Chapter-4
Optical Characterization and Magnetic Moment

4.1   Characterization of crystals

The present chapter deals with the characterization schiffbase and crystals by

(I)   IR Spectral studies,

(II)   Reflectance Spectroscopy Analysis.

(III)   Magnetic Moment Study

4.2   Infrared Spectroscopy

The atoms of a molecule behave as if they were connected by flexible spizings, rather than by rigid bound resembling the connectors of a ball and stick model. Their component parts can oscillate in different vibrational modes, designed by such terms as rocking, scissoring, twisting, wagging and symmetrical and asymmetrical stretching. When inform red radiation is passed through a sample of a given compound its molecules can absorb radiation of the energy (and frequency) needed to bring about transition between vibration ground states and vibration excited states.

For example, a C-H bond that vibrates 90 trillion times a second must absorb infrared radiation of just that frequency to jump to its first vibration excited state. This absorption of energy at various frequencies can be detected by an infrared spectrometer, which plots the amount of infrared radiation transmitted through the sample as a function of the frequency (or wavelength) of the radiation. An infrared spectrum consists of comparatively broad absorption bands rather than sharp peaks such as those seen in NMR spectra. The bands are also usually "INVERTED"-a deep valley rather than a peak represents strong absorption.

Infrared spectroscopy is extremely useful [1-5] in qualitative analysis. It can be used both to detect the presence of specific functional groups and other structural features from band positions and intensities, and to establish the identify of an unkmency compound with a known standard. The fingerprint region of the infrared spectrum, (1250-670 cm^{-1}, 8-15 lym) is best for showing that two substances are identical, since the distinctive patterns found in this region are usually characterizes of the whole molecule and not of isolated groups[6-9]. Infrared spectra can also be used in establishing the purity of compounds, monitoring reaction rates, measuring the constructions of solubility's, determining the structures of complex molecules, and carrying out theoretical studies of hydrogen bonding in other phenomena[10-12].

Infrared spectroscopy has been a workhorse technique for materials analysis in the laboratory for over seventy years. An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. Because each different material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum[13-16]. Therefore, infrared spectroscopy can result in a positive identification (qualitative analysis) of every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present[17-21]. With modern software algorithms, infrared is an excellent tool for quantitative analysis

FT-IR stands for Fourier Transform InfraRed, the preferred method of infrared spectroscopy. In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint no two unique molecular structures produce the same infrared spectrum. This makes infrared spectroscopy useful for several types of analysis[22].

Fourier Transform Infrared (FT-IR) spectrometry was developed in order to overcome the limitations encountered with dispersive instruments. The main difficulty was the slow scanning process. A method for measuring all of the infrared frequencies simultaneously, rather than individually, was needed. A solution was developed which employed a very simple optical device called an interferometer. The interferometer produces a unique type of signal which has all of the infrared frequencies "encoded" into it. The signal can be measured very quickly, usually on the order of one second or so. Thus, the time element per sample is reduced to a matter of a few seconds rather than several minutes. Most interferometers employ a beam splitter which takes the incoming infrared beam and divides it into two optical beams. One beam reflects off of a flat mirror which is fixed in place. The other beam reflects off of a flat mirror which is on a mechanism which allows this mirror to move a very short distance (typically a few millimeters) away from the beam splitter. The two beams reflect off of their respective mirrors and are recombined when they meet back at the beam splitter. Because the path that one beam travels is a fixed length and the other is constantly changing as its mirror moves, the signal which exits the interferometer is the result of these two beams "interfering" with each other. The resulting signal is called an interferogram which has the unique property that every data point (a function of the moving mirror position) which makes up the signal has information about every infrared frequency which comes from the source. This means that as the interferogram is measured; all frequencies are being measured simultaneously. Thus, the use of the interferometer results in extremely fast measurements. Because the analyst requires a frequency spectrum (a plot of the intensity at each individual frequency) in order to make identification, the measured interferogram signal can not be interpreted directly. A means of "decoding" the individual frequencies is required. This can be accomplished via a well-known mathematical technique called the Fourier transformation. This transformation is performed by the computer which then presents the user with the desired spectral information for analysis.

The fundamental absorption refers to band or to exciting transitions, i.e. to the excitation of an electron from the valence band to the conduction band.

The fundamental absorption, which manifests itself by a rapid rise in absorption, can be used to determine the energy gap of the semiconductor. However, because the transition are subject to certain selection rules, the estimation of the energy gap from the "absorption edge" is not a straightforward process-even if competing processes can be accounted for.

Because the momentum of a photon, h/λ (λ is the wavelength of light thousands of angstroms), is very small compared to the crystal momentum h/a ('a' is the lattice constant, a few angstroms), the photon-absorption process should conserve the momentum of the electron. The absorption coefficient α(hν) for a given photon energy hν is proportional to the probability p_{if} for the transition from the initial state to the final state and to the density of electrons in the initial state n_i and also to the density of available (empty) final state n_f , and this process must be summed for all possible transitions between states separated by an energy difference equal to hν.

The main types of light absorption in this type of crystals occurs because of

1. **Intrinsic, or fundamental light absorption** results in the transition of electrons from the bound to the free state, i.e. from the valence to the conduction band. Intrinsic absorption is possible if $\hbar\omega \geq \Delta E_0$. Depending on the forbidden band width it takes place in the visible or in the near infrared part of the spectrum.

2. **Impurity absorption** is due to the ionization of the impurity atoms, i.e. the transition of electrons from impurity atoms to the conduction band or from the valence band to the impurity level.

3. **The absorption by free charge carriers** takes place as a result of their motion induced by the electric field of the light wave. The wave spends some of its energy to accelerate the carriers and is thereby attenuated.

4. The light wave interacts with the lattice vibrations with the resultant change in the number of optical photons. This absorption is termed **lattice absorption**.

5. Light absorption accompanied by the formation of bound electron-hole pairs is termed **exciting absorption**.

6. **Internal-band absorption** is observed in solids with a complicated band pattern, such as the valence band of germanium and silicon.

7. Light absorption by an ensemble of free electrons and holes is termed **plasma absorption**.

4.2.1 Experimental

Infrared scanning for the schiffbase and crystals were made in the range 4000-600cm^{-1} in KBr. AR grade KBr was used for this purpose. It was first fused, powdered and dried in vacuum. The absence of moisture in this dried KBr pellet was checked by scanning the IR spectra of purified KBr. Then the pellet of KBr with polymer was prepared as under.

A mixture of 4mg of pure dried sample and 1 gm KBr powder was ground in a mini ball mill for about 10 minutes. The resulting mixture was placed on the disc and compressed at high pressure about 20,000 psi giving the transparent pellet. The IR spectrum of this transparent pellet was scanned on Nicolet FTIR-760 spectrophotometer shown in figure 4.1.

4.2.2.1 F.T.I.R Spectrometer

Figure 4.1: FTIR spectrometer

Make Model: Perkin Elmer Spectrum GX

Brief Description: FT-IR Spectrometer Perkin Elmer Spectrum

     GX Range: 30 - 15600 cm^{-1}

ATR accessory for reflectance measurement; IR Quant software; Spectrum search software.

Specifications:

- Sample: Solid, Liquid or Gas
- Operating Mode:- NIR and MIR
- Scan Range: 15600 to 30 cm^{-1}
- Optical system: Source NIR: 15,200 – 1,200 cm^{-1}
- Beam splitter KBr: 7,800 - 370 cm^{-1}
- Detector MIRTGS: 10,000 - 220 cm^{-1}
- Optimum Range: 7,800 - 1,200 cm^{-1}
- OPD Velocity: 0.20 cm/s
- Inferferogram Direction: Bi-Direction
- Scan Time: 20 scan/second
- Resolution: 0.15cm^{-1}
- Single Beam/Ratio: Single
- Detector: MIRTGS

4.2.2 Results and Discussion:

The anticipated IR spectral frequencies of all the samples are given in Table 3.1. The infrared spectra of crystals and schiffbase are shown in figures 4.2 to 4.4. The inspection of the infrared spectra of all the samples reveals followings.

(I)   All the IR spectra are identical in almost all aspects. The important bands   are observed at their respective positions.

(II)   The band at $1406\underline{+}14$ cm^{-1} is due to –N=N- group.

(III)   The bands at 3200-3650 cm^{-1} are due to –CH$_3$ linkage.

(IV)   The bands at 2780-2820 cm^{-1} are due to –CH$_2$- linkage.

(V)   A broad band appeared in the region of 3400-3360 cm^{-1} may be assigned to the stretching vibrations of phenolic hydroxyl (-OH) groups of 8-quinolinol moeity.

A strong band of sharp or moderate intensity at 1420 cm^{-1} may be attributed to inplane deformation of hydroxyl (-OH) group of oxine.

Two medium bands at 1090 and 1280 cm^{-1} are attributed to C - O stretching and -OH bending vibrations of -C-OH group of oxine.

Table-4.1

Anticipated IR spectral features for crystals and Schiffbase.

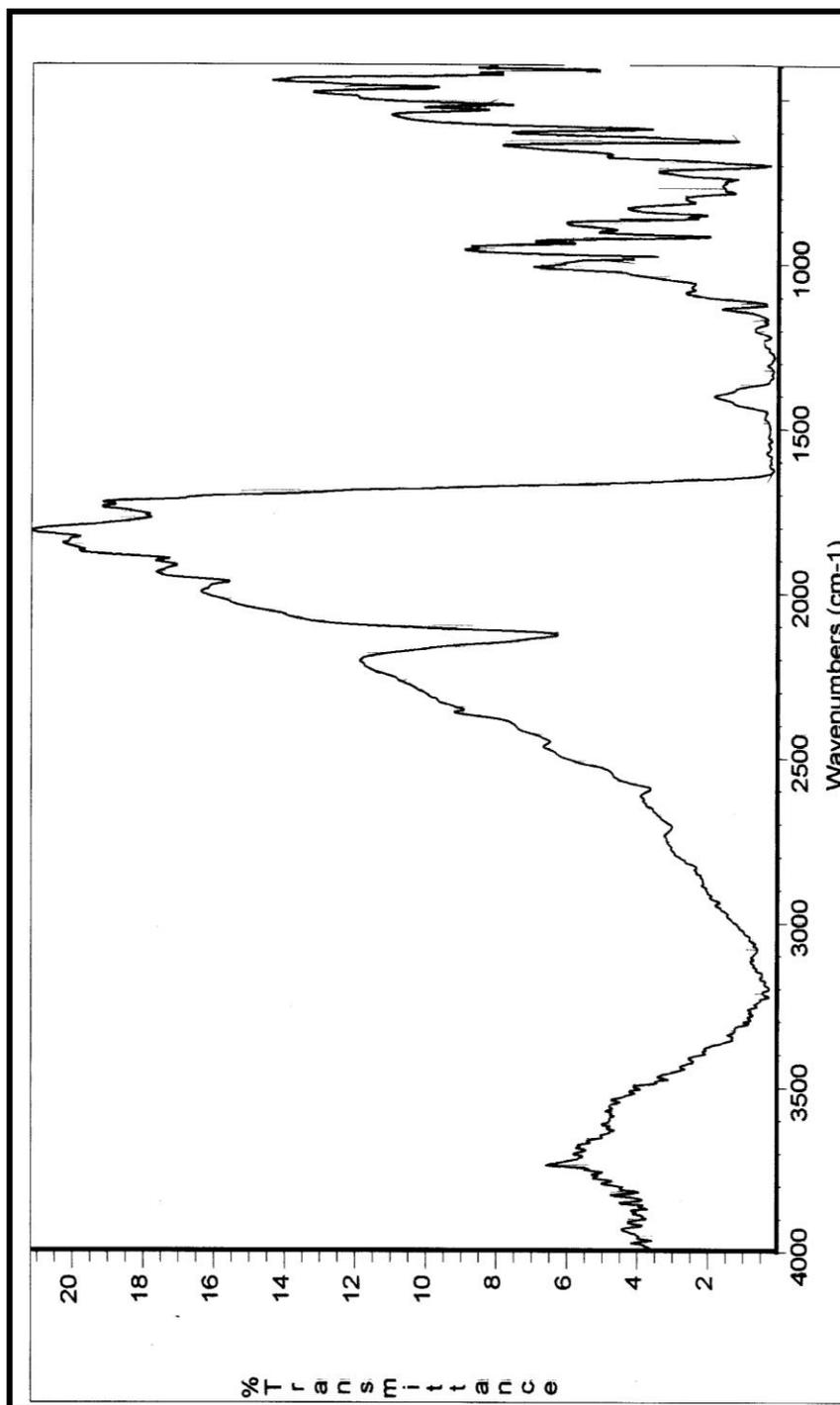| Sr.No.	GROUPS	IR frequencies(Cm^{-1})
1.	-N=N-	1406 ± 14
2.	Aromatic.	3050, 1600, 1010
3.	-OH of Quinoline moieties	3400-3360 1420 1090, 1280
4.	$-CH_2-$	2780-2820
5.	$-CH_3-$	3200-3650

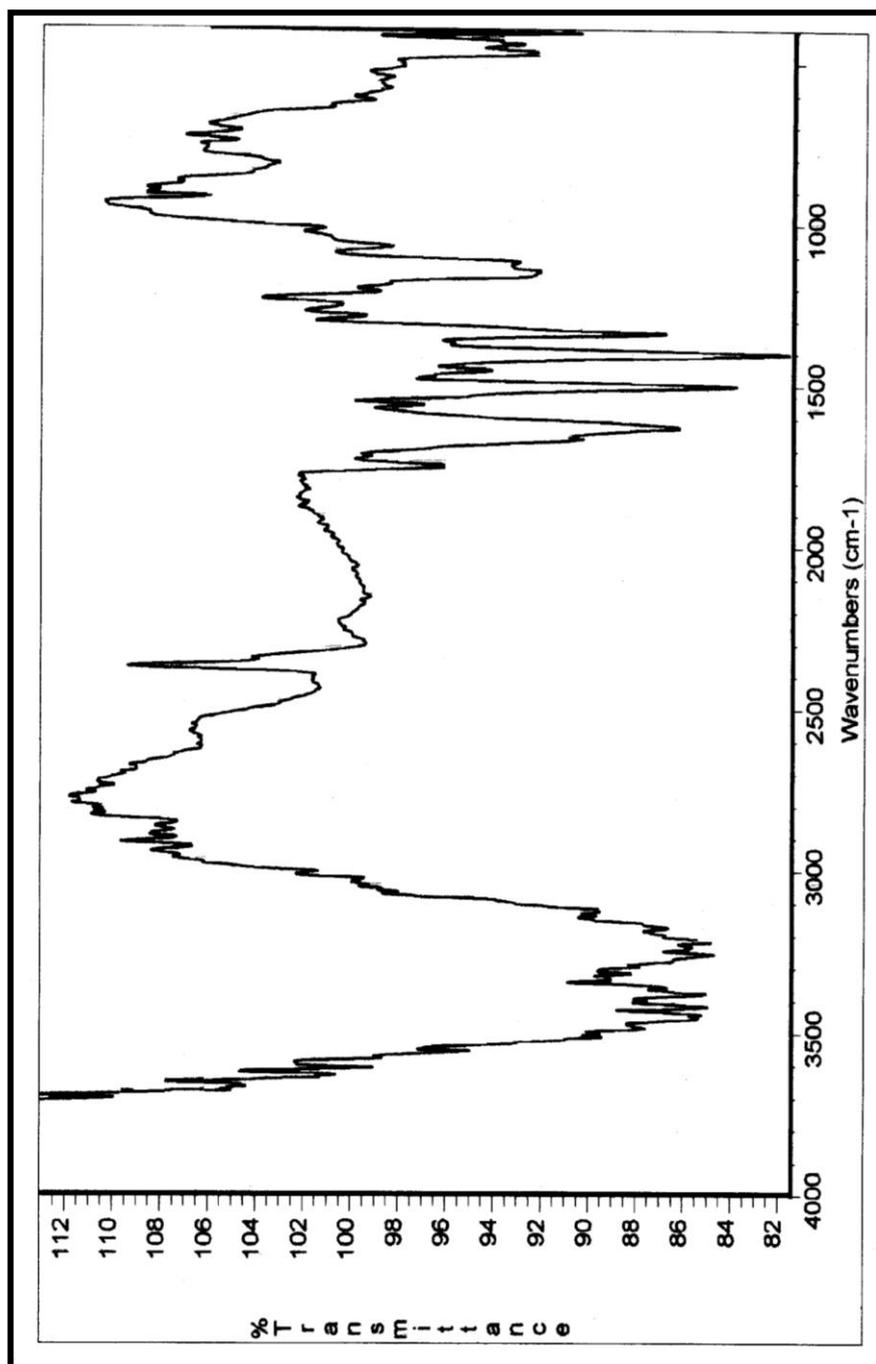**Figure 4.2 IR Spectrum of Schiffbase**

Figure 4.3 IR Spectrum of Cu(II) crystal
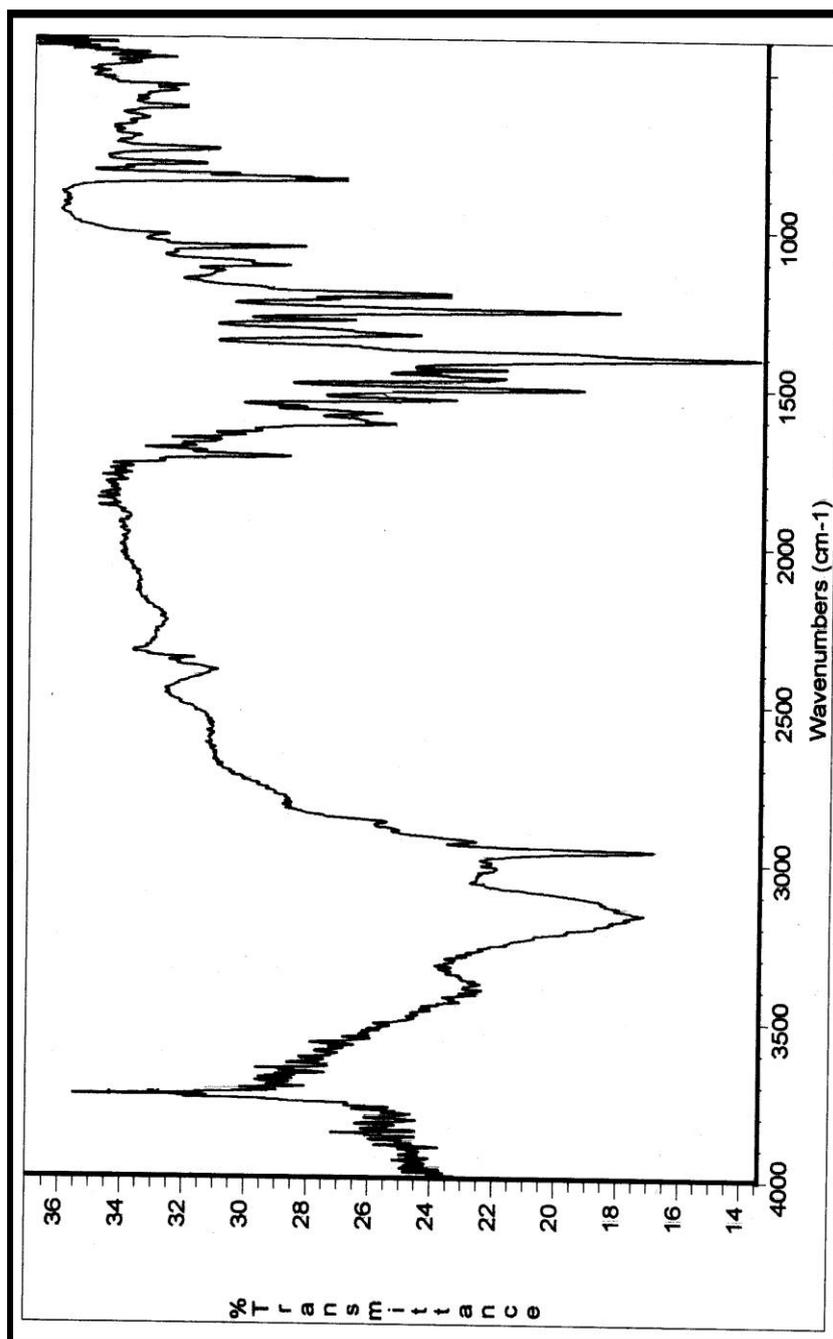
Figure 4.4 IR Spectrum of Ni(II) crystal

4.3   Reflectance spectral study

Ultraviolet-visible spectroscopy or ultraviolet-visible spectrophotometry (UV-Vis or UV/Vis) refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet-visible spectral region. This means it uses light in the visible and adjacent (near-UV and near-infrared (NIR)) ranges. The absorption or reflectance in the visible range directly affects the perceived color of the chemicals involved. In this region of the electromagnetic spectrum, molecules undergo electronic transitions. This technique is complementary to fluorescence spectroscopy, in that fluorescence deals with transitions from the excited state to the ground state, while absorption measures transitions from the ground state to the excited state

Since most transition metal coordination compounds have unique visible and ultra violet spectra, diffuse reflectance spectroscopy is considered as especially useful technique in the study of the geometry and electronic structure of metal chelates [23]. This technique is especially important for the study of transition metal compounds because the chemistry of the structure of these compounds in solid state is not that well studied, as than chemistry in aqueous solution. Hence the reflectance spectroscopic technique is among the most important of the methods available for investigating the solid-state properties such as stereochemistry, spectral properties, photochemical and thermal reactions and analytical applications. One of the most interesting results of research in diffuse reflectance spectroscopy has been the great similarity between the spectra of many metal chelates. Since all present metal chelates are in powder form, attempts are made to obtain diffuse reflectance spectral data of these metal chelates with a view to investigate structural aspects of these chelates. The fundamentals of this technique are briefly discussed in the present section.

A metal coordination compound may exhibit four types of transitions in UV-visible spectra in the range of 200 to 800 nm.

➢ Pure d-d transitions.

➢ Charge transfer transitions.

➢ Internal ligand transitions.

The two most important types of absorption bands of transition metal coordination compounds in the visible and ultraviolet region are those due to charge-transfer (CT) between the metal ions and the ligands and due to d-d (or f-f) transitions. From the position of the absorption bands due to d-d transitions the absorption coefficient values for the absorption bands can be calculated from reflectance values using Kubelka-Munk theory [24]. A fairly large number of studies of diffuse reflectance spectra of transition metal coordination compounds has been made in terms of the ligand field theory [25] which reveals that in the recent years application of diffuse reflectance.

Reflectance spectroscopy is used for samples that are difficult to analyze by transmission. The samples can usually be analyzed as is without the need for preparation or any modification. Reflectance measurements can be divided into two basic categories – internal or external reflectance. The technique of Attenuated Total Reflection (ATR) is employed for internal reflectance measurements as the beam of infrared radiation passes through an ATR element (crystal) in contact with the sample[26-30]. For external reflectance measurements, the infrared beam of radiation is reflected directly from the sample surface. This type of external reflectance measurement can also be divided into two types – Diffuse or Specular[31-35].

UV/Vis spectroscopy is routinely used in the quantitative determination of solutions of transition metal ions highly conjugated organic compounds, and biological macromolecules.

● Solutions of transition metal ions can be colored (i.e., absorb visible light) because d electrons within the metal atoms can be excited from one electronic state to another. The colour of metal ion solutions is strongly affected by the presence of other species, such as certain anions or ligands. For instance, the colour of a dilute solution of copper sulfate is a very light blue; adding ammonia intensifies the colour and changes the wavelength of maximum absorption (λ_{max}).

- Organic compounds, especially those with a high degree of conjugation, also absorb light in the UV or visible regions of the electromagnetic spectrum. The solvents for these determinations are often water for water soluble compounds, or ethanol for organic-soluble compounds. (Organic solvents may have significant UV absorption; not all solvents are suitable for use in UV spectroscopy. Ethanol absorbs very weakly at most wavelengths.) Solvent polarity and pH can affect the absorption spectrum of an organic compound. Tyrosine, for example, increases in absorption maxima and molar extinction coefficient when pH increases from 6 to 13 or when solvent polarity decreases.

- While charge transfer complexes also give rise to colours, the colours are often too intense to be used for quantitative measurement.

The Beer-Lambert law states that the absorbance of a solution is directly proportional to the concentration of the absorbing species in the solution and the path length. Thus, for a fixed path length, UV/Vis spectroscopy can be used to determine the concentration of the absorber in a solution. It is necessary to know how quickly the absorbance changes with concentration. This can be taken from references (tables of molar extinction coefficients), or more accurately, determined from a calibration curve.

A UV/Vis spectrophotometer may be used as a detector for HPLC. The presence of an analyte gives a response assumed to be proportional to the concentration. For accurate results, the instrument's response to the analyte in the unknown should be compared with the response to a standard; this is very similar to the use of calibration curves. The response (e.g., peak height) for a particular concentration is known as the response factor.

The wavelengths of absorption peaks can be correlated with the types of bonds in a given molecule and are valuable in determining the functional groups within a molecule. The Woodward-Fieser rules, for instance, are a set of empirical observations used to predict λ_{max}, the wavelength of the most intense UV/Vis absorption, for conjugated organic compounds such as dienes and ketones. The spectrum alone is not, however, a specific test for any given

sample. The nature of the solvent, the pH of the solution, temperature, high electrolyte concentrations, and the presence of interfering substances can influence the absorption spectrum. Experimental variations such as the slit width (effective bandwidth) of the spectrophotometer will also alter the spectrum. To apply UV/Vis spectroscopy to analysis, these variables must be controlled or accounted for in order to identify the substances presen

The instrument used in ultraviolet-visible spectroscopy is called a UV/Vis spectrophotometer. It measures the intensity of light passing through a sample (I), and compares it to the intensity of light before it passes through the sample (I_o). The ratio I / I_o is called the transmittance, and is usually expressed as a percentage (%T). The absorbance, A, is based on the transmittance:

A = − log(%T / 100%)

The UV-visible spectrophotometer can also be configured to measure reflectance. In this case, the spectrophotometer measures the intensity of light reflected from a sample (I), and compares it to the intensity of light reflected from a reference material (I_o)(such as a white tile). The ratio I / I_o is called the reflectance, and is usually expressed as a percentage (%R).

The basic parts of a spectrophotometer are a light source, a holder for the sample, a diffraction grating in a monochromator or a prism to separate the different wavelengths of light, and a detector. The radiation source is often a Tungsten filament (300-2500 nm), a deuterium arc lamp, which is continuous over the ultraviolet region (190-400 nm), Xenon arc lamps, which is continuous from 160-2,000 nm; or more recently, light emitting diodes (LED) for the visible wavelengths. The detector is typically a photomultiplier tube, a photodiode, a photodiode array or a charge-coupled device(CCD). Single photodiode detectors and photomultiplier tubes are used with scanning monochromators, which filter the light so that only light of a single wavelength reaches the detector at one time. The scanning monochromator moves the diffraction grating to "step-through" each wavelength so that it's intensity may be measured as a function of wavelength. Fixed monochromators are used with CCDs and photodiode arrays. As both of these devices consist of many

detectors grouped into one or two dimensional arrays, they are able to collect light of different wavelengths on different pixels or groups of pixels simultaneously.

A spectrophotometer can be either single beam or double beam. In a single beam instrument (such as the Spectronic 20), all of the light passes through the sample cell. I_o must be measured by removing the sample. This was the earliest design, but is still in common use in both teaching and industrial labs.

In a double-beam instrument, the light is split into two beams before it reaches the sample. One beam is used as the reference; the other beam passes through the sample. The reference beam intensity is taken as 100% Transmission (or 0 Absorbance), and the measurement displayed is the ratio of the two beam intensities. Some double-beam instruments have two detectors (photodiodes), and the sample and reference beam are measured at the same time. In other instruments, the two beams pass through a beam chopper, which blocks one beam at a time. The detector alternates between measuring the sample beam and the reference beam in synchronism with the chopper. There may also be one or more dark intervals in the chopper cycle. In this case the measured beam intensities may be corrected by subtracting the intensity measured in the dark interval before the ratio is taken.

Samples for UV/Vis spectrophotometry are most often liquids, although the absorbance of gases and even of solids can also be measured. Samples are typically placed in a transparent cell, known as a cuvette. Cuvettes are typically rectangular in shape, commonly with an internal width of 1 cm. (This width becomes the path length, L, in the Beer-Lambert law.) Test tubes can also be used as cuvettes in some instruments. The type of sample container used must allow radiation to pass over the spectral region of interest. The most widely applicable cuvettes are made of high quality fused silica or quartz glass because these are transparent throughout the UV, visible and near infrared regions. Glass and plastic cuvettes are also common, although glass and most plastics absorb in the UV, which limits their usefulness to visible wavelength.

Specialized instruments have also been made. These include attaching spectrophotometers to telescopes to measure the spectra of astronomical features. UV-visible micro spectrophotometers consist of a UV-visible microscope integrated with a UV-visible spectrophotometer. These are commonly used for measuring thin film thickness in semiconductor manufacturing, materials science research, measuring the energy content of coal and petroleum source rock, and in forensic laboratories for the analysis of microscopic amounts of trace evidence as well as questioned documents.

A complete spectrum of the absorption at all wavelengths of interest can often be produced directly by a more sophisticated spectrophotometer. In simpler instruments the absorption is determined one wavelength at a time and then compiled into a spectrum by the operator. By removing the concentration dependence, the extinction coefficient (ε) can be determined as a function of wavelength

4.3.1 Experimental

The reflectance spectra of the poly azo chelates in the visible region were recorded against MgO on Beckman-DK-2A spectrophotometer. The assignment significant bands present in the reflectance spectra of each of the metal chelates are furnished in Tables 3.6 to 3.8 and typical spectra are shown in Figs 3.11 to 3.13.

4.3.1.1 UV-VIS-NIR spectrophotometer

Figure 4.5 UV-VIS-NIR Spectrophotometer

Small Description:

UV-VIS-NIR Spectrometer Perkin Elmer Lambda 19 Range: 185-3200 nm: Diffuse reflectance attachment; Standards for wavelength and absorption calibration validation traceable to NIST All types of measurements/studies in the region including Absorbance, Transmission and Reflectance spectra; Quantitative analysis.

Specifications:-

- Double Beam, Double Monochromator, Ratio Recording
- Lamp: Deuterium (UV), Tungsten-Halogen (VIS/NIR)
- Detectors: Photomultiplier tube for UV/Vis
    Lead-Sulphide cell (PbS) for NIR
- Wavelength Range: 185-3200 nm for Absorbance/Transmission and 200-2500 for Reflectance

- Scan Speed: 0.3 to 1200 nm/min

- Wavelength Accuracy: ± 0.15 nm for UV/VIS & ± 0.6 nm for NIR

- Base line flatness: ± 0.001 A° , 4 nm slit

- Ordinate Mode: Scan, Time Drive, Wavelength Programming, Concentration

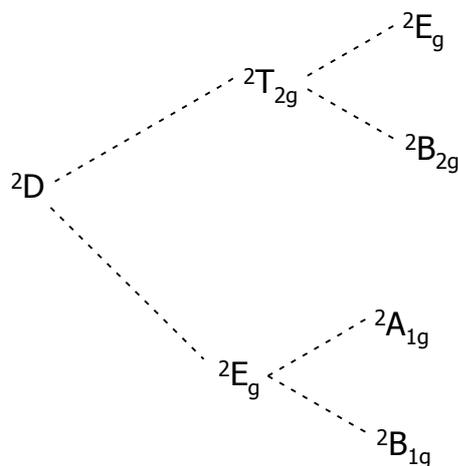- Photometric Accuracy: ± 0.003 A° or ± 0.08 %T

4.3.2 Results and discussion of magnetic moments and Reflectance spectral data co-relation

In the present section, the results of the characterization of metal chelates(Crystals) by magnetic susceptibility measurement and reflectance spectral study are discussed in terms of structure-property relationship[36-37].

(i)   Metal chelates(Crystal) of Cu^{2+}

Literature survey reveals that the electronic configuration of Cu^{2+} is $3d^9$, having an unpaired electron in its sub-shell. Compounds containing Cu^{2+} are considered to exhibit magnetic moment close to the value (1.73 B.M.). However, the magnitude of magnetic moment (μ_{eff}) is found to be dependent on electronic spin and orbital motion and therefore many Cu^{2+} containing compounds exhibits theoretical magnetic moment 1.73 B.M. (no orbital contribution) to a value of 3.0 B.M. However, the measured μ_{eff} usually ranges from 1.7 to 2.2 B.M. In an octahedral field, the ground state of Cu^{2+} ($3d^9$) is subjected to considerable John-Teller distortion. In practice, majority of the green or blue crystals are tetragonally distorted with four short co-planar bonds and two longer axial bonds and in the case of extreme distortion, the crystals would be four coordinated and square planner. Cu^{2+} crystals posses a wide variety of structures. For most of the geometries a very broad band with a peak minimum near 15,000 cm^{-1} is observed. Thus the electronic spectrum of Cu^{2+} is often of little value in assignment of the molecular structure of the chelates. Tetragonal distortion is the most common example of
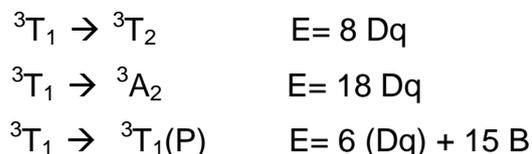
Cu^{2+}coordination. Perusal of the literature reported two distinct absorption bands in the electronic spectra of octahedral crystals [26-28]. The energy levels of the axially elongated chelates are shown below:

$$^2D \longrightarrow {^2T_{2g}} \longrightarrow \begin{cases} ^2E_g \\ ^2B_{2g} \end{cases}, \quad ^2E_g \longrightarrow \begin{cases} ^2A_{1g} \\ ^2B_{1g} \end{cases}$$

The ground state of copper (II) ion in an elongated tetragonally distorted octahedral crystal field of D_{4h} symmetry is a single electron in $d_{x^2-y^2}$ (B_{1g}), orbital or a $^2B_{1g}$ spectroscopic state. The transitions in a tetragonal field are assigned as $^2B_{1g} \dashrightarrow {^2A_{1g}}$, $^2B_{1g} \dashrightarrow {^2B_{2g}}$ and $^2B_{1g} \dashrightarrow {^2E_g}$ and they occur in the range 12,000-17,000, 15,000-18,000 and 17,000 to 20,000 cm^{-1} respectively. The six coordinated copper (II) chelates are almost always distorted from a regular octahedral structure with the axial ligands of octahedron further away from the metal ion than the equatorial ligands due to John-Teller distortion. In the present work, the magnetic moment (μ_{eff}) of all Cu^{2+} complexes are found to be in the range of 1.9-2.0 B.M. indicating the distorted octahedral geometry for these metal complexes. These findings are in agreement with data reported by several research workers [29,30]. The two absorption bands are observed in the region 15625-16000 cm^{-1} and 23625-24000 cm^{-1}, in electronic spectra of Cu^{2+} metal chelate(crystal) of each of the ligands may be assigned to $^2B_{1g} \dashrightarrow {^2A_{1g}}$ and charge transfer transition respectively. These results reveal the **distorted octahedral geometry** for these crystals.

(ii)   Metal chelates(Crystal) of Ni^{2+}

Magnetic moment values 2.83 B.M. suggest tetrahedral geometry in high spin complexes. According Tanabe –Sugano diagram six coordinated Ni(II) crystals belong to $3d^8$ system and there are three spin allowed transition mainly

$$^3T_1 \rightarrow {}^3T_2 \qquad E= 8\ Dq$$
$$^3T_1 \rightarrow {}^3A_2 \qquad E= 18\ Dq$$
$$^3T_1 \rightarrow {}^3T_1(P) \qquad E= 6\ (Dq) + 15\ B$$

The crystal of Ni(II) has shown electronic transitions at 5154 cm^{-1} (υ_1), 11494 cm^{-1} (υ_2) and 13333cm^{-1} (υ_3) respectively.

The value 5154 cm^{-1} at which the first transitions occur is too high for a tetrahedral crystal. So the transition at 13333 cm^{-1} is taken as υ_2 and hence Dq is 5154 cm^{-1}. The calculated value for B is 633 cm^{-1} and β^o is 61 %.

Table-4.2: Reflectance spectral data of Cu^{2+} Chelates

Metal Chelates	Observed transition energies (cm^{-1})	
	CT	$^2B_{1g} \rightarrow {}^2A_{1g}$
Cu(II)	23370	15650

Table-4.3: Reflectance spectral data of Ni^{2+} Chelates

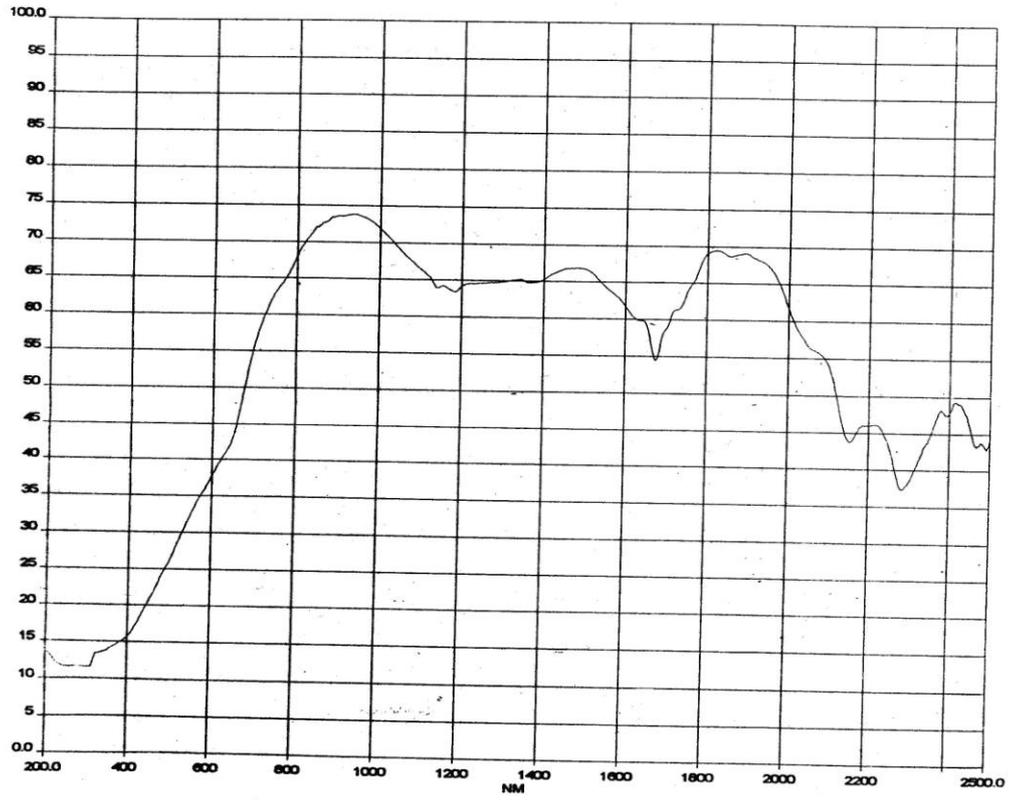| Metal Chelates	Observed transition energies (cm^{-1})		
	$^4T_{1g}(F) \rightarrow$		
	$^6T_{2g}(\upsilon_1)$	$^4A_{2g}(\upsilon_2)$	$^4T_{1g}(P)$
Ni(II)	24660	19990	8792

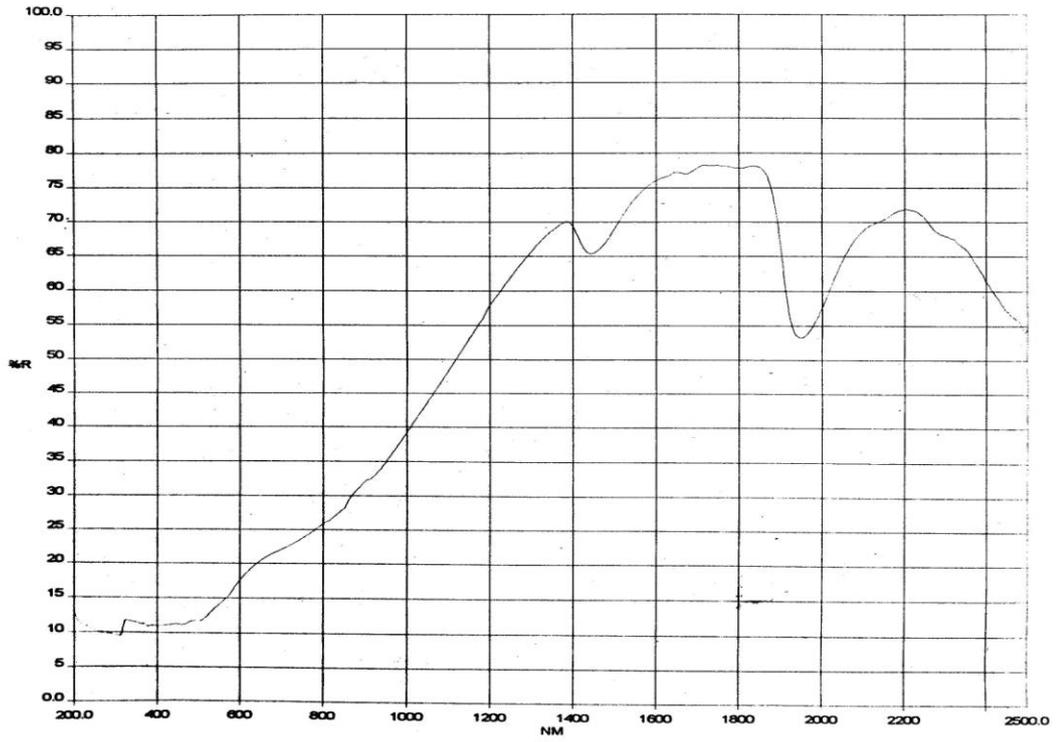**Fig. 4.6 Reflectance spectrum of Cu(II) crystal**

Fig. 4.7 Reflectance spectrum of Ni(II) crystal

4.4   Magnetic susceptibility

The magnetic susceptibility of crystals is considered as one of the intrinsic property and therefore the magnetic behavior of the crystals can be predicted on the basis of it structural unit. Thus in the estimation of molar magnetic susceptibility (ξm) of crystals, the molecular mass of the structural unit is accounted. The study of magnetic properties provides valuable information about valence type of bond and stereo chemical aspects of transition metal chelates(crystals). The magnetic susceptibility is defined as the extent to which a material is susceptible to magnetization by applying magnetic field to it. Magnetic effect are of two types, one diamagnetism arising from the orbital contribution of the electron regarded as charged particles and the other paramagnetism associated with spin and orbital angular momentum of electrons. While ferromagnetism is a sub division of the paramagnetism and known as "cooperative phenomena". It arises when more than one paramagnetic center within sample interact magnetically with one another. It occurs only in those organic molecules contaminated with impurities having domains or lattices particles containing electron with parallel spins. Diamagnetism, a universal property of the materials arises from the interaction of paired electrons with the magnetic field and is independent of both temperature and applied magnetic field. While paramagnetism occurs in only those compounds containing unpaired electrons in their free radical and is independent of applied field, but inversely proportional to the temperature. In organic molecules, paramagnetism occurs in only two classes of compounds those containing transition metal ion (such as metal complexes) or organic compounds containing unpaired electron (such as free radicals). The method is based on measuring the force resulting from the interaction between a magnetic field and magnetic moment induced in the sample by the magnetic field, assuming that it varies only as a function of "ξ", the component of the force per unit volume of the sample [38].

4.4.1 Experimental

Principle

Gouy's method was employed for determining magnetic susceptibility of coordinated ligands as they contain transition metals. It consists essentially a Gouy balance in which a long cylindrical sample tube suspended vertically in a magnetic field with lower end in the region of maximum field and the upper end in a region of effectively zero fields. The force exerted on the sample is measured by the conventional weighing technique. The "instrument constant" measurements measured using material of known susceptibility such as using conductivity water or mercury tetrathiocyanatocobaltate (II) [HgCo(CNS)$_4$] as a calibrant [39].

Theory

The equation used for determining specific susceptibility or mass susceptibility (ξ_g) is

$$\xi_g = \frac{\alpha + \beta dw_s}{Ws} \tag{4.1}$$

Where α = Correction factor due to air pocket in the sample

β   = Tube constant

Ws = Weight of sample in gm

dw$_s$ = Weight difference of the tube filled with sample with Magnetic   field off and on.

The value of 'a' is estimated using equation

$$\alpha = KV \tag{4.2}$$

Where,

K = Volume susceptibility of air (0.029 x 10^{-6} cgs unit)

V **=** Volume of air

The tube constant β is determined at different magnetic field strengths using mercury tetrathiocyanatocobaltate (II) as calibrant. The equation used to calculate this constant is:

$$\beta = X_r \frac{Wr-KV}{dWr} \qquad (4.3)$$

Where,

ξ_r Magnetic susceptibility of calibrant (i.e. 16.44×10^{-6} cgs ± 0.5 % at 20 °C)

Wr **=** Weight (gm) of calibrant used in measurement

dWr = Difference in weight (gm) of calibrant with and without magnetic

    field.

K **=** Volume susceptibility of air (0.029×10^{-6} cgs unit)

V = Volume of air

Equation (4.1) is used to calculate the specific susceptibility of metal chelates. From specific or mass susceptibility i.e. magnetic susceptibility per gram of sample, the molar magnetic susceptibility of ($\aleph_m$) of sample can be estimated using the equation

$$\xi_m = \xi_g \times Mcp \qquad (4.4)$$

Where,

Mcp **=** Molecular weight of metal chelate.

A correction is applied for diamagnetism of the ligand and anions using Pascal's constant to give the corrected molar susceptibility as follows.

$(\xi_m') \text{ corr} = \xi_m \text{ Pascal's constant}$ (4.5)

The value of Pascal's constant is taken from literature [40-43]. Then the values of effective magnetic moment μ_{eff} was calculated by the mathematical expression

$\mu_{eff} = 2.83 \sqrt{(\xi_m)_x T}$ (4.6)

4.4.2 Procedure

The general procedure for filling the sample tube is as given below: The finely ground and dried powder of sample was introduced with tapping so that a maximum filling is obtained in a fixed volume. Although experiments have shown that under normal condition of working loose packing or a tight ramming of the powder in the tube does not affect the susceptibility measurements provided corrections are made for the presence of air pockets. The tight ramming is more preferable for a maximum filling and minimizes the changes of preferential orientation of the particles in the field [40]. Such tight ramming was obtained by introducing small and nearly equal proportions of the powder in the tube and packed by pounding with the flat end of the tube after each addition. The empty tube was suspended between the poles of magnet with its tip in the center of the p and e gap. It was then weighed and the "apparent weight" (w) of tube was measured in the presence of magnetic field and in the absence of magnetic field by passing suitable current of 4 and 6 amps [40]. The difference in weight dw corresponding to each current was noted.

Figgis and Lewis [41] recommended mercury tetrathiocynatocobaltate (II) [HgCo(CNS)$_4$] as an all round calibrant because it has mass susceptibility (ξ_g) of 16.44 x 10^{-6} (± 0.5 %) at 20 °C and is said to have exceptionally good packing properties. This reference material was used in the present study. It was filled in the tube up to the mark and weighed as before. The change in weights were noted and used for obtaining tube constant. After this tube was dried and filled up to the same mark with the sample, the weighing procedure with the magnetic field off and on was repeated as before and the change in weight dw$_s$ corresponding to the same fields used for the reference was determined.

The observed value of μ_{eff} is in Bohr magnetron (B.M.) and T is the absolute temperature at which measurement is carried out. The estimated values of magnetic susceptibility (μ_{eff}) of all the metal chelates are presented in Tables: 3.3 and 3.4. results inspection data of magnetic moments reveals that the metal chelates of Cu^{2+} and Ni^{2+} are paramagnetic in nature. The observed value of μ_{eff} of each of the metal complexes is found to be in the expected range as reported in literature [44-45].

Table-4.4

Experimental data of magnetic moment of Crystal

Crystal	$\chi_g \times 10^6$ (cgs)	$\chi_m \times 10^6$ (cgs)	Observed Magnetic moment μ_{eff} (B.M.)	$\mu_{eff} = \sqrt{n(n+2)}$ (B.M.)	Expected μ_{eff} (B.M.)
Cu(II) crystal	28.87	14247	5.88	5.91	5.2-6.0
Ni(II) crystal	9.53	4624	3.35	2.82	2.8-3.4

χ_M **= Molar Conductivity (Ω^{-1} cm^2 mol^{-1})**

χ_g **= Gram Susceptibility (cgs)**

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