Experiments should be reproducible. They should all fail in the same way.

Fitt’s Law of the Lab
The study of electronic and molecular structure of organic ligands and coordination compounds utilizes a number of spectroscopic techniques. The present thesis utilizes the following spectroscopic techniques for the characterization of benzimidazolyl diamide ligands, their copper(II) metallatriangle complexes. Besides this, some of the spectral techniques were useful in characterization of product formed during catalytic oxidation studies.

2.1 Electronic spectroscopy

Electronic spectroscopy acts as a major tool in characterizing the transition metal ion complexes. It helps in determining the stereochemistry and in many cases the coordination number of metal ions. Absorption bands can be assigned to particular transitions, and variation in 10 Dq helps in identifying the nature of ligand bound to metal ions. A d-orbital splitting diagram (Figure 2.1–2.3) for various geometries can be used to predict the electronic spectrum of a transition metal ion in that environment.

**Figure 2.1** Energy level diagram showing the splitting of a set of d-orbitals by octahedral and tetrahedral electrostatic crystal field

**Figure 2.2** Splitting of a set of d-orbitals in O₆ and D₄h crystal fields
The molar extinction coefficient defines the molar absorbance of a transition for the peak wavelength of an absorption band. More significant is the oscillator strength, \( f \), which is a measure of the integrated intensity under the entire absorption profile (\( \varepsilon \) vs. \( \nu \)) and is directly related to a theoretically derivable quantity called the dipole strength \( D \) of the transition. If the band stretches from \( \nu_1 \) to \( \nu_2 \) (in cm\(^{-1}\)), then,

\[
    f = 4.32 \times 10^{-9} \int \varepsilon d\nu
\]

For a gaussian curve

\[
    f = 4.326 \times 10^{-9} \varepsilon_{\text{max}} \nu_{1/2}
\]

where, \( \nu_{1/2} \) is the half band width, it is the width of the band, in cm\(^{-1}\), where the molar extinction coefficient has a value half of its maximum.

**Selection rules for electronic transitions**

In centrosymmetric molecule

1. Electric dipole transitions between states of equal parity are forbidden, (Laporte’s rule). In other words \( d-d \), \( p-p \) and \( f-f \) transitions are forbidden but \( d-p \), \( d-f \) transitions are allowed. Thus \( \Delta l = \pm 1 \), is the criteria for orbitally allowed transitions.

2. Transitions between wave functions of different spin are forbidden, *i.e.* \( \Delta S = 0 \) for spin allowed transitions, (Spin selection rule).

**Band Intensities**

To determine whether a transition is electronically or vibronically allowed or is forbidden, a comparison of band intensities (molar extinction coefficients) of...
various transitions is studied. The allowed electronic transitions such as $\pi \to \pi^*$ transitions of aromatic organic compounds, have molar extinction coefficients ($\varepsilon$) of the order of $10^4$–$10^6$ M$^{-1}$cm$^{-1}$. At the other extreme, laporte and spin forbidden $d$$\rightarrow$$d$ transitions in centrosymmetric molecules [e.g. octahedral Mn(II) species] may have intensities of the order of $10^{-2}$ – $10^{-3}$ M$^{-1}$cm$^{-1}$. For octahedral complexes, the order of spin allowed (but laporte forbidden) transitions fall in the range $1$–$10^2$, spin allowed and laporte allowed (including MLCT also) in the range $10^2$–$10^3$ while charge transfer absorption (spin allowed and Laporte allowed) in the range $10^3$–$10^6$ M$^{-1}$cm$^{-1}$.

The intensity and position of absorption maxima in the electronic spectra of coordination compounds provides useful information around the stereochemistry of central metal ion. The presence of a non centrosymmetric copper(II) ion generally yields a more intense $d$$\rightarrow$$d$ spectrum through $d$$\rightarrow$$p$ mixing. Non-centrosymmetric stereochemistries, such as tetrahedral, trigonal bipyramidal, and square pyramidal, are known to be slightly more intense than the corresponding square-coplanar, tetragonal-octahedral, or rhombic-octahedral geometries. For regular stereochemistries involving similar ligands with equal bonding distance, the crystal field splitting parameter 10 Dq increases in the sequence four coordinate < five coordinate < six coordinate and the spectra occurs at correspondingly higher energies.$^5$

In practice, it is the degree of tetragonal distortion which has the major effect in determining the energy of the bands in the $d$$\rightarrow$$d$ spectrum of a copper(II) complex. The presence of rhombic crystal fields with $\pi$-bonding primarily influences the separation and ordering of the $d_{xy}$, $d_{xz}$, and $d_{yz}$ levels. A square planar (CuN$_4$) complex absorbs in the region of 500-55 nm, compressed tetrahedral (CuN$_4$) complex absorbs in the region 625-833 nm, trigonal bipyramidal (CuN$_5$) complexes absorbs in the region 714-909 nm, square base pyramidal (CuN$_5$) complexes absorbs in the region 588-769 nm and tetragonal octahedral (CuN$_6$) complexes absorbs in the region 570-650 nm.$^5$

Thus the position of bands in the $d$$\rightarrow$$d$ spectrum may provide an idea about the local geometry of the copper(II) complex.
2.2 Infrared spectroscopy

The infrared spectrum of a sample is recorded by passing a beam of infrared light through the sample. When the frequency of the infrared radiation is the same as the vibrational frequency of the bond, absorption occurs. Evaluation of the energy of the transmitted light reveals how much energy was absorbed at each frequency (or wavelength). This can be achieved by scanning the wavelength range using a monochromator. Alternatively, the whole wavelength range is measured at once using a Fourier transform instrument and then a transmittance spectrum is generated using a dedicated procedure. Analysis of the position, shape and intensity of peaks in this spectrum reveals details about the molecular structure of the sample.

The infrared region of the electromagnetic spectrum that may be useful for the study of organic ligands and transition metal ion complexes can be subdivided into:

1. Middle Infrared (vibration - rotation) (200–4,000 cm\(^{-1}\))
2. Near Infrared (overtone region) (4,000–12,500 cm\(^{-1}\))

Selection rules

I. In order for molecules to absorb IR radiation as vibrational excitation energy, there must be a change in the dipole moment (direction or magnitude or both) of the molecule as it vibrates.

II. Only transitions for which \(\Delta v = +1\) can occur shall be IR active. At room temperature most molecules are in the \(v_0\) vibrational level and thus most transitions occur from the \(v_0 \rightarrow v_1\) state. The frequency corresponding to this energy is called the ‘fundamental frequency’. Transitions from \(v_0 \rightarrow v_2\) are referred to as the ‘first overtones’ while that from \(v_0 \rightarrow v_3\) are called ‘second overtones’. The difference in energy between two adjacent levels \(E_v\) and \(E_{v+1}\) is given as

\[
\Delta E = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad (2.3)
\]

Vibrations of polyatomic molecules: A molecule having \(N\) numbers of atoms will have \(3N\) degrees of freedom since each coordination value may be specified quite independent of the others. For a nonlinear \(N\) atomic molecule there are \((3N-6)\) normal modes of vibration where six coordinates describe translational and rotational motion.
of the molecule as a whole. An important use of the infrared spectrum is to determine structural information about a molecule. The absorptions of each type of bond (N–H, C–H, O–H, C–X, C=O, C–O, C–C, C=C, C≡C, C≡N and so on) are regularly found only in certain small portions of the vibrational infrared region. A small range of absorption can be defined for each type of bond. Generally an absorption in the range 3000±150 cm\(^{-1}\) is almost always assigned to the presence of a C–H bond in the molecule; an absorption in the range 1715±100 cm\(^{-1}\) is normally due to the presence of a C=O bond (carbonyl group) in the molecule. The same type of range applies to each type of bond. Figure 2.4 illustrates schematically how these are spread out over the vibrational infrared.\(^7\)

![Figure 2.4 The approximate regions where various common types of bonds absorb (stretching vibrations only)](image)

**Carbonyl Absorption in Amides:** Primary and secondary amides in the solid phase (potassium bromide pellet or Nujol) have broad C=O absorptions in the range from 1680-1630 cm\(^{-1}\). The C=O band partially overlaps the N–H bending band which appears in the range 1640-1620 cm\(^{-1}\), making the C=O band appear as a doublet. In very dilute solution, the band appears at about 1690 cm\(^{-1}\). Tertiary amides, which cannot form hydrogen bonds, have C=O frequencies that are not influenced by the physical state and absorb in about the same range as do primary and secondary amides (1680-1630 cm\(^{-1}\)).

**N–H and C–N Stretching Bands:** A pair of fairly strong N–H stretching bands appears at about 3350 cm\(^{-1}\) and 3180 cm\(^{-1}\) for a primary amide in the solid state (KBr or Nujol). The 3350 and 3180 cm\(^{-1}\) bands result from the asymmetric and symmetric vibrations, respectively. In the solid state, secondary amides give one band at about 3300 cm\(^{-1}\). A weaker band may appear at about 3100 cm\(^{-1}\) in secondary amides; it is
attributed to a Fermi resonance overtone of the 1550 cm⁻¹ band. A C–N stretching band appears at about 1400 cm⁻¹ for primary amides.

**N–H Bending Bands:** In the solid state, primary amides give strong bending vibrational bands in the range from 1640 to 1620 cm⁻¹. They often overlap the C=O stretching bands. Primary amides give other bending bands at about 1125 cm⁻¹ and a very broad band in the range from 750 to 600 cm⁻¹. Secondary amides give relatively strong bending bands at about 1550 cm⁻¹; these are attributed to a combination of a C–N stretching band and an N–H bending band.⁷

**O–H Stretching Vibrations:** Alcohols or phenols show a broad O–H stretching vibration for intermolecular hydrogen bonding in the range from 3400 to 3300 cm⁻¹. Phenols also show the hydrogen-bonded O–H. If the alcohol is diluted with carbon tetrachloride, a sharp “free” (non-hydrogen–bonded) O–H stretching band appears at about 3600 cm⁻¹, to the left of the broad band. When the solution is further diluted, the broad intermolecular hydrogen-bonded band is reduced considerably, leaving the free O–H stretching band as the major absorption. Intermolecular hydrogen bonding weakens the O–H bond, thereby shifting the band to lower frequency (lower energy).⁷ The C=N stretching in imines appears in the range 1690-1640 cm⁻¹ with a medium strong intensity. A C–O stretching band will appear in the spectrum at 1260–1000 cm⁻¹.

Infrared spectroscopy is very useful for the structural identification of transition metal complexes. When a transition metal ion coordinates to an organic ligand, the shift in the characteristics frequency of that particular functional group which coordinates to metal ion to a higher or lower wavenumber is observed compared to the free ligand. For example, if a metal ion coordinates through oxygen of carbonyl group, significant shifts in wavenumber of C=O group is observed.⁸

Infrared spectroscopy is also helpful to find out the binding mode of anion in the transition metal ion complexes.⁹ For example, the acetate anion coordinates to a metal in one of the following scheme (Figure 2.5).
Chapter II

Theory of Techniques Utilized in the Identification of Diamide Ligands and their Copper(II) Metallatriangles

Figure 2.5 Different binding modes of acetate anion with metal ion

Uncoordinated acetate (type I) shows C–O symmetric stretch around 1414-1425 cm\(^{-1}\) and C–O antisymmetric stretch around 1575-1585 cm\(^{-1}\). In unidentate mode (type II), symmetric stretch appears around 1248-1311 cm\(^{-1}\) and antisymmetric stretch around 1623-1771 cm\(^{-1}\). In bidentate coordinated acetate, symmetric stretch appears around 1420-1483 cm\(^{-1}\) and antisymmetric stretch appears around 1590-1640 cm\(^{-1}\) in bridging mode (type IV) and in chelating mode (type III), symmetric stretch appears around 1456-1472 cm\(^{-1}\) and antisymmetric stretch appears around 1537-1550 cm\(^{-1}\).

It is well known fact that in nitrato complex, the nitrate group may be present as a free ion, or as a coordinated ligand. In ionic nitrates,\(^{10a}\) NO\(_2\) asymmetric stretching in ONO\(_2\) group appears very strongly in the range 1390-1350 cm\(^{-1}\) and NO\(_2\) deformation of medium intensity in the range 836-815 cm\(^{-1}\). The N–O stretching appears weak in the range 1100-1000 cm\(^{-1}\) in the infrared spectrum of compounds when the nitrate ion is outside the coordination sphere which appears due to deformation of ion in the field of the crystal.\(^{10b}\) Strong absorption bands in the regions 1530-1480 cm\(^{-1}\) are due to NO\(_2\) asymmetric stretch, 1290-1250 cm\(^{-1}\) are due to NO\(_2\) symmetric stretch, 1034-970 cm\(^{-1}\) are due to N–O stretch, 800-781 cm\(^{-1}\) are due to nonplanar rocking are indicative of nitrato group coordinated to the metal ion.\(^{10c}\)

The thiocyanato SCN group may coordinate to a metal through the nitrogen or the sulphur or both (M–NCS–M). The C–N stretching frequencies are generally lower in the M–NCS complexes than in the M–SCN complexes. The C–S stretching frequency is more useful in distinguishing these two isomers: 780-860 cm\(^{-1}\) for the M–NCS and 690-720 cm\(^{-1}\) for the M–SCN group. The M–NCS group is linear or bent, while the M-SCN group is always bent. Ionic thiocyanato group in KSCN shows C–N stretch at 2053 cm\(^{-1}\) and C–S stretch at 748 cm\(^{-1}\) while NCS bending appears at 486 and 471 cm\(^{-1}\). The NCS group also forms a bridge between two metal atoms (Figure 2.6).
Figure 2.6 Different bridging modes of SCN group

The C–N stretching frequency of a bridging group is generally higher than that of a terminal group. The C–N stretching frequencies of Pt(II) complexes are 2182-2150 cm\(^{-1}\) for the bridging and 2120-2100 cm\(^{-1}\) for the terminal NCS group. Complex I exhibit one bridging C–N stretching, whereas complex II exhibits both bridging and terminal C–N stretching bonds. Complex I, however exists as two isomers, IA and IB which absorbs at 2162 and 2169 cm\(^{-1}\) respectively.\(^8\)

The free perchlorate (ClO\(_4^–\)) ion belongs to the high symmetry point group T\(_d\). Of the four fundamentals, only \(\nu_3\) and \(\nu_4\) are infrared active. If the ion is coordinated to a metal, the symmetry is lowered and splitting of the degenerate modes occurs, together with the appearance of new bands corresponding to Raman active bands in the free ion. Ionic perchlorate shows one band in the region 1170-1040 cm\(^{-1}\) (\(\nu_3\)) and one in the region 935-950 cm\(^{-1}\) (\(\nu_4\)). Unidentate perchlorate shows two bands in the region 1165-1012 cm\(^{-1}\) (\(\nu_3\)) and one around 920 cm\(^{-1}\) (\(\nu_4\)). Bidentate perchlorate shows three bands in the region 935-1270 cm\(^{-1}\) (\(\nu_3\)) and one around 1025 cm\(^{-1}\) (\(\nu_4\)).\(^8\)

2.3 Nuclear magnetic resonance (NMR)\(^{11}\)

2.3.1 \(^1\)H NMR spectroscopy

The nucleus of a proton behaves as a tiny spinning magnet. Since it possesses both electric charge and spin, it can align itself with or opposed to an external magnetic field. It can precess around the axis of an applied external magnetic field, with a frequency called precessional frequency \(v\).
\[ \nu \propto B_o \]  
(2.4)

where, \( B_o \) is external magnetic field

\[ \nu = \gamma B_o / 2\pi \]  
(2.5)

or

\[ 2\pi \nu = \gamma B_o \]  
(2.6)

where, \( \gamma \) is magnetogyric ratio, being the ratio between the nuclear magnetic moment \( \mu \) and the nuclear angular momentum \( I \)

\[ \gamma = \mu / I \]  
(2.7)

The precessing proton will only absorb energy from the radio frequency source. If the precessing frequency is the same as the frequency of the radio frequency beam, the nucleus and the radio frequency beam are said to be in resonance.

**Chemical Shift:** A single proton peak is expected from the interaction of \( rf \) energy and a strong magnetic field for an isolated proton according to the basic equation

\[ \nu_1 = \frac{\nu}{2\pi} B_o \]  
(2.8)

where, \( \nu_1 \) = applied frequency, \( B_o \) = flux density of the stationary magnetic field, and \( \gamma/2\pi \) = constant

But a proton in a molecule is also shielded to a small extent by its electron cloud. The density of the electron charge varies with the chemical environment. This gives rise to small differences in absorption positions. Thus the basic NMR equation for the isolated proton can be modified as:

\[ \nu_{\text{eff}} = \frac{\nu}{2\pi} B_o (1 - \sigma) \]  
(2.9)

where, \( \sigma \) = ‘shielding constant’

Electrons under the influence of a magnetic field circulate and in circulating, generate their own magnetic field opposing the applied field; hence the shielding effect. This effect accounts for the diamagnetism exhibited by all organic compounds. The degree of shielding of a proton on a carbon atom will depend on the inductive effect of other
groups attached to the carbon atom. The difference in the absorption position of a particular proton from the absorption position of a reference proton is called the “chemical shift” of the particular proton. Generally the reference compound used is tetramethysilane (TMS). This is chemically inert, symmetrical, volatile (bp 27°C), and soluble in most organic solvents. It gives a single, intense, sharp, absorption peak and its proton are more shielded than most of the organic protons.

Splitting patterns are produced due to the coupling of proton that have different chemical shifts and is called first order splitting patterns \((\Delta \nu/J \geq 6)\). Two simple rules can be enumerated as:

1. Splitting of a proton absorption by neighboring protons. The multiplicity of the splitting pattern is determined by the number of these protons. The general formula, which covers all nuclei, is \((2nI+1)\), \(I\) being the nuclear spin quantum number.

2. The relative intensities of the peaks of a multiplet also depend on \(n\). The general formula is \((a + b)^n\); when this is expanded to the desired value of \(n\), the coefficients give the relative intensities.

**Coupling constant \((J)\):** The separation between the peaks in a simple multiplet is called the coupling constant, \(J\). The coupling constant is a measure of how strongly a nucleus is affected by the spin states of its neighbor. The spacing between the multiplet peaks is measured on the same scale as the chemical shift, and the coupling constant is usually expressed in Hertz (Hz) as shown in Figure 2.7.

For most of the aliphatic protons in acyclic systems, the magnitudes of coupling constants are near 7.5 Hz. These coupling constants are typical for the interaction of two hydrogens on adjacent \(sp^3\)-hybridized carbon atoms. Two hydrogen atoms on adjacent carbon atoms can be described as a three bond interaction and abbreviated as \(^3J\). Typical values for this observed coupling is approximately 6 to 8 Hz.
In alkenes, the $^3J$ coupling constants for hydrogen atoms that are \textit{cis} to each other are about 10 Hz, while the $^3J$ coupling constants for hydrogen atoms that are \textit{trans} are larger, about 16 Hz. ‘The coupling constants of the groups of protons that split one another must be nearly identical.’ This axiom is useful in interpreting a spectrum that may have several multiplets, each with a different coupling constant. An illustration of this axiom is given in Figure 2.8. The protons in each group interact to the same extent. In this illustration, with the $J$ values given, clearly quartet A ($J = 7$ Hz) is associated with triplet C ($J = 7$ Hz) and not with triplet B or D ($J = 5$ Hz). It is also clear that triplets B and D are related to each other in the interaction scheme.

Two-bond couplings are quite common in NMR spectra. They are usually called geminal couplings because the two nuclei that interact are attached to the same central atom. Two-bond coupling constants are abbreviated as $^2J$. The most common type of two-bond coupling, H–C–H, is frequently negative. The amount of geminal coupling depends on the HCH angle. In general, it has been found that $^2J$ geminal coupling constants increase as the angle decreases. Some $^2J$ coupling constant are shown in Figure 2.9.
In a typical hydrocarbon, the spin of a hydrogen nucleus in one C–H bond is coupled to the spins of those hydrogens in adjacent C–H bonds. These H–C–C–H couplings are usually called vicinal couplings because the hydrogens are on neighboring carbon atoms. Vicinal couplings are three-bond couplings and have a coupling constant designated as $^3J$. These couplings produce spin–spin splitting patterns that follow the $n + 1$ rule in simple aliphatic hydrocarbon chains. Some $^3J$ coupling constant are shown in Figure 2.10.

Under special cases, coupling occurs between protons that are separated by four or more covalent bonds, and these are referred to as long-range couplings. Long-range couplings are common in allylic systems, aromatic rings, and rigid bicyclic systems. This four-bond coupling ($^4J$) is called allylic coupling. The π electrons of the double bond help to transmit the spin information from one nucleus to the other. Some $^4J$ coupling constant are shown in Figure 2.11.
2.3.2 $^{13}$C NMR spectroscopy

The $^{13}$C NMR spectroscopy can be used to determine the number of nonequivalent carbon atoms and to identify the types of carbon atoms (methyl, methylene, aromatic, carbonyl, etc.) that may be present in a compound. Thus, $^{13}$C NMR spectrum of a compound provides direct information about the carbon skeleton present.

The chemical shift values appear over a range (0-200 ppm) much larger than that observed for protons (0-16 ppm). Because of the very large range of values, nearly every nonequivalent carbon atom in an organic molecule gives rise to a peak with a different chemical shift. Peaks rarely overlap as they often do in proton NMR.

Many of the important functional groups of organic chemistry contain a carbonyl group. In determining the structure of a compound containing a carbonyl group, it is frequently helpful to have some idea of the type of carbonyl group in the unknown. Chemical shift data for carbonyl carbons are particularly powerful when combined with data from an infrared spectrum. The probability of finding two $^{13}$C atoms adjacent to each other in the same molecule is even lower. Therefore, homonuclear (carbon–carbon), spin–spin splitting patterns where the interaction occurs between two $^{13}$C atoms is rarely observed. The spins of protons attached directly to $^{13}$C atoms do interact with the spin of carbon and cause the carbon signal to be split according to the $n+1$ rule. This is heteronuclear (carbon–hydrogen) coupling involving two different types of atoms. In $^{13}$C NMR spectroscopy, splitting that arises from the protons directly attached to the carbon atom are studied. To avoid this C–H coupling in $^{13}$C NMR, spectra are recorded as proton decoupled. The decoupling technique obliterates all interactions between protons and $^{13}$C nuclei; therefore, only singlet are observed in a decoupled $^{13}$C NMR spectrum.

2.4 Fluorescence spectroscopy

The emission of light that occurs from electronically excited states is known as luminescence. Luminescence is formally divided into two categories: Fluorescence and phosphorescence, depending on the nature of the excited state.
In case of fluorescence, the electron in the excited orbital is paired to the second electron in the ground state orbital. Consequently, transition to the ground state is spin allowed and occurs rapidly by emission of photon. The emission rates of fluorescence are typically $10^8$ s$^{-1}$, so that a typical fluorescence life time is near 10 ns. Because of the short time scale of fluorescence, measurement of the time resolved emission requires sophisticated optics and electronics. Phosphorescence is emission of light from a triplet excited state. This is a forbidden transition of electron from excited state to the ground state and emission rates are slow ($10^3$ - $10$ s$^{-1}$). Fluorescence typically occurs from aromatic molecule and the fluorescent substance known as fluorophores.

**Fluorescence quantum yields**\textsuperscript{13,14}

The fluorescence quantum yield is the ratio of the number of photons emitted to number absorbed. The process governed by the rate constant $\Gamma$ (emissive rate of the fluorophore) and $K_{nr}$ (rate of non-radioactive decay to $S_0$) both depopulate the excited state.

The Quantum yield is given by

$$Q = \frac{\Gamma}{\Gamma + K_{nr}}$$

The quantum yield can be close to unity, if the radiationless decay rate is much smaller than the rate of radioactive decay, that is $K_{nr} << \Gamma$.

**Fluorescence Quenching:** The intensity of fluorescence can be decreased by a wide variety of process and is known as quenching. Quenching can occur by different mechanism, one being Collisional quenching. This occurs when the excited state fluorophore is deactivated upon contact with some other molecule in solution, which is called quencher. The decrease in intensity in such case is described by the well-known Stern-Volmer Equation:

$$\frac{F_0}{F} = 1 + k[Q] = 1 + k_q \tau_o [Q]$$

where, $K = $ Stern-Volmer quenching constant,

$k_q = $ bimolecular quenching constant,

$\tau_o = $ unquenched life time,

$[Q] = $ quencher concentration
The coordination of a metal ion causes an enhancement of the fluorescence emission, known as Chelation Enhanced Fluorescence effect (CHEF)\textsuperscript{15} or a quenching of the fluorescence, known as Chelation Enhancement Quenching effect (CHEQ)\textsuperscript{16}, both effects can be coupled with a red or blue shift of the emission band. The various mechanisms are described below:

**Paramagnetic fluorescence quenching:** In a wide variety of metal complexes the formally forbidden intersystem crossing (ISC) become faster due to the presence of a paramagnetic atom in the proximity of the fluorophore. This phenomenon is called paramagnetic effect, and it is the principal cause of the fluorescence quenching by the d\textsuperscript{9} Cu(II) ion. Metal complexes containing this metal ion undergo intersystem crossing by excitation, from S\textsubscript{1} to T\textsubscript{1} state of the fluorophore that is deactivated by bimolecular non-radiative processes. For this reason classical probes for Cu(II) and other strongly paramagnetic metal ions such as Fe(III), Cr(III), Co(II) are usually based on the quenching of the fluorescence.\textsuperscript{17}

**Photoinduced Electron Transfer (PET):** PET is a deactivation process involving an internal redox reaction between the excited state of the fluorophore and another species able to donate or to accept an electron. A fundamental point explaining this process is to consider that in the excited state the properties of the species are quite different compared with those of the ground-state. In particular, due to its higher energy content, an excited state is both a stronger reducing and oxidant than the corresponding ground state. Generally, in fluorescent metal sensors, PET takes place from a lone pair of the coordinating atoms (e.g. N, O, S, P) to the HOMO of the excited fluorophore. The presence of a coordinated metal ion lowers the energy of the lone pair involved in the coordination preventing the PET, thus causing the switch-ON of the fluorescence. PET strongly depends on the solvent polarity which affects the oxidation potential of the lone pairs of the coordinating moiety. Higher solvent polarity makes easier the electron transfer; as a consequence, the PET-mediated quenching effect of the fluorescence occurs more quickly in high polar environments.\textsuperscript{18}

**Photoinduced Charge Transfer (PCT):** This mechanism involves the transfer of an electron between electron donor and acceptor functionalities to promoting
fluorescence. PCT sensors incur partial charge transfer of a fully conjugated $\pi$ system. All PCT sensors show an integrative receptor and fluorophore, as opposed to PET sensors which have the electron donor moiety separated by a spacer from the fluorophore. For this reason, in PCT sensors the complexation of the metal ion gives rise to an alteration of electron energy levels causing a fluorescence ‘turn-off’ or ‘turn-on’ and a variation in emission and absorption wavelengths, depending on the type of fluorophore, metal ion and complexation mode.\(^\text{17}\)

**Excimer or exciplex formation:** In this case there is an interaction between excited and ground-state components which is sufficiently strong to give new chemical species called excimers or exciplexes. Excimer and exciplex formation is a reversible process and both can be luminescent chemical entities. The emission of an excimer or exciplex is always at a lower energy compared with the monomer emission, and usually the corresponding band is rather weak and broad. The presence of a metal ion strongly encourages or disrupts excimer or exciplex, affecting the emission spectra. The ratio between the emission intensity of monomer and excimer gives a quantitative measure of the amount of metal ion present in solution.\(^\text{17}\)

### 2.5 Cyclic Voltammetry\(^\text{19}\)

Figure 2.12 (a) illustrates the shape of a voltage-sweep voltammogram with scan rate’s that may vary from 0.1 V/sec to 100 V/sec. For such high scan rates the electrode has essentially a finite and fixed area.

When the reduction process is reversible the peak current is given by the relation.

$$i_p = 0.4463 \text{ nFA (Da)}^{1/2}c$$

with

$$a = \frac{nFv}{RT} = \frac{nv}{0.026} \text{ at } 25^\circ \text{C}$$

where, $v$ is the scan rate in volts per second

Thus in terms of the adjustable parameters the peak current is given by

$$i_p = 2.67 \times 10^5 \text{ n}^{3/2} \text{ AD}^{1/2} \text{CV}^{1/2} \text{ at } 25^\circ \text{C}$$
For a reversible process the peak potential can be related to the polarographic half wave potential $E_{1/2}$ the expression.

$$E_p = E_{1/2} - \frac{RT}{nF} = E_{1/2} - 0.0285/n \text{ at } 25^\circ C$$ (2.13)

Because of the dynamic nature of the voltage sweep voltammetry, irreversible processes give a distinctly different expression for the peak current from those for reversible systems,

$$i_p = 3.01 \times 10^5 n (\alpha n_a)^{1/2} AD^{1/2} CV^{1/2} \text{ at } 25^\circ C$$ (2.14)

where, $n_a =$ number of electrons in the rate controlling step and $\alpha =$ transfer coefficient (normally with a value between 0.3 and 0.7)

**Figure 2.12** (a) Linear voltage-sweep voltammogram with reversal of sweep direction to give a cyclic voltammogram. Initial sweep direction to more –ve voltage; (b) Method of measurement of peak current and peak ratios of cyclic voltammogram

An extension of voltage-sweep voltammetry is called cyclic voltammetry and involves reversing the triangular scan after the peak of the reduction process has been passed. Thus the voltage is scanned negatively beyond the peak and then reversed in a linear positive sweep. Such a technique provides even more information concerning the properties and characteristics of the electrochemical process and also gives insight into any complicating side processes such as pre and post-chemical reactions as well as kinetic consideration.19
For a reversible process the ratio of the peak current for the cathodic process relative to the peak current for the anodic process is equal to unity. To measure the peak current for the anodic process the extrapolated baseline going from the foot of the cathodic wave to the extension of this cathodic current beyond the peak must be used as a reference, as illustrated in Figure 2.12 (b). If a post chemical process destroys the product before the reverse scan occurs then the ratio of the cathodic peak current to the anodic peak current will be greater than unity. The difference and the peak potentials between the anodic and cathodic processes of a reversible reaction is given by the relationships.

\[(E_p)_a - (E_p)_c = \frac{0.0595}{n} \text{ at } 25^\circ \text{C} \quad (2.15)\]

Again, this provides a very rapid and convenient means for establishing the number of electrons involved in the electrochemical reaction.

2.6 Magnetic measurements

The solution magnetic susceptibilities and magnetic moments can be measured by Evan’s method. This method is based on the fact that the resonance condition (magnetic field, frequency) in an NMR experiment for a given nucleus depends, among other factors, also upon the volume susceptibility of the medium surrounding the nucleus. For such susceptibility measurement a set of two coaxial NMR tubes is required (Figure 2.13). Both of the tubes contain a solvent system consisting of a solvent plus a certain percentage of an inert "indicator" compound (tert-butyl alcohol). The inner tube contains in addition to a known amount of the substance of which the paramagnetic moment is to be determined. Owing to the different volume susceptibility of the two solutions the nuclei (protons) of the "indicator" compound in the two compartments are differently shielded. It can be shown that the resulting shift difference (Figure 2.13) of the absorption signals of the "indicator" nuclei in the two compartments is related to the volume susceptibility \(\chi_g\) (eq 2.16) of the two solutions and therefore to the mass susceptibility \(\chi_m\) (eq 2.17) and the magnetic moment \(\mu_{\text{eff}}\) (eq 2.18) of the paramagnetic substance in the inner tube.

\[\chi_g = 3 \times \Delta \nu \text{ (Hz)} / 2\pi \times c \text{ (g/mL)} \times \nu \quad (2.16)\]
\[ \chi_m = \chi_g \times MW \]  
\[ \mu_{\text{eff}} = 2.82 (\chi_m \times T)^{1/2} \]  

where, \( v = \) spectrometer frequency (Hz), \( c = \) concentration in g/mL; \( MW = \) molecular weight

Figure 2.13 Cell assembly for micro technique (left) and two resonance signals of 2% tert-butyl alcohol. Outer Compartment: 2% \( t \)-butanol in water and Inner Compartment: 2% tert-butyl alcohol in water as solvent for 82 mg of anhydrous CuSO\(_4\) in 10 mL of solution (right)

A number of researchers have utilized this method to obtain the solution magnetic moment of transition metal ion complexes.\(^{\text{22}}\)

2.7 Electron paramagnetic resonance spectroscopy\(^{\text{23,24}}\)

Electron paramagnetic resonance is a branch of spectroscopy in which radiation of microwave frequency is absorbed by molecules, ions or atoms possessing electrons with unpaired spins. In EPR different energy states arise from the interaction of the unpaired electron spin moment (given by \( m_s = \pm 1/2 \)) with the magnetic field, the so called Zeeman Effect. The Zeeman Hamiltonian for the interaction of an electron with the magnetic field is given by equation 2.19, while the transition energy between the two \( m_s \) states is given by equation 2.20:

\[ H^* = g\beta Hsz^- \]  
\[ \Delta E = g\beta H \]  

where, \( g = 2.0023, \beta = \) electron Bohr magneton \((9.274096 \pm 0.000050 \times 10^{-21} \text{ erg})\), \( Sz^- = \) spin operator and \( H = \) applied magnetic field strength

EPR spectra are commonly presented as derivative curves, i.e. the first derivative of the absorption curve is plotted against the strength of the magnetic field. While running an EPR spectrum and external standard diphenylpicryl hydrazide, DPPH, is used together with a microwave frequency counter. DPPH has a \( g \) value of
2.0037±0.0002. The field sweep is assumed to be linear, and the \( g \) values of other peaks are calculated relative to the standard. The field axis is in units of gauss and the \( g \) value is reported as dimensionless quantity using

\[
g = \frac{h}{\beta H}
\]

where, \( \nu \) is the fixed frequency of the probe and \( H \) is obtained from the spectrum.

**EPR spectra of transition metal ion complexes**

An important feature of transition metal systems is that the ‘\( g \)’ factor will deviate from 2.0023 and it may be anisotropic.\(^{23}\) This is because many of the molecules contain more than one unpaired electron. These properties give rise to orbital contributions and zero field effects. Spin orbit couplings also give rise to large zero field splittings (of 10 cm\(^{-1}\) or more) by mixing ground and excited states.

**\( g \)-anisotropy:** \( g \)-anisotropy in the system refers to different values of \( g \) for the magnetic field oriented along (\( g_\parallel \)) and perpendicular (\( g_\perp \)) to the molecular \( z \) direction. The \( g \) value for any orientation is given by

\[
g^2 = g_\parallel^2 \sin^2 \theta + g_\perp^2 \cos^2 \theta
\]

Where \( \theta \) is the angle that the principle axis (i.e. the \( g_\parallel \) axis) makes with the applied field. In solid state, all orientations of the crystallite are probable. Absorption will occur at all fields between that associated with \( g_\parallel \) and that associated with \( g_\perp \). But there are more crystallites that have \( g_\perp \) aligned than \( g_\parallel \) and therefore most intense absorption will correspond to \( g_\perp \). Thus two different signals are obtained in an ideal spectrum but due to overlapping features generated by \( g_\parallel \) and \( g_\perp \) in reality makes it
difficult to obtain their values. In frozen solution however a well resolved spectrum can be obtained.

![Diagram](image)

**Figure 2.14** (a) $^2B_{1g}$ ground state (for $D_{4h}$ symmetry) Zeeman and hyperfine splitting diagram (b) powder pattern spectrum of the $^2B_{1g}$ ground state

**Hyperfine couplings and zero field splitting:** Additional features in the epr spectrum of transition metal complexes results from the interaction of electron spin with the nuclear spin. For a copper nucleus, nuclear spin of 3/2 interacts with the electron spin producing a hyperfine splitting of the EPR signal into $2I+1 = 4$ allowed ($\Delta m_1 = 0, \Delta m_s = 1$) transitions (Figure 2.14).

EPR of exchange coupled complexes (dimeric, trimeric etc.) results in exchange narrowing. When exchange interactions are negligible, the single ion resonances are broadened by dipolar interactions, whereas the line shape remains nearly Gaussian. According to Van Vleck’s model, the presence of exchange interaction, the second moment is dependent on the dipolar interaction energy only. On the other hand, the fourth moment is dependent on both dipolar and exchange interactions. The relative decrease of second moment as compared to the fourth moment caused by exchange can be related quantitatively to the well-known exchange narrowing phenomena.\(^{24}\)

**2.8 X-ray crystallography**

**2.8.1 X-ray single crystal diffraction**\(^{25,26}\)

Single crystal X-ray diffraction is a non-destructive analytical technique which provides detailed information about the internal lattice of crystalline substances, including unit cell dimensions, bond-lengths, bond-angles, and details of site-ordering. Directly related is single crystal refinement, where the data generated from the X-ray analysis is interpreted and refined to obtain the crystal structure.
Fundamental principles of single crystal X-ray diffraction: X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference and a diffracted ray. Bragg's Law, \(2d \sin \theta = n\lambda\) relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. The diffracted X-rays are detected, processed and counted. By changing the geometry of the incident ray, the orientation of the centered crystal and the detector, all possible diffraction directions of the lattice can be attained.

Interpretation of data: Structures of a variety of compounds contain several thousand unique reflections, whose spatial arrangement is referred to as a diffraction pattern. Indices \((hkl)\) may be assigned to each reflection, indicating its position within the diffraction pattern. This pattern has a reciprocal Fourier transform relationship to the crystalline lattice and the unit cell in real space. This step is referred to as the solution of the crystal structure. After the structure is solved, it is further refined using least-squares techniques.

Data collection: Once the crystal is centered, a preliminary rotational image is often collected to screen the sample quality and to select parameters for later steps. An automatic collection routine can then be used to collect a preliminary set of frames for determination of the unit cell. Reflections from these frames are auto-indexed to select the reduced primitive cell and calculate the orientation matrix that relates the unit cell to the actual crystal position within the beam. The primitive unit cell is refined using least-squares and then converted to the appropriate crystal system and Bravias lattice. This new cell is refined using least squares routines to determine the final orientation matrix for the sample. After the refined cell and orientation matrix have been determined, intensity data is collected. Generally this is done by collecting a sphere or hemisphere of data using an incremental scan method, collecting frames in 0.1° to 0.3° increments (over certain angles while others are held constant). Data is typically collected between 4° and 60° 20 for molybdenum radiation. A complete data collection may require anywhere between 6-24 hours, depending on the specimen and the diffractometer. Exposure
times of 10-30 seconds per frame for a hemisphere of data will require total run times of 6-13 hours.

**Corrections for background, absorption, etc.:** After the data have been collected, corrections for instrumental factors, polarization effects, X-ray absorption and (potentially) crystal decomposition must be applied to the entire data set. This integration process also reduces the raw frame data to a smaller set of individual integrated intensities. These correction and processing procedures are typically part of the software package which controls and runs the data collection.

**Structure solution and refinement:** High speed computers use direct methods and least-squares to assign phase to strong reflection and iteration produces a refined fit that leads to the initial electron density map. Elements can be assigned to intensity centers, with heavier elements associated with higher intensities. Distances and angles between intensity centers can also be used for atom assignment based on likely coordination. Once the initial crystal structure is solved, its refined to attain the best possible fit between the observed and calculated crystal structure. The final structure solution will be presented with an $R$ value, which gives the percentage variation between the calculated and observed structures.

**2.8.2 X-ray powder diffraction**

Powder X-ray diffraction (PXRD) is a widely used technique for characterizing solid materials. The sample is in a powdery form and consists of fine grains in the form of single crystallites; the crystalline domains are randomly oriented in the sample. When a 2–D diffraction pattern is recorded, it shows concentric rings of scattering peaks corresponding to the various $d$-spacing in the crystalline lattice. The positions and the intensities of the peaks can be used for identifying the underlying structure (or phase) of a solid material. The diffraction lines of graphite are different from diamonds even though they are both made up of carbon atoms. This phase identification is important because the material properties are highly dependent on the structure. A powder sample shows that the diffracted beams form continuous cones. A circle of film is used to record the diffraction pattern. For every set of crystal planes, one or more crystals will be in the correct orientation to give the correct angle to satisfy the
Bragg’s equation. Every crystal plane is thus capable of diffraction, giving the appearance of a continuous line.

Powder X-ray diffraction (PXRD) is one of the most important characterization tools used in solid state chemistry and materials science. We can determine the size and the shape of the unit cell for any compound most easily using the diffraction of x-rays.

\[
2 \times \text{wavelength} = 2dsin\theta
\]

For constructive interference between these waves, the path difference must be an integral number of wavelengths:

\[
n \times \text{wavelength} = 2x
\]

This leads to the **Bragg’s equation** (2.22):

\[
n\lambda \text{ (wavelength)} = 2dsin\theta
\]  
(2.22)

For a number of values of \(n\), main lines are observed and from each of these lines we can calculate the value of \(d\), the interplanar spacing between the atoms in the crystal (Figure 2.15).

**Data collection:** The intensity of diffracted X-rays is continuously recorded as the sample and detector rotate through their respective angles. A peak in intensity occurs when the compound contains lattice planes with d-spacing appropriate to diffract X-rays at that value of \(\theta\). Although each peak consists of two separate reflections (K\(\alpha_1\) and K\(\alpha_2\)), at small values of 2\(\theta\), the peak locations overlap with K\(\alpha_2\) appearing as a hump on the side of K\(\alpha_1\). Greater separation occurs at higher values of \(\theta\). Typically
these combined peaks are treated as one. The $2\lambda$ position of the diffraction peak is typically measured as the centre of the peak at 80% peak height. Results are commonly presented as peak positions at 20 and X-ray counts (intensity) in the form of a table or an x-y plot. Intensity ($I$) is either reported as peak height intensity, that intensity above background, or as integrated intensity, the area under the peak. The relative intensity is recorded as the ratio of the peak intensity to that of the most intense peak ($relative\ intensity = \frac{I}{I_1} * 100$).

**Determinant of an unknown sample:** The $d$-spacing of each peak is then obtained by solution of the Bragg equation for the appropriate value of $\lambda$. Once all $d$-spacings have been determined, automated search/match routines compare the $d$'s of the unknown to those of known materials. Because each compound has a unique set of $d$-spacings, matching these $d$-spacings provides an identification of the unknown sample. A systematic procedure is used by ordering the $d$-spacings in terms of their intensity beginning with the most intense peak. Files of $d$-spacings for hundreds of thousands of inorganic compounds are available from the International Centre for Diffraction Data as the Powder Diffraction File (PDF).

2.9 Gas chromatography / mass spectrometry (GC-MS)$^{28,29}$

GC-MS is a method that combines the features of gas-liquid chromatography and mass spectrometry to identify different substances within a test sample. Applications of GC-MS include drug detection, environmental analysis and in identification of organic compounds. Additionally, it can identify trace elements in materials that were previously thought to have disintegrated beyond identification.

**Instrumentation and analysis:** The GC-MS is composed of two major building blocks: the gas chromatograph and the mass spectrometer (Figure 2.16). The gas chromatograph utilizes a capillary column which depends on the column's dimensions (length, diameter, film thickness) as well as the phase properties (e.g. 5% phenyl polysiloxane). The difference in the chemical properties between different molecules in a mixture will allow separation of the molecules as the sample travels the length of the column. The molecules are retained by the column and then elute (come off) from the column at different times (called the retention time). This allows the mass spectrometer to capture, ionize, accelerate, deflect, and detect the ionized molecules
separately. The mass spectrometer does this by breaking each molecule into ionized fragments and detecting these fragments using their mass to charge ratio. These two components, used together, allow a much finer degree of substance identification than either unit used separately. It is not possible to make an accurate identification of a particular molecule by gas chromatography or mass spectrometry alone.

Figure 2.16 Example of a GC-MS instrument (left) and schematic diagram of GCMS (right)

The mass spectrometry process normally requires a very pure sample while gas chromatography using a traditional detector (e.g. Flame ionization detector) cannot differentiate between multiple molecules that happen to take the same amount of time to travel through the column (i.e. have the same retention time), which results in two or more molecules that co-elute. Sometimes two different molecules can also have a similar pattern of ionized fragments in a mass spectrometer (mass spectrum). Combining the two processes reduces the possibility of error, as it is extremely unlikely that two different molecules will behave in the same way in both a gas chromatograph and a mass spectrometer. Therefore, when an identifying mass spectrum appears at a characteristic retention time in a GC-MS analysis, it typically lends to increased certainty that the analyte of interest is in the sample.

2.10 Scanning electron microscopy

The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. In most applications, data are collected over a selected area of the surface of the sample, and a 2–D image is
generated that displays spatial variations in these properties. Areas ranging from approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 20X to approximately 30,000X, spatial resolution of 50 to 100 nm). The SEM is also capable of performing analyses of selected point locations on the sample; this approach is especially useful in qualitatively or semi-quantitatively determining chemical compositions (using EDS), crystalline structure, and crystal orientations (using EBSD). A typical SEM instrument is shown in Figure 2.17.

![Figure 2.17 A typical SEM instrument, showing the electron column, sample chamber, EDS detector, electronics console, and visual display monitors (left) and a micrograph of pollen grains taken on an SEM show the characteristic depth of field of SEM micrographs (right)](image)

**Application of SEM:** The SEM is routinely used to generate high-resolution images of shapes of objects (SEI) and to show spatial variations in chemical compositions: (1) acquiring elemental maps or spot chemical analyses using EDS, (2) discrimination of phases based on mean atomic number (commonly related to relative density) using BSE, and (3) compositional maps based on differences in trace element "activators" (typically transition metal and rare earth elements) using CL. The SEM is also widely used to identify phases based on qualitative chemical analysis and/or crystalline structure. Surface morphology studies of a number of coordination complexes involving metal ions like Cu(I/II), Co(II), Ni(II), Zn(II), VO(II) and Ru(II) have been studied using SEM in the recent years. Precise measurement of very small features and objects down to 50 nm in size is also accomplished using the SEM. Backscattered electron images (BSE) can be used for rapid discrimination of phases in multiphase samples. SEMs equipped with diffracted backscattered electron detectors (EBSD) can be used to examine microfabric and crystallographic orientation in many materials.
References


59

