1.1 GENERAL INTRODUCTION AND THEORIES OF COORDINATION COMPOUNDS

In the recent years, inorganic chemistry is impressive renaissance in academic and industrial research area. Last few years have been significant in the growth of interest in Inorganic Chemistry. Inorganic chemistry represents the traditional core of chemistry, with a history traceable over thousands of years. But the field of coordination Chemistry has expanded very fast in the recent years and continues to evolve and there is growing emphasis on Coordination Chemistry [1-4]. There are many new directions of Coordination Chemistry in molecular magnetism, supramolecular chemistry, associated developments in catalysis [5, 6] and chelation therapy. Coordination complexes in the development of new architectural materials such as nanostructures and in environmental applications (e.g., “green” catalysts and bioremediation) are on the frontiers of inorganic chemistry in the twenty-first century; however, even these exciting and splashy new systems remain governed by the fundamentals of metal ion chemistry [7]. The study of “Inorganic Chemistry” involves the studies of alkali and alkaline earth metals, transition metals, lanthanides, actinides, metalloids etc. Understanding and predicting the results of the reactions involving transition metals, is an ultimate goal of Coordination Chemistry [8].

The field of coordination chemistry in medicine may usefully be divided into two main categories first, ligands as drugs which target metal ions in some form, whether free or protein-bound; and secondly, metal-based drugs and imaging agents where the central metal ion is usually the key feature of the mechanism of action [9]. A list of clinically used chelating agents may be found in
most pharmacopoeia, while new chelating agents continue to be sought. Although, bioinorganic chemistry has developed from the continuing research in coordination chemistry with its important associations in biology. Bioinorganic chemistry is a specialized field that spans the chemistry of metals containing biomolecules within biological systems [10-12].

At the beginning of 20th century, inorganic chemistry was not a prominent field. It gained importance after the pioneer work of Alfred Werner (1893) [13]. Studies of Werner emphasized on the structure, properties and reaction of a new class, signalized as “Complex Compounds” and awarded Noble prize in 1913 for his coordination theory of transition metal complexes. The term complex in chemistry is usually used to describe molecules or assembles formed by the combination of ligands and metal ions. The ions or molecules surrounding the metal are called ligands, which bind to the metal ion by a coordinate bond. The organic ligands often bind the metal through a donor atom such as oxygen/nitrogen or sulphur; such compounds are considered as coordination compounds [14, 15].

In the past scientists concentrated almost to the study of properties of the coordinated organic part of the complexes i.e. modification of the organic molecule by coordination with metal. Many relevant problems have been discussed in review. The behavior of structure, stability and general properties of transition metal complexes can be explained on the basis of various advance theories. Inorganic chemistry has greatly benefited from qualitative theories. Such theories are easier to learn as they require little background in quantum theory.
Following theories were popularly considered for explaining the nature of metal-ligand bond:

1. Valence bond theory.
2. Crystal field theory.
3. Ligand field theory.
4. Molecular orbital theory.

**VALENCE BOND THEORY:**

In 1927, Valence bond theory was developed by Heitler and London. In 1929, Linus Pauling's [15] "Nature of the Chemical bond" offered valence bond theory as a plausible explanation for bonding in transition metal complexes. His application of VBT to transition metal complexes was supported by Bjerrum's work on stability.

This theory concentrated on the stereochemistry and magnetic properties of central atom/ion in complexes [16, 17]. In this model low-lying, empty d-orbitals of transition metals (as with non-transition elements) are combined with appropriate s and p orbitals to form new hybrid orbitals that accept ligand electron pairs to form a coordinate covalent bond [18].

Postulates put forth by Caven and Lander in 1939, attributed the relationship of color and complex structure to “looseness or an unsaturation in the electronic structures,” or as Fajans stated, “a constraint or deformation of the electron systems of the coordinated molecules,” could not be adequately explained. There were weaknesses in the VBT as applied to complexes; this created the basis for other theories.
In brief, this theory offers only qualitative interpretation of bond type, stereochemical and allied properties.

**CRYSTAL FIELD THEORY:**

Crystal field theory is a model that describes the electronic structure of transition metal compounds, all of which can be considered coordination complexes. CFT was introduced by physicists Hans Bethe [19] in the 1929, it gives a quantum mechanical basis for understanding complexes and was applied to transition metal complexes by Schlapp and John Hasbroack VanVleck in 1930 [20,21]. This accounted nicely for color and magnetic properties of crystalline solids. CFT thus takes a purely electrostatic approach to bonding and though this is not fully realistic, this model is relatively successful at explaining many transition metal complex properties including color. But crystal field theory treats all interactions in a complex as ionic and assumes that the ligands can be approximated by negative point charges.

CFT has been a favorite for the discussions when possible MO and LF theories are more complicated, but provide a more realistic perspective. Crystal field theory was subsequently combined with molecular orbital theory to form the more realistic complex field theory LFT, which delivers insight into the process of chemical bonding in transition metal complexes [22].
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LIGAND FIELD THEORY:

Ligand field theory describes the bonding in coordination complexes. Ligand field theory was developed during the 1930-40 as an extension of crystal field theory. This theory treats the metal- ligand interaction as a covalent bonding interaction; and depends upon considering the overlap between the d-orbitals on the metals and the ligands donor orbital. Three types of interactions are possible i.e., the $\sigma$ overlap, $\pi$ overlap, or the $d\pi-p\pi$ overlap of orbitals involving orbital of metal and the ligands.

Ligand field theory is applicable to interpret stereochemical path for substitution reactions, coordination number, magnetic and thermodynamic properties of the complexes. This theory involve the use of inter-electronic interaction parameters like spin orbital coupling constant $\lambda$, and the Racah parameters B and C are taken into consideration for the orbital overlap [22-24].

MOLECULAR ORBITAL THEORY:

In chemistry, molecular orbital theory is a method for determining molecular structure in which electrons are not assigned to individual bonds between atoms, but are treated as moving under the influence of the nuclei in the whole molecule and providing a more accurate description of the metal–ligand bond [25]. Molecular orbital theory was developed, primarily through the effects of Friedrich Hund, Robert Mulliken, John C. Slater and John Lennard-Jones in the years, after valence bond theory (1927). MO theory was originally called the Hund-Mulliken theory. The molecular orbital theory had become acceptable as a valid and useful theory in 1933. MO theory provides a global, delocalized perspective on chemical bonding [26-28]. MOT uses a linear combination of
atomic orbitals to form molecular orbitals which cover the whole molecule. Molecular orbitals are further divided according to the types of atomic orbitals combining to form a bond. These orbitals are results of electron-nucleus interactions that are caused by the fundamental force of electromagnetism. These are bonding orbitals, anti-bonding orbitals, and non-bonding orbitals. Thus, overall, bonding (and electrons) is far more delocalized (spread out) in MO theory, than is implied in valence bond theory. This makes MO theory more useful for the description of extended systems.

Study of coordination chemistry is now attracting the attention of chemists and workers. Solid metal complexes and their elemental analysis, magnetic susceptibility, molar conductance, mass, IR, $^1$HNMR, UV-Visible and X-ray etc., are being employed for the investigation of the physico-chemical phenomena of active chemical species. The solution study comprises thermodynamic and kinetic aspects. Kinetic study deal with the rate and mechanism of chemical reaction while thermodynamic study show stability and degradation pattern of the complexes [29-32].

1.2 TECHNIQUES IN THE CHARACTERIZATION OF INORGANIC COMPOUNDS

Because of the diverse range of elements and correspondingly diverse properties of the resulting derivatives, inorganic chemistry is closely associated with many methods of analysis. Older methods tended to examine bulk properties such as the electrical conductivity of solutions, melting points, elemental analysis, magnetic susceptibility and solubility. With the advent of quantum theory and the corresponding expansion of electronic apparatus, new tools have been introduced to probe the electronic properties of inorganic
molecules and solids. Often these measurements provide insights relevant to theoretical models. A number of techniques are used for characterizing and determining the molecular structure of ligands with their metal complexes, and also for deciding the stereochemistry of complexes. The choice of method depends upon the physical state of the complex.

Commonly encountered characterization techniques are:

1. Elemental analysis.
4. Infrared absorption spectroscopy.
5. Electronic spectroscopy (UV-Vis).
8. Thermogravimetric analysis.
10. Molecular modeling.

**ELEMENTAL ANALYSIS:**

The molecular formulae of the coordination compounds can be deduced from elemental analysis. For the determination of the metal contents, the complex was decomposed by heating with concentrated nitric acid and the metal was estimated by well-known standard analytical methods [33].
MOLAR CONDUCTANCE:

The electrical conductivity measurements have been used to determine the charge type of the complex molecules. The molar conductance of charged complex falls in a predictable range in a particular solvent at a given concentration. The ions present in solution are responsible for the conductance. A molar conductance may be defined as the conducting power of all the ions produced by one gram mole of an electrolyte in a given solution and it can be expressed by the following relation

\[ \lambda = 1000 \kappa / C \]

Where \( \lambda \) is molar conductance, \( \kappa \) is specific conductance and \( C \) is the concentration in gram mole per liter.

In context with coordination compounds, the determination of molar conductance value is quite meaningful as it assists in deciding whether a negative ion is inside or outside the coordination sphere. Most ions, with the exception of those having long chains (H\(^{+}\), OH\(^{-}\)) and some complex ions have ionic conductance of about 60 S cm\(^{-2}\) mol\(^{-1}\) at 25°C in water. The approximate value of the conductance vary with the change in size of ion, temperature, dielectric constant, relative velocity of ion and viscosity of the solvent [34,35].

MAGNETIC SUSCEPTIBILITY:

The valence d-electrons of transition metal complexes influence properties such as color, reactivity, and magnetism. By investigating these properties for a particular complex, we can gain insight into metal ion electronic structure. Metal complexes exist with either all of their spins paired
(diamagnetism) or with unpaired electrons (paramagnetism). The vector quantity that is the measure of the torque exerted on a paramagnetic compound when in a magnetic field is called the magnetic moment, $\mu$, measured in units of Bohr magnetons, BM [36].

The molar susceptibility is the susceptibility per gram mole, represented as $\chi_m$. Magnetic moments are calculated by the equation.

$$\mu_{eff} = 2.84\sqrt{\chi_m} \text{ T B. M.}$$

Where T is the absolute temperature.

**INFRARED ABSORPTION SPECTROSCOPY:**

Infrared spectroscopy is one of the most popular analytical techniques to identify compound or investigate sample composition. IR spectroscopy is most widely used for information about the mode of linkage, presence of functional group, aromatic ring and sites of attachment of ligand to the metal ion, the nature of coordinate bond and stereochemistry of metal complexes [30,37]. IR spectroscopy exploits the fact that molecules have specific frequencies at which they rotate or vibrate corresponding to discrete energy levels. A compound can vibrate in six different ways: symmetrical and asymmetrical stretching, scissoring, rocking, wagging and twisting, bending [38,39].

It is the subset of IR spectroscopy that deals with the infrared region of the electromagnetic spectrum. The infrared portion of the electromagnetic spectrum is divided into three regions; the near-, mid- and far-infrared. The spectra recorded in the region from 4000-200cm$^{-1}$ helps in interpreting inorganic and coordination compounds and also helps in ascertaining the ligand
chain length, type of bonding, molecular symmetry, isomerism, functional groups and the nature of their attachment to metal.

Due to various donor atoms [40], IR spectrum of a ligand after complexation with metal must differ from that of the free ligand. The difference between the IR spectra of the free ligand and their coordination compounds are usually of following type:

1. Change in band positions.
2. Change in intensity of relative band.
3. Splitting of single peak of ligand into several bands in the complexes.
5. Bands may broaden after coordination.
6. Disappearance of band frequency.

Infrared spectroscopy is widely used in both research and industry as a simple and reliable technique for measurement, quality control and dynamic measurement. With increasing technology in computer filtering and manipulation of the results, sample in solution can now be measured accurately. This technique makes the observations of chemical reactions and process quicker and more accurate. FT-IR has been highly successful for applications in both organic and inorganic chemistry [41].

**ELECTRONIC SPECTRA:**

In the early 1960, inorganic coordination chemistry was growing rapidly, while at the same time, scanning UV/Vis spectrometers were becoming more widely available. In spectrophotometer, absorption or emission of ultraviolet or visible light by a molecule depends on electron transition between molecular
orbital energy levels, just as absorption or emission of electromagnetic radiations by an atom is determined by electron transitions between different energy levels E in the atom.

Many of the properties of metal complexes are dictated by their electronic structures. The electronic structure can be described by a relatively ionic model that ascribes formal charges to the metals and ligands and does not focus on covalency. In metal complexes three types of spectra may be obtained i.e.:

1. d-d (visible)

2. Charge transfer (M-L)

3. Intra ligand (UV)

Most transitions that are related to colored metal complexes are either "d-d transitions" or "charge transfer bands". In a d-d transition, an electron in a d-orbital on the metal is excited by a photon to another d-orbital of higher energy. A charge transfer band entails promotion of electron from a metal-based orbital into an empty ligand based orbital (Metal to Ligand Charge Transfer or MLCT). The converse also occurs: excitation an electron in a ligand-based orbital into an empty metal-based orbital (Ligand to Metal Charge Transfer or LMCT). Charge transfer bands give intense absorption and d-d band are much weaker. Charge transfer bands usually occur at higher energies than d-d transitions.

The strictness of the selection rules is slightly violated or diluted because of the slight mixing or coupling of the orbitals or states in some cases resulting slightly enhanced intensity of the observed bands. From the number, position and intensity of the bands in the spectrum, it is possible to obtain
information, on the symmetry around the central metal ion, relative order of energy levels, 10Dq and other parameters. In addition to this, when the ligand also absorbs in the visible region, the change in absorption bands indicate the complex formation [29,30,42].

**ELECTRON SPIN RESONANCE:**

Electronic paramagnetic resonance (EPR) or Electronic spin resonance (ESR) spectroscopy is a technique for studying chemical species that have one or more unpaired electrons, such as organic and inorganic free radicals or inorganic complexes possessing a transition metal ion. A molecule or an ion having the unpaired electron absorbs electromagnetic radiation of microwave frequency under the influence of a magnetic field. An unpaired electron can move between the two energy levels by either absorbing or emitting electromagnetic radiation of energy by the action of magnetic field. The energy $E$ of transition is given by following equation.

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

Every electron has a magnetic moment and spin quantum number $s = \pm\frac{1}{2}$, with magnetic components $m_s = +\frac{1}{2}$ and $m_s = -\frac{1}{2}$. In the presence of an external magnetic field $H$, the electron magnetic moment aligns itself either parallel ($m_s = -\frac{1}{2}$) or antiparallel ($m_s = +\frac{1}{2}$) to the magnetic field.

If the great majority of ESR measurements are made with microwave frequency $\nu$ fed to the electron and the applied magnetic field is such that $g\beta H = h\nu$, the energy will absorbed by the $m_s = \pm 1$ state and a transition between two $m_s$ state will take place. When an unpaired electron comes in vicinity of a
nucleus with a spin I, an interaction takes place which causes the absorption signal to be split into \(2I+1\) components (due to nucleus spin-electron spin coupling) the energies of the levels are given by the following expression.

\[
E = g\beta h m_s + A m_s m_l
\]

Where \(A\) is the hyperfine coupling constant.

However, the interaction of an unpaired electron, by way of its magnetic moments, with nearby nuclear spins, results in additional allowed energy state and in turn, multi-lined spectra. In such cases, the spacing between the EPR spectral lines indicates the degree of interaction between the unpaired electron and the perturbing nuclei [43].

EPR spectroscopy is important in various branches of science, such as chemistry and physics, for the detection and identification of free radicals and paramagnetic centers. EPR is used to provide information on a radical’s geometry and the orbital of the unpaired electron. Medical and biological applications of EPR also exist. EPR spectra can then give information on the environment of these so called spin-lebel or spin-probes [44,45].

**MASS SPECTROSCOPY:**

Mass spectroscopy is an analytical technique that identifies the chemical composition of compound or sample on the basis of the mass-to-charge ratio of charge particles. The method employs chemical fragmentation of sample into charge particles (ions) and measurements of two properties, charge and mass of the resulting particles, the ratio of which is deduced by passing the particles through electric and magnetic fields in a mass...
spectrometer. This technique has both qualitative and quantitative uses, such as identifying unknown compounds, determining the isotopic composition of elements in a compound, determining the structure of a compound by observing its fragmentation, quantifying the amount of a compound in a sample using carefully designed methods [46,47].

The design of a mass spectrometer has three essential molecules: an ion source, which transforms the molecules in a sample into ionized fragments; a mass analyzer: which sorts the ions by their masses applying electric and magnetic fields; and a detector: which measures the value of some indicator quantity and thus provides data for calculating the abundances of each ion fragment present. Consider a small amount of sample is vaporized into the mass spectrometer where it is bombarded by a stream of high energy electrons. A molecule may simply lose an electron or it may fragment into cations. The fragment ion may in turn break down further. A parent ion results, when one electron is removed from the parent molecule of the substance. The streams of sorted ions pass from the analyzer to the detector, which records the relative abundance of the ion producing the signal. The tallest peak called the “base peak” is arbitrarily assigned an intensity of 100%.

\[
\text{Molecule} \quad \rightarrow \quad \text{Molecular ion} + e^- \\
M(g) + e^- \rightarrow M^+(g) + 2e^-
\]

Each kind of ions has a particular mass to charge (m/z) ratio. A mass spectrum is a plot of relative abundance against the ratio mass/charge (the m/z value).
Mass spectroscopy not only allows the determination of the mass of an unknown compound but also allows guessing the molecular structure especially in combination from the molecular formula. Mass spectroscopy is applicable to wide variety of problems in inorganic and physical chemistry [48, 49].

**FAB MASS:**

In the fast atom bombardment (FAB) equipment usually a relatively high pressure of argon/xenon gas is placed between the ionizer and the sample. Argon/xenon gas is ionized by hot filament-type ion source, then accelerated in an electrostatic field and focused into a beam that bombards the sample. The Ar⁺/Xe⁺ provide high kinetic energy as well as undergo charge exchange with the solvent in which sample is dissolved. The mass spectrum becomes a fingerprint for each compound because no two molecules are fragmented and ionized in exactly the same manner on electron bombardment. There are sufficient differences in these molecule’s fingerprints, to permit the identification of different molecules in the complex mixture. The mass spectrum of a compound can be obtained on smaller sample size (in extremis down to $10^{-12}$ g) than for any other of the main spectroscopic techniques. The principal disadvantages being the destructive nature of the process, which precludes recovery of the sample [47-49].

**THERMAL ANALYSIS:**

Thermal methods of analysis are now used in a very large range of scientific investigations. The term “Thermal analyses” incorporate the techniques in which some physical parameters of the system are determined as a
function of temperature. Accordingly, thermal analysis has been defined as a
group of techniques in which the parameter of a property of a sample is
monitored against time or temperature, while the substance is continuously
heated or cooled. The thermogram obtained may be considered as thermal
spectrum, which characterizes a system, single or multi component in terms of
the temperature dependence of its thermodynamic properties and physico-
chemical reaction kinetics. Among the various thermal analysis techniques the
most widely used techniques are TG, DTG, DTA and DSC.

**Thermo-gravimetric analysis:** It is a type of testing that is performed on
sample to determine changes in weight in reaction to change in temperature.
Such analysis relies on a high degree of precision in three measurements-
weight, temperature and temperature change. The mass versus temperature
curve known as thermogram, provides information concerning the thermal
stability and composition of the initial sample, any stable intermediate and
the residue. Data obtained from TGA are commonly employed in research and
testing to determine characteristics of materials, degradation temperature
and absorbed moisture contents in materials.

**Differential thermal analysis:** Differential thermal analysis (DTA) measures
the thermal effects occurring in the sample by continuously recording the
temperature difference between the sample and reference material as a
function of temperature. Thus, if a physical or chemical change takes place in
the sample, which accompanies absorption or liberation of heat, then a
temperature difference ($\Delta T$) will occur between the sample and an inert
reference material ($\Delta T = T_{\text{sample}} - T_{\text{reference}}$). In the graphical record this will
appear as a positive or a negative peak depending on the nature of heat change, exotherms by ups and endotherms by down in the DTA curve. The method records all the changes in enthalpy whether it is accompanied by a mass change or not such enthalpy change include phase changes due to melting, boiling, evaporation, sublimation, solid state phase transition, chemical reaction and dissociation. Each substance gives a characteristic DTA curve, which can serve as a fingerprint of that substance.

**Derivative thermogravimetry:** The first derivative of the TG curve with respect to time (t) is plotted as a DTG curve with dm/dt as the ordinate showing mass loss downwards and T or t as the abscissa increasing from left to right. The DTG peak temperature and peak high are related to the activation energy and reaction order, and hence, thermal reactions can be characterized by DTG peak temperature and peak height measurements.

Today TG, DTG and DTA separately or simultaneously are used for the kinetic analysis of various reactions such as dehydration, decomposition, oxidative degradation and loss of constituent ligand molecules. Kinetic studies are important in providing essential evidence of the mechanisms of chemical processes occurring in the gas phase, in solutions in a variety of solvents, at gas-solid interface and in the solid state [50-55].

**KINETICS:**

Chemical kinetics deal with a more chemical aspect of chemical phenomena, namely the rate of change from initial to final state under non-equilibrium conditions of TG analysis. This depends upon the path followed by the reactants while getting converted into the products. The rate of reaction at
temperature $T$ is proportional to the probability $p$, the frequency of collisions $n$, the number of particles with energy $E$ and a function of concentration $f(c)$. The parameters $n$, $E$, $Z$ and $K$ constitute of the kinetic parameters [50].

Weight loss at any given temperature may be defined as: Fraction of reaction $\alpha = [W_0 - W_t]/[W_0 - W_\infty]$, where $W_t$ is the indicated weight at time $t$, $W_0$ is the initial weight and $W_\infty$ is the weight at the end of the process under study.

In practice a plot of $\ln (1/\alpha)$ versus $1000/T^2$ (where $T$ is the temperature in Kelvin) is made. This must yield a straight line if the data are accurate and the reaction is of first order. The method is very sensitive to weighing errors. Proof has been offered that if the plot is linear over the total range of decomposition, the reaction must be first order [50,56].

The value of kinetic parameters is calculated by C-R and P-N methods.

1. **Method of Coats and Redfern (C-R)[54]**

   \[
   \log g(\alpha)/T^2 = \log [-\ln (1-\alpha)/T^2] = E/2.303 RT
   \]

   \[
   \log [(ZR/\beta E) (1-2 RT/E)] \text{ for } n = 1
   \]

   This is one of the most widely used method for determining $E$ and $Z$. The model for which the plot of $\log [g(\alpha)/T^2]$ vs $1/T$ gives the straight line, representing the correct mechanism and $E$ as well as $Z$ can be calculated from such a plot.

2. **Method of Piloyan and Novikova (P-N)[55]**

   Piloyan and Novikova suggested a further simplification whereby

   \[
   g(\alpha) = \alpha, \text{ for } 0.05 < \alpha < 0.4 \text{ to } 0.5 \text{ and hence}
   \]

   \[
   \log [\alpha/T^2] = \log [ZR/\beta E] - E/2.303 RT
   \]
This method does not give an insight into the mechanism of reaction but is one of the simplest methods available for the determination of E and Z from TG curves.

The linear fits for different models were investigated. The best fit linear plot with minimum least square error was selected by applying the data to various equations. The values of slope, intercept and energy of activation were obtained from plots i.e. \( \log g(\alpha)/T^2 \) vs 1/T for C-R and P-N methods; the values of intercept and energy of activation were substituted in equation (1) for evaluating the values of Z in case of C-R and P-N methods. The entropy of activation (\( \Delta S^* \)) was calculated by employing equation (2).

\[
\text{Intercept} = \log ZR/\beta E \quad \ldots \ldots (1)
\]

\[
Z = kT_m/h \exp (\Delta S^*/R) \quad \ldots \ldots (2)
\]

or \( \Delta S^* = 2.303 R \log Z h/kT \)

Where \( k \) is the Boltzmann constant, \( h \) the Planck's constant, \( \beta \) rate of heating, R molar gas constant and Tm peak temperature. The value of E, Z and \( \Delta S \) are calculated. The mechanism involved in the decomposition is random nucleation and apparent order of reaction is one [54-56].

**X-RAY DIFFRACTION:**

X-ray powder diffraction is a nondestructive analytical technique which reveals information about the crystallographic structure, chemical composition, and physical properties of materials and thin films. These techniques are based on observing the scattered intensity of an X-ray beam hitting a sample as a function of incident and scattered angle, polarization, and wavelength or energy. X-ray is the region of the electromagnetic spectrum lying between gamma rays...
and extreme ultraviolet corresponding to a wavelength range of about 0.01 to 100 Å. X-ray crystallography is the science of determining the arrangement of atoms within a crystal from the manner in which a beam of X-rays is scattered from the electrons within the crystal. The method has been traditionally applied for phase identification, quantitative analysis and the determination of structure imperfections. In recent years, application has been extended to new areas, such as the determination of moderately complex crystal structure and extraction of three-dimensional microstructural properties [57].

An intuitive understanding of X-ray diffraction can be obtained from the Bragg's model of diffraction. In this model, a given reflection is associated with a set of evenly spaced sheets running through the crystal, usually passing through the centers of the atoms of the crystal lattice. The incoming beam (coming from upper left) causes each scatterer to re-radiate a small portion of its energy as a spherical wave. If scatterers are arranged symmetrically with a separation $d$, these spherical waves will be in synch (add constructively) only in directions, where their path-length difference $2d \sin \theta$ equals an integer multiple of the wavelength $\lambda$. In that case, part of the incoming beam is deflected by an angle $2\theta$, producing a reflection spot in the diffraction pattern, determined by Bragg’s law

$$2d \sin \theta = n \lambda$$

There are many application of powder method. Fundamentally, the powder method may be characterized inorganic, organic and pharmaceutical compounds, minerals, catalysts, metal and ceramics. On the other hand the inorganic chemist frequently characterizes by X-ray diffraction. The technique is a rapid and powerful tool for identification of all crystalline compounds, and it is
especially valuable in the presence of polymorphs or quasi-isochemical compounds [59-61].

MOLECULAR MODELING:

Density functional (DFT) methods [62, 63] have a long tradition in the treatment of such systems and constitute an attractive compromise between accuracy and computational cost. Nowadays, organometallic transition metal complexes of the size of a few hundreds of atoms can be treated entirely at the quantum mechanical level [64]. Furthermore, DFT calculations can be incorporated into mixed quantum mechanical/molecular mechanical (QM/MM) hybrid schemes, in which only the immediate reactive region of the system is treated within the electronic structure approach and the effects of the surroundings are taken into account on the basis of a mechanical force field description. These DFT/MM calculations enable a realistic description of chemical reactions that occur in complex heterogeneous environments, such as homogeneous catalytic processes in solution and enzymatic reaction cycles in explicit protein environment. QM/MM methods also come in as a handy analytic tool, as they allow for an easy dissection of electronic and steric effects of different parts of the reactive system. An additional difficulty in the theoretical description of systems containing transition metals lies in the fact, that these centers can also exhibit a highly dynamical behavior, in which the coordination sphere undergoes, continues changes both in the number and in the geometric arrangements of the ligands. It is therefore advantageous to use a method that can take the molecular dynamics of the system at finite temperature explicitly into account. In 1985, a unified approach of DFT and classical molecular
dynamics (MD) has been introduced by Carand Parrinello (first-principles MD, ab initio MD or Car-Parrinello MD) [65].

1.3 SIGNIFICANCE:

Since the appearance of the earth, aqua complex ions of metals have existed. The subsequent appearance of life may even have resulted from interaction of metal ions with organic ligands through a coordinate bond, which changes drastically the properties of ligand or metal ion alone.

The medicinal uses and application of metal and metal complexes are increasing in clinical areas commercially. Chemistry of metal complexes has progressed enormously perhaps because of their possible applications in the emerging areas like biotechnology and nanotechnology, besides having intellectual challenges involved in their structural arrangements. The design and synthesis of metal chelated multidentate Schiff bases as ligands have received attention due to recent developments in supramolecular chemistry, where ligand geometry and coordination propensity of the metal ion play a significant role. The period since the mid 1980s, has seen a tremendous growth in the use of coordination complexes for catalyzing chain growth polymerization processes. The chemistry of metal complexes with Schiff base ligands and their application have aroused considerable attention, mainly because of preparative accessibility, diversity and structural variability.

It is well known that majority of 3-d transition metals play a significant role in biochemical systems and hence also remembered as life essential elements, though their occurrence in traces and metals use such unique methods of binding to and reacting with biological molecules; they broaden our
understanding of the chemical principles underlying living processes, as well as our ability to detect and treat the diseases that adversely affect them. It is most expected that the trace metals present in the body can help to transport the biomolecules / drug to the site of its physiological action. In biological systems, these metallic ions are incapable of independent existence. The metal ion can not enter into the cell by them. They are however carried by the chelating agents, which depend upon the formation of stable and soluble metal chelates with metal ions. During circulation, they compete with chelating biological sites. They dislodge the bonded metal from the system as soluble chelates. Hence chelating agents must be of low toxicity and unmetabolizable so as to persist unchanged in the biological systems in order to perform their scavenging functions. They must also be capable of penetrating into the metal storage sites. Further chelate should be much less toxic than free meal ions [9, 66-69].

COPPER:

It is one of man’s most important metals. It has wide use as an agricultural poison and as an algicide in water purification. Copper proteins and enzymes play different role in biological system. Metallic copper has antibacterial properties and Cu thiol complexes have found increasing use in the treatment of rheumatoid arthritis. Copper deficiency results in anaemia, and the congenital inability to excrete Cu, resulting in its accumulation, is Wilson’s disease. The presence of copper, in association with protein attracts the attention of bioinorganic chemists. Any copper absorbed in excess of metabolic requirements is excreted through the bile, probably via hepatic lysosomes on average; an adult has about 150 mg of copper in the body of which about 10 to 20 mg is in the liver [70-72].
CHAPTER-1

COBALT:

cobalt discovered by brandt about 1735. cobalt is found in vitamin b-12 (cobamide), which is essential for human nutrition. b-12 (cobamide) is important in the in-vivo synthesis of amino acids used to make protein. deficiency of cobalt can lead to pernicious anemia. some cobalt compounds are able to produce numerical and structural chromosome aberration in plant cells. enzymes or proteins which act as very specific catalysts by incorporating cobalt into the corrine ring in biological systems. these activators are known as “coenzymes”.

cobalt is also used in other magnet steels and stainless steels, and in alloys used in jet turbines and gas turbine generators. the metal is used in electroplating because of its appearance, hardness, and resistance to oxidation. the salts have been used for centuries for the production of brilliant and permanent blue colors in porcelain, glass, pottery, tiles, and enamels. cobalt carefully used in the form of the chloride, sulfate, acetate, or nitrate has been found effective in correcting a certain mineral deficiency disease in animals. cobalt is extensively used as a tracer and a radio therapeutic agent [72,73].

VANADIUM:

as indicated in literature, the knowledge and understanding of vanadium chemistry has undergone incredible growth since the early 1980s. the discovery of the insulin-like properties of vanadate ions spurred research into the clinical use of vanadium compounds as insulin mimics. inadequate glucose metabolism, either through absence of endogenously secreted insulin or insulin resistance,
leads to diabetes mellitus. Currently potential utility of vanadium complexes on anti-HIV was discovered.

Certain vertebrates have an astonishing ability to accumulate vanadium in their blood. A number of nitrogen-fixing bacteria contain vanadium and it has been shown that in one of these, *Azotobacter*, there are three distinct nitrogenase systems based in turn on Mo, V and Fe, each of which has an underlying functional and structural similarity.

Applications of vanadium complexes in catalysis are well illustrated by the increasing number of reports involving vanadium complexes in various aspects of olefin polymerizations. A variety of polymers and polymer molecular weights have been prepared using vanadium co-catalysts (Karol, Gambarotta, Hessen, Sobota, and Tsuschida). Vanadium has good corrosion resistance to alkalis, sulfuric and hydrochloric acid, and salt water, but the metal oxidizes readily above 660°C. Vanadium pentoxide is used in ceramics and as a catalyst. It is also used in producing a superconductive magnet with a field of 175,000 gauss [72, 73-77].
REFERENCES:


CHAPTER-1


