Chapter 2
Reagents and Physicochemical Methods

2.1. Reagents

2.1.1 Metal salts

Most of the metal salts employed for the synthesis of the complexes were BDH AR grade samples. When AR samples were not available, metal salts were prepared from metal carbonates (AR) and the corresponding 50% acid.

Metal perchlorates were prepared from the respective AR metal carbonates and perchloric acid as follows. The respective metal carbonate was dissolved in hot 50% perchloric acid. A slight excess of metal carbonate was used. The undissolved carbonate was removed by filtration and the corresponding salt was separated by evaporating the resulting solution on a steam bath. It was dried under vacuum over P₄O₁₀. Metal bromides and iodides were prepared in similar way from the respective metal carbonate and hydrobromic or hydriodic acid.

Iron(III) thiocyanate was prepared by mixing 30 ml of FeCl₃.6H₂O solution (10%) with 70 ml of KSCN solution (10%). The deep red iron(III) thiocyanate was extracted with ether (75 ml) and was separated by evaporating the ether layer.
All these salts are hygroscopic in nature and therefore kept in a desiccator having a strong dehydrating agent.

2.1.2 Schi ff bases

Two Schi ff bases were used in the present investigation. Both were prepared from 4-aminoantipyrine. The aldehydes used were 4-antipyrine carboxaldehyde and glyoxal. The 4-aminoantipyrine used was supplied by Sigma Chemical Co., USA and 4-antipyrine carboxaldehyde by Aldrich Chemical Co., USA. The glyoxal used was 50% aqueous solution of E. Merck. These chemicals were used as such without any purification.

1,2-(Diimino-4'-antipyrinyl)ethane (GA)

The Schi ff base, 1,2-(diimino-4'-antipyrinyl)ethane (abbreviated as GA), was prepared by refluxing a mixture of ethanolic solutions of glyoxal and 4-aminoantipyrine for about 2 h in 1:2 molar ratio. The compound was separated as yellow solid on cooling. It was filtered and washed with hot acetone to remove the excess reagents. The compound was purified by recrystallisation from hot ethanol and the purity was tested by TLC, IR spectrum and elemental analyses. The elemental analysis data is as shown below.

Found: C = 67.89%, H = 5.72% and N = 19.52%; Calculated for C_{24}H_{24}N_{6}O_{2}: C = 67.29%, H = 5.61% and N = 19.63%.
4-N-(4'-Antipyrmethy1ideoe)aminoantipye (AA)

The ethanolic solutions of 4-aminoantipyrine and 4-antipyrine carboxaldehyde were mixed in 1:1 molar ratio and refluxed for about 2 h. The resulting solution was cooled and the solvent was removed by evaporation. The yellow compound separated was repeatedly washed with acetone to remove any excess reagents present. Finally the compound was recrystallised from ethanol. The purity of the Schiff base was tested by TLC, IR spectrum and elemental analyses. The elemental analysis data is given below.

Found: C = 69.49%, H = 5.75% and N = 17.59%; Calculated for C_{23}H_{23}N_{5}O_{2}: C = 68.83%, H = 5.74% and N = 17.45%.

2.1.3 Solvents used

The following solvents were used in the present investigation: acetone, acetonitrile, benzene, chloroform, DMF, DMSO, diethyl ether, ethanol, ethyl acetate, methanol and nitrobenzene. These solvents were either GPR or AR grade and were purified by standard methods.

2.1.4 Other reagents

Ammonium chloride, ammonium thiocyanate, EDTA, ferric alum, liquor ammonia, murexide indicator, potassium thiocyanate, silver nitrate, sodium chloride, sodium nitrite, sodium thiosulphate and xylenol orange indicator were also used. These reagents were either BDH GPR or E. Merck GR grade.
2.2. Analyses of complexes

2.2.1 Estimation of metal content

Estimation of iron

Weighed quantity (0.1 g) of the complex was digested with con. H$_2$SO$_4$ followed by con. HNO$_3$. A few drops of perchloric acid were also added to the resulting solution. The clear solution so obtained was evaporated to dryness and the residue was then extracted with distilled water. It was then diluted to 50 ml, 1:1 ammonia solution was added in excess to it and boiled for 2-3 minutes to coagulate the precipitate. The precipitate was filtered through a Whatman filter paper and washed several times with distilled water. It was then ignited in a weighed silica crucible and weighed\textsuperscript{87} as Fe$_2$O$_3$.

Estimation of cobalt

Weighed quantity (0.1 g) of the complex was digested with con. H$_2$SO$_4$ followed by con. HNO$_3$. A few drops of perchloric acid were also added to the resulting solution. The clear solution so obtained was evaporated to dryness and the residue was then extracted with 50 ml distilled water. Hexamine buffer was added to the resulting solution till pH was 6. It was then titrated against standard EDTA solution using xylenol orange indicator till the colour changes from red to yellow\textsuperscript{87}.

Estimation of nickel

Weighed quantity (0.1 g) of the complex was digested with con. H$_2$SO$_4$ followed by con. HNO$_3$. A few drops of perchloric acid were also added to the resulting solution. The clear solution so obtained was evaporated to dryness and
the residue was then extracted with distilled water. It was diluted to around 50 ml and 25 mg of murexide indicator was added followed by 5 ml of 1 M NH₄Cl solution. Ammonia solution was then added to it till pH was 7 as indicated by the yellow colour of the solution. It was then titrated against standard EDTA solution near to the end point. 5 ml of concentrated ammonia solution was then added till pH was 10 and the titration was continued till the colour changed to violet.

Estimation of copper

Weighed quantity (0.1 g) of the complex was digested using concentrated sulphuric acid and perchloric acid. The resulting clear solution was evaporated to dryness and the residue was then extracted with distilled water into an iodine flask. Dilute aqueous ammonia solution (1:1) was added to it dropwise until a faint permanent precipitate remained, and this was removed by means of adding a few drops of dilute aqueous acetic acid (1:1) solution. Around 1 g of potassium iodide was then added and the liberated iodine was titrated against standard sodium thiosulphate solution using starch as indicator.

2.2.2 Estimation of perchlorate content

The perchlorate content in the complexes was determined by Kurz method through the reduction of perchlorate to chloride by NaNO₂ at 500 ± 20°C. About 2 g of finely powdered dried sodium nitrite was taken and the bottom of a nickel crucible was covered with a part of it. Then 0.1 g finely powdered complex was introduced and covered with the remaining nitrite, taking care that the sample did not touch the bottom or sides of the crucible. The covered crucible was transferred to a muffle furnace at 500 ± 20°C and removed after 90 min. It was cooled and
the contents of the crucible and particles adhering to the lid were dissolved and transferred quantitatively into a 250 ml beaker using 40 ml distilled water.

The solution containing chloride was acidified with 10 ml 6 N HNO₃, and saturated potassium permanganate solution was added to it until very faint pink colour persisted for a few minutes. 20 ml of 0.1 N silver nitrate solution was added to it followed by 3 ml of nitrobenzene and 1 ml of ferric alum indicator. The excess AgNO₃ was back titrated with 0.1 N KSCN solution, shaking the flask vigorously, until a faint reddish brown colour persisted.⁸⁷

2.2.3 Estimation of halide content

A weighed quantity of complex (0.1 g) was dissolved in AR methanol (50 ml) and 20 ml AgNO₃ (0.1 N) was added to it. The mixture was acidified with 10 ml 6 N HNO₃ and heated on a water bath. The solution was then cooled and titrated against 0.1 N KSCN using ferric alum as indicator.⁸⁷

2.3. Physicochemical methods used in the present study

The complexes were characterised by the following physical methods: molar conductance, magnetic susceptibility, IR, electronic and ESR spectra, thermogravimetry and elemental analyses.

2.3.1 Electrical conductances

The molar conductivities of all the complexes were measured at room temperature (28 ± 2°C) using Toshniwal conductivity bridge (type CL 01.02 A) with dip type conductance cell (type CL 01/01) and platinum electrode
The solvents used in the present study for conductance measurements are acetonitrile, DMF, methanol and nitrobenzene.

The electrical conductivity measurements have been employed for structural studies of complexes. Information regarding the nature of the counter ions in complexes and hence the possible geometry of the metal ion can be obtained from conductivity data. Most useful conductance data are obtained in non-aqueous solvents like nitrobenzene, acetone, acetonitrile, DMF and methanol. Applications of conductance measurements in studies of complexes have been given in the review by Geary. To assist the interpretation of the experimental conductivity of complexes, the reference value for molar conductivities of various types of electrolytes in a number of common solvents are given in Table 2.1.

Table 2.1 Molar conductance* of the complexes dissolved in some selected solvents at 10⁻³ M.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>1:1</th>
<th>1:2</th>
<th>1:3</th>
<th>1:4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrobenzene</td>
<td>20-30</td>
<td>50-60</td>
<td>70-82</td>
<td>90-100</td>
</tr>
<tr>
<td>Acetone</td>
<td>100-140</td>
<td>160-200</td>
<td>270</td>
<td>360</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>120-160</td>
<td>220-300</td>
<td>340-420</td>
<td>500</td>
</tr>
<tr>
<td>DMF</td>
<td>65-90</td>
<td>130-170</td>
<td>200-240</td>
<td>300</td>
</tr>
<tr>
<td>Methanol</td>
<td>80-115</td>
<td>160-220</td>
<td>290-350</td>
<td>450</td>
</tr>
</tbody>
</table>

*Molar conductance in ohm⁻¹ cm² mol⁻¹

Commonly the specific conductivity (K) of a solution is determined by measuring the resistance (R) using an experimental cell of known cell constant and substituting it in the expression:

\[ K = \frac{\text{Cell constant}}{R} \]
The molar conductivity ($\Lambda_m$) is given by the expression:

$$\Lambda_m = \frac{1000 K}{C}$$

where $C$ is the concentration in moles per litre. A Toshniwal conductivity bridge provided with dip type platinized platinum electrode was employed for these measurements. The cell constant was determined by measuring the resistance of an aqueous KCl solution whose specific conductivity is known. Usually solution of the order of $10^{-3}$ M concentration were employed for the conductivity measurements. The value of the molar conductivity of an electrolyte in a particular solvent depends upon various factors like viscosity and polarity of the solvent, mobility of the ions, etc.

### 2.3.2 Magnetic susceptibility

Magnetic moments of all the complexes were measured at room temperature ($28 \pm 2^\circ$C) using Gouy balance with mercury(II) tetrathiocyanatocobaltate(II) as calibrant.

One of the most valuable fields of application of magnetochemistry is the investigation of transition metal complexes. Magnetic moment can provide information on the electronic structure, oxidation state and in some cases on the symmetry properties of central metal ion in complexes.

In complexes the number of unpaired electrons on the central atom is determined by its oxidation state and the ligand field strength. Thus magnetic susceptibility measurement gives an idea about number of unpaired electrons on the central metal ion in the complex and whether it is low spin or high spin. Owing to the orbital moment contribution, the magnetic moment of transition metal
complexes may differ from the spin only value. The magnetic moment furnishes valuable information on the electronic configuration of complexes containing a central atom in an unusual oxidation state. Earnshaw proved, by magnetic measurements, the $t_{2g}^{3}e_{g}^{-1}$ electronic configuration of the central atom in ethylenediaminechromium(II) complexes. The magnetic moment of the above complex is near to the spin only value (4.90 BM).

The intrinsic magnetic moments of atoms and molecules are composed of the vectorial sum of orbital and spin moments of the unpaired electrons. Here three kinds of interactions are possible; i.e., spin-spin, orbital-orbital and spin-orbital interaction. In lanthanide ions, i.e., ions having large multiplet separation, all three interactions play a part. Hence the resultant magnetic moment can be calculated by means of the Russell-Saunders coupling relation.

$$\mu_{\text{eff}} = g[J(J+1)]^{\frac{1}{2}}$$

where $J$ is the total angular momentum, which is the vectorial sum of the total orbital angular momentum ($L$) and the total spin angular momentum ($S$). The term 'g' is the Lande' splitting factor given by the equation.

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

If $L$ and $S$ are not coupled to give a resultant $J$, spin orbit coupling does not occur and $L$ and $S$ align separately with the external magnetic field. In this case the magnetic moment is given by

$$\mu_{\text{eff}} = [4S(S+1) + L(L+1)]^{\frac{1}{2}}$$

For the ions and complexes of the first row transition metals, in some cases, there is no orbital moment contribution to the magnetic moment and the latter is
determined only by the spin only moment of the unpaired electrons which is given by

\[ \mu_{\text{spin}} = [4S(S+1)]^{1/2} \]

The magnetic susceptibilities of the complexes were measured at room temperature using a Gouy magnetic balance. The Gouy tube was standardised using mercury(II) tetrahydrocyanatozincate(II). Diamagnetic corrections for the rest of the molecules were computed from Pascal’s constants. Gram susceptibility was calculated using the formula.

\[ \chi_g = \frac{\alpha + \beta F}{W} \]

where \( \alpha \) = Air displacement constant
\( \beta \) = Gouy tube constant
\( F \) = Change in weight in mg
\( W \) = Weight of sample in g

The effective magnetic moments (\( \mu_{\text{eff}} \)) were calculated from corrected molar magnetic susceptibility (\( \chi_{M'} \)).

\[ \chi_M = \chi_g \times \text{Mol. wt.} \]
\[ \chi_{M'} = \chi_M + D \]

where \( D \) is the diamagnetic correction.

\[ \mu_{\text{eff}} = 2.84 \sqrt{\chi_{M'} \times T} \text{ BM} \]

### 2.3.3 Infrared spectra

In the present investigation, the infrared spectra were recorded in a Shimadzu IR-470 spectrophotometer in the range 4000-400 cm\(^{-1}\) using KBr pellet
technique and in a Bruker IFS 66 v FT-IR spectrophotometer in the range 500-100 cm$^{-1}$ using polyethylene powder.

During complex formation, when the ligands coordinate to the central metal atom, the newly established metal-ligand coordinate bonds change the electronic structure, the state of energy and the symmetry of ligands. These changes affect the vibration of the ligand and consequently its vibrational spectrum. The new molecule (the complex) comprising the ligands will perform new vibrations which are not exhibited by the free ligands. The structure and symmetry of the complex molecule, the strength of its coordinate bonds as well as its interaction with the environment affect the vibrational spectrum of the complex. By these reasons experimental procedures involving the recording and analysis of infrared spectra are used as an important tool in coordination chemistry.

The vibrational spectra of complexes basically consists of three types of vibrations. (a) ligand vibrations characteristic of the free ligand; (b) skeletal vibrations characteristic of the whole complex molecule; and (c) coupled vibrations.

(a) Ligand vibrations characteristic of the free ligand

A polyatomic molecule can undergo a variety of vibrations like stretching, bending etc. If there is a change in dipole moment as a result of these vibrations, the molecule is said to be infrared active. Such molecules absorb radiations in the infrared region and give the spectra characteristic of the molecules.
(b) **Skeletal vibrations characteristic of the whole complex molecule**

When a ligand forms a coordinate bond with the metal ion, the electronic structure and symmetry of the ligand change to some extent, but not much. As a result, the state of vibrational energy of the ligand is affected. Consequently, the complex molecule has to perform new vibrations that are not present originally in the ligand. These bands enable us to find out the coordination sites of the ligand.

(c) **Coupled vibrations**

This type of vibrations may arise from the coupling of the vibrations 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 and hence the spectrum of the ligand is deformed only to a slight extent.

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

Examination of infrared spectrum mainly reveals the following facts:

(i) **The coordination site of the ligand**

When a ligand is coordinated to the metal ion, the symmetry properties of the ligand are not changed totally and hence the interpretation of the bands in the 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 in some cases and decrease in some others depending on the electronic structure of the ligand. It was proved that the frequency of OH stretching vibration decreases with decreasing electron
But the frequency of C=N vibration increases because the decrease in electron density increases the C=N bond order. Thus, the shifts in the 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 and N=O. For example, the IR spectrum of the Schiff base 4-N-(2'-hydroxybenzylidene)aminoantipyrine has a very strong band at 1655 cm\(^{-1}\) due to the C=O stretching vibration. It is shifted to the region 1600-1605 cm\(^{-1}\) upon complexation indicating the coordination of the C=O group to the metal ion. The band at 1590 cm\(^{-1}\) due to the hydrogen bonded C=N (azomethine) group of the same ligand is also shifted to 1560-1575 cm\(^{-1}\) in the complexes indicating the coordination of the azomethine nitrogen to the metal ion. The cases where \(v_{C=N}\) shows an increase in the vibrational frequency on coordination are also known. The retention of the characteristic frequency of certain groups in the IR spectrum of the complex compared to that of the free ligand may be taken as an evidence for the non-participation of those groups in coordination.

(ii) The relative strength of metal-ligand bond

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

(iii) The nature of the anion coordination

The infrared spectra give a lot of information regarding the nature of the anion present, i.e., whether ionic or coordinated and, if coordinated, the status of
the coordination. This is particularly applicable in the case of anions like ClO₄⁻, NO₃⁻, CNS⁻, SO₄²⁻, CO₃²⁻, halides, etc.

**Perchlorate ion**

In a complex, the perchlorate group may be present as ionic 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 T₄ symmetry. It has four normal modes of vibration represented by v₁, v₂, v₃, and v₄, among which v₃ and v₄ are triply degenerate. The non-degenerate v₁ vibration is theoretically forbidden but becomes weakly allowed due to the distortion of the ion in a crystal field of low symmetry. Normally, the v₁, v₂, v₃, and v₄ vibrations 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 thus, the symmetry is lowered to C₃ᵥ. Consequently, both v₃ and v₄ 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, a total of six infrared active bands are obtained in this case. But, when the perchlorate ion is coordinated through two of its oxygen atoms, the symmetry is lowered further to C₂ᵥ. As a result, a total of nine non-degenerate infrared active bands appear in the vibrational spectrum. Thus, it is possible to characterise the perchlorate group by noting the shape and number of bands observed in the infrared spectrum. The possible vibrations of the perchlorate ion both in the ionic and coordinated state are represented in Table 2.2.
Table 2.2  Vibrations of the perchlorate group as a function of symmetry.

<table>
<thead>
<tr>
<th>State of CIO₄⁻</th>
<th>Symmetry</th>
<th>v₂</th>
<th>v₅</th>
<th>v₁</th>
<th>v₄</th>
<th>v₃</th>
<th>v₅</th>
<th>v₄</th>
<th>v₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic CIO₄⁻</td>
<td>Td</td>
<td>A₁(R) (928-936)</td>
<td>E(R) (914-940)</td>
<td>F₂(l,R) (1070-1100)</td>
<td>F₂(l,R) (1070-1100)</td>
<td>F₂(l,R) (618-632)</td>
<td>F₂(l,R) (618-632)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A & 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 nitrate complexes, the nitrate ion can act either as coordinated or as counter ion. The complexes containing both the types are also known. The coordinated nitrate ion may be present as unidentate, bidentate or in a bridging fashion. The different ways of coordination are as shown below.

\[
\begin{align*}
\text{Unidentate} & & \text{Bidentate} & & \text{Bidentate} \\
M-O-N=O & & M-N=O & & M-O-N-O \\
\text{(chelating)} & & \text{(bridging)} &\
\end{align*}
\]

The nitrate ion has a \(D_{3h}\) symmetry and possesses three characteristic bands, \(v_2\) (out of plane deformation), \(v_3\) (asymmetric stretch) and \(v_4\) (in-plane bending) which are normally obtained at around 1390, 831 and 720 cm\(^{-1}\) respectively.\(^{101,102}\) In addition to this, there is another band \(v_1\) (symmetric stretch) which is normally inactive but sometimes becomes weakly active through crystal interaction and appears\(^{102}\) weakly in the region of 1050 cm\(^{-1}\). Out of these bands, \(v_3\) and \(v_4\) are doubly degenerate. But when the nitrate ion is coordinated monodentately, the symmetry is lowered to \(C_{2v}\). Unlike that of the perchlorate ion, the symmetry of the nitrate ion remains the same (\(C_{2v}\)) both in monodentately and bidentately coordinated states. The different vibrational modes assigned to the free nitrate ion and the coordinated nitrate ion are as shown below.

\[
\begin{align*}
\text{NO}_3^- & & D_{3h} & & v_1(A_1) & & v_2(A_2) & & v_3(E) & & v_4(E) \\
\text{NO}_3^- & & C_{2v} & & v_2(A_1) & & v_6(B_1) & & v_1(A_1) & & v_4(B_2) & & v_3(A_1) & & v_3(B_2)
\end{align*}
\]
Thus all the bands described above become active upon coordination and the degeneracy of $v_3$ and $v_4$ is lifted. The band positions may be shifted on coordination and may be different for monodentate and bidentate nitrate ions, but it is very difficult to establish the coordination status from the infrared bands of the nitrate group. In spite of this, the doubly degenerate asymmetric $v_3$ stretching vibration ($E'$ in the $D_{3h}$ symmetry) splits on coordination into two and the magnitude of separation may be taken as a guide in differentiating monodentate coordination from bidentate coordination.\textsuperscript{103} Generally, it is observed that the magnitude of separation of the bands ($v_4 - v_1$) is around 115 cm\textsuperscript{-1}, if the nitrate group is coordinated through only one oxygen atom and around 186 cm\textsuperscript{-1}, if coordinated through two oxygen atoms.\textsuperscript{103,104} It is also suggested that the band around 1750 cm\textsuperscript{-1} attributed to the combination mode ($v_3 + v_4$) could also be used for the structural elucidation of nitrate ion. The uncoordinated nitrate is found to give a comparatively strong and very sharp combination frequency, while the coordinated nitrate gives two frequencies. Generally, for a given metal, the bidentate coordination of nitrate ion results a greater distortion. According to Lever \textit{et al.},\textsuperscript{105} bidentately coordinated nitrate ion shows a separation of 66-20 cm\textsuperscript{-1} while monodentately coordinated nitrate ion exhibits a separation of 26-5 cm\textsuperscript{-1}. Thus, the separation of the combination frequency may be taken as an indication to the degree of metal-nitrate interaction. Curtis and Curtis have shown that the intensities of the bands decrease in the order: ionic > monodentate > bidentate.\textsuperscript{103} Complexes containing bridging nitrate ions usually exhibit a combination band at a higher frequency\textsuperscript{105} near 1800 cm\textsuperscript{-1}. 
**Halide ions**

The $v_{M-X}$ bands appear in the region 400-200, 300-200 and 200-100 cm$^{-1}$ when $X = \text{Cl}^-, \text{Br}^-$ and $\text{I}^-$ respectively.$^{103}$

**Thiocyanate ion**

The SCN group may coordinate to a metal through the nitrogen or the sulphur or both. The factors such as the oxidation state of the metal, the nature of other ligands in the complex and the steric consideration also influence the mode of coordination. The CN stretching frequencies are (around 2050 cm$^{-1}$) generally lower in N-bonded complex than S-bonded complex (around 2100 cm$^{-1}$)$^{103}$ and the bridging (M-NCS-M) complexes exhibit $v_{CN}$ above 2100 cm$^{-1}$. The N-bonded complex also exhibits a single sharp band near 480 cm$^{-1}$ whereas the S-bonded complex shows several bands of low intensity$^{103}$ near 420 cm$^{-1}$.

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

The M-O stretching vibration usually appears$^{106-108}$ in the region 360-580 cm$^{-1}$ while the $v_{M-N}$ appears$^{107}$ at around 460 cm$^{-1}$. Thus a close examination of the lower frequency infrared region helps us a lot to establish the M-O and M-N coordination in complexes.

**2.3.4 Electronic spectra**

Electronic spectral studies of the Schiff bases and the complexes in solution as well as in solid state were carried out on a Shimadzu-UV-160 A spectrophotometer in the range 200-1100 nm and in the range 1100-1500 nm on a
Cary 2390 UV-VIS-NIR spectrophotometer. For the solution state spectral analyses spectroscopic grade acetonitrile was used as the solvent (~10^3 M solutions) and for the solid state, a paste of the substance with Nujol was used.

The absorption of visible or ultraviolet light by molecules results in a change in the energy of the electrons of the absorbing molecules. This change in the electronic structure affects the vibrational and rotational motion of the molecule. Thus the electronic spectrum will consist of bands of several absorption lines. Each band corresponds to a definite change in the electronic energy. The individual lines within the band are due to definite vibrational transition.

In the electronic spectra of transition metal complexes, bands corresponding to three kinds of electronic transitions can be detected: (1) bands due to d-d transitions, (2) bands due to charge transfer transition and (3) bands due to interligand transitions. Since various geometrical arrangements cause different splitting patterns for the five d-orbitals, geometry will have a pronounced effect upon the d-d transitions in a metal complex. In the electronic spectra of transition metal complexes, the d-d transitions appear in the visible spectral region, owing to the low energy separation of the t_{2g} and e_{g} orbitals. The colour of transition metal complexes is generally caused by the d-d transitions. When the water molecules of the aquo complexes are replaced by more strongly coordinating ligands, the energy difference between the d-orbitals will be greater and hence the d-d band will shift towards shorter wavelength. When coordination of new ligand changes the geometry of the complex, the intensity of the band will increase. Thus the molar extinction coefficient of the blue [CoCl_4]^{2-} with tetrahedral symmetry is considerably higher than that of pink [Co(H_2O)_6]^{2+}, which is octahedral.

There are two types of charge transfer transitions. The first one arises from the transition of an electron from an orbital largely belonging to a ligand to an
orbital belonging to the central metal ion. The second one is obtained when an electron is excited from an orbital of the central metal ion to an orbital of the ligand. The former may occur between an oxidisable ligand and a metal atom in a higher oxidation state. The higher the oxidising power of the central atom and the reducing power of the ligand, the smaller the energy and the longer the wavelength necessary for this excitation. The latter case occurs in complexes formed by unsaturated ligands and metals in low oxidation states. The red colour of the iron(II)2,2'-bipyridyl complex, much used in analytical chemistry, is due to such a charge transfer band. Generally, the molar extinction coefficient of charge transfer bands are about a hundred times greater than that of d-d absorption bands.

In the investigation of electronic spectra of complexes with organic ligands, the bands arising from electronic transitions within the ligand must also be considered. They are in the order of increasing energy, σ-bonding, π-bonding, non-bonding (n), (π*)-antibonding and (σ*)-antibonding. In general, bands due to n→π* transitions appear at longer wavelength than those due to π→π* transitions. Generally on coordination, the ligand absorption band will be shifted to a small extent towards shorter or longer wavelengths. The shape of the absorption curve and the values of the molar extinction coefficient will be changed. In these cases the shift of the absorption bands is not characteristic of the nature of coordination.

2.3.5 ESR spectra

X-band ESR spectra of the Cu(II) complexes were recorded in a Varian E-112 EPR spectrophotometer at liquid nitrogen temperature, using DPPH free radical as the ‘g’ maker. In all the spectra, the field set is 3000 Gauss and the scan range is 2000 Gauss.

Nowadays ESR spectroscopy is constantly gaining importance in coordination chemistry. The general theory of the nuclear hyperfine structure of the
ESR spectra of transition metal salts has been given by Abragam and coworkers\textsuperscript{109,110} and it forms the basis of the ESR investigation of metal complexes.

The fundamental principles of electron paramagnetic resonance are essentially the same as those of NMR. Practical difference arise from the fact that the magnetic moment of an electron is substantially larger than that of proton. The energy of resonance absorption is

$$\Delta E = \hbar v = g\beta H$$

where \(v\) denotes the frequency of the radiation used, \(h\) is Planck’s constant, \(g\) is the spectroscopic splitting factor, \(\beta\) is the Bohr magneton and \(H\) is the magnetic field.

In a rigid medium each molecule has an orientation with respect to the magnetic field and the tensor \(g\) and \(A\) can be written as

$$g = (g_i^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta)^{\frac{1}{2}}$$

$$A = \frac{\left( A_i^2 g_i^2 \cos^2 \theta + A_{\perp}^2 g_{\perp}^2 \sin^2 \theta \right)^{\frac{1}{2}}}{g}$$

$$H_i = \frac{\hbar v}{g_i \beta} \text{ and } H_{\perp} = \frac{\hbar v}{g_{\perp} \beta}$$

\(A\) can also be calculated from the equation\textsuperscript{111}

$$A = \frac{g_i^2 + A_i^2}{g_i^2 A_i^2 + g_{\perp}^2 A_{\perp}^2}$$

The average of \(g\), i.e., \(g_{av}\) can be calculated from the equation\textsuperscript{111}

$$g_{av} = \frac{2}{3} g_i + \frac{1}{3} g_{\perp}$$

The steps in interpreting the ESR spectrum were as follows. First the geometrical arrangement and the symmetry properties of the assumed structure
were considered and the wave functions of the central atom and its nearest neighbour atoms were grouped in accordance with these symmetry properties. The expected energy order of the single electron orbital was established on the basis of the crystal field theory, and, the possible bonding configuration being taken into account, the presumed changes of this order were studied. The parameters (g values) which could be evaluated from the spectrum were then calculated for each possible order of energy with the aid of the molecular orbitals constructed from the corresponding atomic orbitals. The results of these calculation were then compared with the values obtained experimentally from the EPR spectrum and thus the only possible order of the energies and the corresponding bonding characteristics were determined.

The interpretation of EPR spectra of transition metal complexes is somewhat complicated by the fact that orbital moments must also be taken into consideration. When these interactions are taken into account precisely, valuable information may be obtained on the fine structure of the energy levels of the central atom. This information is provided by the change in the g-factor, from which conclusions can be drawn on the occupation of the orbitals, the degree of hybridisation and other factors determining the orbital moment contribution.

The change in the intensity of the external magnetic field at the site of the electron may cause the splitting of the ESR lines. The detectability of this splitting depends on the magnitude of this interaction. The hyperfine structure of EPR spectrum thus obtained is indicative of the position of the unpaired electron in the molecule. Thus in transition metal complexes, the contribution of the ligand in binding the unpaired electrons of the central atom can be unambiguously determined.
2.3.6 **Thermal studies**

Thermal methods of analysis have become an important tool in the study of solid state reactions, phase equilibria, measurement of specific heat etc. The study of the reactions involving solids has three aspects, viz., phenomenological, thermodynamic and kinetic. The phenomenological study is mostly concerned with the quantitative and semiquantitative observations 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 the rate of transformations of the reactants into the products and the mechanism of transformations. The present investigation involves mainly the study of the influence of procedural factors on kinetic parameters obtained from non-isothermal kinetic analyses using TG and DTG data.

**Thermogravimetry (TG)**

The present thermal experiments were carried out using either Delta Series TGA 7 thermal analyser or Seiko thermal analyser in an atmosphere of dry nitrogen, from room temperature to about 800°C. The kinetic parameters were calculated by using a computer programme.

Thermogravimetry is defined as a technique whereby the change in mass of a substance is recorded as a function of time or temperature, as it is heated or cooled in a suitable environment at a controlled rate. Mainly two methods are employed in thermogravimetry (1) isothermal or static thermogravimetry, where the sample mass is recorded as a function of time at constant temperature.
(2) non-isothermal or dynamic thermogravimetry, where the sample is heated in an environment whose temperature is changing in a linear rate.

In derivative thermogravimetry (DTG) the derivative of mass change with respect to time is recorded as a function of time or temperature. The derivative curve may be obtained either from the TG curve by manual differentiation methods or by electronic differentiation of the TG signals. The area under the DTG curve is directly proportional to the mass change and the height of the DTG peak at any temperature gives the rate of mass change at that temperature. The DTG curve allows the ready determination of the temperature at which the rate of mass change is maximum (T₉) and the initial temperature (T₁) at which cumulative mass change begins and the final temperature (T₇) at which the cumulative mass change reaches a maximum corresponding to complete reaction.

**Differential thermal analysis (DTA)**

DTA is a thermal technique in which the temperature of a sample is compared with the temperature of a thermally inert material and the temperature difference is recorded as a function of the sample or furnace temperature, as the sample is heated or cooled at a uniform rate. The temperature changes in the sample are due to endothermic or exothermic reactions that occur during the temperature programme and the corresponding deviation from the reference temperature is studied. This difference in temperature between the sample and the reference, i.e., \( \Delta T = T_{\text{sample}} - T_{\text{ref}} \) is recorded as a function of temperature.

In non-isothermal method, the following aspects\(^{112}\) are studied.

(a) **Phenomenological aspects**: This study is used to find the initial temperature (T₁), the final temperature (T₇) and the temperature of maximum mass loss (T₉) from DTG peaks. The TG plateauex gives the percentage mass loss during each stage of
decomposition. The DTA curve identifies the exothermic or endothermic nature of the different changes undergone by the sample.

(b) Kinetic aspects: The non-isothermal thermogravimetric analysis has been used in the investigation of the thermal stability of solid state materials. Using this method, the kinetic parameters can be calculated over an entire range of temperature in a continuous manner. The kinetic equation for the thermal decomposition is derived based on the following assumptions.

\[ \frac{d\alpha}{dt} = K \cdot f(\alpha) \]  \hspace{1cm} (1)

where \( K \) = specific rate constant, \( \alpha \) = amount of sample undergoing reaction, \( f(\alpha) \) = conversion function.

For a linear heating rate \( \phi \), \( T = T_0 + \phi t \)

where \( T_0 \) - temperature of initiation

\[ \frac{dT}{dt} = \phi \]  \hspace{1cm} (2)

Substituting (2) in (1)

\[ \frac{d\alpha}{dT} = \frac{K \cdot f(\alpha)}{\phi} \]  \hspace{1cm} (3)

The temperature dependence of the specific rate constant \( K \) is expressed by the Arrhenius equation

\[ K = A \cdot e^{E/R \cdot T} \]  \hspace{1cm} (4)

where \( A \) = pre-exponential factor, \( E \) = energy of activation, \( R \) = gas constant and \( T \) = temperature in Kelvin scale.
Substituting (4) in (3)

\[
\frac{d\alpha}{dT} = \frac{A \ e^{-E/RT}}{\phi} \cdot f(\alpha)
\]  

(5)

On integration, taking initial temperature as zero (this assumption is correct as no reaction occurs between \(T = 0\) and \(T = T_i\)).

\[
\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\phi} \int_0^T \ e^{-E/RT} \ dT
\]

\[
g(\alpha) = \frac{A}{\phi} \int_0^T \ e^{-E/RT} \ dT
\]  

(6)

where \(g(\alpha)\) is the conversion integral.

Coats and Redfern\textsuperscript{113} evaluated the temperature integral with the aid of the Rainville function.\textsuperscript{114} The temperature integral thus obtained is

\[
\ln \left[ \frac{g(\alpha)}{T^2} \right] = \ln \frac{A R}{\phi E} \left[ 1 - \frac{2RT}{E} \right] - \frac{E}{RT}
\]  

(7)

This equation is known as Coats-Redfern equation. A plot of L.H.S. of the equation against \(1/T\) is a straight line, from the slope and intercept of which one can calculate the energy of activation (\(E\)) and the pre-exponential factor (\(A\)).

The entropy of activation (\(\Delta S\)) can be calculated using the equation.

\[
A = \frac{\kappa T_s}{h} e^{\Delta S / R}
\]

where \(k\) = Boltzmann constant

\(h\) = Planck's constant

\(\Delta S\) = Entropy of activation.
(c) Mechanistic studies: The mechanism of solid state reactions is quite complex and includes several elementary steps such as: (1) sorption phenomenon (adsorption and desorption) (2) reaction on atomic scale (homogeneous or interphase reactions) (3) nucleation of a new phase (in bulk or at the surface of the reacting solid) (4) transport phenomenon (diffusion and migration).

The kinetic equations which govern the reaction mechanism are based on the assumption that the form of $g(\alpha)$ depends on the reaction mechanism. For the present study the nine mechanism based equations proposed by Satava\textsuperscript{115} (Table 2.3) have been used.

<table>
<thead>
<tr>
<th>Equation No.</th>
<th>Form of $g(\alpha)$</th>
<th>Rate controlling process</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\alpha^2$</td>
<td>One dimensional diffusion</td>
</tr>
<tr>
<td>2</td>
<td>$\alpha + (1-\alpha)\ln(1-\alpha)$</td>
<td>Two dimensional diffusion</td>
</tr>
<tr>
<td>3</td>
<td>$[1-(1-\alpha)^{1/3}]^2$</td>
<td>Three dimensional diffusion, spherical symmetry—Jander equation</td>
</tr>
<tr>
<td>4</td>
<td>$(1-2/3\alpha)-(1-\alpha)^{2/3}$</td>
<td>Three dimensional diffusion spherical symmetry—Ginstling–Brounshtein equation</td>
</tr>
<tr>
<td>5</td>
<td>$-\ln(1-\alpha)$</td>
<td>Random nucleation—One nucleus on each particle—Mampel equation</td>
</tr>
<tr>
<td>6</td>
<td>$[-\ln(1-\alpha)]^{1/2}$</td>
<td>Random nucleation—Avrami equation I</td>
</tr>
<tr>
<td>7</td>
<td>$[-\ln(1-\alpha)]^{1/3}$</td>
<td>Random nucleation—Avrami equation II</td>
</tr>
<tr>
<td>8</td>
<td>$1-(1-\alpha)^{1/3}$</td>
<td>Phase boundary reaction, cylindrical symmetry</td>
</tr>
<tr>
<td>9</td>
<td>$1-(1-\alpha)^{1/3}$</td>
<td>Phase boundary reaction, spherical symmetry</td>
</tr>
</tbody>
</table>

2.3.7 Analysis of carbon, hydrogen and nitrogen

The determination of the percentage of carbon, hydrogen and nitrogen in the complexes was carried out using a HERAEUS CHN rapid analyser.