EXPERIMENTAL TECHNIQUES

The different techniques are used to study structural features, nature of bonding and properties of the metal complexes. All such physiochemical techniques helps to ascertain the exact structure of metal chelates.

3.1 Magnetic susceptibility:

One of the most valuable fields of magnetochemistry is the investigation of transition metal complexes. The measurement of magnetic properties can provide information of the electronic structure, oxidation state and in some cases the symmetry properties of the transition metal central ion and nature of bonding in the complexes.

All substances possess magnetic properties and are affected in some way by the application of a magnetic field. The chemistry of the transition elements provides the most interesting field for magnetic investigation. This is due to the fact that the influences of neighbouring groups on the $d$ electrons of the metal ions are sufficiently strong to affect significantly their magnetic properties. The study of magnetic properties provides the mechanism of these interactions and can yield valuable information about the bonding and structures of transition metal complexes. Thus magnetochemistry is one of the most valuable techniques in the investigation of transition metal complexes [1-3].

The magnetic moment can be calculated by determining the magnetic susceptibility. This is a most useful parameter in the establishment of number of unpaired electrons and their distribution in orbitals around the central metal ion. The number of unpaired electrons and electronic configuration of the central metal ion decides the geometry of the metal complexes. The proper interpretation of observed magnetic data on the basis of valence bond and crystal field theories, is useful to obtain valuable information about oxidation state of the metal ion, type of bonding and structure of transition metal complexes. The magnetic properties of the metal complexes shows whether inner or outer d-orbitals are used and whether d-electrons are paired or unpaired in the complexes. This is useful in distinguishing the high spin and low spin metal complexes.

The ratio of intensity of magnetization induced due to the applied magnetic field is called as magnetic susceptibility. The intensity of magnetic field induced in
the substance depends on paired or unpaired electrons present in the orbitals of metal ion, based upon which the substances are classified as diamagnetic and paramagnetic. The induced magnetization in diamagnetic substance is always opposite in direction to the lines of forces of the external field, which results in a negative susceptibility of the diamagnetic material which ranges from $10^{-6}$ to $10^{-5}$ CGS units. Paramagnetism arises in substances containing unpaired electrons and induced magnetic field is parallel to the lines of force of external field. They have positive susceptibility in the order of $10^{-5}$ to $10^{-3}$ CGS units. The diamagnetic susceptibility is independent of the temperature while paramagnetic susceptibility varies inversely with the absolute temperature.

3.1.1 Experimental method:

The determination of magnetic susceptibility involves measurement of the force exerted by a homogeneous magnetic field on the sample under study. If the force acting on the sample under investigation is known, the magnetic susceptibility of the compound can be determined and from this, the value of the magnetic moment can be calculated.

Gouy’s method was used for the measurement of magnetic susceptibility of the compounds at room temperature. Gouy’s balance consists of an electromagnet with a suitable power supply and a single pan-semi microbalance, E-Mettler-Zurich, Swiss-make-H-1640 with maximum capacity 80 gm and a precision ± 0.01 mg.

The electromagnet consists of cylindrical poles, 15 cm in diameter tapering at ends at an angle of 45° and ending in circular faces, 3.5 cm in diameter. A gap of 4 cm is maintained between the two poles. The magnetic assembly having an electromagnet with capacity up to 7000 oersteds was placed around the tube, with a current of 6 amps fed by a suitable power supply.

The specimen tube made up of Pyrex glass, 14 cm in length and 3.5 mm in diameter with a Teflon stopper was used to hold the sample tube. The tube was supported and suspended freely in the magnetic field with the help of clean silver chain in such a way that its lower end was located at the center of the pole gap. The empty clean and dry tube was weighed successively when current is off and on with 4 amps and 6 amps. The field strength of the magnet and position of tube with respect
to poles remain unchanged during every measurement. The mean of five readings gave the value \( W_g \) for the empty tube.

### 3.1.2 Calibration of the specimen tube:

For accurate measurement of the magnetic moments, the tube constant was determined by using a substance of known magnetic susceptibility at room temperature. The standard substance used was mercury tetrathiocyanato-cobalt (II), which was prepared by the standard method given in the literature \(^1\). The measurement of the force developed on the specimen tube was recorded with two independent fillings of the substance. The compound under investigation was filled in a glass tube and packed in such a way to eliminate any air pockets. The gram susceptibility of the standard substance was taken as \( 16.44 \times 10^{-6} \) CGS units. The tube constant (\( \beta \)) was determined at room temperature, and was used for the calculation of magnetic susceptibility of metal complexes.

A typical data of the calibration is as follows:

- Weight of empty tube \( = 13.42435 \) gm.
- Weight of empty tube in the presence of magnetic field \( = 13.42150 \) gm.
- Force on the empty tube in the presence of magnetic field \( = 0.00285 \) gm.

<table>
<thead>
<tr>
<th>Weight of Hg[Co(NCS)(4)] (gm)</th>
<th>Temperature, ( ^0K )</th>
<th>Force on the sample (gm)</th>
<th>( \beta \times 10^6 ) (CGS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.28280</td>
<td>299</td>
<td>0.0200</td>
<td>232.46</td>
</tr>
</tbody>
</table>

### 3.1.3 Sources of error:

The main source of error in the Gouy’s method for solids arises from the improper packing of the sample. This can be reduced by repeating the measurements on homogeneously repacked samples until relatively constant values of gram susceptibility \( \chi_g \) are obtained. Agreement within 1 % is to be considered good.

### 3.1.4 Measurement of magnetic susceptibilities of metal complexes (Gouy balance method):

The finely powdered metal complex was filled in the experimental tube up to reference mark. The precaution was taken to ensure tight and uniform packing without any air gap in the column of sample. The teflon stopper was tightly fixed on the tube and the tube was suspended between the electromagnetic poles with the help
of silver chain suspension from the pan of the balance. Similar measurements were recorded which are described earlier.

From the experimental data, the magnetic susceptibility ($\chi_g$) of metal complexes was calculated from the following expression.

$$\chi_g = \frac{\beta \Delta \omega}{W}$$

Where,
- $\chi_g$ = susceptibility per gram of the substance.
- $\beta$ = tube constant (characteristic of the tube.)
- $\Delta \omega$ = force exerted by W gm of substance.
- $W$ = weight of the substance.

The molar susceptibilities ($\chi_M$) of complexes were then calculated by the expression.

$$\chi_M = \chi_g \times \text{Molecular weight}$$

The magnetic moments ($\mu_{\text{eff}}$) of the complexes were calculated from the value of $\chi_M$ by the equation.

$$\mu_{\text{eff}} = 2.84 \sqrt{\chi_A T}$$

where,
- $\mu_{\text{eff}}$ = Magnetic moment of the metal ion in Bohr magnetrons (B. M.)
- $T$ = Temperature in Kelvin scale.
- $\chi_A = \chi_{\text{corr.}} = \chi_M - \chi_{\text{diamagnetic (L)}}$

Magnetic susceptibilities obtained by subtracting the diamagnetic susceptibility of ligand molecule calculated by using Pascal’s constants.

$$\chi_{\text{diamagnetic (L)}} = \sum \chi_{\text{atomic correction}} + \sum \chi_{\text{multiple bonds}}$$

The reproducibility of magnetic susceptibility measurements of the complexes was within $\pm$ 2%. The diamagnetic susceptibility, ($\chi_{\text{diamagnetic}}$) of ligand molecules have calculated from Pascal’s constants $^{3,4}$. 

---

Chapter-III

62
3.2 Solution Conductivity:

It is one of the recent methods for studying the complexes. The solution conductivity depends on the concentration of solute and the number of charges on ions, which are formed on dissociation of an ionic material \(^5\). The solution of an electrolyte conducts electric current by migration of ions under the influence of electric field. Hence an ability of any ion to transport charge depends on mobility of ions. Therefore by measuring the solution conductivity one can decide the electrolytic or non-electrolytic nature of the metal complexes, which helps in ascertaining its ionic and covalent nature.

The molar conductivity $\mu_v$ of a solution of solute is a measure of the number and rate of migration of anions and cations in one mole of the solute. By comparison of molar conductivities of complexes with that of known simple ionic materials, the total number of charges on the species formed, when the complex dissolve can be deduced, this decides the composition of complexes by cryoscopy measurement together \(^6\).

3.2.1 Measurement of solution conductivity:

The solution conductivities of $10^{-3}$ M solutions of all metal complexes in DMF were measured on “EQUIPTRONICS” digital conductivity meter EQ-660 with range 20$\mu$Ω to 20 mΩ at 298 K temperature. As the conductivity of solution rises by about 2 percent per degree, the temperature must be controlled. A simple conductivity meter with dip type cell electrodes with cell constant 1.001 was used for this purpose. The instrument and conductivity cell were calibrated using 0.005M KCl, solution at room temperature.

In practice, the observed conductance ($x$) of solution was measured and specific conductivity $K_v$ was calculated by multiplying the cell constant with observed conductance. Finally from specific conductivity and molarity ($M$) of solution, the molar conductivity $\mu_v$ was calculated by equation \(^7\).

$$\mu_v = \frac{K_v \times 1000}{M}$$

Where, $M$- Molarity of a solution.

The molar conductivity has the unit $S \ cm^2 \ mol^{-1}$ or ohm$^{-1} \ cm^2 \ mol^{-1}$. The molar conductance values are interpreted with the help of literature data \(^8\-\!^10\).
3.3 Electronic absorption spectroscopy:

When continuous radiation passes through a transparent material, a portion of radiation may be absorbed and when residual radiation is passed through a prism, it gives a spectrum, called absorption spectrum. The absorption of ultraviolet (UV) or visible light results in a change in the energy of electrons of the absorbing molecule. The electronic spectrum consists of several absorption bands. Each band corresponds to a definite change in the electronic energy and individual lines within the band are due to specific transitions.

The structure of metal complexes can be predicted from the interpretation of their electronic absorption spectra and comparing them with the spectra of corresponding ligands. The complexes can be identified by their characteristic absorption bands, which is based on the positions of maxima and minima in the absorption spectra along with the molar extinction coefficient values. In the spectra of transition metal ions, basically bands are of three types,

I) Bands due to d-d transitions.

II) Charge transfer bands.

III) Bands due to electron transfer within the ligand.

In the transition metal complexes, a visible spectra arises when an electron is excited between $t_2g$ and $e_g$ orbitals with different energy levels. Charge transfer bands may arise from the transition of an electron from an orbital of ligand to the central metal atom. The molar extinction coefficient of a charge transfer band is about hundred times than that of d-d transition bands.

By recording absorption spectra of known molecule, the wavelength of radiation absorbed is correlated with the characteristic structural features. This information is then used in determining the structure of unknown molecules from their spectra\[11-12\]. In more stable complexes, the change in the spectrum of the ligand will depend on the degree of covalency of the metal ligand bond. The magnitude of the shift depends on the coordination number of the central atom and its ionic radius. In complexes, stability increases back coordination and charge transfer bands also appear besides the bands of the ligands. The UV/Vis spectroscopy is, therefore a powerful tool, for structure elucidation.
The correct interpretation of the absorption bands gives an insight into the energy of orbital, mode of bonding in the complexes and their geometries. By this means, it is possible to distinguish tetrahedral, octahedral, and square planar complexes and whether the shape is distorted or regular. Both the intensity and wavelength of absorption band is associated with resonance states of molecule. The intensity of absorption band is associated with energy difference between the ground and excited state of molecule. In general, there is an increase in intensity as the length of conjugation chain increases.\cite{13}

Most organic molecules absorb in the near UV region (200-400 nm) in which the solution is colorless where as transition metal complexes absorb in the visible region (400-800 nm) because of coloured solutions.

### 3.3.1 Scanning of UV/Vis. Spectra:

All Ru(III), Rh(III), Pd(II), Pt(IV) and Ir(III) complexes of Schiff bases in the present study are soluble in DMF/DMSO. Therefore absorption spectra of solutions were recorded on Jasco UV-530 spectrometer in the region 190-1100 nm using quartz optic tube of 2cm path length. Absorption spectroscopy of ligand is based on n→π* and π→π* transition. Many inorganic species show ligand to metal charge transfer (LMCT) transition and metal to ligand (MLCT) transitions (not as common as LMCT). Transition probably in ligand field transitions (d-d) transition is determined by the spin selection rule and the orbital selection rule.

### 3.4 Infrared spectroscopy:

IR radiation refers to that part of electromagnetic spectrum which is in between visible and microwave region. IR radiation occurs when the frequency of alternating field associated with the incident radiation matches a possible change in the vibration or rotational frequency of absorbing molecule. When the carbon skeleton of a molecule vibrates, all the bonds stretch and relax in combination. However some bonds stretch essentially independent of the rest of the molecule. This occurs if the bond is either,

1) Much stronger or weaker than others nearby, or

2) Between atoms that are much heavier or lighter than their neighbors.

Indeed, the relationship between the frequency of the bond vibration, the mass of the atoms is same as Hook’s law for a simple harmonic oscillator.
\[ \nu = \frac{1}{2} \pi c \sqrt{\frac{f}{c}} \]

The absorption of Infrared radiations causes an excitation of molecule from a lower to higher vibrational level. Each type of bond has a different natural frequency of vibration and since same type of bond in two different compounds is in two different environments, no two molecules of different structure have exactly the same infrared absorption pattern or infrared spectrum. Thus, the infrared spectrum can be used for molecules as a fingerprint, used for humans. Absorption of energy from infrared radiation occurs when the frequency of alternating field associated with the incident radiations matches a possible change in the vibration or rotational frequency of the absorbing molecule. It is suggested that, when metal ion combines with the ligands to form complex, its vibration spectrum is expected to change. The change in the vibration can be related to molecular symmetry or with the change in the individual frequency. A molecule can undergo two types of vibrations, stretching (\(\nu\)) and bending (\(\delta\)-deform). Stretching vibrations have higher frequencies than deformation.

Some of the important applications of IR spectroscopy are the identification of major types of bonds, various functional groups, hydrogen bonding in metal complexes and cis-trans isomers. One of the best features of IR spectroscopy in qualitative analysis is that, the absorption or lack of absorption in the specific frequency region can be corrected with specific stretching and bending modes and in some cases, with the relationship of these groups to rest of the molecule.

IR absorption occurs not only with organic molecules but also with covalently bonded metal complexes, which are generally active in the longer wavelength IR region. The inorganic complexes derived from organic chelating groups have a tendency to absorb in the IR region 400-660 cm\(^{-1}\) which is of greatest significance in the study of metal complexes\(^{[14]}\). IR studies thus provide much useful information about metal complexes.

**Scanning of IR spectra :**

The infrared spectra of ligands and metal complexes were recorded on a Jasco FTIR-4100 spectrometer over the range 4000 cm\(^{-1}\) to 400 cm\(^{-1}\) using KBr pellet technique.
3.5 Thermal analysis

Thermogravimetric analysis (TGA) is an experimental technique in which the weight or strictly speaking, the mass of the sample is measured as a function of sample temperature or time. The sample is typically heated at constant heating rate (so-called dynamic measurement) or held at a constant temperature (isothermal measurement), but may also be subjected to non-linear temperature programs such as those used in sample controlled TGA (so-called SCTGA) experiments. The choice of temperature programme will depend upon the type of information required about the sample. Additionally, the atmosphere used in the TGA experiment plays an important role and can be reactive, oxidizing or inert. Changes in the atmosphere during a measurement may also be made.

TGA is commonly employed in research and testing to determine characteristics of materials such as polymers, to determine degradation temperatures, absorbed moisture content of materials, the level of inorganic and organic components in materials, decomposition points of explosives, and solvent residues. It is also often used to estimate the corrosion kinetics in high temperature oxidation.

Thermogravimetric techniques have a very wide field of applications. The technique can be used in the examination of absorptive surfaces, together with the nature and processes involved in thermal decomposition and oxidation processes. The technique has also been applied to the examination of water of crystallization and in forensic work involving the identification and comparison of varnishes and other surface coatings. Thermo gravimetric analysis has also been involved in determining the age of art treasures, particularly paintings and in determining the stability of explosives. The technique is commonly used to control the dehydration procedures for crops particularly in the control of the drying processes used for tobacco. Thermo gravimetric analysis is also used extensively in the pharmaceutical industry in the examination of drug stability and the rate of degradation of certain drugs when exposed to air.

The majority of compounds, including complexes suffer physical and chemical changes when subjected to heat. Under defined experimental conditions, these changes are characteristic of the substance examined and can be used for its qualitative and quantitative analysis. The techniques in which changes in properties of substance are measured as a function of temperature, in controlled temperature...
program are known as thermo-analytical techniques. These methods are based upon the measurement of dynamic relationship between the temperature and some properties of substance such as mass, heat of reaction or volume.

When the sample to be analyzed is heated, various physicochemical changes like thermal decomposition, oxidation, dipole moment, electrical potential, magnetic susceptibility, crystal structure, electrical conductivity, water evaporation, sublimation may take place with a consequent change in the weight of the sample. Thermal decomposition studies of the substance are very useful in predicting the thermal stability of the substance. Chemical changes in the substance can be studied with the help of thermogravimetric analysis (TGA) and differential thermal analysis (DTA) and therefore thermal properties are among the important properties of substances. In the present study, we have used TGA and DTA techniques.

### 3.5.1 Thermo gravimetric analysis (TGA):

Thermogravimetry is a technique in which the change in the weight of a substance when heated or cooled at a controlled rate is recorded as a function of temperature and/or time. A plot of sample weight change as a function of temperature provides both qualitative and quantitative information of sample. It directly records the loss in weight as a function of temperature for transitions that involve dehydration or decomposition. Thermogravimetric curves are characteristic of a given compound or a material due to the unique sequence of physical transition and chemical reactions that occur over definite temperature ranges. Changes in weights are the results of breaking or formation of various bonds and evolution of volatile or heavier reaction products\(^\text{[15]}\). Kinetic studies of thermal decomposition reactions of a substance are of great importance in calculating various parameters like energy of activation (Ea), free energy change (ΔF), pre-exponential factor (Z), order of reaction (n), and entropy of activation (ΔS), which directly govern the factors of thermal stability of any substance.

The course and character of the TG curves are influenced by several experimental factors such as rate of heating, the atmosphere of the furnace, the geometry of the furnace and sample holder, particle size, heat of reaction and compactness of the sample.
3.5.2 Differential thermal analysis (DTA) :

The technique firstly developed by E.S.Watson and M.J O’ Neill in 1962 and introduced commercially at the 1963 Pittsburgh conference on analytical chemistry. The first adiabatic differential scanning calorimeter that could be used in biochemistry was developed by P. L. Privaiov and D. R. Monaselidze in 1964. The term DSC was coined to describe this instrument which measures energy and allows precise measurement of heat capacity. It may be stated that a single thermal property is not sufficient to characterize a chemical reaction or system, but that as many thermal methods as possible be employed.

Differential thermal analysis (DTA) is a thermal technique in which the heat effects, associated with physical or chemical changes are recorded as a function of temperature or time as the substance is heated at a uniform rate. Heat or enthalpy changes, either exothermic or endothermic are caused by phase transitions. Generally phase transitions, dehydration reactions, and some decomposition reactions produce endothermic effect, whereas crystallization, oxidation and some decomposition reaction produce exothermic effects. The heat effects occurring during these chemical and physical changes are measured by differential thermal analysis. Each substance will give a DTA curve whose number, size; shape and position of various endothermic and exothermic features serve as a means of qualitative information of the sample. The endotherms or exotherms can be used to calculate the heat of reaction or heat of phase transition. The area (A) of DTA peak is given by

\[
A = \pm \frac{G \ m \ \Delta H}{K}
\]

Where, \( G \) = sample geometry,

\( m \) = sample mass,

\( K \) = constant,

\( \Delta H \) (enthalpy change) = - ve \rightarrow \text{exothermic}

\[= + \text{ ve} \rightarrow \text{endothermic} \]

DTA is used to study the thermal stability of large number of metal complexes and organic compounds.

The thermogravimetric studies of metal complexes find extensive applications in determining the purity, metal-ligand bond strength and melting points\[16,17\]. The
simultaneous use of TG and DTA for the study of metal complexes provides the useful information. The TG is most useful when it complements DTA. The similarity in the values of thermodynamic and kinetic parameters indicates the basic steps involved in the thermal degradation of chelates are same [18]. The simultaneous use of TGA and DTA plays an important role in the study of thermal behaviour of the inorganic substances.

3.5.3 Scanning of TG-DTA curves:

The simultaneous thermo gravimetric and differential thermal analyses of representative metal complexes were performed on SDT Q600 V20.9 Build 20. in an inert nitrogen atmosphere over a temperature range of 0°C to 1000°C. The heating rate was 10°K min$^{-1}$ and flow rate of air 10 ml/min. The reference substance used was $\alpha$-Al$_2$O$_3$ in platinum crucible and samples weighed in the range 4 to 7 mg.

3.6 Powder X-ray diffraction:

X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. Max von Laue, in 1912, discovered that crystalline substances act as three-dimensional diffraction gratings for X-ray wavelengths similar to the spacing of planes in a crystal lattice.

X-ray diffraction is now a common technique for the study of crystal structures and atomic spacing. X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons toward a target by applying a voltage, and bombarding the target material with electrons. When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced. These spectra consist of several components, the most common being $K_{\alpha}$ and $K_{\beta}$. $K_{\alpha}$ consists, in part, of $K_{\alpha 1}$ and $K_{\alpha 2}$. $K_{\alpha 1}$ has a slightly shorter wavelength and twice the intensity as $K_{\alpha 2}$. The specific wavelengths are characteristic of the target material (Cu, Fe, Mo, Cr). Filtering, by foils or crystal monochromaters, is required to produce monochromatic X-rays needed for diffraction. $K_{\alpha 1}$ and $K_{\alpha 2}$ are sufficiently close in wavelength such that a weighted average of the two is used. Copper is the most common target material for single-crystal diffraction, with Cu$K\alpha$ radiation = 1.5418Å. These X-rays are collimated and directed onto the sample. As the sample and detector are rotated, the intensity of the reflected X-rays is recorded. Fig. 3.1 shows the schematic diagram of X-ray spectrometer.
When the geometry of the incident X-rays impinging the sample satisfies the Bragg’s Equation, \( n\lambda = 2dsin\theta \) (Fig.3.2) constructive interference occurs and a peak in intensity occurs.

This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, counted and processed by scanning the sample through a range of 2\( \theta \) angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d-spacing allows identification of the mineral because each mineral has a set of unique d-spacing. Typically, this is achieved by comparison of d-spacing with standard reference patterns.
The X-ray diffraction is a powerful method to understand the structure of the compounds. X-ray method, can determine the structure and symmetry properties of complexes. It gives information of inter atomic distance, bond angles and electronic arrangement in a complex.

It is possible to observe the molecules indirectly by using X-ray radiation of very small wavelength of the order of $10^{-8}$ cm and involves the studies of crystalline solids by the phenomenon of X-ray diffraction. When the beam of monochromatic X-ray strikes the plane of atoms in the crystal, an interference phenomenon is observed. Bragg’s equation gives the relation between inter planar distance and the diffraction angle.

$$n\lambda = 2d \sin \theta$$

Where,

$n =$ order of reflection.

$\lambda =$ Wavelength of X-rays.

d = inter planar distance and

$\theta =$ Angle of diffraction.

Constructive interference of the radiation from successive planes occurs when the path difference is an integral multiple number (n) of wavelength. This is the Bragg’s law. All crystals of a substance possess the same elements of symmetry. Bragg pictured the diffraction effect or a reflection of X-rays from the lattice planes of the crystal. The atoms in the plane are being responsible for scattering of the X-rays to an extent, dependent upon the number of its electrons. This has made a new and significant tool available to the crystallographers and as a result, an extensive amount of work on single crystal was carried out to reveal the internal structure of the compound and is a convenient and practical means for qualitative identification of crystalline compounds. Now a day, XRD is a well established and powerful technique to understand the internal structure of solids.

The procedure in analyzing the powder diffractogram of an unknown sample is consisting of measuring the intensities of the peaks, the diffraction angles $\theta$ or 2$\theta$. Once $\theta$ is determined, it is used for calculating the inter planer spacing d of reflection planes from the values of $\lambda$ of X-rays used, and then the dimensions of unit cell are
determined. Powder diffraction technique is very important method for the identification of unknown compound and applicable to all crystalline substances.

3.6.1 Scanning of X-ray powder diffraction and indexing of the data:-

The X-ray powder diffraction pattern of representative metal complex was scanned on Philips 50-70 PW –3710 diffractometer attached to a digital computer along with graphical assembly in which Cu-K radiation source connected with the tube Cu-Ni-40 Kv/40 mA producing 1.543 Å wavelength radiations was used with scanning rate 2°/min. Each test sample of 200-300 mesh size weighing minimum amount, 10 mg, was spread in the form of thin film and spectra were scanned in the range of 20 = 5 to 100°.

The data obtained was deduced using computer program Powder-X. The preliminary data in the form of 2θ and intensity ratio were fed to the computer and corresponding h, k, l values were assigned to each peak. The programme calculates the lattice parameters a, b, c (Å) and α, β, γ (degree) along with standard deviation in each. The crystal volume is also obtained from the unit cell data.

The pyknometric densities of each of the complexes were determined using specific gravity bottle by the principle of Archimedes. The density is related to the formula factor as follows:

\[ D = \frac{Z \times F \times M}{V} \]

Where,

\( Z = \) Number of formula units in the cell.
\( F = \) Formula weight of compound.
\( M = \) Mass of hydrogen atom in amu.
\( V = \) Crystal volume.

The calculated densities were correlated with the experimentally obtained densities. The observed densities were used to fix the value of Z to the nearest whole number. By using literature values for definite crystal system, probable space group was assigned to each of the complexes.

Once the dimension of the unit cell, the density and the chemical composition of crystals are known, the number of atoms per unit cell can be established. From the space group, number of atoms in equivalent position contained by the unit cell can be deduced. In this way the unit cell represents the lattice structure of a crystal.
3.7 $^1$HNMR spectroscopy:

Nuclear magnetic resonance involves the interaction between an oscillating magnetic field of electromagnetic radiation and the magnetic energy of the hydrogen nucleus or some other type of nuclei [23]. The sample absorbs electromagnetic radiation in the radio wave region. Proton nuclear magnetic resonance (¹H NMR) spectroscopy is concerned with the proton (¹H) nuclei having spin quantum number I=1/2. In this technique, the absorption of radiofrequency radiation by an organic molecule induces changes in the magnetic properties of ¹H atomic nuclei in that molecule. The frequency at which proton absorbs energy depends on the electronic environment. So, by ¹H NMR spectroscopy, it is possible to locate the protons with different environment which absorbs at different frequencies. The resulting spectrum can be integrated for the number of chemically equivalent protons present in the molecule.

As any spinning charged body generates magnetic field, the proton possessing both electric charge and mechanical spin also generates magnetic field and behaves like tiny spinning bar magnet. Like all bar magnets, the proton orient itself under the influence of external magnetic field, either aligned ($\alpha$-spin state) with the field or opposite to the field ($\beta$-spin state). Thus, it is said to have precessional motion with frequency ($\nu$) directly proportional to the strength of external field ($B_0$). If the precessing proton is irradiated with beam of radiofrequency radiation, it will absorb the radiation energy from the source only when its precessional frequency is same as that of the frequency of incident rf-radiation. When such situation arises, flipping of the spin of proton from $\alpha$-spin to $\beta$-spin takes place, and the proton is said to be in a state of resonance with the radiofrequency radiation and hence the term proton nuclear magnetic resonance. At resonance, there is a continuous excitation and relaxation of proton. In ¹H NMR, the precessional frequency of proton under resonance is measured. Actually protons differently situated in the molecule are magnetically non-equivalent and come successfully into resonance as the field is varied. The energy of resonance is dependent upon the electronic environment about the nucleus. The electron density around proton, shields the nucleus from the influence of applied field ($B_0$), so that the field experienced by the nucleus is different than the applied field. This affects the precessional frequency of the nucleus. More the electron density, greater the shielding effect, lower would be the precessional frequency. The opposite of this character is deshielding effect caused by less electron density. Greater the deshielding effect, higher the precessional frequency. The effective field is given by
\[ B_{\text{eff.}} = B_0 (1 - \delta) \]

Where - \( \delta \) is shielding constant.

The value of \( \delta \) is different for different protons of different functional groups. The required applied field will also be different for different functional group protons. The areas under the peaks are in direct ratio to the number of equivalent protons. Since the precessional frequency (\( \nu \)) is proportional to applied magnetic field (\( B_0 \)), by holding the radio frequency constant at 60 or 100 MHz, and varying \( B_0 \), an increase or decrease in the precessional frequencies of all the proton nuclei can be achieved until each turn reach 60 to 100 MHz and come to resonance with the radio frequency source. In a typical proton spectra, the differences in the position of absorption peaks are small, usually of the order of a few hundred Hz compared to the absolute value of the frequency which is around 107 Hz. The position of an absorption peak in the spectra is therefore denoted not by its absolute frequency value, but by the relationship to that of a reference compound, Hz up field or downfield from the reference. The normal reference compound is tetramethylsilane [(CH\(_3\))\(_4\)Si. TMS] in which all the protons are equivalent and highly shielded and exhibit a single band at high applied field well beyond the band due to protons in most organic compounds. The proton nuclei in vast majority of organic compounds absorb downfield from the TMS peak. In a proton spectrum, the position of an absorption peak relative to that of reference compound TMS is referred as chemical shift.

In order to make direct and rapid comparison between spectra recorded on instruments operating at different frequencies, the chemical shift is normally quoted on the \( \delta \) (delta) scale which is independent of the instruments operating frequency. The \( \delta \) value is obtained by dividing the position in Hz by the instrument frequency in MHz and is expressed in parts per million (ppm). These values can be calculated using the expression:

\[ \delta_x = \frac{\nu - \nu_{\text{TMS}}}{\nu_0} \]

Where \( \delta_x \) = Chemical shift
\( \nu_x \) and \( \nu_{\text{TMS}} \) = Frequencies in Hz of the signal for sample x and TMS respectively.
\( \nu_0 \) = Operating frequency of the instrument in MHz.
Factors such as electro negativity, density of electron cause particular nuclei to appear at different chemical shift (\(\delta\)). The scale is from up field to downfield (\(\delta = 0\) to \(\delta = x\)). The scanning of \(^1\)H NMR spectra of ligands is done as discussed earlier in Chapter II.

### 3.8 Mass spectroscopy:

Mass spectrometry (MS) is an analytical technique that ionizes chemical species and sorts the ions based on their mass to charge ratio. In simpler terms, a mass spectrum measures the masses within a sample. Mass spectrometry is used in many different fields and is applied to pure samples as well as complex mixtures. A mass spectrum is a plot of the ion signal as a function of the mass-to-charge ratio. These spectra are used to determine the elemental or isotopic signature of a sample, the masses of particles and of molecules, and to elucidate the chemical structures of molecules, such as peptides and other chemical compounds. Mass spectrometry is the most accurate method for determining the molecular mass of compound. In this technique molecules are bombarded with a beam of energetic electrons. The molecules are ionized and broken up into many fragments, some of which are positive ions. Each kind of ion has a particular ratio of mass to charge i.e. m/e ratio. For most of ions, the charge is one and thus, m/e ratio is simply the molecular mass of the ion. The molecular ion is called parent ion and is usually designated as \(M^+\). The set of ions is analyzed in such a way that a signal is obtained for each value of m/e. the intensity of each signal represents the relative abundance of the ion producing the signal. The largest peak in the structure is called the base peak and its intensity is taken as 100.the intensities of other peaks are represented relative to the base peak. The mass spectrum is a plot representing the m/e values of various ions against their corresponding relative abundances. The peak on the extreme right corresponds to the molecular mass of the original molecule. In aromatic compounds, \(M^{+}+ 1\) and \(M^{+}+ 2\) peaks are also noticed.
3.9 References:


*****