t_{2g}^5 e_g^2 \) and for stronger fields \( t_{2g}^6 e_g^1 \). An octahedrally coordinated cobalt(II) ion should have three spin-allowed transitions, from the ground state \( ^4T_{1g}(F) \) to \( ^4T_{2g}(F), ^4A_{2g}(F) \) and \( ^4T_{1g}(P) \). The first and last are observed around 20.00 and 8.50 kK, while the middle one is difficult to observe.

V. ELEKTRON SPIN RESONANCE SPECTROSCOPY

Absorption of the radiation of microwave frequency of molecules containing unpaired electrons is called electron spin resonance 218-220, and such electrons have a great tendency to show fine structure in their resonances due to coupling with spinning nuclei in their vicinity. Since electrons always possess a spin, they also have a magnetic moment, and hence the basic magnetic resonance theory applies to electrons as
well as to spinning nuclei. The electron spin magnetic moment is about 1000 times as great as a typical nuclear magnetic moment.

In ESR, a transition between the two different electron spin energy states occurs upon absorption of a quantum of radiation in the radiofrequency or microwave region. The energy $E$, of the transition is given by:

$$E = h\nu = \frac{\hbar I}{I} = g\beta H \quad -------- (1)$$

where $h, \nu, \beta$ and $H$ stands for Planck's constant, frequency of radiation, Bohr magneton and field strength, respectively; term "g" is called the spectroscopic splitting factor which is not a constant but a tensor quantity. Magnitude of "g" depends upon the orientation of the molecule containing the unpaired electrons with respect to the magnetic field. If the paramagnetic radical or ion is located in a octahedral or tetrahedral (i.e. Cubic crystalsite) site, the 'g' value is independent of the orientation of the crystal site but in lower symmetry the g-value depends upon the orientation of the crystal and is said to be anisotropic. Thus, we can say that the magnitude of the g-tensor provides definite information about ground and excited states of electrons in complexes.

Expressions for the g-values for copper(II) in a tetragonal field are: $^{221,222}$
\[ g_{11} = 2 \cdot 8 \lambda / (E_2 - E_0) \] \hspace{1cm} (2)

\[ g_1 = 2 \cdot 2 \lambda / (E_3 - E_0) \] \hspace{1cm} (3)

where \( E_0, E_2 \) and \( E_3 \) denote energies and \( \lambda \), spin orbit coupling constant.

VI. NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

The discovery of nuclear magnetic resonance spectroscopy by Purcell and Bloch in 1946, has now been recognized as a very important and powerful tool for the structural elucidation of inorganic complexes, mainly because

(a) the chemical shift leads to the identification of the groups present in the molecule.

(b) the area under the lines is proportional to the number of protons in the group.

(c) the fine structure of the line give information about neighbouring groups in the molecule.

Nuclear magnetic resonance is the study of transitions between magnetic energy levels of atomic nuclei that arises by placing a nucleus in a strong magnetic field. This transition corresponds to a change in the angle that the axis of the nuclear magnet makes with the applied magnetic field. This,
particular change can be brought about through the application of electromagnetic radiation whose magnetic vector component is rotating in a plane perpendicular to the main magnetic field.

Amines ordinarily give rise to single, sharp absorption lines, a behavior that indicates rapid chemical exchange of the amine hydrogen atoms. Aliphatic amines absorb in the region 7.8 - 9.7° and aromatic amines in the region 5.3 - 7.4°. These absorption values are shifted to higher field on dilution with inert solvents. Because the nitrogen nucleus has a spin of unity (I = 1), the absorption of a proton attached to nitrogen will in theory be split into a triplet, This behavior is observed for amines in acid solution.

In paramagnetic complexes, the effect of unpaired electrons in the metal ion are transferred to the ligand through the formation of covalent bonds e.g. in Co$^{2+}$($I = \frac{7}{2}$) complexes, the shifts are due to paramagnetic term which arises from a magnetic field — induced mixing of the $^{1}T_{1g}$ state with the ground state$^{223-226}$. The contribution to the chemical shift from this effect is inversely proportional to the energy separation of the two states.

In many paramagnetic complexes, the NMR spectra cannot be obtained because the unpaired electrons broaden the spectra by both dipolar and electron spin-nuclear spin coupling mechanisms.