Experimental

2.1: Materials and Methods

2.1.1: Glassware

Glassware fitted with interchangeable standard conical ground joints were used throughout. All glassware were cleaned with alkali solution (5% NaOH solution in 1:1 water-methanol mixture) or an appropriate acid. They were then rinsed thoroughly with water followed by acetone and dried in an electric oven at 110-120 °C for about 3-4 h prior to each experiment. These were cooled in desiccators or assembled hot and protected from atmospheric moisture either by anhydrous calcium chloride guard tubes or by flushing with oxygen free nitrogen gas.

Special types of weighing pipette, transfer tubes and other glassware were used for air sensitive compounds. Originally calibrated burettes, pipette and standard volumetric flasks were used. A special type of filtration assembly fitted with G-3 crucible was used for filtration of air sensitive compounds. Fractionating columns of various lengths assembled with still head for condensing and collecting the solvents were use for drying and distillation of various solvents. The melting points were determined in capillary tubes and are uncorrected.

2.1.2: Materials

The analytical Grade (AR) chemicals were used in all the experiments. Wherever AR grade chemicals were not available, LR grade chemicals were used after purification. All the solvents used during the present investigation were dried using appropriate reagents and purified according to standard methods [221]. The solvents were refluxed using fractionating columns and then distilled out. Following solvents were used during the experimental work.

Nitrogen gas used during the present investigation was of commercial grade. Trace amount of moisture and oxygen if present at all, were removed by passing nitrogen gas through Fieser’s (potassium hydroxide pellets + sodium dithionite + anthraquinone -2-sulphonic acid) solution and conc. H₂SO₄. Analysis was carried out using double distilled water.

Acids used during experimental work such as Hydrochloric acid, Sulphuric acid and Nitric acid were of AR grade (s d fine-CHEM make).

2.2: Analysis and instrumentation
2.2.1: Analysis

The ligands and their complexes prepared during the present investigation were analyzed by following methods.

a) Microanalysis

Microanalysis (C,H,N,S) of all the compounds were carried out in the Sophisticated Analytical Instrument Facility, IIT Bombay using Thermo Finnigan, Italy Model FLASH EA 1112 Series elemental analyzer.

2.3: Instrumental techniques

During recent years, due to the advancement in instrumental techniques physico chemical methods have been widely applied to characterize coordination compounds and to study their structural aspects. The term ‘structure’ is widely interpreted to study the properties of coordination compounds including (a) oxidation state of central metal atom, (b) coordination number of the central metal atom, (c) nature and sites of bonding of ligand molecule to the central metal atom and (d) probable structural chemistry of the complex. These physico-chemical methods used to study the structural aspect can be divided into two categories.

a) Macroscopic technique: Although these techniques do not give structural details, but help in providing useful information about purity and other properties of compounds related to their structures. These techniques include melting point, boiling point, decomposition point, molecular weight, solubility and thermal analysis etc.

b) Spectroscopic techniques: These techniques provide specific structural information and a site of bonding, the techniques includes infrared spectroscopy, nuclear magnetic resonance spectroscopy, ultraviolet-visible spectra spectroscopy and x-ray powder diffraction. Each of these techniques has certain limitation and to get clearer and complete information about various techniques as possible, considering their application.

2.3.1: Infrared Spectroscopy

Infrared spectrum originates from different modes of vibration of atoms in the molecule and rotation of the molecule. For infrared absorption to occur two major conditions must be
fulfilled. First, the energy of radiations must coincide with the energy difference between the excited and ground state of the molecule. Second, the vibration must implore a change in dipole moment of the molecules. Stretching and bending (deformation) are the two kinds of fundamental vibrations for molecule. These vibrations are not random events but can occur only at specific frequencies governed by the atomic masses and strengths of the chemical bonds, expressed as,

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

Whereas $\bar{\nu}$ = frequency of vibration
c = velocity of light
k = force constant
$\mu$ = Reduced mass of the atom involved

The infrared spectral range of greatest use is from 4000 to 200 cm$^{-1}$. In the group frequency region 4000-1400 cm$^{-1}$ the principal absorption bands may be assigned to vibration units consisting of only two atoms but may be assigned to vibration units consisting of only two atoms of a molecule, that is, unit. Which are more or less dependent only on the function group giving absorption and not on the complete molecular structure.

The approximate position of some infrared absorption bands are given in Table No. 2. The major bands in the spectra between 1400-650 cm$^{-1}$ (fingerprint region) are single bond stretching frequencies and bending vibration of polyatomic system. Which involve motion of the bonds linking a substitute group to the remainder of the molecule? This region of the spectrum, which is rich in absorption bands and shoulders, gives discernible differences spectra, even for similar molecules, which show similar spectra in the group frequency region. The far infrared region 670-620 cm$^{-1}$ is the particularly suited to the study of organometallic and inorganic compounds. Where atoms are heavy and whose bonds are indicated to be weak. Metal-ligand stretching vibrations appears in this far infrared region.

The intensity of an infrared absorption bond is proportional to the square of the rare of change of dipole moment, with respect to the displacement of the atoms, correspondingly C=C, C=O stretching vibration produce weak and strong bonds respectively.

As this thesis comprises of coordination compound of transition metal salts likes [Mn$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, Pd$^{2+}$and Pt$^{2+}$ with some organometallic compounds [222]. It will be worth discussing some of the modes given in figures of infrared region.
Approximate ranges of some infrared absorption bands.

<table>
<thead>
<tr>
<th>Linkage</th>
<th>positions wave No. cm(^{-1})</th>
<th>positions wave No. (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-H</td>
<td>3300-3700</td>
<td>3.03-2.70</td>
</tr>
<tr>
<td>N-H</td>
<td>3300-3370</td>
<td>3.03-2.97</td>
</tr>
<tr>
<td>C-H (aromatic)</td>
<td>3000-3100</td>
<td>3.33-3.23</td>
</tr>
<tr>
<td>C-H (aliphatic)</td>
<td>2700-3000</td>
<td>3.70-3.37</td>
</tr>
<tr>
<td>-C-O</td>
<td>1000-1050</td>
<td>10.00-9.52</td>
</tr>
<tr>
<td>-C=O (aldehyde)</td>
<td>1720-1740</td>
<td>5.81-5.75</td>
</tr>
<tr>
<td>&gt;C=O (ketone)</td>
<td>1705-1725</td>
<td>5.86-5.80</td>
</tr>
<tr>
<td>&gt;C=O (acid)</td>
<td>1550-1650</td>
<td>6.45-6.06</td>
</tr>
<tr>
<td>&gt;C=N</td>
<td>1590-1660</td>
<td>6.29-6.02</td>
</tr>
<tr>
<td>-C≡N</td>
<td>2100-2250</td>
<td>4.76-4.44</td>
</tr>
<tr>
<td>-C≡C-</td>
<td>2100-2250</td>
<td>4.76-4.44</td>
</tr>
</tbody>
</table>

The usual approaches have been tolerant the position and separations of the asymmetric and symmetric carboxylate frequencies in the compound to there of an authentic ionic salts[223].

Unidentate coordination removes equivalence of the carbon-oxygen bond in the anion, and has a metal-oxygen distance considerably shorter, than the next shortest metal-oxygen contact. Such as arrangement increase, but increase the separation delta values[224]. Both the symmetrical bridging and chelating carboxylate and nitrogen of the amide group maintain the equivalence of the carbon-oxygen bond and metal-nitrogen bonds found in the free ions[225] and it has been suggested that bidentate coordination should give separation similar to the ionic values. It has also been suggest, both the symmetry frequencies may shift, in the some direction also the separation is significantly less than these for ionic values are considered and indicative of the chelating or bridging groups[226]. Generally smaller delta values for chelating than bridging may be anticipated, as in the chelating systems. The splitting in the infrared absorptions can be attributed

i) Two coordination modes[227].

ii) Equilibrium between dimmer, polymeric from[228].

iii) Vibration coupling between neighboring group[229].

iv) Solid state effect[230].
Some application of infrared absorption is:

1. Infrared spectrum cannot commonly distinguish between the pure and impure samples, but the spectrum of a pure sample has fairly sharp and well-resolved absorption bands as compared to that of an impure one.
2. Sites and nature of bonding of ligand molecules with the central metal atom can be ascertained.
3. Progress of reactions can be monitored.
4. Stereochemistry of a compound can be deduced i.e cis or trans.
5. Identity of two samples can be established by comparing their spectra, recorded in the same medium.

**Instrumentation:**

The infrared spectra (4000-500cm\(^{-1}\)) of the complexes were recorded using in KBr pallets with Scanning speed of the 20 minute per spectrum.

2.3.2: Ultra violet-Visible Spectroscopy

Observations in this region are subject to two limitations:

I. The sparingly soluble nature of the complexes in solvents transparent.
II. The high absorption of the ligands compared to that of metal ions.

The absorptive of the organic ligands marks any splitting or structure developed by the metal ion that may arises from complexation. Hence, one can look for bond shifts and intensity alteration of the ligands alone. In some the total disappearance of the ligand bands is also observed[231]. The absorption of light energy by organic compounds in the ultraviolet region involves promotion of electrons in \(\pi\), \(\sigma\) and \(\eta\) orbital from the ground state to higher energy states. These higher energy states are described by molecular orbital that are vacant in the ground state or unexcited state and commonly called anti bonding orbital.

The electronic transitions (\(\rightarrow\)) that are involved in the ultra violet-Visible region are of the following type; \(\sigma \rightarrow \sigma^*\), \(\eta \rightarrow \sigma^*\), \(\eta \rightarrow \pi^*\) and \(\pi \rightarrow \pi^*\). The energy required for \(\sigma \rightarrow \sigma^*\) transition is very high, consequently compound in which all valance shell electron are involved in single bond formation, such as saturated hydrocarbon, do not show absorption in the ordinary ultra violet-Visible region. An exception is cyclo propane, which shows \(\lambda_{max}\) at about 190 nm.
Compound containing non-bonding electrons are oxygen, nitrogen, sulphur and halogen atoms are capable to showing energy than $\eta \rightarrow \sigma^*$ transition, which are lower in energy than $\sigma \rightarrow \sigma^*$ transitions. Consequently molecules containing non-bonding electrons usually exhibit absorption in the ordinary ultra violet-visible region.

Whether an organic compound contains a particular spectral pattern above 210 nm or not, it will generally show some absorption that increase in intensity towards shorter wavelength in the region. The absorption is due to part of $\eta \rightarrow \sigma^*$ transition near 200nm, if the molecule contain oxygen, nitrogen, Sulphur and halogen atom. This absorption $\eta \rightarrow \sigma^*$ is generally called the end of absorption.

Transition to anti bonding $\pi^*$ orbital are associated only with unsaturated centers in the molecule. These are of still lower energy requirements and occur at longer wavelengths, usually well within the region of the ordinary ultraviolet-visible spectrophotometer. R-CHO and R-C=O exhibit an absorption of low intensity around 285 nm, which is attributed to $\eta \rightarrow \pi^*$ transition and an absorption of high intensity and 180nm, which attributed to $\pi \rightarrow \pi^*$ transition. The $\pi \rightarrow \pi^*$ transition are of intermediate energy, absorption owing to these transition are usually between these owing to $\eta \rightarrow \pi^*$ and $\eta \rightarrow \sigma^*$ transition. The high-energy transitions ($\sigma \rightarrow \sigma^*$) occur at shorter wavelength and low energy transition, ($\eta \rightarrow \pi^*$) occur at lower wavelength.

Identical functional group in different molecules will not necessarily absorb at the same wavelength. The energy change for a particular transition dictates the position of absorption of a given group. Transition in identical functional group in different molecules will not necessarily have exactly the same energy requirement because of different structural environments. The magnitude of the mole of extinction coefficient for a particular absorption is directly proportional to the probability of the particular electronic transition, the more probable a given transition longer the extinction coefficient.

In visible region of spectrum interest centers around the effect of chelating on the absorption bands of the metal ion and influence of the solvent on these absorption of the complex formation is generally, reflected either in alternation in the intensity or shift in the position of absorption maximum or some time both. However, generally a splitting of the absorption band
was also observed, the rare earth metal ions shows band of medium to high intensity in aqueous solution.

Moeller [232] also proposed that every η, d band in the range 510-1000 nm was split in to two or more inflections indicating interaction between the ethylene diamine tetra acetate and the Nd $^{3+}$ ion in the solution. The study of the spectra of transitional metal ion complexes [233] in non aqueous medium revealed that the enhance stability of the chelate is reflected in the spectral alterations.

Certain absorption bands of rare earth ions show interaction due to complex formation, while most of the other bands remain unaffected. The transition involved in these hypersensitive bands as they are often called obeys. The selection rule $J\pm 2$ i.e $J$ value of excited level [234] to the bond observed in the rare earth due to hypersensitive transition is due to the in homogeneity of the solvent. The polarity of the solvent molecule also plays a part in hypersensitive transition. By as examination of the spectra of anhydrous salts of rare earth Pr$^{3+}$, Nd$^{3+}$, Sm$^{3+}$ and aqueous solution The red shift of anhydrous salts compared to those of the aqua ion solution[235].

The phenomenon of red shift was expending by Ephraim partly as contraction in high electrostatic bonding. Jorgenson called this is Nephelauxetic effect, which means an expansion of an electron, could influence by the ligand [236]. It gives the qualitative picture of the same proposed [237] a linear relationship between the wave number of the band of the complex $\tilde{\nu}$. The stabilization of the lowest sub shell of the ground state.

However, the spectra of Cu$^{2+}$ion complexes with different ligands keeping the coordinating atom unchanged [238]and observed that relationship given by the Jorgenson correlated the Nephelauxetic effect with the change in the inter electronic repulsion parameters. He has not taken in to account the infrared bands.

Sinha’s used the original relationship by plotting $\tilde{\nu}$ complex Vs $\tilde{\nu}$ aquo. Which gives better results one should actually use $\tilde{\nu}$ Fi ($\tilde{\nu}$ Fi = wave number of the free ion instead of aqua ions) because the aqua ions produce slight Nephelauxetic effect, the aquo ion was used, as the free ion level is not experimentally known and it is only recently they are being measured.
Study of the Nephelauxetic effect in some Ln$^{3+}$ complexes with pyridine-2- amnoxine

Angelov[239] stated that, it was well established that complex formation with lanthanide ions might lead to splitting and shift in the narrow $f-f$ bands. This evidently decreases the inter electronic repulsion within the 4f shell leading to weak covalent bonding between the lanthanide (III) ion. The donor atoms and hence in such complexes the mutilate intervals of the central metal ion are usually decreased and shifted towards lower numbers was observed. The shifted transition has been compared with the corresponding as in the lanthanide (III) aquo ions. Thus the level of Nephelauxetic effect was calculated using the relation

\[ \beta = \frac{\nu_{\text{complex}}}{\nu_{\text{aquo}}} \]

Further the covalence parameter $b^{1/2}$ has been connected to the Nephelauxetic effect parameter by using this relation

\[ b^{1/2} = \left[\frac{1}{2} \left( 1 - \beta \right) \right]^{1/2} \]

\[ \beta \text{- the average value of } \nu_{\text{complex}} / \nu_{\text{aquo}} \]

The calculated the $b^{1/2}$ value and found that the order covalence in amine complexes of Oxygen donor atoms. Further, a scale ($\delta\%$) to express the covalence of metal- ligand bond with Nd$^{3+}$ (III) complexes [240-241]the parameter of co-valence ($\delta\%$) is expressed as:

\[ \delta = \frac{1 - \beta}{\beta} \times 100 \]

($\beta$= average value of $\nu_{\text{complex}} / \nu_{\text{aquo}}$)

Taking as much transition as possible depending upon the ligands value may be either positive (covalent bonding) or negative (ionic bonding). All through the absolute value of $\delta$ are less important[242]. They may be conveniently used in ascending the relative covalent character of the complex.

**Instrumentation:**

The complexes were prepared in methanol and alcohol. Most of the complexes are colored. The Visible spectra recorded using dimethyl form amide, dimethyl sulfoxide and ethanol the range of spectra is 280-900nm.

**2.3.3: Magnetic moment**
Magneto chemistry is a powerful technique in the study of stereochemistry of metal complexes. Some metal ions possess unpaired electrons and some are having paired electrons. When the substance placed in magnetic field the magnetic moment induced in it. The magnitude of magnetic moment depends upon the paired and unpaired electrons present in the orbits of the metal ion. The study of magnetic properties can yield valuable information about the bonding and structure of metal complexes. Magnetic induction (β) produced by magnetic moment of strength of H is related to the intensity of the magnetism induced (I) in a material as:

$$\beta = \mu H = 4\pi I + H$$

Whereas $\mu$=magnetic permeability of the substance.

The intensity of magnetism induced (I) is equal to the product of, the strength of magnetic field (H). The volume susceptibility (K) and specific (X) i.e. susceptibility per gm can be calculated as $X=K/9$

Whereas $K/9$= density of material.

The molar susceptibility Xm can be expressed as

$$X_m = \text{specific susceptibility} \times \text{molecular weight of substance}$$

$$= X_g \times \text{M.wt}$$

The magnetic moment ($\mu_{\text{eff}}$) of the substance can be calculated by using the equation.

$$\mu_{\text{eff}} = 2.84 \sqrt{X'm \times \frac{T}{B \times M}}$$

Where $X'm$=corrected molecular susceptibility and $T$ = temp in Kelvin.

Depending upon the numerical value of $\mu_{\text{eff}}$ i.e magnetic moment, the number of electrons is decided. The range of $\mu_{\text{eff}}$ value as per the number of unpaired electrons is given by the formula:

$$\mu_{\text{eff}} = \sqrt{n (n+2)}$$

Where $n$ = number of unpaired electron.

Instrumentation:

Gouy balance was used to carry out susceptibility measurement of representative complexes, at room temperature on Faraday Electro – balance. The tube constant was determined by HgCO (CNS)$_4$ [mercury tetra thio canto cobalt (II)] as the standard material. The compound
in form of fine powder was packed densely in the Gouy tube and weight was recorded at various fields 4 amp and 6 amps. Susceptibility was correlated for the presence of diamagnetic components and the magnetic movement values were deduced.

2.3.4: X-ray powder diffraction

X-ray get diffraction by crystal, as their wavelength is of the same order of interplanar distance in crystal. The Bragg’s Equation can represent the necessary condition for diffraction,

\[ 2d \sin \theta = n \lambda \]

Whereas

- \( d \) = Interplanar spacing.
- \( \theta \) = Angle of reflection.
- \( n \) = Order of diffraction
- \( \lambda \) = Wave length of X-ray in \( \text{Å} \)

The target elements used commercially, Ag, Mo, Cu, Ni, Fe, and Cr giving wave length range 0.56 to 2.29 \( \text{Å} \) use for analytical purpose. X-ray diffraction data for single crystals allow the definitive establishment of both coordination number and molecule geometries for solid complexes, to the extent that, data of this type established the arrangement of nearest neighbor atoms, along with the central lanthanide (III) atoms. All types of compounds are similarly treated and a decision as to what arbitrary. Here in the term complex is restricted to a species containing a lanthanide (III) ion and a recognized ligand. Which can be regarded as an entity that could exist in solution and could undergo reaction as such?

In this sense, anhydrous chloride of the Yttrium chloride type structure would not qualify as a complex even though in its crystal structure. These exists octahedral arrangement of six chloride ions around each lanthanide ions. Which are linked by shored edges\(^\text{135}\) however, a hydrated chloride, containing the group \([\text{Ln} (\text{H}_2\text{O})_6 \text{Cl}_2]\) would so quality\(^\text{136}\). The rare earth chelate of the type \(\text{ML}_3\) have been shown to react with alkali metal ions and an addition ligand to form complex chelate of \(\text{M}' \text{ ML}_4\). \{Where \(\text{M}' = \text{alkali metal, } \text{M}=\text{rare earth metal, } \text{L}=\text{ligand}\}\) A large cationic size and the lack of directional and strongly covalent nature in bond formation makes situation early for the lanthanide ions to exhibits various coordination number\(^\text{137-138}\) irrespective of whether the bonding in the complex species is electrostatic or covalent. The most probable special position of the donor atoms with respect to the central atom is predictable in terms of electron pair, ligand or columbia repulsion of the requirement of maximum symmetry [243].
2.3.4.1: Indexing X-ray powder diffraction

The inter planar spacing $d_{hkl}$ were calculated from $2\theta$ value using relation $d = \lambda \cdot 2\sin \theta$ and correlated to $1/d^2$. The entire indexing was done with the help of reciprocal lattice concept using the following linear equation for all crystal systems:

$$1/d_{hkl}^2 = (ha^*)^2 + (lc^*)^2 + 2ha^*kb^*\cos \gamma^* + 2kb^*ic^*\cos \alpha^* + 2lc^*ha^*\cos \beta^*.$$  

Where as $a^*$, $b^*$, $c^*$, $\alpha^*$, $\beta^*$ and $\gamma^*$ are reciprocal lattice parameters. The following relations between the dimensions of the direct reciprocal lattice were used, which is necessary for ito’s method of calculating angular as well as linear parameters.

Various computer programs like powdin and Powdout, celerel were used in succession to index the powder data and to obtained lattice parameter.

2.3.4.2: Program used for indexing the data

a) **Program bar**: The recorded data in the form of $1/d^2$ were fed to the computer, all the difference were calculated as required for Hess[244]and lipson[245] method. All valve were arranged in increasing order than plotted on an extended bar diagram with accuracy $4 \times 10^{-4}$ from the recurring difference, final $a^*^2$, $b^*^2$ and $c^*^2$ were selected by trial and error method.

b) **Back-cal and powdin and out program**: If the lattice parameters in the form of $a^*^2$, $b^*^2$, $c^*^2$, $2a^*b^* \cos \gamma$, $2b^*c^* \cos \alpha$ and $2c^*a^* \cos \beta$ are fed to the computer in order to evaluate the lattice parameters $a$, $b$, $c$, $\cos \alpha$, $\cos \beta$ and $\cos \gamma$, all the possible combination of $h$, $k$, $l$ planes and the corresponding $1/d^2$. After using program bar, if the appropriate $a^*^2$, $b^*^2$, $c^*^2$ were obtained. Then the back-cal program can be used to calculate $h$, $k$, $l$ combinations and corresponding $1/d^2$ value in increasing order. These values can be readily compared and checked with observed data. These values also check on powdin program.

c) **X-ray program**: This program of least square method on the weight aged percentage.

$$\frac{F_i - Y_i}{Y_i}$$

Where $F_i = 1/d^2$ (calculated) and $Y_i = 1/d^2$ (observed).

2.3.4.3: Density and space group determination
The densities of indexed complexes were determined by ‘Flotation method’ using toluene solvent. The relationship between volumes of the unit cell ‘V’ expressed in terms of $A^3$ and density ‘D’ in grams $cm^3$. The relationship is given by following expression.

$$D = \frac{Z \times F}{N_A \times V \times \left(1.66 \times Z \times F\right)}$$

Where, $F = $ formula weight of complex.

$Z = $ Number of formula units present

$N_A = $ Avogradro constant – $6.022 \times 10^{23}$ mol$^{-1}$

Using the X-ray data, crystal lattice density of each complex were calculated. Also, densities of these complexes were determined using specific gravity bottle. Subsequently the observed density of the complex was used to evaluate formula factor $Z$. The value of $Z$ and the volume obtained from X-ray data were used to calculate actual density of the complexes. Data from international tables of X-ray crystallography[255] and the $Z$ value were used to assign an appropriate space group to the indexed crystal system.

**Instrumentation:**

X-ray powder diffraction patterns were obtained by using nickel filtered CuKα radiations. Joel8030 double Gonio meter X-ray diffraction wide-angle goniometry with a Geiger Muller counter was employed to record the patterns. Using silicon slandered performed the alignment and calibration of the goniometry. A thin layer of the sample was spread evenly as a glass slide using amyl acetate solution. Secondary speed $2\theta = 1^\circ$ per minute and scanning is different i.e. 10 to 40$^\circ$ were used. Diffraction pattern were recorded on a chart and from the chart recordings. The inter planar d-spacing and the diffraction line interstices were determined.

**2.3.5: Thermo Gravimetric Analysis**

Thermogravematric methods involve techniques such as Thermogravematric analysis is a technique whereby the weight of a substance, in an environment heated or cooled at a controlled
rate, is recorded as a function of temperature or time. The following factors, which affect Thermogravimetric analysis curve, are,

i] Rate of heating.

ii] Atmospheric of the furnace.

iii] Nature, shape and material of construction of the sample holder.

iv] Weight of the sample taken for analysis.

v] Compactness of sample


Thermogravimetric analysis provides a qualitative measurement of any weight change associated with a transition. Thermogravimetric analysis curve are characteristic for a given compound or system because of the unique sequence of physico-chemical reactions. Which occurs over definite temperature ranges and at rates that is function of the molecular structure. Some of the applications of this technique are:

I) To determine the purity and thermal stability of a substance.

II) To deduce the molecular weight of the starting material from the total weight loss, once the reduces is identified.

III) To determine the composition of a compound heated up to a specific temperature and to follow the reaction involved in its decomposition, it use together with some other techniques.

**Differential Thermal Analysis:**

In this technique the difference in temperature between substance and thermally inert reference material are continuously recorded as a function of temperature or time, and the reference as both are subjected to a predetermined rate of heating/cooling in an environment. Some of the factors, which affect differential thermal analysis curve, are;

I. The rate of heating.

II. The gaseous environment around the sample.

III. Geometry of the material of construction of the sample.

IV. Furnace characteristic. {Types of winding show direct effect on differential thermal analysis curve}

V. Initial weight and particular size of the sample.

*Some Applications are:*
I. The melting point of a substance can be determined; therefore, this technique can be used as a check for the purity of a substance.

II. From the area under the peak, the heat of reaction can be calculated.

III. It can be used for identifying the substance. The differential thermal analysis curves of no two substances are identical and it serves as a fingerprint for a substance.

IV. Differential thermal analysis can also be used for constructing phase diagrams of multi-component systems.

V. The identification of new intermediate compounds.

VI. It can be distinguished between a phase change and decomposition, if used along with Thermogravimetric analysis.

Instrumentation:

The thermal and differential analyses of complexes were heated from 25-1000 °C at a heating rate 1 min/10 °C in N₂. Only ten mg sample was required. Intermediates were identified by percentage weight loss.

2.3.6: Scanning Electron Microscopy (SEM)

The scanning electron microscope (SEM) is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. Basic operation of an SEM involves the production of electrons which are accelerated toward the specimen while being confined and focused by apertures and electromagnetic leavened. Once the beam impinges on the surface of the specimen, electron interactions occur with the sample resulting in electrons that can be detected to reveal topographic, size, and structure of the sample.

Images presented in the current work were obtained using FEI Quanta -200 Scanning Electron Microscope (SEM) with an operating voltage of 20 kV.

2.3.6.1: Preparation Method of Nanoparticles

Equi-molar solutions of metal and organometallic ligand were mixed. Then these solutions were concentrated by heating at 50-60 °C in water bath near about seven hours. Than this solution were centrifuges for 5 hours at 4000 rpm. The Nanoparticles were formed. The results of Nanoparticles were mentioned in Chapter-III,IV,V and VI in detail with its images.

2.3.7: Electrolytic conductivity
Electrolytic conductivity is a measure of the ability of a solution to carry an electric current. The solutions of electrolytes conductivity of ions are under the influence of an electric field. The standard unit of conductance is specific conductance $K$, expressed in $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. The observed conductance of a solution depends inversely on the distance $d$ between the electrodes and directly upon their area $A$,

$$\frac{1}{K} = \frac{A}{d}.$$  

For a given cell with fixed electrodes, the ratio $d/A$ is a constant, called cell constant. The electrical conductance of a solution is a summation of contributions from all the ions present. It is depend upon the number of ions per unit volume of the solution and upon the velocities with which these ions move under the influence of the applied electromotive force. In order to express the ability of individual ions to conduct, a function called the equivalent conductance ($\Lambda$) is employed.

$$\Lambda = 1000 \times \frac{K}{C_s}$$

Where $C_s$ is concentration of the solution in gram equivalent per liter. Similarly, molar conductance can be calculated by expressing concentration of the solution in mole per liter.

**Instrumentation:**

Conductivity measurements were carried on Toshaniwal digital conductivity meter CL 01.10A, using $10^{-3}$ molar solution at room temperature. The conductivity measurements were performed in dimethyl sulphoxide and dimethyl formamide using as a solvent. Formula weights of the complexes were considered as their molecular weights for preparation of solution. Standardization was done by using 0.01 molar potassium chloride solution, prepared in distilled water.

**2.3.8: Determination of metal-ligand ratio**

The metal-ligand ratio of the complexes were determined by taking known weight of the complex in platinum crucible, heating it about 800-900 ºC. The complexes decompose and convert into metal oxide. It is found that the entire complexes metal ligand ratio is 1:1 and 1:2, which is agree with elemental analysis of the complexes.

**2.3.8.1: Mohr’s method**
The Mohr method was first described in 1865 by K.F. Mohr, a German pharmaceutical chemist, who did much pioneering work in the development of titrimetry, first described the Mohr’s method in 1865. Because chromium (VI) is a carcinogen. This method is commonly used for estimation of chlorines [246].