CHAPTER-II
EXPERIMENTAL TECHNIQUES

In this Chapter, a brief discussion about the theory and instrumentation of various spectroscopic techniques employed in the thesis are presented. Since the main technique used is Electron Paramagnetic Resonance spectroscopy, it is discussed in a detailed way. Also are discussed various related necessary information for the understanding of these spectroscopic techniques.

II.1. EPR SPECTROSCOPY

EPR spectra are recorded in pure paramagnetic samples, if co-operative phenomena are to be studied. In these samples, the paramagnetic centers are too close so that the spectrum is strongly affected by dipolar interactions as well as spin exchange between neighbouring centers. Hence, in order to derive information confined to individual paramagnetic entities, they need to be separated, i.e., magnetically diluted. In solutions, this condition is readily achieved at reasonably low concentrations. In solids, there are two common methods.

First method is to dope the paramagnetic impurity in a diamagnetic lattice. If the dopant concentration is quite low (of the order of 1 mole % or less), the dopant centers are sufficiently far away and the desired isolation is achieved. This leads to well-resolved spectra free from dipolar and exchange effects and the treatment of the system as independent centers is reasonably justified. Such doping is quite common with transition metal complexes. In these cases, the dopant substance does not necessarily have the same crystal structure as the host lattice. Experiments show that the environment of the host is invariably imposed on the dopant, thus making it possible to study the dopant complex under circumstances that do not exist in its pure form.

Another common method to produce the paramagnetic centers in a diamagnetic lattice is radiation damage using UV, X-ray or γ-rays. The technique may be employed in a pure host lattice or a doped host lattice. However, this technique has not been employed in the present thesis.
CRYSTAL GROWTH

The main technique involved in crystal growth is slow evaporation method. Growing crystals by allowing a saturated solution of a material by evaporation is the simplest method [1, 2]. Crystals are grown with little knowledge of fine details such as evaporation of solvent or temperature change. However, care must be taken to prevent the solution becoming too much supersaturated for crystals would then appear spontaneously throughout the solution. The factors that control the growth process are (a) character of the solution (b) effect of additives and (c) operating variable such as the degree of supersaturation and the temperature range.

The choice of solvent is an important factor that determines the growth of a crystal from solution. Growth of a large crystal is virtually impossible unless a solvent is found in which the solute is appreciably soluble. Various solvents, such as ethanol, methanol, water etc. are used depending on the complex solubility. The rate of growth of the crystal is dependant on the temperature at which the solution is maintained. At higher temperatures, the growth rate will be high. All the crystals are grown at room temperature.

INSTRUMENTATION

The basic principles and the elementary details of an EPR spectrometer are so well known. The details of instrumentation and measurement techniques are discussed extensively in literature [3-6]. From the resonance condition \( h\nu = g\beta B \), it follows that the EPR spectra could be measured by using fixed frequency and variable field or fixed field and variable frequency; it is always convenient to follow the former procedure. Depending upon the frequency of resonance, EPR spectrometers are classified as S, X, K, Q band spectrometers, the most common one being X and Q. At X-band, the frequency is normally around 9 GHz, with the free-electron resonance field at \( \sim 320 \) mT, while at Q-bands, the corresponding values are 35 GHz and 1200 mT. The approximate frequency ranges and wavelength of these bands are given below:

<table>
<thead>
<tr>
<th>Bands</th>
<th>S</th>
<th>X</th>
<th>K</th>
<th>Q</th>
</tr>
</thead>
<tbody>
<tr>
<td>Approximate Frequency (GHz)</td>
<td>3</td>
<td>9</td>
<td>24</td>
<td>35</td>
</tr>
<tr>
<td>Approximate Wavelength (mm)</td>
<td>90</td>
<td>30</td>
<td>12</td>
<td>8</td>
</tr>
<tr>
<td>Approximate Field for ( g = 2 ) (mT)</td>
<td>110</td>
<td>320</td>
<td>850</td>
<td>1250</td>
</tr>
</tbody>
</table>
In order to observe a well resolved spectrum, the spectrum is to be recorded under optimum conditions of microwave power, modulation amplitude, spectrometer gain, filter time constant, scan range and scan time. The work described in this thesis is carried out on a JEOL JES-TE100 ESR spectrometer operating at X-band frequencies, having a 100kHz field modulation to obtain a first derivative EPR spectrum. DPPH, with a g value of 2.0036 is used for g-factor calculations. Low temperature measurements are done using a quartz Dewar, whose tail fitted into the EPR cavity.

Crystals are mounted at one end of a perspex rod (with ‘quick-fix’), which fitted in the ESR cavity. A large protractor, calibrated in degrees, attached to the other end enabled accurate rotations of the crystal about a preferred axis. The error in mounting the crystal is about ±2° and that in orientation is about ±1°.

INTERPRETATION OF EPR SPECTRA

In order to calculate g and A values, the following expression is used.

\[ g = \left( \frac{g_{\text{DPPH}} B_{\text{DPPH}}}{B} \right) \]  

where B is the magnetic field position at the EPR peak, B_{DPPH} is the field position corresponding to DPPH and g_{DPPH} is the g-value of DPPH which is equal to 2.0036. Alternatively, the g-value is calculated directly using the spectrometer frequency (v) at which resonance occurs. The expression is

\[ g = \left( \frac{hv}{\beta B} \right) \]  

The hyperfine (hf) coupling constant ‘A’ is given by the field separation between the hyperfine components. If the spacing is unequal, an average of them is taken to be the value of A. For n number of hyperfine lines, the average hyperfine value is

\[ A = \left( \frac{B_n - B_1}{n-1} \right) \]  

where, \( B_n \) is the field position for the \( n^{\text{th}} \) hyperfine line and \( B_1 \) is the first hyperfine line field position.

Spectra are measured both in single crystal and poly-crystalline forms. A brief outline of the interpretation that is used is given below.
POWDERS AND GLASSES

In powders and glasses, the observed spectrum is a result of superposition of all possible orientations of single crystals giving rise to statistically weighted average. The theory of powder line shapes in EPR is discussed in detail [7-9]. A brief pictorial summary of the evaluation of principal magnetic tensors for a few representative examples is given in Figure II.1. In normal circumstances, the principal values can be evaluated from powder data. However powder line shapes become complicated when more than one type of species is present and or when hyperfine lines overlap, and especially so when the tensors do not coincide. The first two complications can be circumvented to some extent by measuring the spectra at two different frequencies (X and Q bands) and sorting out the field-dependent and field-independent terms in the Hamiltonian. Some times power saturation techniques [3, 4] and temperature variation also help.

However, the orientation of the magnetic tensors relative to crystallographic axes and hence w.r.t. molecular framework cannot be obtained from powder data. In such a case, measurements have to be done on single crystals. Nevertheless, powder data is obtained easily with a single measurement and often acts as a useful check in the interpretation of single crystal data. There is almost a parallel analogy between powder and single crystal data in EPR and X-ray crystallography.

SINGLE CRYSTALS

Many authors [10-15] have described in detail the evaluation of the principal values of magnetic tensors from single crystal measurements. The method consists of measuring the variation of $g(\theta)^2$ for rotations about three mutually perpendicular axes in the crystal, which might coincide with the crystallographic axes or which are related to the crystallographic axes by a simple transformation. From the maxima and minima obtained in the three orthogonal planes, the matrix elements of the $g^2$ tensor are derived easily [10]. A Jacobi diagonalization of this matrix gave the Eigen-values corresponding to the principal values of the $g$ tensor and the transformation matrix, which diagonalises the experimental $g^2$ matrix, gives the direction cosines of these tensors with respect to the three orthogonal rotations. Complications arise, when more than one magnetically distinct site per unit cell are present, since, there is no a priori predictability of the relations between sites and spectra.
Figure II.1. Schematic diagram summarizing the evaluation of principle values of magnetic tensors from powder data based on the delta function line shape.
in the three planes. This led to several possible permutations leading to many $g^2$ tensors. A careful examination, however, invariably leads to the identification of the proper combinations and the corresponding direction cosines. In the case of hyperfine tensor, when $g$ is not highly anisotropic, the same procedure as above could be adopted. When this is not the case, Schonland has suggested, that it is necessary to follow the variation of $g^2A(\theta)$ in the three principal planes. The reason for this is as follows:

The Hamiltonian for a paramagnetic system, including only the electronic Zeeman and Hyperfine terms is expressed as

$$H = \beta (g_{11}B_1S_1 + g_{22}B_2S_2 + g_{33}B_3S_3) + (A_{11}S_1l_1 + A_{22}S_2l_2 + A_{33}S_3l_3) \quad \ldots [4]$$

Let $(n_1,n_2,n_3)$ be the direction cosines of the magnetic field $B$ with reference to the axes of the $g$ and $A$ (hyperfine) tensors. Here, it is assumed that $g$ and $A$ tensors are coincident. If $M$ and $m$ are the electron and nuclear spin quantum numbers, then the energy levels are given by:

$$E_{M,m} = g\beta BM + \beta KMm \quad \ldots [5]$$

Here $g$ and $K$ are given by the equations

$$g = (g_{11}^2n_1^2 + g_{22}^2n_2^2 + g_{33}^2n_3^2)^{1/2} \quad \ldots [6]$$

and

$$K = 1/g \left[ g_{11}^2A_{11}^2n_1^2 + g_{22}^2A_{22}^2n_2^2 + g_{33}^2A_{33}^2n_3^2 \right]^{1/2} \quad \ldots [7]$$

The magnetic field $B_m$ where the transition $|M,m> \leftrightarrow |M+1,m>$ takes place is given by

$$hv = g\beta B_m + \beta Km \quad \ldots [8]$$

i.e.

$$B_m = hv/g\beta - Km/g$$

If $A$ is hyperfine splitting parameter and the lines are centered around $hv/g\beta$, then

$$A = K/g \quad \ldots [9]$$

In order to evaluate the matrix elements of the hyperfine tensor, one has to consider the angular variation of $(gK)^2$, since $(gK)$ has a linear angular dependence on $g$. Therefore,

$$(gK)^2 = g^4A^2 \quad \ldots [10]$$

From this equation, the matrix elements of the hyperfine tensor matrix could be evaluated using the same procedure used to get $g$ tensor matrix.

Schonland has indicated the probable errors in the method described to get the principal values of $g$ and hyperfine tensors. But, the errors are very small compared with the experimental errors involved, such as mounting the crystal along the specified axis.
DIRECTION COSINES OF THE SUBSTITUTIONAL SITES

The single crystal x-ray analysis data provides the positional parameters p, q, r and the unit cell dimensions a, b, c and \( \alpha, \beta, \gamma \). For crystal system with non-orthogonal crystal axes, the positional parameters p, q, r of the various atoms can be changed over to an orthogonal framework and the Cartesian co-ordinates x, y, z are calculated by using the relation

\[
\begin{pmatrix}
x \\
y \\
z 
\end{pmatrix} = \begin{pmatrix}
a & b \cos \gamma & c \cos \beta \\
0 & b \sin \gamma & (c/sin \gamma)(\cos \alpha - \cos \beta \cos \gamma) \\
0 & 0 & d
\end{pmatrix} \begin{pmatrix}
p \\
q \\
r 
\end{pmatrix}
\]

[11]

where, \( d = \sqrt{c^2 - c^2 \cos^2 \beta - (c^2 / \sin^2 \gamma)(\cos \alpha - \cos \beta \cos \gamma)^2} \)

By setting the metal atom as the origin, one can get the co-ordinates of the various atoms surrounding the metal. The normalized Cartesian co-ordinates of these atoms give the direction cosines of the metal-ligand bond of the co-ordination polyhedron. The direction cosines of these metal-ligand bonds are to be compared with the direction cosines of the g and A- tensors, obtained by the procedure described in the previous section. Sometimes, it is found that the magnetic tensor directions coincide with some of the bond directions, which is not so in low symmetry cases.

SIMULATION OF EPR SPECTRA

The EPR spectra are simulated using standard Bruker WIN-EPR program and EPR-NMR program, developed by Prof. John A. Weil and his group [16]. The program uses exact diagonalisation and includes various options such as simulation of powder spectrum, simulation of single crystal spectrum at a particular variation or obtaining spin Hamiltonian parameters such as g, A, D tensors, by inputting the line positions obtained during crystal rotations. This program has been used heavily in the present thesis.
11.2. MAGNETOCHEMISTRY

Magnetism has played an important role in understanding the structural and electronic factors that govern the spin exchange phenomenon in inorganic and bioinorganic chemistry [17-20]. The binuclear copper complexes are useful models to study the intramolecular exchange interactions, i.e., interaction between the metal ions through the intervening bridging ligand, which leads to low lying states of different multiplicities [21]. Depending upon the spin of the ground state, the complexes will display either ferromagnetic or antiferromagnetic properties. The theory behind this exchange interaction is not only applicable to dimeric complexes but also to polymeric complexes, a field of much research activity in superconductivity and molecular based ferromagnets. Hence, the study of exchange interaction and an understanding about the factors controlling the magnetic behaviour of the binuclear copper complexes is essential for proper tuning of the expected magnetic properties in synthetic magnetic materials.

The binuclear copper complexes are divided into three types based on the extent of interaction between the metal centers [22].

1. Non-interacting type: In these cases, the magnetic property of the complex is same in dimer and monomer. The distance between the two metal ions is more than 6 Å or the orbital planes of metal ions are orthogonal to each other.

2. Strongly interacting type: Due to the direct interaction between the copper atoms, the complex exhibits diamagnetism. The intermetallic distance is less than 2 Å.

3. Weakly interacting type: The intermetallic distances ranges between 3 and 6 Å. The mixing of the metal magnetic orbitals happens through a filled intervening ligand orbital. This interaction produces low energy molecular states with different multiplicity ($2J<1000 \text{cm}^{-1}$). This interaction is often termed as superexchange interaction, results in interesting magnetic properties depending upon the spin of the ground state $S=1$ (ferromagnetic) or $S=0$ (antiferromagnetic) [23,24].

The exchange interaction in copper dimer is explained based on orbital model proposed by Hay and co-workers, which is grounded on the basis of magnetic orbitals and overlap density between the magnetic orbitals [22]. If the ground state is $S=0$, then the
interaction will be antiferromagnetic and the interaction will be ferromagnetic when $S = 1$. In this model, the singlet-triplet energy gap $J$ characterizing the nature and magnitude of exchange interaction results from the competition between two driving forces, one favours the singlet ground state ($J_{AF}$) and another favours triplet ground state ($J_F$). If the interaction is weak enough, the $S = 1$ and 0 states can be best explained by Heilter-London wave function built from magnetic orbitals and energy for the metal – metal charge transfer configuration is very high than the ground state configuration of A-B, the $J$ can be explained by the combination of the antiferromagnetic ($J_{AF}$) and ferromagnetic ($J_F$) components. The most frequently encountered situation is the one where the antiferromagnetic interaction predominates due to the stabilization of the singlet ground state with respect to triplet excited and the pure Heilter–London wave function is no longer valid to describe the $S = 0$ and $S = 1$ states.

For experimental convenience, the magnetic interaction between the spins $S_A$ and $S_B$ for atoms A and B respectively is given in the form suggested by Heisenberg [25], Dirac [26] and Van Vleck [27]. If $|S_A| = |S_B|$ then the total number of possible molecular states is equal to $S_A$ with total spin $S = 0, 1, \ldots \ldots 2S_A$ and the energy difference between the states $S$ and $S-1$ is given by

$$E(S) - E(S-1) = -2JS$$

In the case of $S_A = 1/2$, the triplet-singlet energy gap

$$E(1) - E(0) = -2J$$

In practice, the extent of interaction in dicopper complexes is determined by performing variable temperature magnetic susceptibility measurement and fitting the experimental susceptibility values to the theoretical values defined by Bleaney-Bowers equation [28]

$$\chi^m = (Ng^2\beta^2/3kT) [3 + \exp (-2J/kT)]^1 (1-P) + (0.45P/T) + N$$

Here $\chi^m$ is the molar magnetic susceptibility /mole corrected for diamagnetism using Pascal’s constant, $P$ is the percentage of monomeric, impurity, $J$ is the coupling constant, $N$ is the temperature independent paramagnetism (TIP) which has been fixed as $120 \times 10^{-6}$ cm$^3$ mol$^{-1}$ and other symbols have their usual meanings. The effective magnetic moment is calculated using the relationships $\mu = 2.828 (\chi^m T)^{1/2}$. The discrepancy factor between the
theoretical and experimental susceptibility values is evaluated using the relationship $R(\chi) = [\Sigma (\chi_{\text{obs}} - \chi_{\text{calc}})^2 / \Sigma (\chi_{\text{obs}})^2]$.

Based on theoretical and magneto-structural studies carried on several binuclear copper (II) complexes, it has been suggested that following factors effect superexchange interaction in binuclear copper complexes:

1. Geometrical factors [29-35] such as geometry around copper atoms Cu...O...Cu bridge angle, dihedral angle between the X-Y plane of the complex, etc.
2. Electronegativity [29, 36-38] and mode of bonding [39] of the directly bound ligands.
3. Chelate ring size [37, 40,41] and
4. Electronic and steric factors induced by the groups attached to the ligand frame work [40, 42-47].

II.3. SINGLE CRYSTAL X-RAY DIFFRACTION

The diffraction pattern produced by a single crystal is measured by using a three circle diffractometer. The computer linked to the diffractometer determines the unit cell dimensions and the angular settings of the diffractometer's three circles that are needed to observe any particular (hkl) reflection. The computer controls the settings, and moves the crystal and the detector for each one in turn. At each setting, the diffraction intensity is measured, and making measurements at slightly different settings assesses background intensities. Computing techniques are now available not only to automatic indexing but also the automated determination of the shape, symmetry and size of the unit cell. Several techniques are now available for sampling large amount of data including area detectors and image plates, which sample whole regions of diffraction patterns simultaneously. The interpretation of the data from a diffractometer in terms of the structure of the crystal involves structure factors, electron density, phase problems and structure refinement.

The mathematical principles involved and experimental details of single crystal diffraction techniques are covered in detail in the literature [48-53]. In this section, only a brief outline of the method of solving crystal structure based on the intensity data collected on a Siemens SMART-CCD-three circle diffractometer is described.

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For single crystal X-ray data collection, crystals free from defects such as twinning, cracks, mosaicity etc are essential. Crystals suitable for X-ray diffraction are chosen by examination of them under a polarizing microscope. Crystals stable to X-rays at ambient atmosphere is mounted on a glass fiber, which is fixed on a pip, using glue. This is then mounted on a goniometer head, which has two arcs and two slides to precisely position the crystal at the center of the goniometer. The diffracted X-rays obey Bragg’s law

$$n \lambda = 2 d_{hkl} \sin \theta$$  \hspace{1cm} (2.1)

where \(d_{hkl}\) is the interplanar spacing of a set of parallel planes having Miller indices \((hkl)\), \(2\theta\) is the angle between incident and diffracted rays and \(\lambda\) is the wavelength of incident radiation. The intensity data are collected at room temperature using the Siemens SMART-CCD area detector three-circle diffractometer equipped with a graphite monochromated Mo \(K\alpha\) \((\lambda = 0.71073 \text{ Å})\) radiation.

The unit cell dimensions are determined using the method of shortest vectors and are refined by the method of least squares fit of a few reflections chosen from different zones of the reciprocal lattice [48]. Systemic absences and equivalence’s of series of reflections are verified to determine the space group. Once the space group is known, the optimum instrumental parameters are chosen for data collection. Variable scan rates are employed to collect the intensity of reflection based on the ratio of the standard deviation to the net count of reflections. There are two important geometrical factors, viz., polarization and Lorentz factors, which affect the intensities. Hence, polarization and Lorentz corrections are applied.

The structure solution by X-ray method depends on the solution of ‘phases’. The phases depend on atomic positions, which are unknown. This is called phase problem in crystallography and it has been solved by the ‘direct methods’. With the knowledge of morphology of the crystal and direction cosines of the incident and diffracted beams with respect to the direction of the axes of the reciprocal unit cell numerical absorption correction is applied. The program (SHELDRICK, 1996 SADABS) is used for the absorption correction.

Once an approximate chemically meaningful structure is obtained, the actual atomic positions are calculated using the least-squares refinement procedures [54, 55]. The X-ray structure reported in this thesis is solved by SHELXS 86, a FORTRAN program for the solution of crystal structure [56] and refined using (SHELXS-97) [57].
II.4. REDOX PROPERTIES OF BINUCLEAR COPPER (II) COMPLEXES

The study of electrochemical behaviour of dinuclear copper complexes gain momentum from metalloprotein chemistry. The dicopper site in coupled dicopper proteins undergoes two cooperative one electron transfers at the same potential [58]. A vast number of binuclear copper(II) complexes have been studied with the use of cyclic voltammetry and coulometry [59-62]. The electrochemical studies distinguish three types of electrochemical behaviour, i.e., reversible, quasireversible and irreversible electron processes. In some cases, the electron transfer involves either simultaneous or sequential two electron transfer. The nearly diamagnetic triketonate dicopper(II) complexes have two reversible one electron transfer at negative potentials [63-65] and a macrocyclic dicopper(II) complex with no apparent magnetic interaction between the two copper ions is found to undergo reversible electrochemical process at nearly same potential [66]. However, most of the phenoxo bridged dicopper(II) complexes behave quasireversible property involving two sequential one electron transfer reduction and either two sequential single electron transfer or single step two electron transfer oxidation. The actors that are responsible for a electrochemical process to be quasi reversible or irreversible are the inability of the complexes to adopt the required stereochemical changes, speedy chemical reaction accompanied by electrochemical processes, decomposition of the exogenous ligand prior or subsequent to electron transfer.

The following factors affect the electrochemical behaviour of the binuclear copper complexes.

1. Geometrical factors
2. Nature of the donor atoms
3. Electronic and steric factors of the groups attached directly to the donor atoms or to the peripheral region of the ligand framework
4. Flexibility of the ligand
5. Chelate ring size.
6. Ligand unsaturation and conjugation and
7. Solvent effects.

Molecules that contain two or more chemically equivalent and reversible redox sites exhibit thermodynamically controlled electrochemistry [67]. For a molecule with two metal
centres, the redox potential and the stability of the one electron reduced mixed valent species, defined by the conproportionation constant, $K_{\text{con}}$ are related in the following way.

\[
E_1^\text{I} \quad E_2^\text{I} \\
\text{Ox-Ox} \rightleftharpoons \text{Ox - Red} \rightleftharpoons \text{Red - Red} \\
K_{\text{con}} \\
\text{Ox-Ox + Red - Red} \rightleftharpoons 2(\text{Ox - Red}) \\
E_1^\text{I} - E_2^\text{I} = -0.0591 \log K_{\text{con}}
\]

Based on the $K_{\text{con}}$ values, the two metal centre complexes are classified into three classes. When $K_{\text{con}} = 4$, the system is a totally non interacting type or case and the oxidation state of one site is not affected by the oxidation site of another site. If $K_{\text{con}} < 4$, it indicates that the addition of second electron is easier when compared to the first, i.e., $E_1^\text{I} - E_2^\text{I} < 0.0356$ V and the mixed-valent species is unstable with respect to disproportionation. This process is always accompanied with processes [68,69] such as bond breaking, rotation about a bond or protonation, after the addition of the first electron thereby making the addition of second electron easier. When $K_{\text{con}} > 4$, the addition of the second electron is more difficult when compared to the first, i.e., $E_1^\text{I} - E_2^\text{I} > 0.0356$ V and the mixed-valent species is stable with respect to disproportionation.

II.5. INSTRUMENTS USED

All the melting points are uncorrected and determined using open capillary tube. The C, H, and N content of the ligands and complexes are obtained using Heraeus Elemental Analyser. The metal contents present in the complexes are determined by gravimetric estimation. $^1$H NMR spectra of the ligand are obtained in CDCl$_3$ using Varian NMR Spectrometer mode EM 390 operating at 90 MHz or GSX 400 MHz NMR Spectrometer. The mass spectra of the ligand is obtained using MASPEC/msw 9629. The IR spectra of the ligand and complexes are recorded in KBr discs using IFS66V FT-IR spectrometer in the scan range 400-4000 cm$^{-1}$ (MIR) and also in the same instrument in the polyethylene in the range 10-600 cm$^{-1}$ (FIR)/ABB Bomem MB 1.4 FTIR spectrometer 500-4000 cm$^{-1}$. The use of IR spectroscopy very well elucidates the difference in shift of the stretching frequency absorption between the ligand and complexes. Electronic spectra of the ligand and
complexes are measured on a Hitachi 320 Double Beam Spectrophotometer (or) Hewlett Packard 8025 A diode array spectrophotometer. Methanol is used as the solvent for all measurements. The use of UV-Visible spectroscopy can also be utilized to find out the difference in absorption between the ligand and complex. The intra ligand charge transfer transition and d-d transitions could well be studied. The LMCT transition could also be identified. Variable temperature magnetic measurements are performed on PAR Model 155 vibrating sample magnetometer operating at the field strength 5000 Gauss. The instrument is calibrated with the use of metallic nickel supplied with the instrument. The variable temperature magnetic susceptibility data are fitted to the Bleaney- Bowers equation to calculate the best fit parameter, -2J, P and g.

The work described in this thesis was carried out on a JEOL JES-TE100 ESR spectrometer operating at X-band frequencies, having a 100kHz field modulation to obtain a first derivative EPR spectrum. DPPH, with a g value of 2.0036 was used for g-factor calculations. The cyclic voltammograms are recorded using a Perkin Hitachi model 057 X-Y recorder. A three electrode cell assembly is used in which the working and the counter electrodes are platinum foil and the reference electrode is saturated silver/silver chloride electrode. Supporting electrolyte used is tetra butyl ammonium perchlorate (TBAP), DMF/Acetonitrile solvents are used for measurements.

All the chemicals and solvents used in the preparation of complexes are obtained from standard chemical companies and used after proper purification, whenever necessary.
REFERENCES


(1979).
