Chapter II

Characterization Techniques
Experimental:
The synthesis of the various cobalt complexes are described in detail in Chapter III. However the characterization techniques of all the investigations are explained in this chapter.

2.1. Chemical analysis
To characterize a sample, chemical analysis is the fundamental contrivance available in the laboratory. The percentage of hydrazine and metal ions are determined by the standard chemical methods [44].

Estimation of Hydrazine: Hydrazine estimation was done under Andrew’s conditions [44].

\[ \text{IO}_3^- + \text{N}_2\text{H}_4 + 2\text{H}^+ + \text{Cl}^- \rightarrow \text{ICl} + \text{N}_2 + 3\text{H}_2\text{O} \]

Thus \( \text{KIO}_3 = \text{N}_2\text{H}_4 \)

To the known amount of sample taken in a glass stoppered bottle, 15 mL of concentrated hydrochloric acid, HCl and 10 mL of double distilled water was added followed by carbon tetra chloride, CCl₄. Standard potassium iodate, KIO₃ (5.350 g/L) was then added drop-wise from the burette with constant stirring and shaking the bottle until the CCl₄ layer decolorizes indicating the end point.

Percentage of hydrazine in the sample was then calculated by using the relation.

\[ 1 \text{ mL of } 0.025 \text{ M KIO}_3 = 0.0008103 \text{ g of N}_2\text{H}_4 \]

Estimation of Cobalt: The Cobalt content of the various complexes was estimated by ethylene diamine tetra acetic acid (EDTA) complexometric titrations [44]. A
standard solution of 0.02 M EDTA was prepared by directly weighing disodium salt of EDTA and dissolving it in double distilled water. This EDTA solution was standardized by titration with zinc sulfate, ZnSO$_4$$\cdot$7 H$_2$O. A known weight of the sample, 100 mg of cobalt complex was dissolved in 1:1 HCl and heated in boiling water bath till dissolution. This was then diluted with distilled water and the volume was made to 100 mL. 25 mL of the sample was taken. A pinch of buffer Hexamine and ammonium hydroxide, NH$_4$OH were added to adjust and maintain pH = 6. A few drops of xylene orange were added as an indicator. This solution was then titrated against 0.02 M EDTA till color changes from orange red to yellow indicating end-point.

Amount of metal ions present was calculated by the following relation

1000 mL of 1M EDTA = 58.933 g of Co

'x' mL of 0.02 M EDTA = 'y' g of Co

25 mL of the sample contains 'y' g of Co

Therefore 100 mL of the sample contains 'z' g of Co

\[
\text{Amount of Co ('z' g)} \times 100 = \% \text{ Co}
\]

Weight of sample

2.2. Infra red Spectroscopy (IR)

Infrared (IR) Spectroscopy is a precious tool for analyzing samples. It is based on the fact that a molecule will have a number of fundamental vibration frequencies and each fundamental frequency may be associated with the absorption of radiation of its own frequency. It has been widely used for identifying the organic ligands bound to the metal ion; metal oxygen bonds as well as the adsorbed species on the
catalyst surface. IR instrument can be divided into two classes namely dispersive and non dispersive. The dispersive type of instrument is similar to UV-visible spectrophotometer while the non dispersive type has an interferometer in the place of monochromator and the instrument is called as Fourier Transform Infra-red Spectroscopy (FTIR). The different components of FTIR are 1) Source, 2) Michelson Interferometer, 3) Sample compartment, 4) Detector. The spectrum of the sample can be interpreted for the functional groups present by matching the corresponding group frequencies.

Infrared spectra of the metal precursors and their decomposed product were recorded on SHIMADZU FTIR instrument, model IR Prestige -21 fitted with diffuse reflectance accessories. The samples were mixed with spectroscopic grade KBr and ground well. IR spectra were scanned in the frequency range of 4000-400 cm\(^{-1}\) and the samples were recorded in percent transmittance (%T) mode against wave number (1/\(\lambda\)) cm\(^{-1}\).

2.3. Magnetic Susceptibility using Gouy’s balance

The most common modus operandi employed for measuring magnetic susceptibility is the Guoy's method wherein the sample under examination is placed in a magnetic field and its weight is measured. The pole pieces of the magnet are usually cylindrical so that the magnetic field is symmetrical about the axis of the magnet. The magnetic field is strongest at the centre where the bottom of the sample column is placed. The magnetic field falls off in radial directions so that it is very small at the top of the column. The sample is taken as a uniformly packed solid in a glass
tube suspended from the balance. Under these conditions, there is an apparent change in the weight of the sample when the magnetic field is turned on. The change in weight of the sample is related to the magnetic susceptibility of the magnetic substance in the sample. Magnetic susceptibility is the ratio of the intensity of magnetization of the specimen of the material and the strength of the magnetic field applied. It measures how easily the specimen can be magnetized.

The magnetic susceptibilities of the various cobalt complexes were brought into being by the Gouy method at room temperature with a field of the order of 8500 gauss using mercury tetrathiocyanatocobaltate (Hg[CoSCN]₄) as the standard reference material.

2.4. Thermal Analysis

Thermal analysis is comprehensively used in the characterization of materials, chiefly for metal precursors. The techniques include Isothermal weight loss, Thermo gravimetric Analysis (TGA), Differential Thermal Analysis(DTA) and Differential Scanning Calorimetry (DSC).

(i) Isothermal weight loss:

Isothermal weight loss concedes examination of weight loss. The various cobalt complexes were weighed in silica crucibles. The initial weight of the crucible and samples were noted. The crucibles containing the samples were placed in a muffle furnace and the temperature was slowly raised to 700°C. The weight loss of the cobalt complexes were measured by finding the difference in the final and initial weight of the crucibles + sample. The isothermal weight loss % was then calculated.
(ii) Thermogravimetric (TG) and differential scanning calorimetric (DSC)/

Differential Thermal analysis (DTA)

Thermogravimetry (TG) provides quantitative scrutiny of mass loss with thermally induced transitions. It also provides information regarding the thermal stability of the material. The changes in physical and chemical properties of the material can be monitored as a function of temperature. Thus the reaction mechanisms can be predicted based on the thermal data. Essential components of a TG analyzer are 1) Furnace, 2) Sample crucible with thermocouple, 3) Automatic recording balance and 4) Printer/plotter. Differential Scanning Calorimetry (DSC) analysis /Differential Thermal analysis (DTA) provides the differential heat flux between the sample and reference material as a function of temperature. The different components of a DSC instrument are 1) Sample and reference container, 2) Average temperature amplifier, 3) Differential temperature amplifier, 4) Programmer. Differential Thermal analysis (DTA) is one of the oldest and simplest thermal techniques used for the study of physical and chemical transformations in materials associated with the energy changes. In DTA, the temperature difference $T$ between the sample and the thermally inert reference is measured as a function of temperature/time when both are heated simultaneously at the predetermined constant heating rate in the controlled atmosphere. Thermogravimetric (TG) and differential scanning calorimetric (DSC) analysis were performed on NETZSCH DSC-TG; STA 409PC. The heating rate was maintained at $10^\circ C \text{ min}^{-1}$. The analysis was carried out in air.
2.5. Electron spin resonance spectroscopy (ESR)

Electron Spin Resonance (ESR) is a branch of spectroscopy in which electromagnetic radiation, usually of microwave frequency is absorbed by molecules, ions, or atoms possessing electrons with unpaired spins, i.e. electronic spin $S > 0$, which is a common feature of transition metals. The reversal of spins of these unpaired electrons in an applied magnetic field is recorded. The spectra are obtained by varying magnetic field at constant microwave frequency. The condition for absorption of resonant energy is $E = gBeH$

Where $Be$ is a constant, i.e. the Bohr Magneton (BM), $H$ is the strength of the applied magnetic field, the factor ‘$g$’ is the gyro magnetic ratio and has a value of 2.0023 for a free electron. ESR spectra are usually represented as the first derivative of the absorption. From ESR spectra we can obtain information on the paramagnetic ion and its immediate environment in the host structure. The Electron spin resonance (ESR) spectra were recorded on Bruker BioSpin Gn, with Field sweep width 8000 G and Microwave frequency 9.425 GHz. Reference compound used was DPPH (2,2-Diphenyl-1-Picrylhydrazyl) with $g$ value of 2.0036. The samples were scanned as solid at room temperature; and 120K as well as dissolved in dimethyl formamide (DMF) and scanned at 120K.
2.6. X-Ray Photoelectron spectroscopy (XPS)

X-Ray Photoelectron Spectroscopy known as XPS or ESCA (Electron Spectroscopy for Chemical Analysis) has the ability to measure binding energy variations resulting from their chemical environment.

It measures the kinetic energy of the electrons that are emitted from matter as a consequence of bombarding it with ionizing radiations or high energy particles. There is direct ionization of an electron from either a valence or an inner shell. The kinetic energy $E$ of the ionized electron is equal to the difference in energy of the incident radiation $E_i$ and the binding energy of the electron $E_g$. Measurement of $E_i$ and $E_g$ therefore provides a means of the identification of the atoms. The ionizing radiation used is X-Rays and hence this technique is also known as X-Ray photoelectron spectroscopy (XPS). XPS analysis was done at 298K using Mg $K_a$ radiation on a VG Microtech Multilab ESCA 3000 spectrometer. Binding energy (BE) calibration was performed with Au (4f/2) core level at 83.9 eV. Al K alpha was used for nitrogen 1s level. All other core levels were recorded with Mg K alpha. Sample surfaces were scraped before analysis. Measurement conditions and parameters were verified to get the right carbon peak position ($C\ 1s = 248.8\ eV$), assuming an error lower than 0.2 eV. Spectra were fitted with Gaussian-Lorentzian (80-20% respectively) peaks, considering a Shirley baseline.

2.7. X-Ray diffraction (XRD)

The X-Ray diffraction technique is most extensively used for characterization of different crystalline solids. The position and intensities of X-Rays diffracted by a
crystalline solid provide a lot of information such as crystal structure, composition of the solid, particle size etc. X- Rays are a form of electromagnetic radiation of very short wavelength from 0.1 to 100 Å and are produced when high speed electrons are stopped by a solid object.

In a crystal different atoms and molecules are arranged in different planes in a systematic and repetitive manner. These inter-planar distances are of the same order of magnitude as the wavelength of the characteristic X-Rays emitted by the target. Hence the crystal planes act as a diffraction grating to the X-Rays and diffraction occurs. The necessary condition for X-Ray diffraction to occur is represented by Bragg's equation, \( n\lambda = 2d \sin \theta \) where \( n \) is an integer (1, 2, 3 etc.) called the order of reflection, \( \theta \) is the glancing angle of incident X-Ray beams on the crystal surface, \( d \) is the inter-planar spacing and \( \lambda \) is the wavelength of X-Rays. The phase identifications of the powdered samples, precursors and oxides of the cobalt chloride complexes were studied through powder diffraction technique. This method uses sample in powder form. Different components of powder diffractometer are evacuated X-Ray tube (source), sample compartment and detector. X-Ray diffraction studies of the decomposed products of the complexes were carried out on PHILIPS-X'Pert Industry using Co Kα radiation and of the precursors by X'Pert Graphics using K alpha radiation.
2.8. Ultra violet- Visible Spectroscopy (UV-Vis) and Diffuse Reflectance Spectroscopy (UV-DRS)

Transitions of electrons between outermost energy levels are associated with energy changes in the range $10^4$ to $10^5$ cm$^{-1}$ or $10^2$ to $10^3$ kJ mol$^{-1}$. These energies span the range from the near infrared through the visible to the ultraviolet and are therefore often associated with color. Various types of electronic transition occur and may be detected spectroscopically.

A reliable technique to find the unknown concentration of a moiety in the samples by finding the absorbance is Ultra violet -Visible Spectroscopy (UV-Vis). The concentration of hydrazine in the boiler feed water was pronounced by using a Shimadzu UV-2450 UV—Visible Spectrometer measured at a wavelength of 460 nm. Ultra violet -Diffuse Reflectance Spectroscopy (UV-DRS) is an authoritative technique to identify and characterize the metal ion coordination. It is a non destructive technique that uses the interaction of light, absorption and scattering, to produce a characteristic reflectance spectrum, providing information about the structure and composition of the medium. It also provides the information regarding the band gap of the materials, above all the semi conducting metal oxides. The diffuse reflectance spectra of dry samples, precursors were recorded using a Shimadzu UV-2450 UV—Visible Spectrometer equipped with a diffuse reflectance accessory in the wavelength range of 800–200 nm. BaSO$_4$ was used as a reference.
2.9 **Home-built De-aerator:** In order to study the oxygen scavenging action, we designed and fabricated a home-built de-aerator consisting of a large cylindrical stainless steel drum of length 50 cm, diameter 36 cm and 50L capacity, with electrical heating arrangement to maintain and raise the temperature of water to 90-100°C, continuous controlled stirring arrangement using a stirrer, a long stainless steel rod of length 29 cm with small stainless steel rods of length 6 cm and diameter 1 cm, welded to it horizontally and a rectangular acrylic plate of length, breadth and thickness 24.7 cm, 22.3 cm and 0.4 cm respectively. This plate has small holes and is fixed or joined to the long stainless steel rod. This arrangement was done to introduce and ensure good and proper agitation of the water containing dissolved oxygen; the major approach to reduce or bring down the dissolved oxygen level being, efficient mechanical de-aeration. Arrangement for inlet of water and two outlets; one for sampling of water and the other for washings or clean-up process were also made.

![Figure 2.1: Home built de-aerator (1) front view (2) top view (3) internal view](image-url)
2.10 Winkler’s Method:

The Winkler’s Method is a technique used to measure dissolved oxygen in freshwater systems. Dissolved oxygen is used as an indicator of the health of a water body, where higher dissolved oxygen concentrations are correlated with high productivity and little pollution. This test is performed on-site, as delays between sample collections and testing may result in an alteration in oxygen content. This method uses titration to determine dissolved oxygen in the water sample. A sample bottle is filled completely with water; no air is left to skew the results. The dissolved oxygen in the sample is then "fixed" by adding a series of reagents that form an acid compound that is then titrated with a neutralizing compound that results in a color change. The point of color change is called the "endpoint," which coincides with the dissolved oxygen concentration in the sample. Dissolved oxygen analysis is best done on the field, as the sample will be less altered by atmospheric equilibration.

A 125 mL glass stoppered bottle was filled carefully with sample water. Immediately, 1mL of manganese sulfate, MnSO₄, was added to the collection bottle by inserting the calibrated pipette just below the surface of the liquid. If the reagent was added above the sample surface, oxygen would be introduced into the sample. The pipette was slowly squeezed, so no bubbles were introduced via the pipette. 1mL of solution of sodium hydroxide, NaOH and potassium iodide, KI was added in the same manner. The bottle was stoppered with care to be sure no air was introduced. The sample was mixed by inverting several times. If oxygen was
present, a brownish-orange cloud of precipitate or floc would appear. Concentrated sulfuric acid, H₂SO₄ was added via a pipette held just above the surface of the sample. The volume of concentrated sulfuric acid added was noted. The bottle was carefully stoppered and inverted several times to dissolve the floc. From this, 50 mL of the sample was taken in a conical flask or stoppered bottle, and 1-2 drops of starch indicator was added and titrated against sodium thiosulfate by slowly dropping titrant solution from a calibrated burette into the flask and continually stirring or swirling the sample water. The color changed from blue to colorless.

The concentration in ppm of dissolved oxygen in the sample

\[ 'x' \times 0.025 \times 8 \times 1000 \]

\[ = \frac{a \times (b - c)}{b} \]

Where,

'\text{x}' = \text{volume of titrant, sodium thiosulfate}

\[ a = \text{volume of sample taken} = 50 \, \text{mL} \]

\[ b = \text{volume of stoppered bottle} = 125 \, \text{mL} \]

\[ c = \text{volume of } H_2SO_4+MnSO_4+NaOH+KI \text{ added} \]
Figure 2.2: (1) sampling (2) appearance of floc (3) floc dissolved using H₂SO₄

2.11 Lovibond Comparator 2000*

The dissolved oxygen content in very minute quantity in the de-aerator and boiler feed water is measured by using indigo-carmine and the apparatus required is the Lovibond comparator. The one used by us was Lovibond Comparator 2000°. The appropriate test disc for dissolved oxygen was selected for its use and inserted into the comparator with values towards the front of the instrument. The disc covered the range 0 to 0.12 mL/L oxygen in steps 0.005, 0.01, 0.015, 0.03, 0.055, 0.08, 0.1, 0.12 mL/L. To convert mL/L to parts per million, the values in mL/L are multiplied by 1.43. The disc was used in conjunction with a special reaction glass vessel which has been developed for use with the Lovibond Comparator. The reagents used were indigo-carmine stock solution (prepared by dissolving 0.018 g indigo-carmine and 0.2 g glucose in 5 mL double distilled water further adding 75 mL glycerol. This
reagent is stable for 90 days if stored in a refrigerator and for 6 weeks at ambient
temperature if stored in the dark), potassium hydroxide (KOH) (37.5 g dissolved in
62.5 mL of distilled water) and leuco reagent (freshly prepared in a small bottle by
mixing 8 mL of indigo-carmine stock solution and 2 mL of KOH). After
thoroughly mixing, the reagent was allowed to stand until the initial dark red color
changed to lemon yellow in approximately 10 minutes. The water sample was taken
and the reagents were added in the absence of atmospheric oxygen. Sampling was
carried out by the “Submerged Bottle Method”. With a dropping pipette the vial
attached to the inner surface of the special reaction vessel was filled with leuco
reagent. Any entrapped air bubbles were allowed to rise and disperse, so that the
vial was completely full and free of air. It was then sealed by means of a glass ball
which was placed in position by sliding the ball down a glass tube placed over the
end of the vial. The sample was allowed to flow through the reaction vessel for 10
minutes, to remove any reagent on the outside of the vial. The reaction vessel was
then removed from the sampling line and the stopper was inserted under water, to
prevent the trapping of any air. The reaction vessel was then removed from the
water, inverted to allow the ball to fall off the vial and the contents were thoroughly
mixed. This reaction vessel was then placed in the right-hand compartment of the
Lovibond comparator and a sample of water without reagents was placed in the left-
hand compartment to serve as a blank. The color developed in the sample was then
compared with the colors on the disc of the comparator.
2.12 Spectrophotometric Estimation of Hydrazine

In this method, the reddish coloration of a sample brought about by the reaction of p-dimethylamino-benzaldehyde (PDBA) on hydrazine in the boiler feed water was measured at a wavelength of 460 nm. The presence in the feed water of any oxidizing agent and a color resembling the red color or turbidity becomes an obstruction for estimation. As for its measuring range, this method is applicable for the hydrazine content 0.01-0.2 ppm.

Gravimetric Calibration curve: Diluting the standard hydrazine liquid (Dissolve 0.328 g of hydrazine dihydrochloric acid N₂H₄·2HCl together with 74 mL of hydrochloric acid in 100 mL of water, transfer this solution into one litre measuring flask, diluting it to one litre. 1 mL of this solution contains 0.1mg of hydrazine.) with hydrochloric acid (74 mL of hydrochloric acid in a one litre measuring flask and dilute it to one litre with water), a series of hydrazine solutions of 25 mL which contain various amounts of hydrazine in sequential order, in 50 mL stoppered measuring cylinders were prepared. 2 mL of HCl to each cylinder was added. 20 mL of PDBA solution (Dissolve 4 g of PDBA together with 15 mL of hydrochloric acid in 200 mL of ethanol, put the solution in a brown colored bottle and store it in a dark place) respectively was pipetted and added after shaking them well. After thoroughly mixing them, using as a blank sample a solution that has been separately prepared by adding 20 mL of PDBA solution to 27 mL of water (25 mL water + 2 mL HCl) that does not contain any hydrazine, the respective absorbance of the above mentioned solution with various hydrazine contents was measured spectrophotometrically, using a wave length of 460 nm. The spectrophotometer
used here was the one mentioned in section 2.8 of this chapter. Subsequently, a calibration curve that shows the relationship between the absorbance and hydrazine concentration in ppm was drawn.

![Calibration curve](image)

**Figure 2.3: Calibration curve for concentration of hydrazine**

The hydrazine content in the water collected or sampled out from the home-built de-aerator was measured by this method. As mentioned earlier, the measuring range by this method is applicable for the hydrazine content of 0.01 - 0.2 parts per million (ppm). However, the hydrazine concentration in our measurements can be made even well below 0.003 ppm.