Chapter II

Reagents and physicochemical methods

This chapter deals with the details of the reagents used, the methods of preparation of metal salts as well as Schiff base ligands and the various procedural details of different types of physicochemical analyses employed for the structural elucidation of the complexes.

2.1 Reagents

2.1.1 Chemicals used in the synthesis of the Schiff base ligands

4-antipyrine carboxaldehyde, 2-aminomethylpyridine and 3-formylchromone were purchased from ‘Sigma Aldrich Chemicals Co.’ USA. Ethylenediamine was purchased from E.Merck.

2.1.2 Metal salts

The metal salts used in the synthesis of complexes were:

Fe(III)salts: FeCl₃, FeBr₃.6H₂O, Fe(NO₃)₃.6H₂O, Fe(ClO₄)₃.6H₂O and Fe(SCN)₃.6H₂O.

Co(II) salts: CoCl₂.6H₂O, CoBr₂.6H₂O, CoI₂.6H₂O, Co(NO₃)₂.6H₂O and Co(ClO₄)₂.6H₂O.

Ni(II) salts: NiCl₂.6H₂O, NiBr₂.6H₂O, NiI₂.6H₂O, Ni(NO₃)₂.6H₂O and Ni(ClO₄)₂.6H₂O.

Cu(II) salts: CuCl₂.2H₂O, CuBr₂.4H₂O, Cu(NO₃)₂.3H₂O, Cu(ClO₄)₂.6H₂O.

A R grade chlorides of Fe(III), Co(II), Ni(II) and Cu(II) and nitrates of Fe(III), Co(II) and Cu(II) were purchased from E.Merck, India. The bromides, perchlorates and iodides of all metals and nitrate of Ni(II) were
prepared from the metal carbonates of the corresponding acids by the following procedure. The analar BDH metal carbonates were dissolved in corresponding 50% acids and the resulting solution is filtered out and evaporated over a steam bath. The crystalline solids obtained were dried under vacuum over phosphorus(V)oxide.

Ferric thiocyanate was prepared by a reported method [152]. Aqueous concentrated solutions of FeCl$_3$.6H$_2$O and ammonium thiocyanate were mixed in the ratio 1:3 by weight. The deep red ferric thiocynate formed was extracted with ether. The ether layer was then evaporated to get the salt in the solid form.

2.1.3 Solvents

The solvents used in the present investigation are acetone, acetonitrile, ethanol, ethylacetate, methanol, DMF, DMSO and nitrobenzene. All solvents were AR grade.

2.1.4 Other reagents

Acetic acid, ammonium chloride, ammonium thiocyanate, EDTA, ferric alum, liquor ammonia, murexide indicator, oxalic acid, hydrazine hydrate, potassium dichromate, potassium iodide, potassium thiocyanate, silver nitrate, sodium chloride, sodium nitrite, sodium thiosulphate and xylenol orange indicator are also employed at different stages. The reagents are either BDH or E.Merck GR grade and used without further purification.

2.1.5 Schiff bases

The two Schiff bases used in the present investigation are

1) 2,3-dimethyl-4-formyl-[2′-(aminomethyl)pyridine]-1-phenyl-3-pyrazolin-5-one (DFAPP)
2) ethylenediaminobis(chromone-3-carbaldehyde) (FCED)

2,3-dimethyl-4-formyl-[2′-(aminomethyl)pyridine]-1-phenyl-3-pyrazolin-5-one

The ligand, DFAPP, was prepared by the condensation of antipyrine-4-carboxaldehyde and 2-(aminomethyl)pyridine in ethanolic medium. To a boiling solution containing 10 mmol (1.0815 g) 2-(aminomethyl)pyridine in ethanol (20 ml), 10 mmol (2.1624 g) of antipyrine-4-carboxaldehyde in ethanol (30 ml) was added and refluxed on a steam bath for about 6 h (Scheme 1). The light brown crystals obtained after cooling the resulting solution were filtered out and washed with cold ethanol to remove the unreacted reactants, if any. It was then recrystallised from ethyl acetate and dried over phosphorus(V)oxides under vacuum [153]. DFAPP is light yellow in colour, its molecular formula is C_{18}H_{18}N_{4}O and molecular mass is 306.37.

Scheme 1. 2,3-dimethyl-4-formyl-[2′-(aminomethyl)pyridine]-1-phenyl-3-pyrazoline-5-one (DFAPP)

The yield: 85%. m.p.148°C. Anal. Cal. for C_{18}H_{18}N_{4}O : C, 70.57; H, 5.92; N, 18.29. Found: C, 70.47; H, 5.87; N, 18.26%. IR (cm⁻¹): 1660 (-C=O), 1562 (-CH=N-), 1460, 698 (Pyridyl N). ¹H NMR (δ): 8.42 (s,1H, -CH=N-), 7.23-7.67 (m, -Ph), 7.14-8.67 (m, py. ring), 3.71 (s,2H, -N-CH₂-), 3.34 (s,3H, -N-CH₃), 2.55 (s,3H, -N-CH₃). ¹³C NMR (δ): 166.71 (C12) UV-VIS (λ_max/μm): 335 (n - π*), 247 (π- π*).
Ethylenediaminobichromone (3-carbaldehyde) (FCED)

An ice cold solution of 3-formylchromone (0.348 g, 2 mmol) in absolute ethanol (30 mL) was added dropwise to an ice cold solution of ethylenediamine (0.062 g, 1mmol) in absolute ethanol (10 mL). The mixture was stirred at this temperature for 24 hours (Scheme 2). The white precipitate obtained was collected by filtration and washed several times with cold ethanol. It was then recrystallized from ethanol and dried over phosphorus(V)oxide under vacuum. FCED is pale yellow in colour, its molecular formula is C_{22}H_{16}N_{2}O_{4} and molecular mass is 372. Yield: 82%. m.p.188 °C. Anal.Cal. for C_{22}H_{16}N_{2}O_{4} : C, 70.96; H, 4.30; N, 7.52. Found: C, 70.93; H, 4.26; N, 7.46%. IR(cm⁻¹): 1643 (-C=O), 1587 (-CH=N-). ¹H NMR(δ): 8.162 (s,1H, -CH=N-), 7.01-7.93 (m, 2-Ph), 2.839 (s, 4H, -CH₂-CH₂-). ¹³C NMR (δ):162.01 (C10, C13) UV-VIS (λ_{Max/mm}): 273(π- π*), 372 (π - π*).

Scheme 2. Synthesis of ethylenediaminobichromone (3-carbaldehyde) (FCED)

2.2 Analysis of the complexes

2.2.1. Estimation of metal content

Estimation of Iron

About 0.1 g of the complex was accurately weighed and digested with con.H₂SO₄ followed by con.HNO₃. Few drops of perchloric acid were
added to the resulting solution. The clear solution so obtained was evaporated to dryness and the residue was then extracted with distilled water. The resulting solution was diluted to 50 mL, 1:1 ammonia solution was added in excess and boiled for few minutes to coagulate the precipitate [154]. The precipitate was filtered through a Whatman No.41 filter paper and washed several times with distilled water. It was then ignited in a weighed crucible and weighed as Fe$_2$O$_3$.

**Estimation of Cobalt**

About 0.1 g of complex was accurately weighed and digested with con.H$_2$SO$_4$. Few drops of perchloric acid were added and heated till a clear solution was obtained. The solution was evaporated to dryness and the residue was extracted with water. Hexamine buffer was added to the resulting solution till the pH was 6. It was then titrated against standard EDTA solution using xylenol orange indicator till the colour changes from red to yellow orange [154].

**Estimation of Nickel**

About 0.1 g of complex was accurately weighed and digested with con.H$_2$SO$_4$. Few drops of perchloric acid were added and heated till a clear solution was obtained. The solution was evaporated to dryness and the residue was extracted with water and diluted to 50 mL. Few drops of murexide indicator solution was added followed by 5 mL 1M NH$_4$Cl solution. Ammonia was added to it till the pH was 7 as indicated by yellow colour of the solution. It was then titrated against standard EDTA solution until the end point was approached. 5 mL of con.ammonia solution was then added till the pH was 10 and the titration continued until the colour changed to bluish violet [154].
Chapter II

Estimation of Copper

About 0.1 g of complex was accurately weighed and digested with con.H$_2$SO$_4$. Few drops of perchloric acid were added and heated till a clear solution was obtained. The solution was evaporated to dryness and the residue was extracted with distilled water to an iodine flask. 1:1 aqueous ammonia solution was added to it dropwise until faint permanent precipitate was obtained. The precipitate was just dissolved in the minimum quantity of 1:1 aqueous acetic acid solution and then added two more drops. About 1 g of potassium iodide was added and liberated iodine was titrated against standard sodium thiosulphate solution using starch as indicator [154].

2.2.2 Estimation of perchlorate content

The estimation of perchlorate was done by Kurz method [155]. In this method the perchlorate was reduced to chloride and then estimated by Volhard [154] method. About 2 g of finely powdered and dried pure sodium nitrite was taken and a part of it was transferred into a nickel crucible. About 0.1 g of complex was accurately weighed and transferred into the crucible in such a way that no sample was in direct contact with the crucible. The remaining sodium nitrite was then added to cover the complex completely. The crucible covered with its lid was then placed in a muffle furnace and heated for about 90 minutes at a temperature of 500 ± 20 °C. The contents were cooled and transferred quantitatively into a 250 mL beaker using 40 mL distilled water.

The solution containing chloride was acidified with 10 mL 6N nitric acid and saturated potassium permanganate solution was added to it until a very faint pink colour persisted for a few minutes. 20 mL of 0.1N silver nitrate solution was added to it followed by 3 mL nitrobenzene and 1 mL
ferric alum indicator. The excess silver nitrate was back titrated with 0.1 N potassium thiocyanate solution with vigorous shaking until a faint reddish brown colour persisted. From the titre value, the percentage of perchlorate content in the complex was calculated.

2.2.3 Estimation of halide content

The halide content in the complex was estimated by Volhard method [154]. About 0.1 g of the complex was accurately weighed out into a 250 mL conical flask. The complex was dissolved in 50 mL methanol and 20 mL of silver nitrate (0.1 N) was added to it followed by 10 mL of 6N nitric acid. The mixture was heated on a water bath for about 1h. The solution was cooled and excess of silver nitrate was back titrated against 0.1 N potassium thiocyanate solution using ferric alum as indicator. From the titre value, the percentage of halide present in the complex was calculated.

2.3 Physicochemical methods used in the present study

The physicochemical methods adopted for characterization of complexes involve elemental analysis, molar conductance in non-aqueous solvents, FT-IR, UV-Vis and EPR spectra, magnetic susceptibility measurements as well as TG/DTA. In addition single crystal X-ray diffraction technique was also employed in the characterization of a few complexes.

2.3.1 Elemental analysis

The elemental analysis could quantify the solvent or water of crystallization and the metal to ligand ratio. So it is very useful in assigning the empirical formula of the complex.
A CHN Analyzer is a scientific instrument which can determine the elemental composition of a sample. The name derives from three primary elements measured by the device: carbon (C), hydrogen (H) and nitrogen (N). Percentage composition of sulphur (S) and oxygen (O) can also be estimated. The CHNS (O) analyzer finds utility in determining the percentage of carbon, hydrogen, nitrogen, sulphur and oxygen of organic/inorganic compounds, based on the principle of “Dumas method” which involves the complete and instantaneous oxidation of a sample by “flash combustion”. The combustion products are separated by a chromatographic column and detected by the thermal conductivity detector (T.C.D), which gives an output signal proportional to the concentration of individual components of the mixture. The built-in chromatographic column converts the compound and elutes it in the form of NO₂, CO₂, SO₂, and H₂O which are then detected with the help of Thermal Conductivity Detector. This method finds greatest utility in finding out percentages of C, H, N, S, (O) in organic/inorganic compounds which are generally combustible at 1800°C.

The chemical composition of all the complexes were evaluated by analyzing for C, H and N percentage by using Elementar Vario EL III analyzer.

2.3.2 Electrical conductance

Measurements of molar conductance is an important tool that gives valuable information about the coordination number, structure of the complexes and nature of counter ions present in the complexes. It also helps us to confirm the electrolytic nature and thereby the number of ions present outside the coordination sphere. In some cases coordinated groups are found
to be displaced by solvent molecule [156, 157]. In such cases the electrolyte type remains unchanged, where the neutral ligand is displaced by a neutral solvent molecule, but it will be affected in other cases where an anion is displaced by a neutral molecule.

Molar conductance of a solution is obtained from the measured value of specific conductance. The specific conductance \(K\) is related to the resistance \(R\) by expression.

\[
K = \frac{\text{Cell constant}}{R}
\]

Molar conductance \(\Lambda_m\) can thus be calculated using the relation

\[
\Lambda_m = \frac{1000K}{C}
\]

Where ‘\(C\)’ is the concentration in moles per litre.

Molar conductances of all complexes are measured at room temperature (28± 2 °C) using Toshniwal conductivity bridge (type CL 01.02A) with a dip-type conductance cell (type CL 01/01) and platinum electrode (cell constant = 0.9835). The cell constant is determined by measuring the resistance of an aqueous solution of potassium chloride whose specific conductance is known accurately. Generally 10^{-3} M solutions are used for measurements. The solvents used in present study for measurement of conductance are acetonitrile, DMF, methanol, nitrobenzene and ethanol.

Geary has studied the conductance of different electrolytes in various solvents [158]. The molar conductance values of different electrolytes in a number of solvents are summarized in the Table 2.1.
Table 2.1 Molar conductance\textsuperscript{a} of the complexes dissolved\textsuperscript{b} in some selected solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Electrolyte type</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1:1</td>
</tr>
<tr>
<td>Acetone</td>
<td>100-140</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>120-160</td>
</tr>
<tr>
<td>DMF</td>
<td>65-90</td>
</tr>
<tr>
<td>Methanol</td>
<td>80-115</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>20-30</td>
</tr>
<tr>
<td>Ethanol</td>
<td>35-45</td>
</tr>
</tbody>
</table>

\textsuperscript{a} in ohm\textsuperscript{-1}·cm\textsuperscript{2}·mol\textsuperscript{-1} \textsuperscript{b}10\textsuperscript{-3} M solution.

2.3.3 Infrared spectra

Infrared spectroscopy has been very extensively used in coordination chemistry and possibly no other technique has contributed as much to the growth of coordination chemistry. IR spectroscopy plays an important role in determining the site of coordination, the nature of metal-ligand bonds as well as for elucidating the structure of coordination compounds. Studies of the effect of coordination on the IR spectrum of metallic complexes afford valuable information on the nature of metal-ligand bond and stability of the complexes. Coordination usually causes 1) Appearance of new bands in the spectrum. 2) Frequency shift of bands and 3) Intensification of spectra. The newly formed metal-ligand bonds consequently change the electronic structure, the energy state and the symmetry of the complex. These changes affect the vibrational modes of bonds in the ligand, which consequently change the nature of vibrational spectrum also. By coordination all the
fundamentals are more or less shifted according to their modes of vibration. As the metal-ligand bond becomes stronger, their shifts to lower or higher frequencies increase.

The vibrational spectra of complex basically consist of three types of vibrations [159]

i) Ligand vibrations characteristic of the free ligand,

ii) Skeletal vibrations characteristic of whole complex molecule and

iii) Coupled vibrations.

i) **Ligand vibrations characteristic of the ligand**

Molecular vibrations which lead to change in the dipole moment of the molecule will give rise to absorption spectrum. A large change in dipole moment will usually give rise to strong absorptions.

ii) **Skeletal vibrations characteristic of whole complex molecule**

When a coordinate bond is formed between a metal atom or ion and ligand, the electronic structure and symmetry of ligand change to some extent. As a result the vibrational energy state of the ligand is changed. The complex molecule has to perform new vibrations that are different from original ligand. This causes changes in the IR frequency that enables one to find the coordination sites in ligand molecule.

iii) **Coupled vibrations**

This type of vibration may arise from coupling of vibration of two ligands or of a ligand vibration and a skeletal vibration or of
various skeletal vibrations. The coupling, if any, takes place only to a slight extent.

Other factors that normally affect the vibrational spectrum of a complex molecule are structure, strength of metal-ligand bond, interaction with solvents etc.

A detailed study of infrared spectrum mainly reveals the following facts.

a) **The coordination site of the ligand**

When a ligand is coordinated to the metal atom or ion the symmetry properties of the ligand are not changed totally and hence the interpretation of the bands in vibrational spectrum of the complex is possible. The electron density of the donor atom decreases upon coordination to a metal ion. As a result the bond order and consequently the stretching frequency may increase or decrease depending on the electronic structure of the ligand. It was proved that the frequency of OH stretching vibration decreases with decreasing electron density since the strength of OH bond is lowered by a decrease in electron density on oxygen [162]. But the frequency of C=N vibration increases because the decrease in electron density increases the C=N bond order [162]. Thus the shifts in characteristic vibrational frequencies of the ligand on complexation yield valuable information about the mode of coordination particularly of groups like C=O, P=O, S=O, C=N or N=O. For example the infrared spectrum of 4[N-(4-dimethylaminobenzylidene)amino]antipyrine, shows very strong bands at 1650 cm\(^{-1}\) due to \(\nu(C=O)\) mode and another strong band at 1590 cm\(^{-1}\) due to \(\nu(C=N)\) mode of vibrations. In complexes these bands are shifted to lower wave numbers and appear in the 1620-1590 cm\(^{-1}\) and 1575-1530 cm\(^{-1}\) region respectively. The shifts to lower
wave numbers in these complexes suggest that both, the carbonyl and azomethine group, are coordinated to metal ions [160]. In some cases ν(C=N) shows an increase in vibrational frequency on coordination [159]. The non-participation of some groups in coordination is indicated by retention of characteristic frequency of these groups in infrared spectrum of the complex compared to the free ligand.

b) **The relative strength of metal-ligand bond**

In complexes the vibration of metal-donor atom bond gives direct information about the strength and character of coordinate bond. When the ligand is coordinated to metal atom or ion, the electron density on donor atom decreases and this drainage of the free electron pair from free ligand increases the metal ligand bond strength.

c) **The nature of anion coordination**

The infrared spectra give a lot of informations regarding the nature of anion present, ie, whether ionic or coordinated and if coordinated, the status of coordination. This is particularly applicable in the case of anions like ClO$_4^-$, NO$_3^-$, CNS$^-$, SO$_4^{2-}$, CO$_3^{2-}$ and halides.

**Perchlorate ion**

In complex, the perchlorate ion may be present as uncoordinated and/or monodentately or bidentately coordinated. The vibrational spectrum plays an important role in establishing the nature of perchlorate ion in a complex. The ionic perchlorate has a tetrahedral structure having $T_d$ symmetry. It has four normal modes of vibration represented by $v_1$, $v_2$, $v_3$ and $v_4$ among which $v_3$ and $v_4$ are triply degenerate. The non-degenerate $v_1$ vibration is theoretically forbidden but becomes weakly allowed due to crystal field of low symmetry. Normally $v_1$, $v_2$, $v_3$ and $v_4$ occur around 460,
625, 932 and 1100 cm\(^{-1}\) respectively and all these are raman active. When the perchlorate ion is coordinated monodentately, one of the oxygen atoms behaves differently from the other three and symmetry is changed to \(C_{3v}\). Consequently both \(\nu_3\) and \(\nu_4\) vibrations split into two, out of which one is doubly degenerate in each set. In addition to this the bands around 932 and 460 cm\(^{-1}\) become infrared and raman active. Thus total six infrared active bands are obtained in this case. But when the perchlorate is coordinated through two of its oxygen atoms, the symmetry is changed to \(C_{2v}\). As a result a total of nine degenerate infrared active bands appear in the vibrational spectrum [163]. Thus it is possible to characterize the perchlorate group by taking into account the number of bands observed in the infrared spectrum. The possible vibrations of the perchlorate ion both in the ionic and coordinated status are given below.
Table 2.2  Vibrations of perchlorate ion as a function of symmetry

<table>
<thead>
<tr>
<th>State of ClO$_4^-$</th>
<th>Symmetry</th>
<th>$v_1$ (1, R)</th>
<th>$v_2$ (1, R)</th>
<th>$v_3$ (E)</th>
<th>$v_4$ (E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monodentate</td>
<td>C$_{3v}$</td>
<td>ClO$_4^-$ Str</td>
<td>ClO$_4^-$ Rocking</td>
<td>E$_3$ (R)</td>
<td>E$_3$ (R)</td>
</tr>
<tr>
<td>O*-ClO$_3^-$</td>
<td>C$_{2v}$</td>
<td>A$_1$ (R) (928-936)</td>
<td>A$_2$ (R) (928-945)</td>
<td>Cl-O$_2$* S.str</td>
<td>Cl-O$_2$* S.str</td>
</tr>
<tr>
<td>Ionic ClO$_4^-$</td>
<td>Td</td>
<td>E (R) (458-476)</td>
<td>E (R) (458-476)</td>
<td>E$_2$ (1, R) (1070-1100)</td>
<td>E$_2$ (1, R) (1070-1100)</td>
</tr>
<tr>
<td>Bidentate</td>
<td>C$_{2v}$</td>
<td>A$_1$ (R) (928-945)</td>
<td>A$_2$ (R) (928-945)</td>
<td>Cl-O$_2$* S.str</td>
<td>Cl-O$_2$* S.str</td>
</tr>
<tr>
<td>O*-ClO$_2$</td>
<td></td>
<td>A$_1$ (R) (1025-1038)</td>
<td>A$_2$ (R) (1025-1038)</td>
<td>Cl-O$_2$ a.Str</td>
<td>Cl-O$_2$ a.Str</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B$_1$ (1, R) (1170-1215)</td>
<td>B$_1$ (1, R) (1170-1215)</td>
<td>Cl-O$_2$* Q.Str</td>
<td>Cl-O$_2$* Q.Str</td>
</tr>
</tbody>
</table>

A and B- Non-degenerate; E-doubly degenerate; F-triply degenerate; I-Infrared active; R-Raman active; S-Symmetric; a-antisymmetric; O*coordinated oxygen; Str-stretching
Nitrate ion

In a nitrato complex, the nitrate ion may be present as a free ion or a coordinated ligand bound in a unidentate, bidentate or intermediate fashion or may be bridging. Moreover in complexes containing several nitrate groups, more than one coordination mode may be present. The different ways of coordination are shown below.

The free NO$_3^-$ ion has relatively high symmetry (D$_{3h}$). Thus its IR spectrum is fairly simple. The totally symmetric N-O stretching ($\nu_1$) mode is not IR active but sometimes become weakly active through crystal interaction and appears in the region of 1050 cm$^{-1}$. Three more characteristic bands $\nu_2$ (out of plane deformation), $\nu_3$ (asymmetric stretch) and $\nu_4$ (in plane bending) are obtained around 1390, 831 and 720 cm$^{-1}$ respectively. Out of these bands $\nu_3$ and $\nu_4$ are doubly degenerate. When NO$_3^-$ is coordinated monodentately, the effective symmetry is lowered to C$_{2v}$ causing degeneracy to split and all modes become IR active [168]. The symmetry of nitrate ion remains the same both in monodentately and bidentately coordinated species. Useful structural information can be derived from consideration of combination bands exhibited by nitrato complexes. The different vibrational modes assigned to the free nitrate ion and the coordinated nitrate ion is as shown below.
The doubly degenerate asymmetric $\nu_3$ stretching vibration splits on coordination into two and the magnitude of separation may be taken as a guide in differentiating monodentate coordination from bidentate coordination. The magnitude of the splitting depends on metal-nitrate interaction and is generally larger for bidentate than for monodentate coordination for a given metal and oxidation state. Generally it is observed that the magnitude of separation between the bands ($\nu_4 - \nu_1$) is around 115 cm$^{-1}$ if the nitrate group is coordinated through only one oxygen and around 186 cm$^{-1}$ if coordinated through two oxygen atoms. It is also suggested that the bands near 1750 cm$^{-1}$ assignable to combination mode ($\nu_4 + \nu_1$) could also be used for structural elucidation of nitrate group. The ionic nitrate group is found to give one comparatively strong and very sharp combination frequency while the coordinated group gives two frequencies. Generally for a given metal, the bidentate coordination of nitrate ion results greater distortion [166]. According to Lever et al, bidentately coordinated nitrate ion shows a separation of 66-20 cm$^{-1}$ while monodentately coordinated nitrate group exhibits separation of 26-5 cm$^{-1}$. Thus, separation of combination frequency may be taken as an indication of degree of metal nitrate interaction [167]. Curtis and Curtis have shown that intensities of bands decrease in the order ionic $>$ monodentate $>$ bidentate [165]. Complexes containing bridging nitrate groups usually exhibit a combination band at higher frequency near 1800 cm$^{-1}$. 
**Thiocyanate ion**

The thiocyanate group may coordinate to a metal through the nitrogen or sulphur or both. In general first transition series metals form M-N bonds whereas second half of the second and third transition series form M-S bonds. Other factors such as oxidation state of the metal, nature of the other ligand in the complex and steric condition influence the mode of coordination. The C-N stretching frequencies are generally lower in N-bonded complexes (near and below 2050 cm\(^{-1}\)) than S bonded complexes (near 2100 cm\(^{-1}\)). N- bonded complexes exhibit a single sharp (NCS) band near 480 cm\(^{-1}\) whereas S bonded complex shows several bands of low intensity near 420 cm\(^{-1}\) [168-170]. NCS groups also form a bridge between two metal atoms. The CN stretching frequency of a bridging group is generally higher than the terminal group. For example \([\text{HgCo(NCS)}_4\text{(Co-NCS-Hg)}]\) absorb at 2137 cm\(^{-1}\) whereas \((\text{NEt}_4)_2[\text{Co(-NCS)}_4]\) absorb at 2065 cm\(^{-1}\)[163].

**Halide ions**

Halides are the most common ligands in coordination chemistry. Terminal M-X stretching bands appear in the regions of 750-500 cm\(^{-1}\) for M-F, 400-200 cm\(^{-1}\) for M-Cl, 300-200 cm\(^{-1}\) for M-Br and 200-100 cm\(^{-1}\) for M-I. Halogens tend to form bridges between two metal atoms. In general bridging MX stretching frequencies are lower than the terminal M-X stretching frequencies [163].

**Metal-oxygen and metal-nitrogen vibrations**

The M-O stretching vibration usually appears in the region 360-580 cm\(^{-1}\) while M-N stretching vibration appears at around 450 cm\(^{-1}\). Thus a close
examination of the lower frequency infrared region helps to establish M-O and M-N coordination in complexes [171-174].

In present investigation, the infrared spectra are recorded in a Perkin Elmer Spectrum 400 Spectrometer in the range 4000-100 cm$^{-1}$.

### 2.3.4 NMR spectra

NMR is a phenomenon which occurs when nuclei with a net spin are immersed in a static magnetic field and exposed to a secondary oscillating magnetic field. NMR signals are generated by scanning a range of magnetic field strengths which interact with the spinning nuclei of molecule and align themselves with the external magnetic field generated by the instrument. For this, a constant radio frequency is permitted to pass through the sample molecule. When precessional frequency of the nuclei become equal to the constant radio frequency that surrounds the molecules, resonance occurs and the nuclei absorb energy from radiation which is detected by the instrument as NMR absorption signal [175].

The following are the results obtainable by NMR technique

* The position of resonance frequency provides information on chemical environment of the magnetic nuclei in the molecule.

* The relative ratio of equivalent nuclei in the molecule can be determined from the intensity distribution of the corresponding resonance lines.

* Analysis of fine structure permits, on the basis of the differences in the values of the spin-spin coupling constant, the determination of spacial arrangement of the nuclei.
Depending on chemical environment of the nucleus, the precise resonance frequency will be shifted from that of resonance frequency of the reference compound (commonly used is TMS) and is called the chemical shift ($\delta$). The magnitude of chemical shift depends on the degree of shielding of a magnetic nucleus from applied field by secondary magnetic field created by the electron cloud surrounding the nucleus. It may be expressed as:

$$\delta = \frac{\text{Distance downfield from TMS (Hz)}}{\text{Spectrometer operating frequency (MHz)}} = \text{Parts per million (ppm)}$$

$^1$H NMR spectra

Proton NMR was the first and is the most commonly used spectroscopic techniques among other NMR techniques. Protons in identical chemical environments are chemically equivalent and produce similar chemical shifts. The multiplicity of a signal in proton NMR spectra is given by $(n+1)$, where $n$ is the number of the coupling protons on neighbor atoms. In contrast to carbon, proton NMR spectra tend to be much more complicated in appearance due to the smaller chemical shift range and wide variation in the magnitude of coupling constants.

The interpretation of $^1$H NMR spectra of diamagnetic complexes is straightforward, but that of the paramagnetic complexes is complicated due to the following reasons.

- Signal broadening due to various relaxation phenomena
- Large shift (isotropic shift) of resonance signal

This means that the signals appear, in most cases, at field outside the usual region of 0-10 ppm in proton NMR. This shift is due to both contact and pseudo contact interactions.
The structural information obtainable from proton NMR is

- The number of $^1$H NMR signals gives the number of chemically equivalent protons (protons in same chemical environment) in a molecule.

- The positions of signals in comparison to the reference compound tell the kind of protons responsible for the signal.

- The intensity (area measurement) of the signal gives the relative number of protons responsible for each signal.

- The splitting of signals is caused by (and therefore tells us the number of) protons bonded to adjacent carbons.

The difference in resonance between a nucleus bound in paramagnetic complex and the same nucleus in an analogous diamagnetic complex is defined as the isotropic shift ($\Delta \nu$) of paramagnetic complex. Generally, the isotropic shift of nuclei in a paramagnetic complex is given by the sum of Fermi and Pseudo contact interaction terms [176]. Total shift is given by the equation

$$\Delta_{\text{total}} = \Delta_c + \Delta_{pc}$$

Where $\Delta_c =$ Fermi contact term and $\Delta_{pc} =$ pseudo contact term.

The Fermi contact term ($\Delta$) is a through-bond interaction and is related to the amount of covalency in the metal-ligand bond. It is given by the equation,

$$\Delta_c = \frac{\Delta \nu_{\text{com}}}{\nu_0} = -\left(\frac{A}{h}\right)\left(\frac{g_j \beta (g_j - 1) J(J+1)}{3kT_1}\right)$$
where

\[ \Delta \nu^{\text{con}} = \text{Induced shift in Hz} \]
\[ \nu^0 = \text{Larmor frequency} \]
\[ g_j = \text{Lande' splitting factor (g), given by the equation,} \]
\[ g_j = \frac{1+S(S+1)+J(J+1)-L(L+1)}{2J(J+1)} \]

\[ \frac{A}{h} = \text{Scalar electron-nuclear hyperfine interaction in Hz} \]
\[ J = \text{Total angular momentum quantum number} \]
\[ B = \text{Bohr magneton} \]
\[ \gamma_1 = \text{Nuclear magnetic ratio} \]

The pseudo contact interactions result from electron dipole and nuclear dipole interactions which are not averaged to zero by tumbling of aromatic complex in solution since its magnetic susceptibility is anisotropic.

The proton NMR spectra can conveniently be used to study the coordination sites of ligands and the form in which the ligands get coordinated to the metal ion. The change in N=CH proton signal can be taken as an evidence for coordination of the azomethine nitrogen [177,178]. The acid proton attached to carboxylate ion and the hydrogen atom attached to the amino group is unstable and are affected by the electronic configuration of the molecule caused by coordination. Thus, the absence of proton signals from –COOH, -OH and –NH groups indicates the substitution of hydrogen by the metal ions [179-181]. The absence of a proton signal
corresponding to water molecule indicates the absence of coordinated or lattice water molecule in the complexes [182].

13C NMR spectra

Carbon-13 NMR signals are generated by the same fundamental basis as proton signals, but the magnetic field strength is different and scanning range is twenty times wider. Only 1.1 % of naturally occurring carbon is 13C. Non-equivalent carbons which have different electron environment will generate different 13C signals. A 13C NMR spectrum consists of discrete, sharp lines corresponding to each non-equivalent carbon atom in the range of zero to 220 ppm with respect to reference peak of TMS.

The informations we get from 13C NMR spectra are

- The number of signals tells us the number of different carbons or set of equivalent carbons.
- The splitting of signal gives the number of hydrogens attached to each carbon [183].
- The chemical shift gives the hybridisation of each carbon atom.

The major strength of 13C NMR is the ability to observe the characteristics of carbonyl carbons. The main factor affecting the chemical shift is the electron density around the nuclei involved. As the electron density increases, the peak will undergo downfield shift. Quantitative information cannot easily be extracted from 13C spectra as in proton spectra.

13C NMR spectra can conveniently be used to study the coordination sites of ligands containing carbonyl groups and the form in which it get coordinated to the metal ion [184, 185]. The change in C=O signal can be taken as the evidence for the coordination of carbonyl oxygen.
coordination through the ring nitrogen such as pyridine and pyrazolones can be established taking changes in chemical shift of the carbons in the ring [186].

In the present investigations, Schiff base ligands are subjected to NMR studies. The $^1$H NMR and $^{13}$C NMR were recorded on a Bruker AV-400 spectrometer by dissolving them in suitable solvents (DFAPP in DMSO-d6 and FCED in acetone-d6). Due to paramagnetic nature of the complexes $^1$H NMR and $^{13}$C NMR spectra could not be studied.

2.3.5 Electronic spectra

One of the physical techniques used for studying transition metal complexes is electronic absorption spectroscopy. The electronic absorption spectrum often provides quick and reliable information about the arrangement of ligands around the metal ion. For example, octahedral complexes are readily distinguished from tetrahedral ones on the basis of position and intensity of their absorption bands. The number of bands, their frequencies and molar absorptivities should all be considered while making the assignments. Electronic transitions occur when electrons within the molecule or ion move from one energy level to another. This causes changes in vibrational and rotational motion of the molecule. Thus electronic spectrum will consist of bands of several absorption lines. Each band corresponds to definite change in electronic energy state. Four general types of electronic transitions are possible in transition metal complexes.

1. The d-d transition. In this case transition may occur between the split d levels of central atom giving rise to d-d or ligand field spectra. The spectral regions of these bands spread near IR, Visible and UV. The great variety of colours found in transition metal complexes is due to
these transitions. In practice the region generally scanned is 1000 to 333 nm although some d-d transitions do occur up to 200 nm due to charge transfer and/or interligand transitions.

2. **Ligand to metal charge transfer transitions.** In this type the ligand has a pronounced reducing ability and the metal ion has oxidizing properties. Such a transition occurs when the ligand has relatively high energy filled orbital and the metal ion has low lying empty orbital. Metal halo complexes such as \([MX_6]^{n-}\) (where \(X = \text{Cl, Br or I}\)), potassium permanganate and potassium ferrithiocyanate are examples of complexes exhibiting \(L \rightarrow M\) charge transfer transition.

3. **Metal to ligand charge transfer transitions.** This transition is possible when metal ion has some reducing character. Also the ligand must possess low lying empty orbital \((\pi^*)\) and the metal ion has filled orbital which are above the highest filled ligand orbital. The best known examples exhibiting \(M \rightarrow L\) charge transfer transitions are orthophenanthroline and dipyridyl complexes of such oxidisable transition metal ions as iron(III) and copper(II). A low valent metal carbonyl also exhibits such a charge transfer transition. For example \(\text{Cr(CO)}_6\) has an intense band around 277 nm which has been assigned to charge transfer transition from a filled metal orbital to ligand antibonding orbital.

4. **Intra ligand electronic transitions which involve electrons being excited**

These transitions generally occur with energies found in the UV region and associated with the electronic excitation from one ligand orbital to another. The energies of the orbitals are in the
increasing order: $\sigma$-bonding $< \pi$ bonding $< (n)$ nonbonding $< \pi^*$-antibonding $< \sigma^*$-antibonding.

In general bands due to $n\rightarrow\pi^*$ transitions appear at longer wavelength than those due to $\pi\rightarrow\pi^*$ transitions. Generally on coordination the ligand absorption bands will be shifted to a small extend towards shorter or longer wavelengths.

Electronic spectral studies of the Schiff bases and the complexes in solid state were carried out using a Shimadzu UV-160A spectrophotometer in the range 200-800 nm and on a Carey 2390 UV-VIS-NIR spectrometer in the range 800-1500 nm.

2.3.6 EPR spectra

EPR spectra gives valuable information regarding the concentration of the sample examined, the nature of bonding and delocalization in favourable cases. EPR is a branch of absorption spectroscopy in which a molecule or ion having unpaired electrons absorb electromagnetic radiation of microwave frequency under the influence of magnetic field. This phenomenon is known as electron paramagnetic resonance (EPR) and it is exhibited by paramagnetic substances. EPR spectra have significant applications in transition metal ions or complexes containing unpaired electrons.

The energy of resonance absorption is

$$\Delta E = h\nu = g\beta H$$

where $\nu$ denotes the frequency of radiation used, $h$ is Planck’s constant, $g$ is the spectroscopic splitting factor, $\beta$ is the Bohr magneton and $H$ is the magnetic field strength.
The splitting of EPR line due to an interaction between the nuclear spin and electron spin of same atom is known as hyperfine splitting. The number of hyperfine splitted lines is given by the total number of orientation of the nuclear spin, ie, by \((2I+1)\). These lines are equally separated with a spacing \(A\) (where \(A\) is called hyperfine splitting constant). The isotropic hyperfine splitting constant, which is the value of \(A\) in solution and is related to the parallel \((A_\|)\) and perpendicular \((A_\perp)\) components of hyperfine splitting constants as \(A_{av} = \frac{1}{3} (2A_\| + A_\perp)\). The hyperfine interaction resulting from the ligand donor atoms is called super hyperfine interaction.

The ‘\(g\)’ factor for a free electron is 2.0023. A free radical also has the same \(g\) value. This is because in a free radical the unpaired electron is not confined and can move about freely over the orbital. In transition metal complexes, on the other hand, the unpaired electron is localized in a particular orbital because of loss of orbital degeneracy and spin-orbit coupling. As a result the \(g\) value for a complex is different from 2.0023. The \(g\) value of a transition metal complex depends on relative magnitude of spin orbit coupling and the crystal field.

The ‘\(g\)’ value of a transition metal complex give very important information about the structure of the complex. In the EPR study of the complexes using single crystals, \(g_Z\) value is equivalent to \(g_\|\), the \(g\) value obtained when the \(Z\) axis is parallel to the external magnetic field. The \(g_\perp\) value is the \(g\) value obtained in any direction in the plane perpendicular to this direction. The \(g_{av}\) value for a tetragonal complex is given by \(g_{av} = \frac{1}{3} (2g_\| + 2g_\perp)\).

For tetragonally compressed copper(II) complexes \(g_\perp > g_\|\) where \(g_\| = 2\) and for tetragonally elongated copper(II) complexes \(g_\| > g_\perp > 2\) if
unpaired electron resides in the $d_{x^2-y^2}$ orbital, while $g\perp > g\parallel = 2$ if unpaired electron is in the $d_{x^2}$ orbital.

The value of $g\parallel$ is a parameter indicative of covalency. For a covalent complex $g\parallel > 2.3$ or more. For a square planar copper(II) complex, the $g$ value is expressed as

$$g\perp = 2.002 - \frac{2k\perp \lambda}{\Delta E_{xz}}$$

and

$$g\parallel = 2.002 - \frac{8k\parallel \lambda}{\Delta E_{xy}}$$

where $k$ is the orbital reduction factor, $\lambda$ is the spin orbit coupling constant, $\Delta E_{xz}$ is the energy of $^2B_1g \rightarrow ^2E_g$ transition and $\Delta E_{xy}$ is the energy of $^2B_1g \rightarrow ^2B_2g$ transition. Combining the above two expressions,

$$G = \frac{g\parallel - 2.002}{g\perp - 2.002} = \frac{4k\parallel \Delta E_{xz}}{k\perp \Delta E_{xy}}$$

The value of $G$ indicates the strength of the ligand, whether strong or weak. $G$ value below 4 indicates negligible ionic character in the complexes. In the case of copper(II) complexes the in-plane $\sigma$ covalency parameter $\alpha_{Cu}^2$ is related to $A\parallel$, $g\parallel$ and $g\perp$ according to Kivelson and Neiman equation [187].

$$\alpha_{Cu}^2 = - (A\parallel/0.036) + (g\parallel - 2.002) + 3/7 (g\perp - 2.002) + 0.04$$

The $\alpha_{Cu}^2$ value accounts for a fraction of unpaired electron density on copper(II) ion. The smaller the value of $\alpha_{Cu}^2$ the greater is the covalency in the metal-ligand bond.
The X-band EPR spectrum of copper(II) complexes were recorded in a varian E-112 EPR Spectrophotometer at liquid nitrogen temperature using DPPH free radical as ‘g’ marker. In all the spectra, the field set is 3000 Gauss and the scan range is 2000 Gauss.

2.3.7 Magnetic susceptibility

Magnetic measurements can provide information on electronic structure, oxidation state and in some cases the symmetry properties of the transition metal central atom. Magneto-chemistry is used to investigate the magnetic properties of transition metal complexes. Magnetic moment can provide information about the oxidation state of the metal ion, electronic structure and symmetry properties of the complexes. This would give a clear idea about the number of unpaired electrons in the central metal atom or ion in the complex.

In first row transition metals, the spin only magnetic moment can be calculated using the equation,

\[ \mu_{(s,o)} = \left[ 4S(S+1) \right]^{1/2} \]

Gram susceptibility was calculated using the formula

\[ \chi_g = C_{bal} \times 1 \times \frac{(R-R_0)}{10^9} \]

where \( C_{bal} \) = a constant for the balance, \( l \) = length of sample in cm, \( m \) = mass of sample in gram, \( R \) = balance reading with the sample and \( R_0 \) = balance reading without the sample. Molar susceptibility was calculated using the expression,

\[ \chi_m = \chi_g M \]
where $M = \text{molar mass of the sample}$. Diamagnetic corrections are computed from Pascal’s constants. The corrected molar susceptibility values were calculated using the expression,

$$\chi_A = \chi_m + \chi_{\text{dia}}$$

The effective magnetic moments were calculated from the corrected molar susceptibility values using

$$\mu_{\text{eff}} = 2.828(\chi_A T)^{1/2} \text{ BM.}$$

Magnetic susceptibility measurements were performed on pulverized samples at room temperature on a Sherwood Magway MSB MK1 balance. The diamagnetic corrections were calculated using pascal’s constants.

### 2.3.8 Thermal analysis

Thermal methods of analysis may be defined as those techniques in which change in physical and/or chemical properties of a substance are measured as a function of temperature. The thermal study of reactions involving solids has three aspects. They are phenomenological, thermodynamic and kinetic. The phenomenological study is concerned with the quantitative observation occurring during the reactions. The thermodynamic aspect is static in nature. It is related to the initial, final and equilibrium states of the system and the driving force behind the transformations. The kinetic approach is mainly concerned with rate of transformations of reactants into the products and the mechanism of transformations. In present work, mainly we look into the phenomenological aspects using TG and DTA data. In thermo gravimetric analysis, the mass of sample is recorded continuously as a function of temperature or time as the temperature of the sample is increased (usually linear with time). A plot of mass or mass percent as a function of time is called thermogram or thermal
decomposition curve. TG also provides a quantitative measurement of any weight change associated with transition. The changes in mass are as a result of rupture and formation of chemical bonds at elevated temperatures and evolution of some volatile products. TG curves are characteristic for a given compound because of a sequence of physicochemical reactions, which occur over definite temperature ranges. These changes are a function of its temperature dependent molecular structure. From such curves, the thermodynamics and kinetics of various chemical reaction mechanisms and an idea of intermediates and final products could also be obtained. In DTA (differential thermal analysis) the material under study and an inert reference are made to undergo identical thermal cycles while recording any temperature difference between sample and reference. This differential temperature is then plotted against time, or against temperature (DTA curve). Changes in the sample, either exothermic or endothermic, can be detected relative to the inert reference. The area under a DTA peak is enthalpy change and is not affected by heat capacity of the sample.

TG and DTA studies have much more importance in the case of coordination compounds. This may be due to the fact that on varying the temperature, the complexes may change into another product with the removal of ligands, anions and coordinated or uncoordinated solvent molecules. These modified high temperature compounds can have completely modified novel structures, which could be interesting. From this aspect it is possible to find out thermal stability of a substance, the initiation temperature ($T_i$), the final temperature ($T_f$), the temperature of maximum loss ($T_s$), the physicochemical reactions which takes place over definite temperature ranges, the intermediates formed and final product of the reaction.
The thermal studies were undertaken in a Perkin Elmer STA 6000 thermal analyser in nitrogen atmosphere in temperature range 30-900 °C with a heating rate 10°C min⁻¹.

### 2.3.9 Single crystal X-ray diffraction analysis

Single crystal X-ray diffraction (SXRD) is a non-destructive analytical technique which provides detailed information about the internal lattice of crystalline substances, including unit cell dimensions, bond angles, bond lengths and detailed site-ordering. SXRD is performed by analyzing the pattern of X-rays diffracted by an orderly array of many identical molecules. Many pure compounds like small molecules, organometallic complexes, proteins and polymers solidify into crystals under proper conditions. When solidify into crystalline state these individual molecules typically adopt one of only a few possible 3D orientations. When monochromatic X-ray beam is passed through a single crystal, the radiation interacts with electrons in atoms resulting in scattering of radiation to produce a unique image pattern. Computational analysis of a set of images results a 3D structure of the molecule.

Crystallography is the only technique that enables the acquisition of full detailed structural information including the relative position of atoms as well as their motion in the solid state. Since chemical and physical properties of a material depend on its structure, this information is essential and consequently crystallography has become one of the most valuable characterization techniques available to modern chemist. However, modern crystallographic analyses provide not only the positions of the atoms and corresponding bond distances, angles and related features within a material, the far more important and interesting aspects like the correlation of structural features with the
physical properties. This can include optical, magnetic and conductive effects as well as the structural behaviour under external stimulus or in different chemical environments. The resulting knowledge increases our understanding of complex underlying process, ultimately aiding to design of new materials in which desired chemical or physical properties are enhanced.

The sample in SXRD is a single crystal. A single crystal has a continuous and unbroken lattice on the entire sample and it is optically clear with no grain boundaries. Furthermore, in SXRD, as an additional distinction the size of single crystal should be small preferably within the range from 0.1 to 0.2 millimeters. They are normally selected using an optical microscope equipped with a polarizing attachment. A selected crystal is fixed on tip of a thin glass fibre using epoxy or cement or in a loop including specific oil, which fits into the goniometer head of the diffractometer. The crystal is then aligned along the direction of the beam. Once the crystal is mounted on the diffractometer, the reflection intensity data are collected. Complete data collection may require 3 to 12 h. Some of the measured intensities enable the calculation of unit cell parameters. Then all the intensities are indexed and a list of hkl reflections will be obtained. The precise measurement of the relative intensities of reflection is termed intensity data collection. A structure has been determined and hence the approximate positions of the atoms, refined by nonlinear least-square techniques to give the best fit between the calculated and observed intensity data for the specimen. The next step is the computation of the structure by Fourier synthesis and refinement of structural parameters to optimize the fitting between observed and calculated intensities in the diffraction pattern. The refinement process yields very accurate values for atomic positions from which bond lengths, bond angles and other structural parameters may be calculated.
Quality of the solution of a crystal is assessed by the values of R1, wR2 and GooF. R1, often called R-value, which is the agreement between the calculated and observed models. Ideal solutions would have R-values of zero, however, due to random errors, this is never achieved. R-values (listed as percents) of less than 5% are considered good solutions; high quality samples will often result in R-values lower than 2.5%. wR2 is similar to R1, but refers to squared F-values. These result in wR2 always have a higher value than R1. The final value, GooF, refers to “goodness of fit” of the solution. In addition to difference in F values, the GooF take the number of observed reflections and parameters used into account. At the end of refinement GooF should approach 1. Structure refinement is greatly aided by software packages. Probably the most widely used package of software is the SHELXTL program suite. The different programmes in this suite, including XPREP, XP and SHELXL, allow for initial solution of the phase problem, imaging of the crystal and refinement of the structure.

In present investigation, it could be able to solve the structure of three compounds using the single crystal XRD analysis. The X-ray single crystal data were collected using MoKα (λ = 0.7107 Å) radiation on a BRUKER APEX II diffractometer equipped with CCD area detector. Unit cell refinement (Bruker, 2006) [188] data reduction (SAINT) and the structure solution as well as refinement (SHELXL97) [189] were carried out using the software package of SMART APEX. All structures were solved by direct method and refined in a routine manner. In most cases, non-hydrogen atoms were treated anisotropically. Whenever possible, the hydrogen atoms were located on a different Fourier map and refined. In other cases, the hydrogen atoms were geometrically fixed. Molecular graphics were generated using softwares Mercury 2.3 [190], ORTEP 3 [191] and Diamond 3 [192].