Chapter-I Introduction

1.1. Literature survey of coordination chemistry

Coordination chemistry is basically the chemistry of the electron accepting tendency of metal ions surrounded by donating groups i.e. ligands. Coordination compounds are formed between a metal atom or ion and a molecule with one or more unshared pair of electron referred as ligand. Formation of complex involves reaction between Lewis base (Ligands) and a Lewis acid (metal or metal ion) with the formation of coordinate covalent (or dative) bond between them. The model utilizes hybridization of metal s, p, and d valence orbital’s to account for the observed structures of magnetic properties of complexes. Metal chelates in which the donor atoms are attached to each other as well as to metal so that the metal becomes a part of heterocyclic ring.

A coordination complex is the product of a Lewis acid-base reaction in which neutral molecules or anions (called ligands) bond to a central metal atom or ion by coordinate covalent bonds. The Coordination Number (CN) is the number of donor atoms bonded directly to the central metal atom. Ligands which donate a single pair of electrons to a central metal atom are called monodentate, if they donate two pairs of electrons they are called bidentate and if they donate more than two pairs of electrons they are called polydentate ligands. Bidentate ligands are also called chelating ligands. Complex that contain chelating ligands are called chelate.

According to Werner theory atoms possess two types of valency called primary or principal valency and secondary or residual or auxiliary valency. While ordinary molecules results from the satisfaction of primary valencies, utilization of the secondary valencies leads to the formation of coordination compounds. The bidentate and other higher polydentate ligands form closed rings on binding to a metal ion and hence, were called chelating ligands by Morgan and the closed ring formed was called a chelate ring. The most important factors that govern the CN of a complex are 1) The size of the central metal atom or ion. 2) The steric interaction between ligands. 3) Electronic interactions between the central atom or ion and the ligands.

In 1931 Pauling give valence bond theory (VBT) considered that the formation of complex involves reaction between Lewis acid (ligand) and Lewis
base(metal ion) with the formation of coordinate covalent bond which is based on revolutionary idea of hybridization of atomic orbitals. According to this theory, the central metal ion makes available equal number of empty orbitals to its coordination number. The orbital’s shows the certain type of hybridization such as sp, sp\(^2\), sp\(^3\), dsp\(^2\), d\(^2\)sp\(^3\) which gives shape to molecule linear, trigonal, tetrahedral, square planar, octahedral and pentagonal bipyramidal respectively. The filled ligand orbitals overlap with hybrid orbital’s of metal ion and forms coordinate covalent bond. This theory takes into account the splitting of the degeneracy of the d orbitals in the field of ligands. The extent of splitting depends upon the metal d orbital’s, nature and number of ligands and determines magnetic and spectroscopic properties of coordination compounds.

The crystal field theory was proposed by Bethe and Van Vleck in 1935 proved to be far more widely accepted in explaining the bonding properties of coordination complexes than the valence bond theory. According to this theory bonding between a central metal ion and the ligand in a complex is purely electrostatic. The interaction of transition metal ion with the surrounding ligand produces crystal field effect. The energies of the d orbital’s of the metal ions split by electrostatic field. The crystal field splitting is measured in terms of the energy difference between t\(_{2g}\) and e\(_g\) orbitals. The resulting energy difference is identified by 10Dq. The CFT explains the magnetic and spectral properties of transition metal complexes quantitatively. The difference in the energy levels of t\(_{2g}\) and e\(_g\) orbital’s vary with the nature of ions, nature of ligands and the geometries of complexes formed, they absorb radiations in different regions in visible light.

According to the molecular orbital theory, the orbitals are associated with the molecule as whole. The formation of overlapping takes place atomic orbitals of metal ion and orbitals of ligand. Two atomic orbitals one from each bonded atom whose energies are comparable and which posses a large amount of overlap to form two molecular orbitals. One of these molecular orbitals is lower in energy than either of the atomic orbitals from which it was formed and hence gives rise to attractive state. The other molecular orbital is higher in energy and therefore gives rise to a repulsive state. This high energy molecular orbital is termed as antibonding orbital, since electrons placed in this kind of orbital decreases the stability of the bond. The antibonding orbitals are represented by superscript asterisks. The probability of finding the electrons in the bonding molecular orbital
increases whereas it decreases in the antibonding molecular orbital. The lower energy molecular orbital is called bonding orbital, since electrons placed in such an orbital increase the stability of the bond. The bonding molecular orbital are represented by $\sigma, \pi, \delta$ etc where as the corresponding antibonding molecular orbitals are represented $\sigma^*, \pi^*, \delta^*$ etc. The shape of the molecular orbitals formed depend upon type of combining atomic orbitals $^{10}$.

Transition metal complexes with heterocyclic organic molecules containing Oxygen, nitrogen, sulphur donor atoms as ligands have been amongst the widely studied coordination compounds and find remarkable applications in different fields. The chelating characters of heterocyclic molecules towards transition metals are very interesting. Some heterocyclic molecules coordinate to the metal ion through nitrogen, oxygen atom. The presence of N, O, S, hetero atom in heterocyclic molecule extra stability to metal complexes through chelation. In the present work of studies the complexation of heterocyclic molecules 2,4 Diamino 5Hydroxy Pyrimidine (DAHP), 2-amino 4Methyl Pyridine (AMPY), 2Amino-5Bromo Pyridine (ABPY), 1,5 Dimethyl 2 Phenyl 4 Aminopyrazolone and N-(2-[(5-[(dimethylamino)methyl]furan-2-yl)methylthio]ethyl)-N-methyl-2-nitroethene-1,1-diamine studied extensively. Metal-based drugs are of a increasing interest research area for organic, inorganic, pharmaceutical and medicinal chemistry and have concentrated much attention as an approach to new drug development $^{11}$.

Transition metal complexes are cationic, neutral or anionic species in which a transition metal is coordinated by ligands. Research has shown significant progress in utilization of transition metal complexes as drugs to treat several human diseases $^{12}$.

Literature survey reveals that a metal chelates plays an important role in the development of co-ordination chemistry. The chelating agents are poly functional heterocyclic molecules which have tendency to form transition metal chelates. $^{13-14}$ The nitrogen donor ligand have been studied widely for their coordination ability due to their stability in biochemical processes$^{15-20}$. The increasing is interest in the coordination chemistry of various metal ions with organic molecules which acting as multidentate N-N and N-O donor with the formation of mono or polynuclear metal chelates$^{21-23}$. The Polydentate ligands bind the metal ion in metal chelates using coordinate covalent or ionic bonds$^{24-26}$. 

1.2. **Coordination tendency of ‘d’ block metal ions**

The ‘d’ block elements called transition elements. The elements which partly filled ‘d’ sub shell in their elementary form. The transition elements are so good at forming complexes is that they have small, highly charged ions and have vacant low energy orbital’s to accept lone pair of electrons donated by other group and ligands\(^{27}\).

The transition metal atoms or the cations derived from them have an ability to form complex compounds with certain molecule (e.g. Co, No, NH\(_3\) etc). or ions (e.g.F\(^-\), Cl\(^-\), CN\(^-\) etc). These molecules contains one or more lone pair of electrons which they can easily donate to the transition metal atom or cation thus complete the vacant orbital’s of those atoms or cations those the formation of M-L coordinate bonds. The tendency of transition metal atom or cation to form complex compounds.

Due to small size of the transition metal atoms or their cations and high effective nuclear charge they have a high positive charge density makes the atom or cations to attract or accept the lone pair of electrons from the ligands. The transition metal atom have a vacant orbital’s (n-1) d orbital’s in which they can accept the lone pair of electrons donated by the ligands and thus can form L-M coordination bond\(^{28}\). The chemistry of transition metals is associated with coordination compounds there are some important aspects of their behavior that are related to other type of compounds. Transition metal atoms have great tendency to form complex with different ligands. The ligands containing lone pair of electrons which donates to the transition metal cation. The transition metal cation are very small in size and hence have high positive charge which makes it easy for transition metal cation which accept the lone pair of electrons from ligand\(^{29}\). Charge in colour, Solubility, PH, Chemical properties, polarographic measurements, Oxidation potential, conductance measurement are indicated as formation of metal complexes. The charge in colour is indication formation of complex. The displacement of one or more usually weak acidic protons of the ligand to metal ion. Thus the charge in PH is indication for complex formation\(^{30}\). Benzoxazines are very important heterocyclic compounds of oxygen-nitrogen with a variety of
biological activities, such as antimicrobial, antifungal agents. Anantha Lakshmi et al. have been synthesized Cr(III), Mn (II), Fe (III), Co (II) and Ni (II) complexes of N-(2-nitro)-benzilidene-3-hydrazino benzoxazine-2-one (NBHBO) and characterized by elemental analysis, conductance, thermal, spectral and magnetic data. The chelating agent acts as a bidentate N,N donor towards trivalent and N,O donor divalent metal ions. By using analytical, spectral and thermal data the proposed structure of complex is octahedral.

Study of some d block metal ion complexes of synthesised hydrazone derivatives as chelating agent and characterized by using electronic, infrared., elemental analysis, magnetic properties, conductance measurement, thermal parameters and to determine coordination behavior of metal complexes and its microbial study.

Prashant Singh et al. reported that the metal ion chelates of Co(II), Ni(II) & Cu(II) with a Chelating ligands containing O, N, and S donor atoms obtained from condensation reaction between of 2- Thiienyl glyoxal and 2-Aminopyridine derivatives and characterized by magnetic and spectral study. The antimicrobial activity of the ligand and their complexes have been also studied, showing that the complexes were of more antifungal and antibacterial activity than the chelating agent. Spectral, chemical and physical parameters shows that the ligand behave as tetradeinate with O, N and S donor atoms, suggesting an octahedral arrangement.

Manish Kumar and P.N. Saxena have been studied Ti (III), Mn (III), V (III), Co (III), Fe (III), Ru (III) and Rh (III) complexes were prepared using chelating agent 5-bromo salicylaldehyde-2-furoic acid hydrazide have been characterized by elemental analyses, melting points, molar conductance, magnetic susceptibility measurement, electronic and infra red spectral studies. The results suggest that the complex an octahedral arrangement. The ligand has behaved in dibasic tridentate nature. The infrared spectral study of this transition metal complexes revealed non-participation of furan ring oxygen in coordination with the metal ions.

1.3. Chelating tendency of heterocyclic compounds-survey

The heterocyclic organic compounds are of great importance in the theoretical and practical fields and they play a significant role in many biological systems. Pyridine derivatives are very important in biological actions such as antituberculor,
fungicidal, antitumor and antibacterial activities. Heterocyclic compounds are widely distributed in nature and biological systems. Metal complexes becomes more important in biochemical, analytical and antimicrobial applied fields. Various heterocyclic, such as Furan, thiazole, pyrazoline, hydrazones occupy an important position, due to their increasing activities in multifunctional systems. The heterocyclic compounds have applications in the synthesis of various organic derivatives and different metal ion chelates. Heterocyclic compounds contains N,O, S donor atoms, they act as good organic chelating agents and provides extra stability to metal ion chelates.

Heterocyclic compounds are extensively used in synthesis of transition metal ion chelates. The heterocyclic ligand containing nitrogen donor atom plays important role in coordination chemistry. Polydentate donor centre of amino heterocycles plays a significant role in the study of coordination compounds. The transition metal complexes containing pyrimidine ligands are commonly found in biochemical compounds and play an important role in drug interaction with biomolecules as catalysts. Some sulphur containing heterocyclic chelating agents are carcinostatic (anticancer), antibacterial and antifungal.

References indicates that some transition metal ion chelates with heterocyclic chelating agent have significant role in various biological processes such as photosynthesis, electron transfer reaction and in respiration process, N$_2$ fixation, nitrogenase enzyme synthesis, oxygen activation, oxygen transport in the body and detoxification of reactive oxygen species.

Schiff bases are synthesized by amino compound with an active carbonyl compound. Schiff bases are considered as very important organic ligands which have wide application in many biological study. In azomethine derivatives, the C=N linkage is essential for biological activity, several azomethines were studied to enhance antibacterial, antifungal, anticancer activities. Schiff bases and their complexes were recently found to have significant antitumor and biological activity. Amino acid-based Schiff bases are very effective metal complexes are models for a number of important biological activities. The study of coordination chemistry of Schiff bases derived from pyridine received much attention.
Yang et al\textsuperscript{61} reported that the chelating agent 5-methoxy-4'-bromo-2,2'-[ethylenedioxybis(nitrilomethylene)]diphenol (H\textsubscript{2}L) has been used to synthesis of Ni(II) chelates. The results shown slightly distorted octahedral coordination geometry around each Ni(II) atom.

Pulin Nath et al\textsuperscript{62} reported Cobalt(II), nickel(II), copper(II) and zinc(II) complexes are new multidentate ligands, the proposed structure of the complex shows octahedral geometry with potential antimicrobial activity. The metal chelates are coloured insoluble in common organic solvents but soluble in DMF and DMSO. From conductance measurements the results shows all the metal chelates have 1:2 metal ligand ratio. Results indicates that the metal complexes are non electrolytic in nature.

Vali G et al\textsuperscript{63} reported that the metal complexes of o-Benzoyl N-2-pyridyl benzamide has been prepared 100ml solution of ligand (0.005M) in aqueous ethanol were added to a solution of metal salts100ml (0.0025M) in an aqueous ethanol. The solution was stirred for five hours and allow to stand for overnight. The precipitate were filtered, the precipitate were purified. The yield of the product is recorded 50-60%. The complexes shows absorption spectra in the region 210-570 nm. All the metal ion complexes were found coloured. IR spectral values of o-Benzoyl N-2-pyridyl benzamide metal complexes indicates presence of M-N&M-O bonding.

The Pyrozoline derivatives are much more attention in the field of chemistry and it has been synthesized from 4-acetyl-3-methyl-1-(4’methylphenyl)-2-pyrazolin-5-one with 2-amino-4-phenyl-5-methyl thiazole and was characterized by elemental analysis, mass spectra, $^1$H NMR spectra, $^{13}$C NMR spectra and FTIR spectra. This chelating agent used for synthesis complexes of Mn, Fe, Co, Ni and Cu forms complexes and it were characterized by elemental analysis, Magnetic susceptibility, electrical conductance, electronic spectra, infrared spectra and TGA analysis. The M:L ratio of complexes were found to be 1:2 with octahedral arrangement. Thermo gravimetric analysis of ligand and its metal complexes are used to get an idea about thermal stability of these metal complexes and to decide whether the water molecules are inside or outside the inner coordination sphere of the central metal ion. It also suggest the general scheme for thermal decomposition of metal complexes. All the compounds were tested for their antimicrobial activity. The result indicates that the
growth of the tested organism was inhibited by most of the compounds. From the results following structure were proposed\textsuperscript{64}

1.4. Different characteristic features to identify metal ion chelates

The procedural details of synthesis, characterisation of metal chelates are given in each topic. The metal chelates are formed when the ligand solution is added to a solution of metal ion in proper reaction condition. The composition and structure of the metal chelates can be determined by various physical, chemical and spectral characteristics. The change in colour of solution is indication of complex formation. Coordinate complex contains coordinate linkages they are less soluble in aqueous solutions. Complexes are more soluble in non polar solvents. This decrease in the solubility of the compound in polar solvents indicates complex formation. Generally ligands are weak acids or bases. The change in pH value is indication of complex formation. The decrease or increase in the value of electrical conductance of the solution in which complex formation occurs. The absorption of light in the visible region by a metal ion depends on electron transitions within the ion depends upon ligand to metal bonding. Thus the metal ion containing d electrons give variable colours depending on the nature of the ligand attached with the metal ion. Polarography is a powerful tool in the study of complex compounds. Polarographic technique provide certain information which is used for the detection of complex formation. This method is based on the fact that when a ligand is added to a metal ion, the characteristic half wave potential of the metal ion is shifted which indicates the formation of complex between the metal and the ligand. There is decrease in ionic activity of the metal and hence an increase in its oxidation potential when combines with ligand to form complex. During recent years the chemical methods have been supported by the x ray structure determination of complex compounds. This method is applicable for solid crystalline compounds\textsuperscript{65,66}.
1.5. Methods adopted for characterisation

The different analytical & physicochemical methods for the characterisation of ligand and metal complexes are discussed in each topic.

(a) Physical Parameters: After synthesis of metal complexes they will be characterized by physical parameters like yield, colour, decomposition point, molar conductance were measured. the melting points were determined by open capillary method and are uncorrected.

Conductance measurement: By measuring the solution conductivity, one can decide the electrolytic or non-electrolytic nature of the metal ion chelate, which gives information regarding the electrolyte nature of a compound. The instrument was standard by using 0.1N KCl solution whose specific conductance values is known. The molarities of solution was $1\times10^{-3}$ M. The conductance values of metal ion chelates were measured using conduct meter Equitronics model no.EQ661. The solvent used as DMSO or DMF.

Magnetic susceptibility: The measurement of magnetic properties can provide information regarding the metal complexes may possess different geometry depending upon electronic configuration of metal ion. Magnetic properties of a coordination compounds can provide information about the number of unpaired electrons, types of bond present and stereochemistry of coordination compounds. Diamagnetic compounds with all electrons paired and are slightly repelled by magnetic field. When there are unpaired electrons, the sample is paramagnetic and is attracted into a magnetic field, the measure of these magnetism is called as magnetic susceptibility. Gouy method using Hg[Co(NCS)$_4$] as standard used for determining magnetic susceptibility that requires only an analytical balance and small magnet. The solid compound is placed in small glass tube. A small high field U shaped magnet is weighed with sample compound between the poles of the magnet and with a reference compound of known magnetic susceptibility. With the diamagnetic sample, the tube and magnet repel each other and magnet appears slightly heavier. With the paramagnetic sample the tube and magnet attract each other and magnet appears slightly lighter.
(b) **Chemical parameters** : M:L ratio was determined by usual method. The known weight of complex is heated previously weighed platinum crucible. The complex is heated slowly in beginning and later on strong flame from the difference in weight gives weight of residue. From the weight of residue M:L ratio was determined. The elemental analysis for carbon, hydrogen, nitrogen in the ligand and synthesized metal chelates were carried out on Thermo Finnegan elemental analyser at SAIF IIT, Pawai, Mumbai.

**Determination of Metal ions :**

The % of metal is determined by gravimetric method as well as EDTA method.

(i) **Dissolution of metal complex**

Weigh about an 80 mg of metal complex and transfer into a 250 ml beaker. Then add 15 ml of conc. HNO$_3$ and the solution were heated upto dryness at least two times. It was then extracted with small volume of distilled water. Then contents were transferred into a 250 ml standard flask and make the solution upto the mark by adding distilled water. Then metal ion were carried out by using reported method.

(ii) **Preparation and standardization of EDTA solution :**

Weigh accurately 3.7224 gm disodium salt of EDTA on watch glass and transfer into the beaker. Add to it small quantity of distilled water and shake well, the compound is dissolved completely and transfer into 1000 ml of standard volumetric flask and make up the solution by adding distilled water. It is standardized with Zn$^{+2}$ solution prepared from zinc pellets, using buffer of 10 P$_{H}$ and Erichrome black-T indicator. The accurate concentration were determined.

**Estimation of Manganese (II) :-**

In diluted solution of metal ion complex, 0.3 g hydroxyl ammonium chloride were added to prevent oxidation. The solution were warmed and neutralized with sodium hydroxide solution. Also add 3 ml of triethanol amine to keep the manganese in solution and was made alkaline with aqueous ammonia. Then 2 ml of pH 10 buffer solution was, followed by few drops of Erichrome black T as an indicator .

This solution titrated against 0.01M EDTA solution from burette, till the colour solution changes from red to blue. By using following relation % Mn determined.
1 ml 0.01M EDTA = 0.5493 mg of Mn (II).

**Estimation of Iron (III):**

Take 25 ml solution of Fe(III) complex in conical flask was made acidic with 10-15 ml concentrated hydrochloric acid and heat it up to the boiling. Add dropwise acidic SnCl₂ solution with continuous shaking till the yellow colour just disappears. After that add few drops of SnCl₂ in excess so that Fe(III) is completely reduced to Fe(II). The solution were cooled and add 5 ml of 10% aqueous mercuric chloride (HgCl₂) to remove the excess of SnCl₂, silky white precipitate is formed. The 10 ml phosphoric-sulfuric acid mixture (2.5% 200 ml H₂SO₄ + 85% 2.5 ml H₃PO₄) and 5 drops of 0.2% aqueous solution of sodium diphenylamine sulphate were added.

The Fe(III) solution titrated against 0.01N K₂Cr₂O₇ (Potassium dichromate) solution until a grey blue colour appear near the end point, continue the titration until by adding of one drop gives violet blue coloration even vigorous shaking.

1 ml 0.01M K₂Cr₂O₇ = 0.5585 mg of Fe(III).

**Estimation of Cobalt (II):**

Transfer the sample solution into a conical flask, then add 3-4 drops of freshly prepared indicator solution (0.5% aqueous solution) of xylenol orange. Then granules of powdered hexamine were added with continuous stirring until the yellow colour of the solution changed to deep red (pH = 6), followed by 0.5 ml addition of 0.001 M solution of 1,10- phenanthroline to improve the correct estimation of the end point. The contents were then titrated against 0.01 M EDTA solutions, until the colour changes from red to yellow orange.

1 ml of 0.01M EDTA = 0.5893 mg of Co (II).

**Estimation of Nickel (II):**

The complex solution were treated with 50 mg of muroxide indicator (1% mixture of it in potassium nitrate, followed by 10 ml of 1M ammonium solution), the pH of the solution was raised to about 7 by adding ammonia solution drop wise, till the solution attains yellow colour. This content were titrated against 0.01M EDTA solutions, near the end point 10 ml of ammonia solution were added to make it alkaline, with constant shaking, colour changes from yellow to bluish violet at the end point.

1 ml 0.01 ml EDTA = 0.5871 mg of Ni (II).
**Estimation of Copper (II) :-**

To the metal ion solution add 10 ml of 1 M ammonium chloride solution to prevent increase of $P^H$. The acidic solution of Cu (II) ions were neutralized with ammonia and $P^H$ and maintain the PH about 8. Add to this solution 3 to 4 drops muroxide indicator and titrated against 0.01M EDTA solution with constant stirring until the colour changes from orange yellow to violet at the end point.

$1 \text{ ml} \ 0.01\text{M EDTA} = 0.6354 \text{ mg of Cu (II)}$.

**Estimation of Chlorides : -**

The estimation of chlorides ware carried out by Volhard’s method$^{76-78}$. Transfer10 ml of complex solution into conical flask and add to it 5 ml of 6M nitric acid in it and chloride solution was then treated with a 20 ml of standard 0.01M silver nitrate solution. Then 2-3 ml of nitrobenzene and 1 ml of iron (III) indicator were added with vigorous shaking to coagulate the precipitate. The residual excess of silver nitrate was titrated with standard 0.01 M potassium thiocynate solution, until a permanent faint reddish-brown precipitate appears. A blank titration were performed without the sample solution by following same procedure under similar experimental conditions. The difference of these two readings were used to find out the volume of 0.01M silver nitrate consumed by chloride ion. The % of Cl in respective metal ion complex was determinedby using following relation.

$1 \text{ ml} \ 0.01\text{M AgNO}_3 = 0.3545 \text{ mg of Cl}$

**Thermogravimetric analysis :-** Thermogravimetry is an analytical technique in which to study nature of decomposition of complex. It is a technique where by the weight of substance in an environment heated or cooled at a controlled rate is recorded as a function of temperature or time. A thermogram of sample gives thermal behavior of metal complexes .The TGA curves gives valuable information of metal complexes. The horizontal portion of curves indicates that there is no weight change .This information provides thermal stability .The curved portion indicate weight losses, another information from TG curve is that how much weight is loss by heating the temperature. From this data inorganic chemist can determine the composition of a compound and can follow the reactions involved in its decomposition.
Thermogravimetry is mainly concerned with the change in weight of sample as its temperature changes. First this determines the temperature at which the material losses the weight. This loss indicated decomposition or evaporation of the sample. Second the temperature at which no weight loss takes place is revealed, which indicates stability of the complex. These temperature ranges are physical properties of chemical compounds can be used for identification\textsuperscript{79,80,81}. The thermal behaviour of metal chelates indicates weight the hydrated metal complexes lose molecules first followed by decomposition of chelating agent molecule in a different stages. The thermogravimetric analysis of these metal complexes were carried out and to understand the stability of complexes and behaviour, decomposition pattern and weight of residue\textsuperscript{82-85}. Thermogravimetric analysis of metal complexes are applied for information regarding thermal stability of newly synthesized metal complexes. It decides whether the water molecule inside or outside the coordination sphere of the central metal ion. Also it suggest the general scheme for thermal decomposition of complexes, generally the loss of lattice water molecule will be present at a lower temperature than that of coordinated water\textsuperscript{86-91}.

In the present investigation thermo gravimetric analysis were recorded by instrument Thermal Analyzer (TG-DSC) instrument SDTQ 600 V20.9 in nitrogen atmosphere @ 10\degree c/min. heating rates 10\degree c/min\textsuperscript{-1} under nitrogen atmosphere and weight loss measured from ambient temperature to 1000\degree c\textsuperscript{92-95}.

(c) Spectral parameters

(1) Electronic spectra: UV-visible spectra gives valuable information regarding the structure of the complex. The spectral characteristic of substance arise from the materials to absorb characteristic frequency in the different regions of electromagnetic spectrum. The chelating agent which are heterocyclic organic compound have absorption in ultraviolet region. Chelation of ligand with transition metal ions. Some changes will take place in the electronic properties of the system. The new absorption bands in visible region due to d-d transitions and charge transfer spectra from metal to ligand (M$\rightarrow$L) or ligand to metal (L$\rightarrow$M). It can be examined and gives information regarding structure and geometry of metal complexes. The electronic spectra of chelating agent and complexes were recorded in the region 200-1000 nm UV-Visible spectrophotometer Thermo Evolution 300 in DMSO solution at Vishnu Chemicals, Jeedimetla, Hyderabad.
(2) **IR spectra** : The IR spectra provide valuable information about the nature of functional group attached to the central metal ion. The IR spectrum of the complexes compared with those of ligand in order to determine the coordination sites that may involve for chelation. It is an important and powerful analytical technique useful for chemical identification. When coupled with intensity measurements, this technique can be used for quantitative analysis. It is an important method over the other usual methods for structural analysis which gives valuable information about the structure of molecules, M-L bonding sites quickly without any evaluation method.

(3) **X-Ray powder Diffraction** :-

The X–ray diffraction is a powerful method to determine crystal structure. XRD can provide information regarding the structure of metal ion chelates. It will also give information about interatomic distance, bond angles and electronic arrangement in a metal ion chelate.

When a beam of monochromatic X-ray strikes and might be diffracted while passing through a crystal where it acts as a three dimensional diffraction grating and produce interference effect. It is possible to observe the molecules indirectly by using X-ray radiation of very small wavelength of the order of $10^{-8}$ cm and involves the studies of crystalline solids by the phenomenon of X-ray diffraction. When the beam of monochromatic X-ray strikes the plane of atoms in the crystal, an interference phenomenon is observed. Bragg’s equation gives the relation between the wavelength of X-ray($\lambda$), incident angle of X-ray($\theta$) and interlayer distance($d$).

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

Where,

$n$ = order of reflection.

$\lambda$ = Wavelength of X-rays.

$d$ = interplanar distance and

$\theta$ = Angle of incident.

The diffractometer were recorded on X-ray diffractometer. The study of intensity of X-ray spectra gives information about arrangement of planes of different atoms in space. The crystal lattice may be regarded as parallel planes passing through lattice
points known as lattice planes. The lattice planes can be chosen in different ways. Miller indices are a set of integers (h,k,l) planes. By using X-ray powder diffractogram consisting of measuring the intensities of an unknown sample were recorded each reflux position and reflux height in terms of intensity, the diffraction angles $\theta$ or $2\theta$. The data obtained was indexed using powder X computer software. Once $\theta$ is determined it is used for calculating the inter planer spacing $d$ of reflection planes from the values of $\lambda$ of X-rays used, and then the dimensions of unit cell are determined. Powder diffraction technique is an important tool for the determination of unknown compound and used to all crystalline substances.

XRD patterns of the selected metal complexes in powder form were recorded on Philips PW 1050/70 X-ray diffraction machine attached with X-ray Diffractometer which is equipped with Cu-K$\alpha$ target tube ($A = 1.54056\text{Å}$) at Department of Physics Shivaji University, Kolhapur.

1.6. Literature survey regarding corrosion inhibition :-

The cobalt (II) complexes of macrocyclic bidentate corrosion inhibitors for iron in perchloric acid has been studied$^{103}$. Certain references indicates that heterocyclic molecules containing nitrogen, oxygen, sulfur atoms works as good corrosion inhibitors$^{104-108}$. The corrosion inhibition effect of nitrogen containing amino acid L-typtophan on mild steel in 0.1M HCl solution was studied by weight loss technique. The result indicates that L-typtopham acts more anodic than cathodic inhibitor$^{109}$. The corrosion inhibiton effect of the complexes of Zn(II) Mn(II) Co(II) Cu(II) with acetylacetonate as ligand on the mild steel in Phosphoric acid were studied. The results indicates that the acetylacetonate complexes of Zn(II) Mn(II) Co(II) Cu(II) as new corrosion inhibitor in 1M H$_3$PO$_4$.$^{110}$ Sourav K R, Saha et al$^{111}$ reported that the effect of Schiff base 2(2-Hydroxybenzilideneamino) phenol (HBAP) and its corrosion inhibition effect of d block metal ion complexes as Mn-HBAP, Co-HBAP and Ni-HBPA on chrome steel in 0.1 N Nitric acid solution. From the result it is shown that inhibition efficiency increases with increase concentration. It shows that NiHBAP complex highest inhibition efficiency as compared to HBPA ligand Mn-HBPA CoHBAP. While HBPA ligand has less corrosion inhibition efficiency.

The thioburetes and their molybdenum and tungsten complex has been studied as corrosion inhibitors in mild steel in 0.1N H$_2$SO$_4$ solution. The mass loss experiment
were carried by using mild steel. The test specimen for the mass loss determination washed with soap, then tap water and distilled water & degreased with Acetone. The sample were dried & stored in vacuum desiccator before immersed in test sample solution. The beaker containing 300 ml of 0.1 N sulphuric acid solution, the specimen immersed in a beaker. The I.E. were determined. After 24 hour using 10, 20, 50, 100 and 150 ppm of inhibitor after 24 hour immersion time, the specimen were removed from solution, washed with distilled water dried and weighted and record the weight. All the above inhibition property. Thioburates and methoxyl phenyl derivatives behaves as corrosion inhibitors. The inhibition property of thioburetes increases of forming molybdenum and tungsten ions complexes

1.7. **Biochemical importance of heterocyclic metal ion chelates-survey** :-

The treatment of some diseases depends on metabolism of inorganic constituents. The metal complexes have been used in pharmaceutical and agricultural industry. Certain references indicates that when metal ion interacts with antibiotics which may enhance antimicrobial activity as compared to ligand. Metal ion chelates play important role in various chemical processes. Hemoglobin, the oxygen carrier of blood is iron complex of a protein. Chlorophyll containing the green pigment in plants and is helpful for photosynthesis, the primary source of energy for all organisms is the magnesium chelate. Hemocyanin, which transports oxygen in invertebrate animal blood, is a copper chelate. Vitamin B<sub>12</sub> is cobalt chelate. The important application of coordination compounds in living systems. The coordination complexes which are found in minerals, plants and animals are of great significance because they exhibit important functions in the environment. The synthesis of organic chelating agents that can coordinate with transition metal ions has a increasing applications is one of the most intellectual attractive and experimentally demanding for research and development of coordination chemistry.

The reaction obtaining energy for living system are basically inorganic, the reactions are made possible in complex biochemical system. The ternary complex of CO(II) & Ni(II) containing alanine & nucleic acid constituents adenine guanine & cytosine adenosine, guanosine, cytidine have been synthesized and characterized elemental analysis, IR, UV, 1HNMR and EPR spectral data. The metal complexes of monohydroxamic acids is of great importance to its biological importance and
which are used as an oral source of iron anemia & manganese deficiency\textsuperscript{117,118}. The biomolecules which contain iron are the most important group which can be divided into heme non heme type. The iron porphyrin (heme) proteins appears in a large number of systems and have diverse role including oxygen transport and storage hemoglobin & myoglobin, for catalytic dehydrogenation or oxidation of organic molecule (peroxides cytochrome) & for reduction & electron transport. Hemerythrin is non heme iron protein used by sipunculid& brachiopod marine invertebrates for oxygen transfer and storage\textsuperscript{119}. Certain metal ion chelates are known to enhance potential activities in the areas of biological, clinical, analytical, catalytic, microbial, insecticidal, antibiotic, growth factors, food additive, etc. It may be due to unused coordination sites present on the ligand systems\textsuperscript{120,121}.

### 1.8. Microbial activities of heterocyclic metal ion chelates :-

Nirdosh patil et al\textsuperscript{122} has been reported that synthesis, characterization of and antimicrobial activity of Co(II), Ni(II) & Cu(II) complexes with ligand derived from pyrozoline derivatives. These complexes and chelating agent were screened for their antibacterial & antifungal activities. The most of the complexes shows remarkable antibacterial activity.

The synthesis, spectral antifungal activity of Di(p-chloro phenyl) thiosemicarbazone & its Cr(III) & Co(II) metal complexes have been studied &characterization by spectral studies. The ligand and complexes have been screened pathogenic fungi & were found good fungicidal properties. on the basis of characterization of metal complexes & assigned to an octahedral geometry\textsuperscript{123}. pyridine -2-aldoxim is an heterocyclic molecule containing both and aromatic nitrogen heterocyclic and an oxime group at ortho position. Synthesis characterization of transition metal complexes with pyridine 2 aldoxime have been studied and characterized by by electronic absorption, infrared spectra. The most of the complexes shows remarkable activity against E. coli S. aures & C albicans\textsuperscript{124} from the result of inhibition zone of metal complexes at 10mg/ml concentration against bacteria result found that cobalt complex showed maximum antibacterial activity against bacillus subtilis bacteria as compared to as chelating agent. The synthesized metal complexes as equally or lesser inhibitor than the parent compound. The copper complex showed no inhibition zone agent against Ecoli bacteria \textsuperscript{125}. The binary and ternary complexes
of transition metal and inner transition metal have been prepared by reaching metal salts with antiulcer drug namely omparazole and uracil /adenine. The ligand and the synthesized metal ion chelates have been studied for their antibacterial activity against pseudomonas dominate, Escherichia coli, Streptococcus faecali bacteria’s and antifungal activity towards Aspergillus niger. The increased activity depends upon chelation theory attributed to the positive charge of metal shared donor atoms present in the ligand which increases lipholicity of complexes due to delocalization of chelate ring. This may be due to more stability of metal ion chelates.
1.9. References


(81) B.K. Sharma, Instrumental Methods of Chemical analysis,(2010).


