STUDIES ON TRANSITION METAL COMPLEXES OF SOME OXYGEN, NITROGEN/SULPHER DONOR LIGANDS

THESIS SUBMITTED TO
DR. BABASAHEB AMBEDKAR MARATHWADA UNIVERSITY
AURANGABAD- 431 004.

FOR THE AWARD OF THE DEGREE OF
DOCTOR OF PHILOSPHY
IN CHEMISTRY

BY

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CERTIFICATE

This is to certify that the work embodied in the thesis entitled, "STUDIES ON TRANSITION METAL COMPLEXES OF SOME OXYGEN, NITROGEN/SULPHER DONOR LIGANDS" was carried out by **Shri. Vishwas Ganpatrao Mane**, for his Ph. D. degree under my supervision. This work is original and has not been submitted for any degree of this or other university.

Place: AURANGABAD

Date: _ _ / 05/2007

Dr. B. R. Arbad

(Research Guide)

With Love and Respect

DEDICATAD TO

MY BELOVED AND ENCOURING

MOTHER

SMT. SUNILA (BAI) GANPATRAO MANE-PATIL

IN THE MEMORY OF

MY FATHER

LATE. BHAI. GANPATRAO BHAGWANRAO MANE-PATIL

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VISHWAS G. MANE

Research fellow.

DECLARATION

The research work embodied in this thesis has been carried out by me under the guidance of **Dr. B. R. Arbad,** Profesor, Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad. The work is original and has not been submitted for any research degree of this or other university.

Place: AURANGABAD

VISHWAS G. MANE

Date: _ _ / 05/2007

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ABSTRACT OF THE THESIS

ENTITLED

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STUDIES ON TRANSITION METAL COMPLEXES OF SOME OXYGEN, NITROGEN/SULPHER DONOR LIGAND

- **INTRODUCTION:-**

Transition metal complexes have a prominent role in modern coordination chemistry because of their role in catalytic processes, biological systems and medical science. They have paramount applications in the field of food and dye industries, analytical chemistry, biology, and agriculture, polymer science, in liquid crystal devices and as myocardial perfusion imaging agents.

Studies in coordination behaviour of potentially important ligands containing various functional groups with transition metal ions is one of the subjects of interest. The development of numerous newer organic chelating agents that can coordinate with transition metal ions has opened up a broad scope to research scientist in this field. The transition metal complexes of bidentate, tridentate, tetradentate organic ligands/Schiff bases containing oxygen-nitrogen, oxygen-sulphur, oxygen-nitrogen-sulphur as a potential sites have been reported.

Schiff bases (imines) are an important class of ligands in coordination chemistry and have many applications in various fields. Schiff bases have notable contribution in the development of coordination chemistry. The fact is supported by number of publications in this field. The Schiff base is a compound containing azomethine group which are also referred as azomethines, imines and anils. The chemistry of Schiff base (imines) complexes have been reported with wide applications in food industries, dye industries, analytical chemistry, catalysis, fungicidal and agrochemical activity. The transition metal complexes of various Schiff bases derived from salicylaldehyde, 2-hydroxy-1-naphthaldehyde, 2-hydroxy acetophenone, dehydroacetic acid and different amines have been reported from this laboratory due to their novel chemical, electronic and magnetic properties.

From earlier reported study, it is planned to undertake a detailed and comprehensive investigation of metal complexes of Schiff bases using various modern techniques. The proposed work includes synthesis and characterisation of Schiff bases (ligands) and study of their coordination behaviour towards transition metal ions. The results obtained from various physicochemical experimental techniques are used for determine the structure of complexes.

The work to be presented in the thesis is divided in to six chapters

CHAPTER 1

INTRODUCTION:-

Schiff bases, their metal complexes along with applications, importance have been discussed briefly, followed by the general introduction to coordination chemistry and its theories. A brief survey of literature on previous studies on metal chelates of salicylaldimines, 2-hydroxy acetophenoneimines, ketoimines, Schiff bases of DHA and some other metal complexes have been discussed.

CHAPTER 2

SYNTHESIS AND CHARACTERISATION OF SCHIFF BASES AND THEIR METAL COMPLEXES:-

The experimental procedures followed in the synthesis of Schiff base ligands have been given. The characterisation of ligands by elemental analysis, electronic absorption, and PMR spectroscopy has been included. General methods of synthesis of Cu (II), Ni (II), Co (II), Fe (III) and Mn (II) complexes with Schiff bases have been described.

CHAPTER 3

EXPERIMENTAL TECHNIQUES:-

A brief account of various experimental techniques used for the study of coordination complexes is given. The experimental details of measurement of magnetic susceptibility, solution conductivity, electronic absorption spectra, infrared spectra, X-ray powder diffraction and thermal analysis of complexes are given.

CHAPTER 4

RESULTS AND DISCUSSION OF MAGNETIC SUSCEPTIBILITIES, ELECTRONIC ABSORPTION SPECTRA, THERMOANALYTICAL AND X-RAY POWDER DIFFRACTION STUDIES OF METAL COMPLEXES:-

The experimental data on conductivity, magnetic susceptibility, electronic absorption spectra, thermoanalytical and X-ray powder diffraction measurements of Cu (II), Ni (II), Co (II), Fe (III), and Mn (II) complexes of Schiff bases are presented and discussed in this chapter.

The discussion is mainly concerned with magnetic susceptibilities, electronic absorption spectra and ligand field parameters of metal complexes, in relation to their probable stereochemistry in the light of ligand field theory and information available in the literature on similar compounds. It also includes discussion on conductivity and elemental analysis.

The discussion on thermal decomposition behaviour of metal complexes on the basis of simultaneous TG-DTA curves is confined and thermal kinetic parameters are calculated.

The unit cell data and crystal lattice parameters of metal complexes calculated from strong refluxes in the XRD pattern by using computer program are presented and discussed with respect to lattice parameter, density, porosity percentage, crystal system and probable space group.

CHAPTER 5

RESULTS AND DISCUSSION OF INFRARED SPECTRAL STUDIES OF LIGANDS AND THEIR METAL COMPLEXES:-

The infrared spectral data of ligands and their metal complexes are discussed with respect to frequencies of different groups involved in complex formation. The assignments of absorption frequencies for different groups are empirical and tentative and are based on information cited in literature on similar transition metal complexes.

The chapter also devote for presenting conclusions of present investigation drawn on the basis of various physicochemical and spectral analytical technique employed in characterization of metal complexes.

CHAPTER 6

STUDIES OF ANTIFUNGAL ACTIVITY:-

The brief biology of fungi is discussed with fungal growth, biotechnological, industrial, economic importance and harmful effects.

The experimental procedure of screening of antifungal activity of Schiff bases and their metal complexes is described. The experimental data in terms of yield of MDW and percentage inhibition of fungal growth are presented and discussed from the point of view of comparative fungal toxicity of ligand and their metal complexes.

The physicochemical study of Schiff bases and their transition metal complexes is used to study the structure of complexes, nature of bonding involve and the effect of substituents on the complexes. The comparative study of Schiff bases and their metal complexes towards biological activity is also studied in the present work.

With this aim in view, the present study deals with the synthesis of solid complexes of Cu(II), Co(II), Ni(II), Mn(II) and Fe(III) with Schiff bases derived from dehydroacetic acid and aromatic amine-

3-chloro aniline
3-amino phenol
3-methoxy aniline
3, 4-dichloro aniline
3-bromo aniline
3-amino benzoic acid
3-methyl aniline
2-ethoxy aniline

The characterization of Schiff bases is carried out by elemental analysis, PMR, IR and electronic absorption spectra. The characterization of complexes is done by elemental analysis, electronic absorption spectra, conductometry, thermal analysis, IR spectroscopy and X-ray powder diffraction techniques.

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MANE V. G.
(Research Fellow)

Prof. B. R. ARBAD
(Research Guide)

CHAPTER -I

INTRODUCTION

1.1 INTRODUCTION TO COORDINATION CHEMISTRY.

1.2 SCHIFF BASES AND THEIR METAL COMPLEXES.

1.3 APPLICATIONAL IMPORTANCE OF SCHIFF BASES AND THEIR METAL COMPLEXES.

1.4 LITERATURE SURVEY ON PREVIOUS RELATED STUDY.

1.5 AIM OF THE PRESENT INVESTGATION.

1.6 REFERENCES.

CHAPTER -1

INTRODUCTION

1.1 INTRODUCTION TO COORDINATION CHEMISTRY:

In recent days large area of inorganic chemistry research is acquired by coordination chemistry due to its interesting and significant properties. Coordination chemistry has always been challenge. Earlier there were mysteries about structure and bonding. The rapid developing field of bio-inorganic chemistry is centered on the study of coordination compounds present in living organisms. Many biologically active compounds are coordination complexes. The similar types of synthesized complexes have served as model of such biologically active compounds. The bio-inorganic chemistry is largely concerned with coordination chemistry.

The modern study of coordination chemistry begins with Alfred Werner[1]. Werner was the first who could able to explain the nature of bonding in complexes in 1893. He proposed that in coordination compounds the metal exhibits two types of valencies that are primary and secondary. The primary valency is ionisable and non-directional; where as secondary valency is nonionisable and directional. Soon after the development of electronic theory of valency; the Lewis, Kossel, Langmur, Sidwick, and other[2] cleared the ideas of primary (oxidation state) and secondary (coordination number) valencies in complexes.

In the complex, the metal ion is present at the center and has capacity to accept lone pair of electrons. The negative, neutral or positive species containing one or more unshared pair of electrons and capable to donate such lone pair of electron to the central metal are called as ligand. The stability of complexes have explained by Sidwick with the help of the fact that central metal ion acquires the same effective atomic number

(EAN) as the next inert gas configuration. Actually some compounds obey EAN rule where as some do not.

The nature of bonding and properties of coordination complexes is explained by different theories. The brief account of some important theories are given as-

In 1931 Pauling gave valence bond theory (VBT), which is based on revolutionary idea of hybridization. According to this theory, the central metal ion makes available equal number of empty orbitals to its coordination number. These orbitals undergo particular type of hybridization such as sp, sp^2, sp^3, dsp^2, d^2sp^3, d^3sp^3 which gives shape to molecule linear, trigonal, tetrahedral, square planer, octahedral and pentagonal bipyramidal respectively. The filled ligand orbitals overlap with hybrid orbitals of metal ion and forms coordinate covalent bond. This theory explains mainly electronic structure of central metal ion, shapes of complexes, magnetic moments and stereochemistry; however, it does not give proper explanation of maximum pairing, the spectra of the complexes and quantitative interpretation of magnetic properties.

Crystal field theory (CFT) developed by Bethe[3] and Van Vleck[4] is another approach to study the complexes. According to this theory, the bond between metal and ligand is neither due to sharing of electron nor due to interaction of atomic orbitals. The bond between metal and ligand is purely electrostatic. The interaction of d-orbitals of central metal ion with the surrounding ligands produces crystal field effect. The electric field due to the ligands lifts the degeneracy of the five d-orbitals of central metal ion and splits them into two energy sublevels t_{2g}-triplet and e_g-doublet. The energies of these sublevels depend upon the type of geometry. The energy difference between t_{2g} and e_g levels is known as crystal field stabilization energy and is denoted by Δ or 10Dq. The magnitude of 10Dq or Δ depends upon the nature of ligand and charge on the central metal ion. CFT interprets the magnetic and spectral properties of transition metal complexes quantitatively.

Application of the molecular orbital theory (MOT) to metal complexes has been developed by Van Vleck[4]. This theory can provide quantitative interpretation for all the properties of coordination complexes. The bonding between metal ion and ligand is considered as purely ionic, purely covalent and intermediate.

Rossotti- Rossotti[5] has defined the coordination complex is a species formed by association of two or more species, each is simple and capable of independent existence. When one of the simple species is a metal ion, then the resulting entity is known as metal complex. The term ligand is applied to the particular molecule or ion which is attached to the central metal ion in the complexes. The common donor atoms present in ligands are N, O and S. If the ligand is attached to a central metal ion by two or more donor atoms forming a heterocyclic ring structure is called as chelate [6], the so formed chelates have exceptionally high stability. The stability of chelate depends upon the size and number of rings formed during chelation. Generally coordination compounds formed of a saturated five membered ring are more stable than those formed of an unsaturated five membered ring. However, a greater stability is achieved with the formation of six member ring. The coordination number of metal is generally 4 or 6.

The formation of covalent bond with metal ion and donor group may proceed with or without replacement of hydrogen atom from an organic functional group. The most common electron donor organic functional groups, which combine with metal ion by replacement of hydrogen as acidic group, are.

-COOH (carboxylic)

$-SO_3H$ (sulphonic)

>C=N-OH (oxime)

-OH (phenolic)

-SH (thiophenolic)

>C=N-H (imine), etc.

The examples of organic functional groups, which form bond with metal ion without replacement of hydrogen ion, are

-OH (alcoholic)

-SH (mercapto)

-O- (ether)

>C=S (thiocarbonyl)

>C=N-R (alkyl imine)

$-NH_2$ (primary amine)

-NHR (secondary amine)

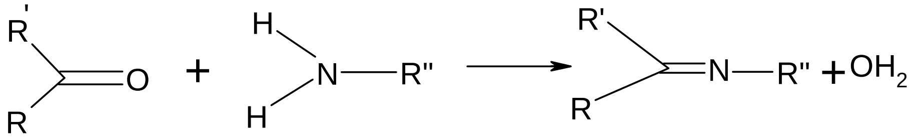
>C=O (carbonyle)

-S- (thioether)

$-NR_2$ (tertiary amine), etc

1.2 SCHIFF BASES AND THEIR METAL COMPLEXES:

Schiff bases are condensation products of amines with active carbonyl compounds. The Schiff bases are also called as imines[7], anils and azomethines. They contain azomethine (>C=N) group and hence can act as effective ligand. Schiff bases have a great contribution in the development of coordination chemistry. This fact is supported by large number of publications in this field[8,9, 10]. Schiff bases are mainly synthesized by condensation of active carbonyl compound with primary amines.



Active carbonyl comp Primary amine Schiff base

(R, R' and R" may be acyclic, alicyclic, aromatic and heterocyclic etc.)

The Schiff bases are more effective as chelating agent when they bear supporting and stabilizing group like –OH in the vicinity of >C=N group. They form five or six membered chelates. Such variables in Schiff bases are responsible to have a great flexibility in the structure with interesting magnetic and spectral properties. Hence variety of Schiff base ligands with diverse structures has been synthesised[11]. Therefore, the chemistry of Schiff base metal complexes attracted many researchers and has been developed rapidly in recent years [12].

Hydrazones, carbazones, semicarbazones, thiosemicarbazones, thiocarbazones, oximes, etc. are some of the important classes of Schiff bases that have been studied extensively[13].

Metal complexes of Schiff bases can be synthesized by several methods[14], but they are mostly prepared by the addition of alcoholic or aqueous metal ion solution to the alcoholic Schiff base solution in presence of sodium acetate or alcoholic or aqueous ammonia. The addition may also be carried out in neutral medium.

Schiff [15, 16] and later on Pfeiffer and coworkers[17] extensively used a unique method in which metal complexes of carbonyl derivative was treated with an alcoholic solution of amine to obtain the metal chelates of desired Schiff bases. Alternatively, the metal complex of amine was treated with carbonyl compound. This method is very useful particularly to synthesize metal chelates of unstable Schiff bases. One of the salient features in the preparation of metal complexes of Schiff bases is pH of reaction medium. It plays a significant role in determining the ultimate composition, constitution, geometry and the structure of resulting complex.

The imines derived from aromatic aldehyde and ketones are relatively stable. The Schiff bases can be classified as monodentate, bidentate, tridentate tetradentate and polydentate ligands. In bidentate Schiff bases, the major donor atoms are NN, ON and SN. Large number of metal complexes of these ligands are reported[18]. The donor atoms in tridentate Schiff bases are NNN, ONN, ONO and ONS, such systems have also contributed in the progress of chemistry of coordination complexes of transition metal ions[19, 20]. Tetradentate[21] as well as polydentate Schiff base metal complexes[22] have also a great deal of contribution in the chemistry of coordination complexes.

1.3 APPLICATIONAL IMPORTANCES OF SCHIFF BASES AND THEIR METAL COMPLEXES: -

The Schiff bases and their metal complexes play an important role in modern coordination chemistry. These compounds possessing novel structural features, interesting spectral and magnetic properties have been the subject of intensive research due to their importance in medical, agricultural, analytical, biological and industrial field. The Schiff base ligands and their metal complexes find applications in the field of food and dyes industry, agriculture, analytical chemistry, catalysis, polymer sciences, biological science as antimicrobial agent, medical science as anticancer, antiseptic, antidiarrhoeal, antiulcer agents, in liquid crystal devices (LCD), metal corrosion inhibition; and as myocardial perfusion imaging agents etc. These compounds are regarded as model system of biochemical interest[23]. Various studies have shown that, the azomethine group (>C=N-) in Schiff base metal complexes has considerable biological significance[24] and found to be responsible for biological activity such as fungicidal and insecticidal[25]. Schiff bases of amino guanidine and aromatic aldehydes were studied for their antiviral, tuberculostatic and antipoliovirus activities[26]. The applicational importance of Schiff base metal complexes in various fields can be given as-

1.3.1 In medical field-

Schiff bases of nitro guanidine with various aldehyde and ketones were studied for their antineoplastic and tuberculostatic activities[27]. Many other metal chelates were studied for antitumour and antineoplastic activities[28]. 2-Pyridine carbaldehyde (2-pyca) and its hydrazones are used to collect semen antipode for cyanide poisoning[29]. The complexes of Schiff bases derived from 2-pyca and amino acids are powerful chelates for antibacterial activities[30]. Schiff bases of dehydroacetic acid with benzoyl hydrazone, salicylic hydrazone and thioseicarbazone and their metal chelates have been studied for their applications in biochemically relevant aspects, chemotherapy and also in the field of agriculture[31]. The imino derivatives of 2-pyca can be used as chemotherapeutic drugs[32].

Interests in Schiff base complexes of Tin (IV) and organotin (II) moieties have been shown because of their potential fungicidal and bactericidal activity[33]. It has been observed that reagents of selective interaction with particular metal ion are very less. Schiff base complexes of thiosemicarbazides and thiosemicarbazones have been paid much attention due to their antitubercular activity. Metal chelates are found to inhibit the tumour growth and such types of metal chelates are used in the treatment of cancer[34, 35]. The Schiff bases derived from thiazole amines are found to be biologically more active due to the presence of thiazole nucleus. These have been found herbicidal properties. The complexes of Schiff bases derived from bezaldehyde and p-amino phenyl thiazol have significant role in anticancer activity [36]. Dunn and Sodnett[37] studied antitumour activity of Schiff bases. The anticancer and antitubercular activities of these compounds have been studied by Muslim et.al.[38]. Anticancer Schiff bases have been prepared by condensation of aniline with substituted benzaldehydes [26].

The reactions catalyzed by vitamin B_6 have been postulated to proceed through the formation of intermediate derived from pyridoxal and amino acids[39]. In the absence of enzymes, these reactions are catalysed by metal ions, i.e. formation of metal complexes of Schiff bases derived from pyridoxal and amino acids as reaction intermediates[40].

Cobalt complexes of Schiff bases derived from salicylaldehyde and diamines have been proposed as models of vitamin B_{12} compounds for similar physiochemical behaviour such as the ability to form stable organo-metallic compounds and also models of naturally occurring oxygen carriers having capacity to take up oxygen reversibly[41]. Cobalt complexes of Schiff bases derived from salicylaldehyde and diamines have proved to be useful in food packages. They have excellent light resistance property and storage ability and hence prevent degradation of food in presence of acidic gases like carbon dioxide[42].

1.3.2 In industrial field-

The Schiff base metal complexes carrying molecular oxygen are useful in biological and industrial processes because of the importance of molecular oxygen in these fields. The industrial chemists are interested in developing the homogeneous analogues to metal catalyzed oxidation reaction where as the biochemists are interested in biological oxygen transport.

The Schiff bases containing oxygen, nitrogen and sulphur as donor atoms extend more contribution. Schiff bases with sulphur as donor atoms have been found to be more selective as analytical reagents due to its large size and less electronegativity. They form stable and intense coloured chelates with certain metal ions[43]. Hence, they are successfully used in dyes and pigment industries. Mixed chelates of Chromium and Cobalt with Schiff bases are used to dye the wool, nylon, silk and leather giving fast bluish green shades[44]. The transition metal Schiff base complexes are useful for mass dyeing of linear polyesters, polyethylene terephthallate fibers[45]. The Schiff base transition metal complexes are used as inorganic polymers in polymer industry[46].

The Schiff base metal complexes exhibit interesting fluorescence property. Aluminum, Zinc, Tin and Yttrium complexes of Schiff bases derived from salicylaldehyde and o-aminophenol have green, bluish green or blue fluorescence. The fluorescence emission is utilized for the fluorimetric determination of these metal ions[47]. Fluorescent Schiff base type benzo crown ethers and their transition metal complexes were synthesized and studied for their fluorescence poperties[48].

Luminescence studies of Cu(II), Ni(II), and Zn(II) Schiff base complexes were carried out to understand the luminescence intensity pattern with increasing distance between two azomethine groups[49]. The Zn-Schiff base metal complex polymer having electroluminescent applications was prepared for electroluminescent (EL) devices [50].

Chemisorption studies of transition metal Schiff base complexes of 1:2 composition of metal: Schiff base were carried out[51]. Photopolymerisation of reactive mesogenic Schiff base and related metallomesogens were carried out and liquid crystal properties of the resulting Zn(II) complex acrylic monomers were reported[52]. Flash photolysis studies on Mn(III) Schiff base complexes carried out for understanding photochemical properties of these compounds[53].

The Mn, Co, and Fe complexes of Schiff bases of specified structure are used as activators in the bleaching of soiled materials[54] such as tea stained cotton fabric. Odourless household oxygen bleaches of Schiff base metal complexes that generate no toxic gases and no pungent odour for removing fungi have been synthesised and their bleaching action[55] studied.

1.3.3 In analytical field-

Schiff base and their metal complexes have variety of applications in analytical chemistry, such as in chromatographic, solvent extraction, separation techniques, qualitative and quantitative analysis.

Mono and diamine Schiff bases were used in developing qualitative test for Cu(II), Ni(II), Co(II), Fe(II), Fe(III), Cd(III), Zn(II), Mg(II) and Pb(II). A coloured precipitate of soluble coloured complex is formed in the P^H range 7-9. The reaction of Schiff bases ethylene bis-(salicylaldene imine) i.e. salen with various metal ions in high P^H range was studied. Copper (II) could be selectively precipitated from ammonical solution even in the presence of large amount of Cd(II) and other ions. Methods for estimation of Cu(II), Ni(II), Fe(III) and Zn(II) in presence of foreign ions have been developed with salen using masking agents[56]. Capitan-Vallvey and co-workers have developed two new methods for the gravimetric estimation of Ni(II) and UO_2(II) using Schiff bases N-(4-methyl-2pyridyl) salicyl-aldimine and N-(6-methyl-2pyridyl) salicyl-aldimine[57]. A highly sensitive and selective specrophotometric determination of trace amounts of

Cu(II), Ni(II) and V(V) ions with tetra dentate Schiff base ligands have been established using reversed phase high performance liquid chromatography[58]. A copper (II) ion selective PVC membrane electrode based on a recently synthesized naphthol derivative Schiff base is developed and successfully applied for the direct determination and potentiometric titration of copper in presence of alkali, alkaline earth, transition and rare earth metal ions in the P^H range 4-7[59].

The Schiff base synthesized from diamino benzene thiol and glyoxal is polymeric and useful to concentrate gold, especially without interference from other metals[60]. Comparative separation of Cu(II), Ni(II) and Pd(II) complexes of Schiff bases carried out by gas chromatography and adsorption liquid chromatography[61]. The effective separation of oxygen from air using Schiff base metal coordination complexes is reported by Li. Guang Quing et.al.[62].

In chromatography, polymeric metal complexes of Schiff bases from diamine, bis(salicylaldehyde) are used as supports and adsorbants and as covalent bond type polymers. The adsorption HPLC resolution of Cu, Ni, Pd chelates of tetradentate β−ketoimine were carried out. The efficiency of polymeric Schiff base complexes as solid phases for chromatographic separation of low molecular weight gases and oxygen selective sorbents from supported Schiff base transition metal ion complexes for gas separation was studied by many workers[63].

Liquid-liquid extraction of metals like Cu, Fe, Ni, Co and Zn using tetradentate Schiff bases as their chelates were reported Lubkeora[64]. Solvent extraction of transition metal ions with acyclic, macrocyclic Schiff bases containing phenol, bisphenol and thiophene sub units were studied[65].

1.3.4 As Catalyst: -

The metal complexes of some Schiff bases are used as catalyst in various organic reactions. Co(II) complex of bidentate Schiff base composed of Salicylidino-N-benzylimine is used as catalyst for oxidation[41]. Coordination compounds with multi metal centers with magnetic interaction are used with considerable importance in the domain of metalloenzymes and homogeneous catalysis[66]. Cobalt and manganese complexes of Schiff bases derived from 2-hydroxy-6-sulfo-1-naphthaldehyde and o-phenylene-diamine, ethylenediamine have been used as catalysts for removal of mercaptans from gas and liquid petroleum fractions[67]. Catalytic activities of Schiff base and their metal complexs have been reported by large number of workers[68].

1.3.5 Biological field: -

Transition metal complexes of macrocyclic Schiff base ligands are useful for preventing superoxide mediated cell damage and for treatment of inflammatory disorders in mammals particularlarly in humans[69]. Technetium complexes with Schiff base and phosphate coordination have been used as myocardial perfusion imaging agents. Some complexes were chosen for further imaging development based on myocardial uptake, rapid blood and liver clearances[70]. Fungicidal and bactericidal activity of transition metal chelates of Schiff bases derived from physiologally active dehydroacetic acid was studied by some workers[31]. A large number of workers have stressed the application importance of Schiff bases and their metal complexes as antimicrobial both antifungal and antibacterial agents[71].

1.4 LITERATURE SURVEY ON PREVIOUS RELATED STUDIES:

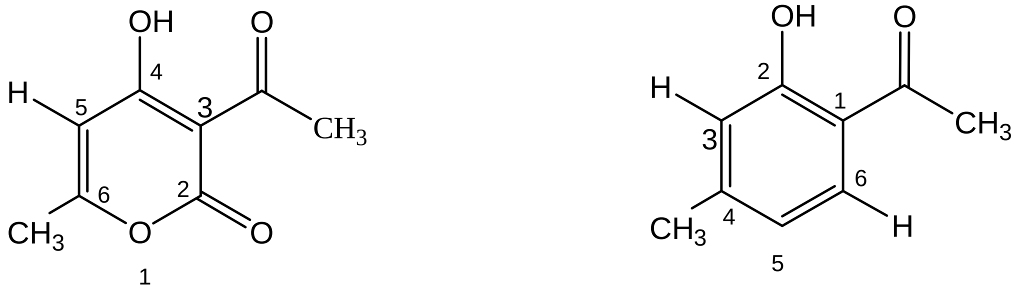
The literature survey reveals that, scope of coordination chemistry is vast. The new horizons of this chemistry extend its tentacles to various interdisciplinary fields. Since the time of Alfred Werner, the coordination compounds attracted many workers. The development of numerous newer organic chelating agents that can coordinate with metal ion has opened up a broad scope to a research scientist in synthetic field. An enormous amount of work has been done on metal complexes both in solution and solid state in the last few decades.

Because of their excellent chelating properties, and diverse structural features, the Schiff bases have been used extensively in the synthesis of metal complexes and contributed to a greater extent for the development of coordination chemistry.

Since transition metal ion, in particular, form many stable complexes that too with Schiff base ligands, the scientists have ventured into the detailed study of transition metal Schiff base complexes with the help of various physicochemical techniques.

The advent of modern instrumental techniques such as X –ray diffraction (XRD), which come to coordination chemist’s rescue and helps to unravel the mysteries of coordination compounds, has made the study of metal chelates more simple and easy to the present day worker.

The oxygen heterocyclic compound, dehydroacetic acid (DHA), [3-acetyl, 6-methyl (2H) pyran 2, 4 (3H) Dione] (I) Fig. 1, which is used in the present work has structure analogous to that of substituted 2-hydroxy acetophenone (II) Fig. l and substituted salicylaldehyde. Dehydroacetic acid is a physiologically active compound and combines with various primary aromatic amines to yield Schiff bases with excellent chelating properties. These Schiff bases of DHA and primary aromatic amine form stable chelates with transition metal ions.



(I) **(II)**

Fig. 1

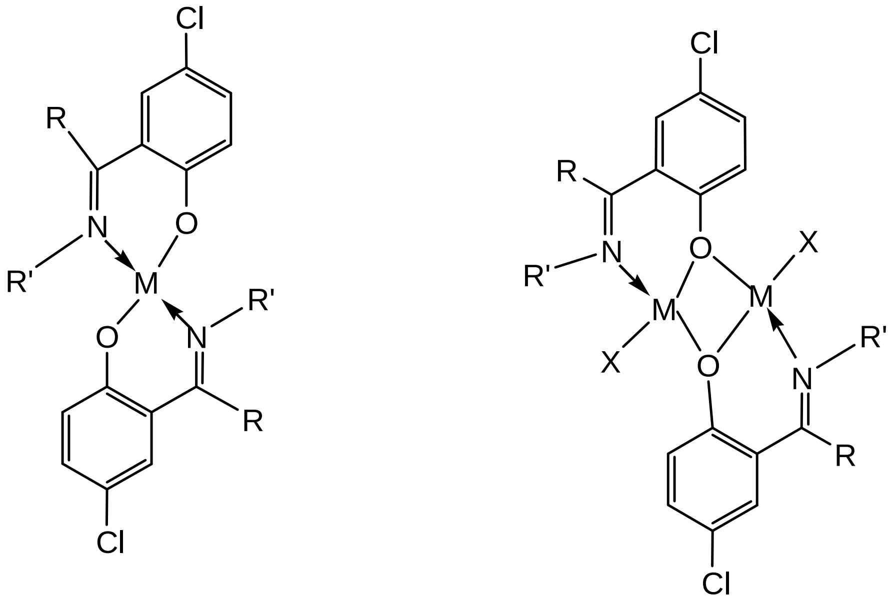
Considering this, a brief survey of literature pertaining to the present investigation on transition metal complexes of Schiff bases reported so far is given as-

1.4.1 BRIEF ACCOUNT OF COPPER (II) COMPLEXES:-

Copper is one of the most important transition metal. It is moderately abundant and is the twenty fifth most abundant in the earth’s crust. It is extensively studied for complexation with various ligands in its most stable oxidation state of +2[82].

Cu(II) ion with its d^9 configuration provides an opportunity for observation of the Jahn-Teller effect. Number of copper (II) complexes with bidentate ligands containing O and N donor atoms has been reported[72,73]. They found to have square planar, tetrahedral and octahedral configuration.

In our laboratory Chondhekar[73] reported both mononuclear and binuclear copper (II) complexes of Schiff bases derived from 5-chloro-2- hydroxy acetophenone and aromatic amines. Mononuclear and binuclear complexes of Cu(II) have been synthesized by the reaction of copper (II) nitrate and copper (II) chloride with Schiff bases in the pH range 6.5-8.0 and 10.55-11.00 respectively. The magnetic moments of mononuclear complexes were in the range 1.87-2.01 B.M. and electronic absorption bands were in the range 13700-14300 cm^{-1} and 18870-20830 cm^{-1}. The magnetic moment of binuclear Cu(II) complexes were observed in the range 1.53-1.86 B.M. which indicates antiferromagnetic interaction between two Cu(II) ions. The electronic absorption bands appeared between 17200-17400 cm^{-1} and 20620-21050 cm^{-1}. Both types of complexes found to be non electrolytic in nature assigned to mononuclear (I) and binuclear (II) complexes is presented below (Fig.2).

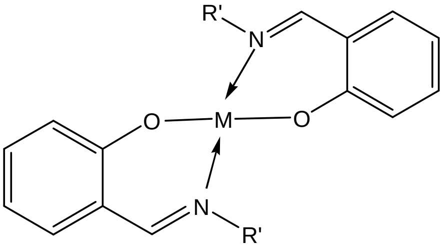


(I) (II)

Fig.2

The metal complexes of salicylaldehyde Schiff base with 2- substituted aniline have been extensively studied by Parashar et.al.[74]. The structure of the metal complexes proposed is given below (Fig.3.).

The μ_{eff}. values of the complexes were in the range 1.73-2.36 BM, which corresponds to one unpaired electron and they possess square planar geometry. It has been reported, that element copper does show anti inflammatory activity on chelation with active organic drugs[75]. This metal is found to increase their antiulcer action. However, the results indicated that the ligands SAA, SAP showed anti-inflammatory activity but their copper chelates did not.



R'=Anthranilic acid,

= 2-amino phenol

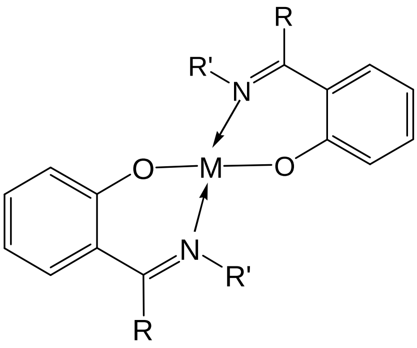
=2-amino thiophenol,

=2-amino pyridine.

Fig. 3

The neutral complexes of salicylaldimines have been extensively studied. These are the 1:1 adduct of salicylaldehyde and primary amines. Imines >C=N form of these exists predominantly as per the appearance of ultraviolet absorption band intensity[76].

The structure of metal complexes of salicylaldimine and β-hydroxy ketone is shown below (Fig.4):



Where

R=H (salicyladimine complex)

R=alkyl (β-hydroxy ketoimine complex)

Fig. 4

The usual planar structure of copper (II) complex is modified by changing the substituent R. The cooper (II) complexes of neutral Schiff base ligands derived by the condensation of ethylene diamine with acetophenone and bezaldehyde have magnetic moments in the range 2.0-2.1 B.M. which is due to tetrahedral geometry[77].

Binuclear salicylaldimine copper (II) complexes have the magnetic moment in the range 1.83 to 1.90 B.M. in both solid state and in benzene. These show a single band in solid and in solution at 6,000 cm^{-1} [78]. Bis (salicyllaldimine) copper (II) complexes have bands at 8500, 13500 and 21000 cm^{-1}.

Binuclear salicylaldimine copper (II) complexes have been studied by Harris et.al.[79]. These complexes are formed due to the property of oxygen in salicylaldimine to change its valency (coordination) from two to three in solution and help in forming oxygen bridge between metal ions. These complexes are stable in solid state. Different complexes of this type have been sudied[80].

The low magnetic moment values in binuclear copper (II) complexes of these ligands were attributed to spin- spin interaction between two copper (II) ions. The bulky aryl substituent azomethine nitrogen prefers trans planar geometry (Fig.5) than cis planar, and further favours conversion to tetrahedral or pseudo-tetrahedral geometry.

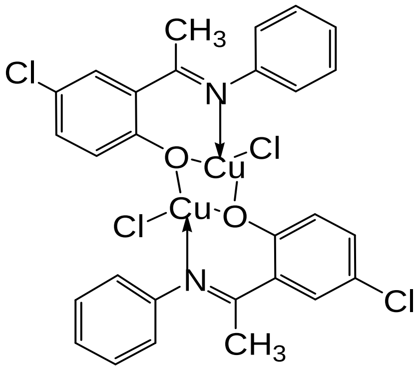


Fig. 5

1.4.2 BRIEF ACCOUNT OF COBALT (II) COMPLEXES:-

Cobalt having odd atomic number with d^7 configuration has low abundance of only 23 ppm by weight in the earth’s crust. Out of the common +2 and +3 oxidation states, +2 state is more stable than +3. However, +3 state is stable considerably and is important in complexes. Co(II) forms tetrahedral or octahedral complexes. Less commonly it forms square planar complexes with bidentate and tetradentate ligands.

Co(II) forms more tetrahedral complexes than any other metal ion[81], octahedral complexes are orange pink in colour while tetrahedral are blue or violet in colour.

Formation of both octahedral and tetrahedral complexes with the same cobalt salt and ligand is common due to small stability difference between these geometries. Sometimes these two geometries are found to be in equilibrium as reported in compounds of $[CoX_2(py)_2]$ type[82]. Planar complexes are formed by tetradentate ligand such as bis (salicylaldehyde ethylene diaminato) ion and porphyrins.

The Co(II) and Ni(II) chelates derived from Schiff bases of bromo-salicylaldehyde and sulphamethoxy pyridazine, sulphamethazole, sulphafurazol have been reported as six coordinated[83]. Cobalt (II) complexes of tridentate Schiff bases were prepared and characterized by various analytical techniques and reported to be six coordinated chelates[84]. The cobalt (II) chelates of Schiff bases 3, 4 and 5-substituted salicylidene and 2-hydroxy acetophenone immine-5-mercapto-1,2,4-triazine were synthesised and characterized by modern techniques and found to exhibit tetrahedral geometry[85].

Chondhekar[86] reported cobalt (II) complexes of bidentate Schiff bases derived from 5-chloro-2-hydroxy acetophenone and aromatic amines. The observed magnetic moments and electronic bands of the chelates with Schiff bases of p-bromoaniline and 1-naphthylamine are suggestive of tetrahedral geometry. However, the low magnetic moments of other chelates supported dimeric nature and further suggested that one nucleus exist as square and other as tetrahedral (Fig 6a, 6b).

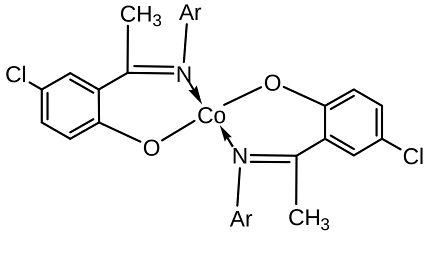


Fig. 6(a)

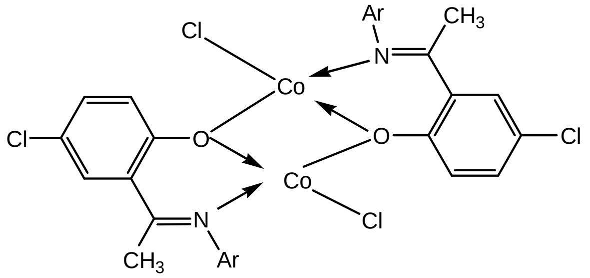
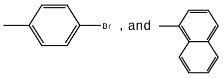


Fig6(b)

Where, Ar=



Vanillin thiosemicarbazone (VTSC) has been used by Kuntebommanahalli et.al.[87] to isolate Co(II) as its complexes of the type $[Co(VTSC)_2(H_2O)_2]Cl_2$. The structure suggested for these complexes is represented in Fig. 7.

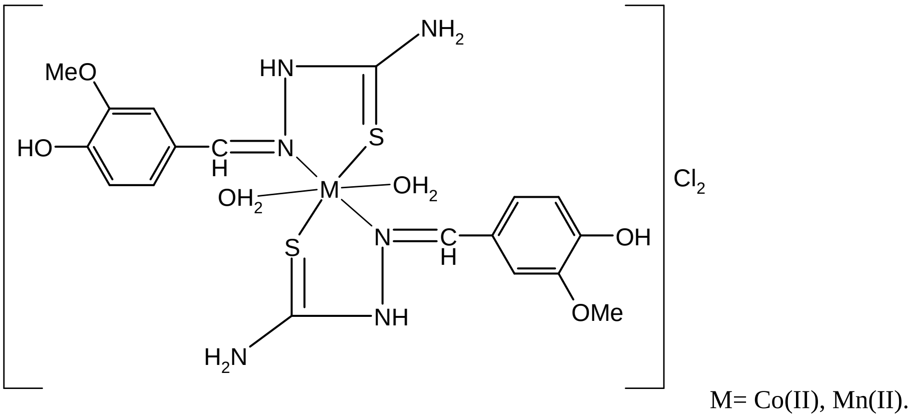
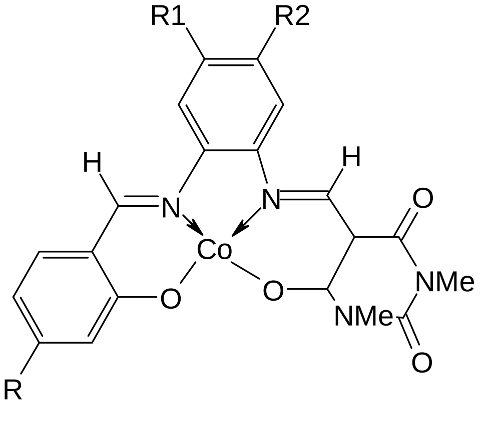


Fig. 7

Sasaki et.al.[88] reported the synthesis of unsymmetrical tetradentate Schiff base ligands and some of their Co(II) complexes. The aromatic aldehyde reacted with o-phenylene diamines in presence of chloroform as solvent which serves to control the formation of monodentate Schiff bases. This was further condensed with 5-formyl-1-dimethyl barbituric acid leading to the formation of non-symmetrical Schiff bases. The resulting Schiff bases were used to synthesize Cobalt(II) complexes of structure in Fig. 8.



Where, 1) R=H, R1=R2=H 2) R=H, R1=H, R2=OMe3) R=H, R1=OMe, R2=H

Fig. 8

Complexes of Cu(II), Ni(II), Co(II),Zn(II) and Mn (II) with tridentate Schiff base ligands were synthesized and charactersied[89]. The Schiff bases used in the synthesis were derived from salicylaldehyde, furfuraldehyde, and o-phenylene diamine. The chelates of ML_2 type reported to exhibit the structure as in Fig. 9a, 9b.

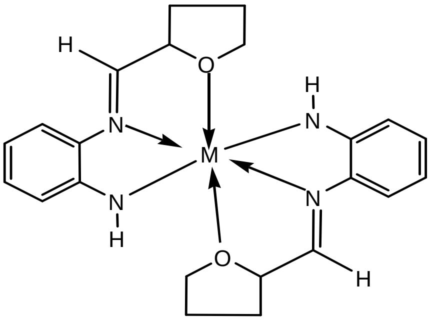


Fig. 9(a)

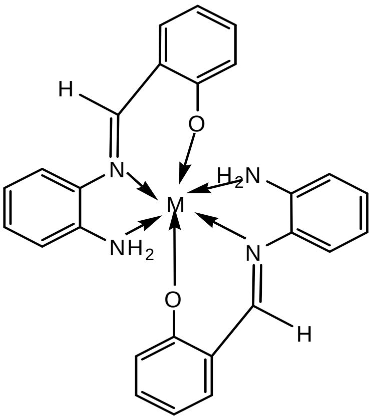


Fig. 9(b)

Where, M= Cu(II), Ni(II), Mn(II), Zn(II) and Co(II).

Khare et.al.[90] synthesized cobalt (II) complexes of 2-furfurylidene-2-aminopyridine, ethyl methylketone-2-aminopyridine (EMKAP) and suggested tetrahedral geometry with magnetic moments 4.01-5.01 B.M.

1.4.2 BRIEF ACCOUNT OF NICKEL (II) COMPLEXES:

Nickel is moderately abundant and is twenty second most abundant element in earth's crust. It exists as Ni (II) in most of its complexes. The Ni (II) ion with its d^8 configuration has coordination number rarely exceeding to six. Though the chemistry of Ni(II) is simple, the Ni(II) complexes are quite complicated. Octahedral and square planar complexes are commonly formed and a few tetrahedral, trigonal bipyramidal structures are also reported[81].

Octahedral and tetrahedral Ni(II) complexes are green, intensely blue, or blue in colour and are paramagnetic as the d^8 ion has two unpaired electrons involving sp^3d^2 and sp^3 hybridization respectively. The square planar Ni(II) complexes are generally red brown or yellow and are diamagnetic under strong field forcing the electrons to pair up with dsp^2-hybridisation .

A number of Ni(II) complexes of bidentate[91], tridentate[92], tetradentate[93] and polydentate[94] Schiff base ligands have been reported.

The existence of equilibria between different structural forms in solution is one of the most remarkable features about the stereochemistry of Ni (II) complexes. This equilibrium is mostly dependent on the concentration and temperature.

Chondhekar[95] reported mononuclear Ni(II) complexes of Schiff bases derived from 5-chloro-2-hydroxy-acetophenone and aromatic amines. The P^H range for the formation of complexes was 6.0-8.0. The range of magnetic moments was 0.5-1.66 B.M. The electronic absorption band appeared in the range 16000-17000 cm^{-1}, and at 21,740 cm^{-1}. The structure (Fig10) assigned to these complexes is diamagnetic trans-square planar.

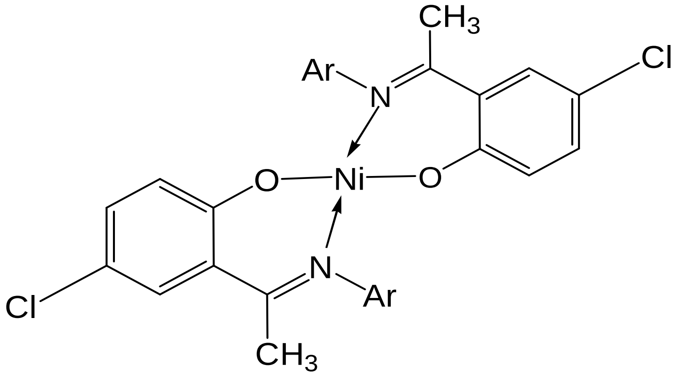


Fig 10

Sharma et.al.[96] synthesised Ni (II) complexes of bidentate Schiff bases derived from salicylaldehyde and 2-substitued anilines. Their square planar geometry was indicated by their diamagnetic nature. It is also supported by the electronic spectra having two bands around 525nm and 415nm probably due to $^1A_1g \longrightarrow {}^1A_2g$ (υ_3) and $^1A_1g \longrightarrow {}^1B_1g$ (υ_2) transitions respectively. The structure as shown in Fig. 11 is assigned to these Ni(II) complexes:

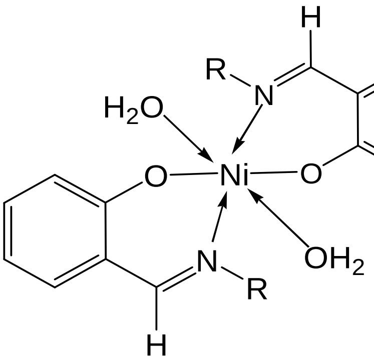


Fig 11

Ni (II) complexes of quadridentate Schiff base derived from ethylene diamine, isopropylene diamines and 2,5-dihydroxy acetophenone, benzophenone were synthesised by Dave et al.[97]. The μeff values of 3.8-4 B.M. and ESR spectral data indicated that these complexes have tetrahedral geometry. The proposed structure for these Ni(II) complexes is presented in Fig.12;

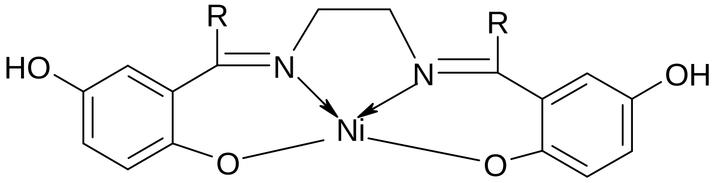
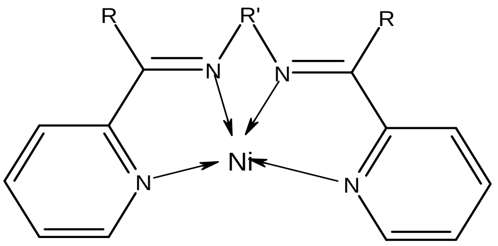


Fig 12

Dey and Sen[98] prepared hydrolytically stable Ni (II) complexes of tetradentate Schiff bases derived from 1,3 –diaminopropane, 1,3-diamino propan-2ol and 2-acetyl pyridine, 2-fomyl pyridine. The metal to ligand ratio was found to be 1:1. The magnetic moments of the chelates were reported to be 3.09 and 3.3 B.M. The following structure (Fig. 13) is proposed to the complexes.



R= -H,

= $-CH_3$

R'= $-CH_2-CH_2-CH_3$

= $-CH_2-CH (OH)-CH_3$

Fig. 13

The Ni (II) complexes of Schiff bases derived from 2-hydroxy-1- naphthaldehyde and different amines were studied[99] and assigned trans, planar geometry to the chelates and suggested the structure as shown in Fig. 14.

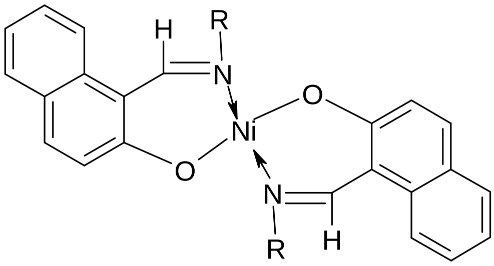


Fig. 14

Mixed ligand complexes of Ni(II) of MLL' type derived from Schiff bases of salicylaldehyde and 2-hydroxyacetophenone were synthesized and reported to have octahedral geometry. However, the mixed ligand chelates of Ni(II) of MLL' type with L, L´ representing Schiff bases of salicylaldehyde and 2-hydrox-1-naphthaldehyde were reported to exhibit square planar gometry[100], having following structure (Fig.15).

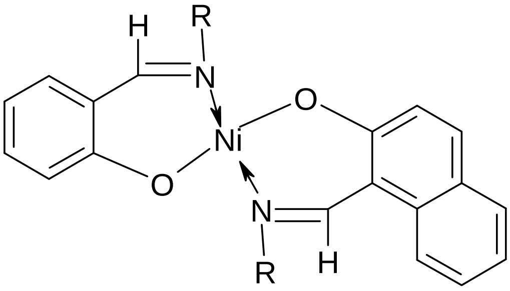


Fig. 15

O-Amino bezaldehyde and o-aminophenol condensed Schiff bases of Ni(II) complexes were synthesized and characterised by Brezina et.al.[101]. using physicochemical techniques. The structure as in Fig. 16 is proposed to these complexes.

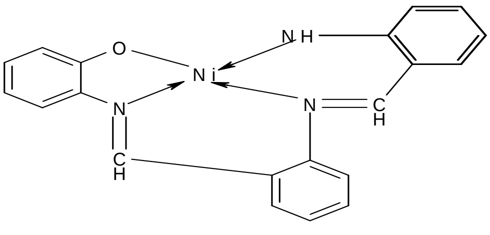


Fig.16

1.4.3 BRIEF ACCOUNT OF MANGANESE (II) COMPLEXES:

Manganese is the twelveth most abundant element by weight in the earth's crust and is biologically important in photosynthesis. Its +2 oxidation state is most stable and found in its complexes having pale colour.

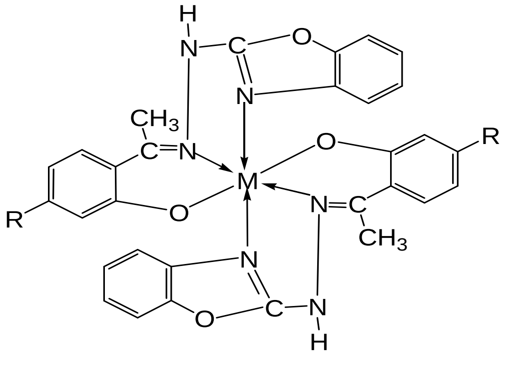
Mn(II) with d^5 configuration corresponding to half filled d shell is more stable than other divalent transition metal ions. Most of its complexes are six coordinated, octahedral and have high spin arrangement with five unpaired electrons[81]. Some complexes have square planar and tetrahedral geometries.

The Mn(II) complexes of bidentate, tridentate and quadridentate Schiff bases have been synthesised and characterised. Bis-(N-methyl salicylaldimino) Mn(II) complexes have been shown to exist as dimer in solid state in which Mn(II) is bound to three oxygen and two nitrogen to give distorted bipyramidal geometry[102].

Venkat Reddy[103] has synthesized Mn(II) chelates of different Schiff bases and proposed the following structures Fig 17a, 17b to these chelates having octahedral geometry with 1:2, M:L ratio.

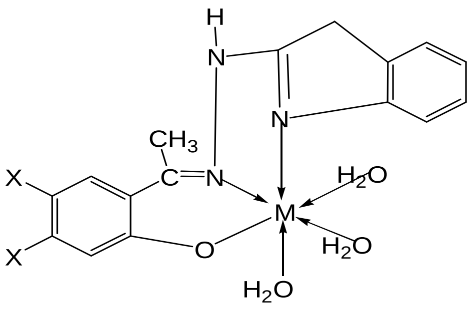
Room temperature magnetic moments of these complexes were found to be in the range 5.3-5.82 B.M. which corresponds to high spin Mn(II) complexes, the 5.3 B.M. is very low as compared to its spin only value of 5.93 B.M.

The subnormal magnetic moment is attributed to the existence of Mn(III) species as well as spin exchange in solid state complexes[104].



R= -H, $-CH_3$; M=Mn(II)

Fig. 17(a)



X=-H, -Cl; M=Mn(II)

Fig. 17(b)

Chondhekar[86] reported Mn(II) chelates of bidentate Schiff bases derived from 5-hydroxy acetophenone and aromatic amines. The complexes reported to possess dimeric tetrahedral geometry on the basis of their spectral and magnetic susceptibility measurements. The electronic absorption bands were observed at 16130-16950 cm^{-1}, 20,000 cm^{-1} and 23810-5000 cm^{-1}. Magnetic moments were found to be in the range 4.86-5.85 B.M. and complexes have 1:1 M:L ratio.

Kuntebommana halli et.al.[87] reported Mn (II) complexes of vanillin thiosemicarbazone (VTSC) having structure similar to that of complexes of Co (II) with same ligand Fig. 7.

Mn(II) complexes of Schiff bases derived from 1-tyrosine hydrazide and 0-hydroxy acetophenone have been reported by Rao et.al.[105]. The interpretation of magnetic moment data revealed the complexes to be octahedral, tetrahedral and supported the proposed structure as in Fig. 18 to these Mn(II) complexes.

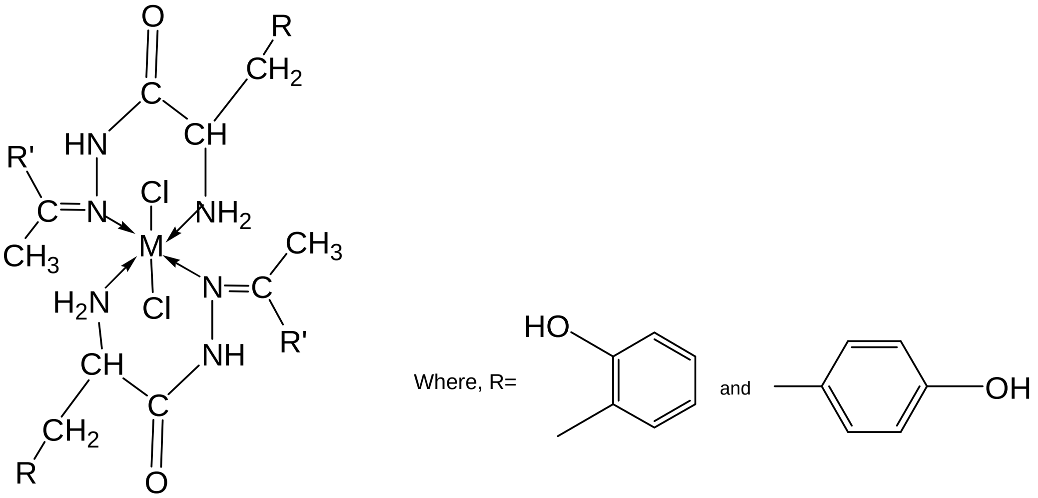


Fig. 18

The Mn(II) complexes of Schiff bases derived from salicylaldehyde and 2-aminobenzopheone-2-thionylhydrazone prepared by Singh et.al.[106] have been exploited for their physicochemical studies. The results indicated the presence of five unpaired electrons with octahedral or tetrahedral geometry of these complexes having polymeric structure as in Fig. 19.

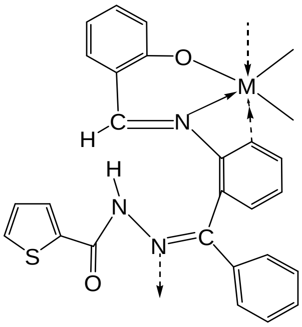


Fig. 19

1.4.3 BRIEF ACCOUNT OF IRON (III) COMPLEXES:

Iron is the fourth most abundant element in the earths crust. It is biologically most important transition element in plants and animals functioning as electron carrier, oxygen carrier, and oxygen storage and forms several unusual complexes[81].

Iron(III) ion with its d^5 configuration has +3 oxidation state and forms octahedral complexes with various ligands. The tetrahedral and square planar complexes of Fe(III) are very less reported as compared to its octahedral complexes. The affinity of iron (III) for amine ligands is very less. No simple amine complexes exist in aqueous solution as addition of aqueous ammonia to iron (III) ion leads to precipitate it as hydroxide.

Iron (III) has affinity towards ligands, which coordinate via oxygen. Octahedral complexes of Fe(III) like $[Fe(CN)_6]^{3-}$ are low-spin with one unpaired electron having a magnetic moment of 1.9B.M., while the complexes $[Fe(H_20)_6]^{3+}$, $[Fe(F)_6]^{3-}$etc are high-spin with five unpaired electrons having a magnetic moment of 5.9 B.M.

The affinity of Fe(III) towards oxygen donor is comparatively greater than nitrogen donor[114]. It has been observed that urea coordinates with Fe(III) via oxygen forming stable complexes. The unidentate ligands with nitrogen donor do not form stable complexes in aqueous solution. The complexes of the type $[Fe\ (NH_3)_6]^{-3}$ are formed with ammonia gas but they are decomposed immediately by water at room temperature with release of ammonia.

Ligands such as bipyridil, phenanthroline have chelating nitrogen donor atoms and form stable complexes with Fe(III). The substitution of metal ion is difficult in such low-spin complexes yielded by strong field ligands. A large number of stable chelates of Fe(III) with many bidentate, tridentate, tetradentate and polydentate Schiff base ligands are reported[107, 108, 109].

Some dimeric complexes such as $[Fe(SAL)_2en]_2$ are reported to have magnetic moment about 1.9 B.M. at 298 ^{0}K. These complexes are believed to have a linear Fe-O-Fe system through which magnetic interaction seems to occur[110]. Spin exchange in solid state also results in subnormal magnetic moments[111].

Dubey et.al.[104] studied the Fe(III) complexes of Schiff bases derived from salicylaldehyde and some amines for their compositions and abilities.

Manganese (II) and Iron (III) complexes of 2-hydroxy, 2-carboxy-phenyl azo-β-diketones are reported to be dimeric[112].

Costamagna[113] systematically surveyed the literature on Cu(II), Ni(II), Fe(III) chelates of 2-hydroxy-1- naphthaldehyde and salicylaldehyde.

Mn(II) and Fe(III) complexes of Schiff bases derived from salicylaldehyde, 2-hydroxy acetophenone and ethylene diamine were synthesized and analysed by Abdula et.al.[114] and found to possess 1:1 and 1:2 metal to ligand ratio having the structure as in Fig. 20a, 20b.

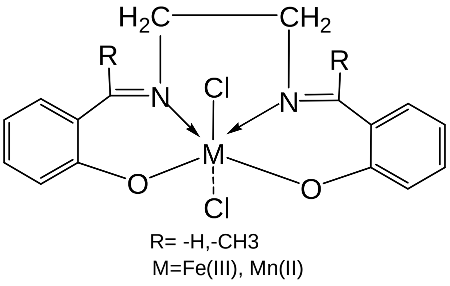


Fig. 20(a)

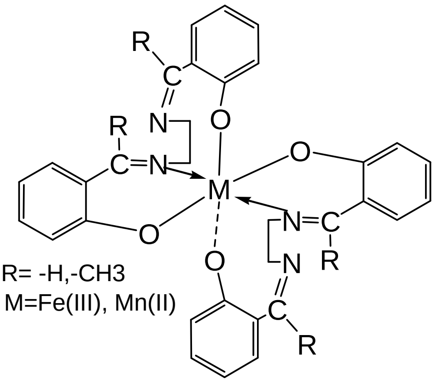


Fig. 20(b)

Venkat Reddy[103] has synthesised and characterised the Fe(III) and Mn(II) complexes of Schiff bases derived from 2-hydroxy actophenone, 2-hydroxy-4-methyl acetophenone, salicylaldehyde, 3;5-dichloro salicylaldehyde, benzoxazole hydrazide and benzimidazole hydrazide and found to possess octahedral geometry. Mehta et.al.[115] reported some six coordinated iron (III) Schiff base complexes.

1.5 AIM OF THE PRESENT INVESTIGATION;

The survey of literature on previous related studies illustrates that, a variety of transition metal complexes of Schiff base ligands formed by the condensation of salicylaldehyde, substituted salicylaldehyde, 2-hydroxy-1-naphthaldehyde, 2-hydroxy acetophenone with substituted anilines, diamines, amino acids, hydrazines, semicarbazides, thiosemicabazides, ethanol amine, thioethanolamine and aliphatic diamines have been synthesized and characterized.

It is well known fact that many organic compounds, the heterocyclic aromatic compounds in particular are physiologically active. Number of heterocyclic compounds like benzoxazole, benzimidazole, benzothiazole, hydrazones and thiosemicarbazones are said to possess a variety of physiological activities such as fungicidal, insecticidal, and anesthetic activities.

The metal complexes of Schiff bases derived from heterocyclic compounds have been a centre of attraction for many workers in recent years. But the chelating abilities of Schiff bases derived from oxygen heterocyclic compounds have received very little attention. One of oxygen heterocyclic is dehydroacetic acid (DHA), [3-acetyl-6-methyl (2H) pyran 2,4 (3H)-dione] which proved its importance in industries because of its physiological activity.

The dehydroacetic acid (DHA) is an important biologically active compound and finds biological and industrial applications. In food technology, it is used as preservative for products such as fish sausages and is used to enhance vitamin C stability, protects vegetables from oxidation during food processing[116]. Coordination of Schiff base of this compound with metal ions such as copper (II) nickel (II).iron (III) often enhances its antifungal activity as reported for pathogenic fungi[117].

In view of this, a brief review of literature related to the present work on transition metal complexes of Schiff bases derived from DHA is summarized in the following paragraphs.

Surya Rao et.al.[118].synthesised Zn(II), Cu(II), Ni(II), Co(II), Fe(II) and Mn(II) chelates of physiologically active Schiff bases and proposed the structure as in Fig. 21

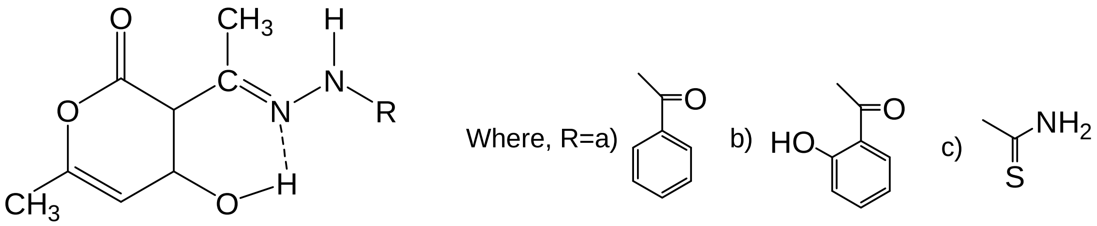


Fig. 21

These metal chelates were found to be stable to air, moisture and decompose at higher temperature. They are insoluble in common organic solvents indicating the bimeric and polymeric nature. Infrared spectra revealed the tridentate nature of ligands with ONO and ONS donor sequence, Fig 22-24. The synthesized compounds were screened for their biological activity. The insecticidal activity of some of the chelates was good and comparable to the commercial pesticides.

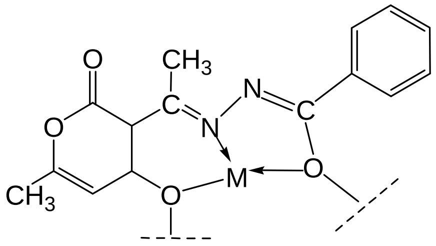


Fig. 22 Polymeric metal chelate of ligand of type (a)

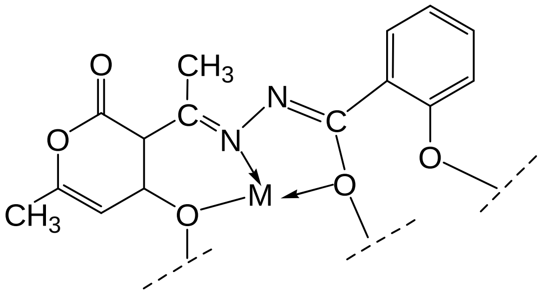


Fig. 23 Polymeric metal chelates of ligand of type (b)

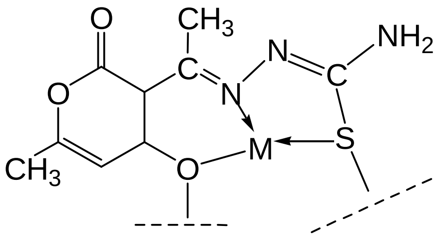


Fig.24 Polymeric metal chelate of ligand of type (c)

Rama Rao[119] synthesised Cu(II), and Co(II) mixed complexes with dehydroacetic acid as primary ligand and heterocyclic bases as secondary ligands. All the complexes were characterized by elemental analysis, magnetic moment, electronic and infrared spectral measurements and found to be octahedral. These $M(LH)_2B$ and $M(LH)_2B_2$ type (where M= Cu(II), Ni(II) andCo (II); LH = dehydroacetic acid, B=2,2-bipyridyl, 1, 10-phenanthroline; B = pyridine) of complexes exhibited fungicidal activity.

Sau Fun Tan[72] synthesised Cu(II), Ni(II) and Pb(II) complexes of quadridentate Schiff bases derived from dehydroacetic acid and amino acids, diamines, aminophenols, and amino alcohols. The complexes were characterized by infrared, electronic spectral and magnetic susceptibility measurements. The following structures (Figs. 25-27) were proposed to these complexes.

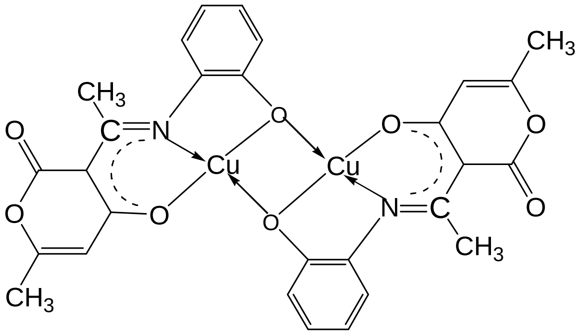


Fig.25

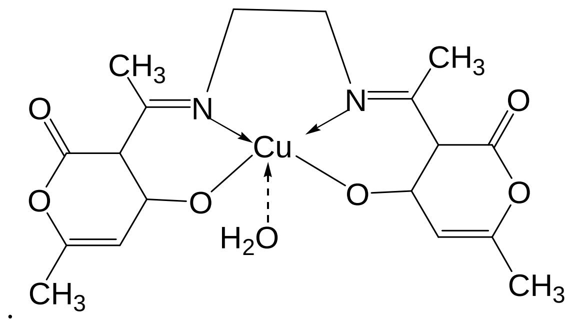


Fig. 26

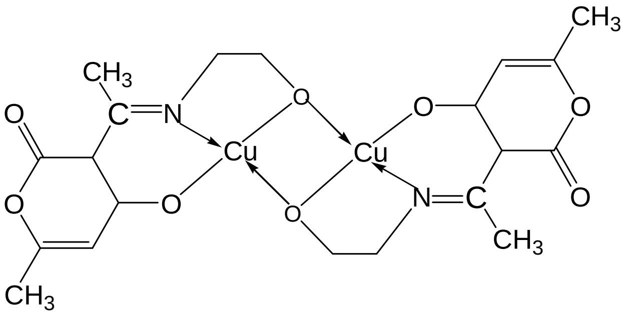


Fig. 27

Rama Rao[120] synthesized Cu(II) Ni(II), Mn(III), Zn(II), Co(II)and Fe(II) complexes of Schiff bases obtained by condensation of dehydroacetic acid and glycine. The complexes were characterized by chemical analysis, and different physicochemical techniques. All the complexes have been reported to have octahedral geometry. The metal chelates of Cu(II), Ni(II), Co(II) and Mn(II) are polymeric and those of Fe(II) and Zn(II) are monomeric.

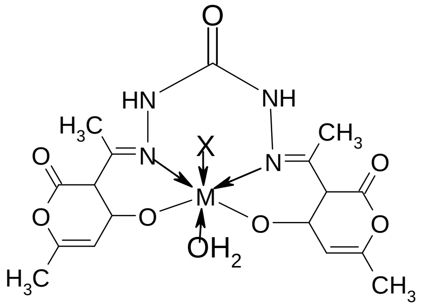
The Cu(II), Zn(II), Ni(II), Fe(II), Co(II) and Mn(II) complexes of Schiff bases derived from dehydroacetic acid and thioethanol amine were studied by Rama Rao et.al.[121]. The chelates of Cu(II) and Zn(II) were reported to have tetrahedral geometry having monomeric structure. The chelates of Ni(II), Fe(II), Co(II) and Mn(II) were found to be bimeric with octahedral geometry.

Rama Rao[122] synthesized Pd(II) and Pt(IV) complexes of DHA and its Schiff bases derived from benzol hydrazine (DBH), thiosemicarbazide (DTS), 2-aminoethane thiol (DHA-2-AET) and ethylene diamine (DHAen). The complexes were studied by physicochemical techniques and found to possess 1:1 M:L ratio except for complexes of DHA. The Pd(II)-DTS, and Pd(II)-DHA-2-AET complexes are dimeric while all other are monomeric. Pd(II) complexes are proposed to be square planar while Pt(IV) complexes possess octahedral geometry

Tan and Ang[123] reported the physicochemical study of Cu(II) and Ni(II) complexes of unsymmetrical bis Schiff bases from ethylenediamine, DHA, aldehyde and ketones. The electronic spectral data suggested that they possess square planar geometry with 1:1, M:L composition.

Abdulla[124] synthesized the dimeric chelates of Ni(II) and Pd(II) with Schiff bases derived from dehydroacetic acid and hydrazine-5-methyl carbodithioate, their acid amides and thiosemicarbazides. The structure of the metal chelates was confirmed by elemental analysis, molecular weight determination, IR, UV-visible and NMR spectral techniques.

Venkateswar Rao[125] synthesised tetradentate Schiff bases from dehydroacetic acid and carbohydrazide Fig. 28 and its complexes with V(IV), Cu(II), Ni(II), Mn(II), Co(II) and Fe(II). The complexes are characterized by magnetic, IR, UV-visible, thermal, mass and ESR spectral study. The complexes are also screened for fungicidal activity against A. niger, order of inhibition is given as Cu(II)>Ni(II)>Fe(II)>Co(II)>Mn(II)>V(IV).



Where, X=H_2O, when M(II)= Mn, Fe, Co, Ni and Cu

X= =O, when M=V

Fig. 28

Venkateswar Rao[126] have also reported the Schiff base derived from dehydroacetic acid and DL-Histadine and its complexes with V(IV), Cu(II), Ni(II), Mn(II), Co(II) and Fe(II).

El-Tabl, et.al.[127] have prepared Cu(II) complexes of Schiff base derived from dehydroacetic acid and thiosemicarbazide Fig.29

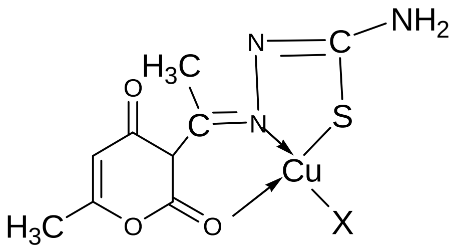
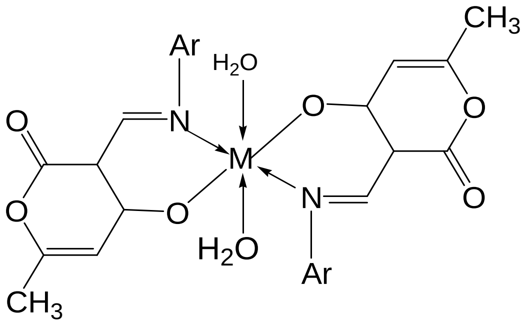


Fig. 29 Where X=Cl, NO_3, Br, Ac.

Sergio Sitran et.al.[128] synthesized mixed acetate-dehydroacetato complexes of lanthanides which were characterized by IR, 1H-NMR, thermoanalytical, and elemental analysis measurements. The influence of solution water content on complex purity is discussed. The NMR spectra assisted in determining the best conditions for the substitution of the acetate group by dehydroacetato anions. Venkat Reddy[129] studied the Cu(II), Ni(II), Co(II), and Mn(II) complexes of Schiff base derived from ethanol amine and dehydroacetic acid pH-metrically and determined their stability constant.

The solid complexes of Cu(II), Ni(II), Co(II), Fe(III) and Mn(II) with bidentate Schiff bases derived from DHA and o-toluidine have been synthesized by Mane et.al.[130]. Thermodynamic kinetic parameters of these complexes for their thermal decomposition were evaluated by Coas-Redfern method from their TG-data and results were used to decide the order of thermal stability of compounds.

Mane et.al.[131] also synthesised the Cu(II), Ni(II), Co(II) and Mn(II) complexes of Schiff bases derived from dehydroacetic acid and aniline, p-chloroaniline, p-iodoaniline, and p-phenetidine and characterized by element analysis, conductance, magnetic, thermal, IR, UV/visible and NMR spectral measurements. They suggested the octahedral geometry to all the complexes and dimeric nature to Mn(II) complexes. The magnetic and spectral studies of Mn(II), Co(II), Ni(II) and Cu(II) complexes of Schiff bases derived from DHA and 4-aminophenol, 4-aminobenzoic acid reported by Shirodkar et.al.[132] also are indicative of octahedral geometry with the structure as shown in Fig 30a, 30b.



Where, M=Cu (II), Ni (II) and Co(II)

Fig. 30 (a)

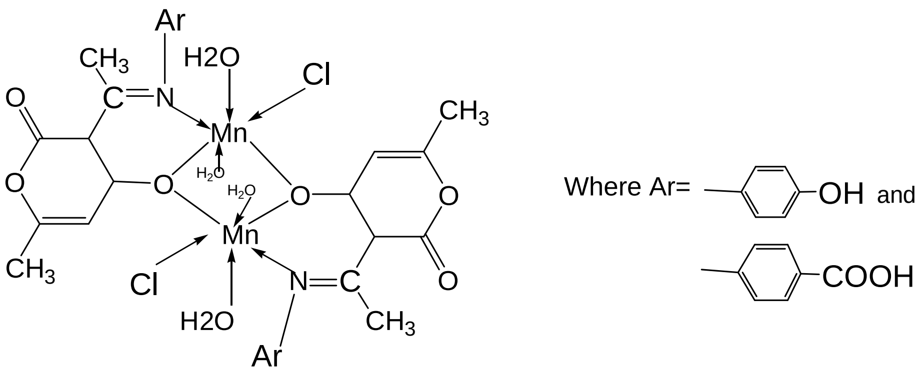


Fig. 30(b)

The fungicidal activities of these complexes were screened against A. Niger. The fungicidal activity of Cu(II), Co(II), Mn(II) and Fe(III) complexes of Schiff bases derived from DHA and p-toluidine, p-bromoanilie, P-anisidine, 2-naphthylamine and o-phenylendiamine were screened against Aspergillus niger by Chondhekar et.al.[133] and proposed to follow the order Cu> Ni> Fe> Mn> Co.

The complexes of these metal ions with some Schiff bases derived from DHA and p-toluidine, P-bromoaniline and p-anisidine which have been characterized by physicochemical methods revealed the monomeric nature with high-spin octahedral geometry except for Mn(II) complexes which are dimeric in nature[134]. The non-isothermal degradation and kinetic parameters of complexes of above metal ions with bidentate Schiff bases of DHA and p-toluidine have also been studied[135]. The values of activation energies (Ea) obtained were used to determine the order of thermal stability of complexes.

Pachling[136]. reported the synthesis and characterization of Fe(III), Cr(III), Cd(II), Hg(II) and Pb(II) complexes of Schiff base derived from DHA and semicarbazide, thiosemicarbazide, ethanol amine, thioethanol amine, 2-hydroxy benzoyl hydrazide, 2-chlorobenzide and benzol hydrazide. The cumulative fungicidal effect of metal and ligands in metal complexes against A. niger reported to follow the order Pd> Hg> Cd> Fe> Cr.

Considering these aspects, studies on transition meal complexes of Schiff bases derived from DHA and some primary aromatic amines have been reported from our laboratory. These Schiff bases and their metal complexes have been proved to have good antifungal activities. Hence in continuation with our earlier reported studies and in view of the significant characteristics of dehydroacetic acid, the present work is undertaken,

With this aim in view, the present study deals with the synthesis of solid complexes of Cu(II), Ni(II), Co(II), Fe(III) and Mn(II) metal ions with the newly synthesized aryl Schiff bases derived from dehydroacetic acid (DHA) and the following primary aromatic amines.

1. m-chloroaniline
2. m-amino phenol
3. m-Anisidine
4. m-Toluidine
5. m-Bromoaniline
6. m-amino benzoic acid
7. o-phenitidine
8. 3,4-dichloro aniline

The characterization of Schiff bases and their transition metal complexes was carried out by various physicochemical and spectroanalytical methods. The fungicidal and bactericidal activity of these Schiff bases and their metal complexes were also screened.

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CHAPTER – II

SYNTHESIS AND CHARACTERISATION OF SCHIFF BASES AND THEIR METAL COMPLEXES

2.1 BASIC REQUIRMENTS.

2.2 SYNTHESIS OF LIGANDS.

2.3 CHARACTERISATION OF LIGANDS.

2.4 SYNTHESES OF METAL COMPLEXES.

2.5 CHARACTERISATION OF METAL COMPLEXES.

2.6 REFERENCES.

CHAPTER: 2

SYNTHESIS AND CHARACTERISATION OF SCHIFF BASES AND THEIR METAL COMPLEXES

2.1 BASIC REQUIRMENTS :-

i) **Apparatus: -** The experimental work was carried out using borosilicate glass apparatus. They were calibrated before use by standard analytical method[1]. All the glasswares used for experimental work scrupulously cleaned by means of chromic acid as cleaning agent followed by tap water and portions of deionised water. Finally they were dried in an electrically heated oven at 100-120°c for about an hour. The chemicals used were weighed on one pan analytical balance with 0.01mg sensitivity.

ii) **Chemicals: -** All the chemicals used for experimental work were of AR-grade.

a) Solvents-

I. **Water: -** Throughout experimental work, the glass-distilled water was used. This was obtained by distillation of metal distilled water in presence of crystals of potassium permanganate in alkaline conduction.

II. **Super dry ethanol /methanol: -** In a 2-liter round bottomed flask 5gm of clean, dry magnesium turning and 0.5gm of Iodine in 75ml absolute ethanol/methanol was added. The mixture was warmed until iodine disappeared and heating was continued till magnesium was converted into ethanolate/methanolate. Then 900ml of commercial absolute ethanol/methanol was added and refluxed for 30 minutes and then distilled. Distilled ethanol/methanol were directly stored in polyethylene vessel and protected from atmospheric moisture[2].

b) Reactants and Reagents

The reactants such as ketones, amines, metal salts, and other chemicals used for the synthesis of Schiff bases and their metal complexes were of AR-grade. The purity of chemicals was checked by routine test like melting point, boiling point, thin layer chromatography etc. The purification of liquid chemicals and solvents were done by distillation as suggested in literature. The A.R.grade chemicals and standards were used as reagents for the determination of metal ions in metal chelates.

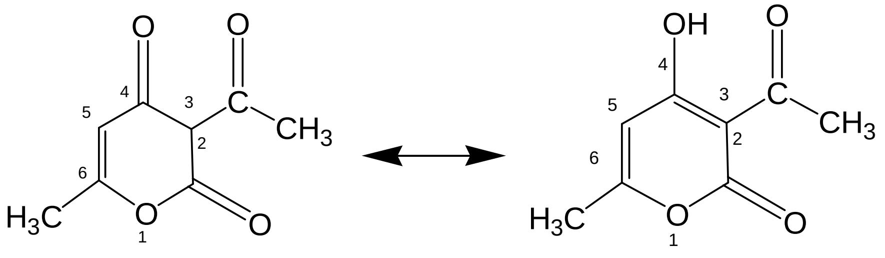
iii) **Measurement of mass: -** For sample weighing up to 100mg or more single pan mechanical analytical balance E-Mettler Zurich, type-MG 60N072840 Swiss made with maximum capacity ranging between 160-200gm having precision ± 0.1 mg was used. For the samples weighing less than 100 mg. a semi micro analytical balance E. Mettler Zurich Swiss made type H-16 GD No. 172989 with maximum loading of 80 gm. having precision of 0.01 mg. was used.

2.2 SYNTHESIS OF SCHIFF BASES:

2.2.1 THEORITICAL ASPECTS:-

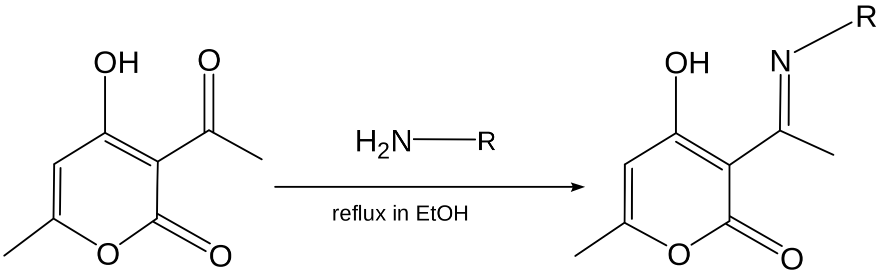
The heterocyclic compound, dehydroacetic acid (DHA) [3-acetyl-6-methyl-(2H) Pyran, 2.4 (3H)-Dione] is a ketone, used for the synthesis of Schiff bases by its condensation with primary aromatic amines.

Dehydroacetic acid (I) exist in solution as an enolised species (II) [3-4] as the acidic hydrogen at C_3 being alpha to carbonyl groups lies in close proximity to all the three adjacent carbonyl groups.



(I) (II)

Dehydroacetic acid (II) undergo condensation with primary amine to form Schiff base (III)



(II) (III)

2.2.2 EXPERIMENTAL ASPECT: -

The Schiff bases were prepared by the standard method, in which equimolar mixture of dehydroacetic acid and amine in dry ethanol were refluxed. The 0.1 mole of DHA and 0.1 mole of amine in 100 ml, ethanol were taken in round bottomed flask and refluxed for about 6 hours. Then it was cooled to room temperature; solid Schiff base got separated, washed with ethanol. It was further purified by recrystallisation from ethanol and dried in vacuum desiccators.

2.3 CHARACTERISATION OF LIGANDS: -

These ligands are stable to air and moisture, soluble in methanol, chloroform, dimethyl formamide, dimethylsulphoxide and insoluble in water. Their structural features are elucidated with the help of element analysis, electronic, infrared absorption and nuclear magnetic resonance techniques.

2.3.1 Elemental analysis, colour and melting point of Ligands:-

All the ligands are white in colour. The melting point, percentage of Carbon, Hydrogen and Nitrogen found and calculated theoretically are given in Table. 2.1.

Table 2.1 Analytical data, molecular weight and melting point of ligand.

Ligand	Symbol	Colour	Found (Calculated)				Mol. Wt.	M.P. ^{o}C
			C	H	N	Cl/Br		
$C_{14}H_{12}ClNO_3$	L1	White	59.80 (60.55)	3.68 (4.36)	4.65 (5.04)	11.86 (12.77)	277.71	120
$C_{14}H_{13}NO_4$	L2	White	64.01 (64.86)	4.49 (5.05)	4.51 (5.4)	-	259.26	188
$C_{15}H_{15}NO_4$	L3	White	64.96 (65.93)	5.12 (5.53)	4.94 (5.13)	-	273.29	108
$C_{15}H_{15}NO_3$	L4	White	69.20 (70.02)	5.47 (5.88)	5.02 (5.44)	-	257.29	118
$C_{14}H_{12}BrNO_3$	L5	White	51.85 (52.20)	3.47 (3.75)	4.02 (4.35)	23.87 (24.80)	322.16	138
$C_{15}H_{13}NO_5$	L6	White	61.98 (62.72)	4.45 (4.56)	4.51 (4.88)	-	287.27	238
$C_{16}H_{17}NO_4$	L7	White	66.18 (66.89)	5.80 (5.96)	4.36 (4.87)	-	287.32	118
$C_{14}H_{11}Cl_2NO_3$	L8	White	53.21 (53.87)	3.11 (3.55)	4.30 (4.49)	21.64 (22.72)	312.5	164

2.3.2 Spectroscopic study of Ligands: -

Among the spectroscopic methods used for structure determination of ligands, the ultra violet visible (uv-visible), infrared (IR), Nuclear Magnetic Resonance (NMR) are the main spectroscopic techniques useful for the structural determination of organic ligands.

a) ELECTRONIC ABSORPTION SPECTRAL STUDY OF LIGANDS (uv-visible spectra) :-

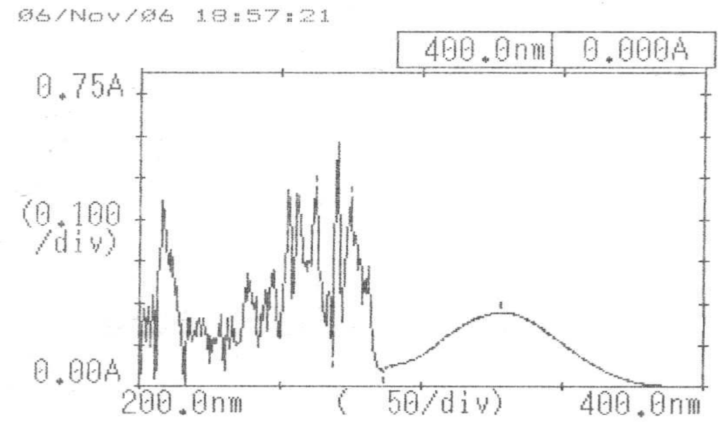
Molecular absorption in the ultraviolet and visible region of the electromagnetic spectrum depends on the electronic structure of molecule. In practice the ultraviolet spectroscopy is primarily used to measure the multiple bonds and aromatic conjugation within a molecule.

The amount of ultraviolet radiation absorbed, changes the electronic energy of molecule resulting in the transitions of valence electrons. These transitions consist of the excitation of an electron from an occupied molecular orbital usually a non-bonding η, or bonding σ and π-orbital to the next higher energy unoccupied molecular orbital, that is an antibonding π* or σ * orbital. The possible transitions are from σ → σ *, η → σ *, π→π* and η→π *. But from these transitions only significant transitions are π→π* and η→π *. The energy required for different transitions is in the order η→π* < π→π* < η→ σ * < σ → σ *. These electronic transitions are designated by the letters assigned as R, K, B and E bands.

Letters assigned for designation of band (Type of band)	Electronic transition	ε max
R	η→π*	< 100
K	π→π*	> 10,000
B	π→π*	~1000 to 5000
E	π→π*	2000 to 14000

The solutions of known concentration ($1x10^{-4}$ M) of Schiff base ligands were prepared in chloroform (A.R.) and their uv/visible (electronic absorption) spectra were recorded on uv/visible spectrophotometer model UV-1601, SHIMADZU, Japan in the range 190-400 nm.. The instrument was calibrated using solution of 0.04 gm. potassium chromate in 0.05M potassium hydroxide solutions. The ligand solution spectra were recorded by filling reference cell with pure solvent.

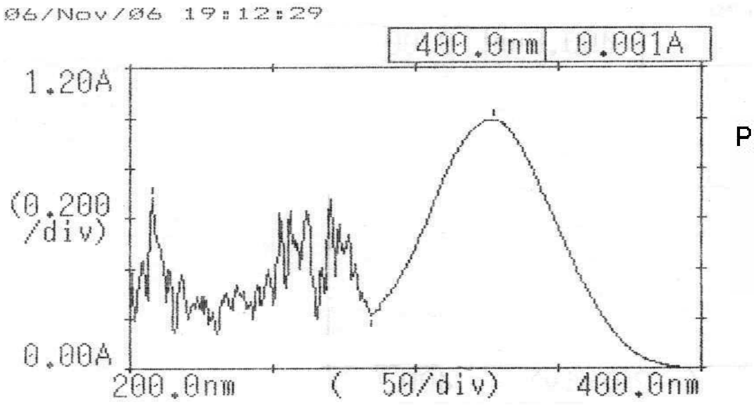
The observed λ max values of Schiff bases are found to be nearly same 326-330 nm. (Table-2.2). The >C = N azomethine π→π* transitions are expected in the range 220 to 230 nm[5]. The present Schiff bases show a weak absorption band in the same region. (Fig. 2.1 to 2.8)



Peak detection

λ	ABS
328.5	0.179
275.0	0.453
262.5	0.477
225.0	0.175

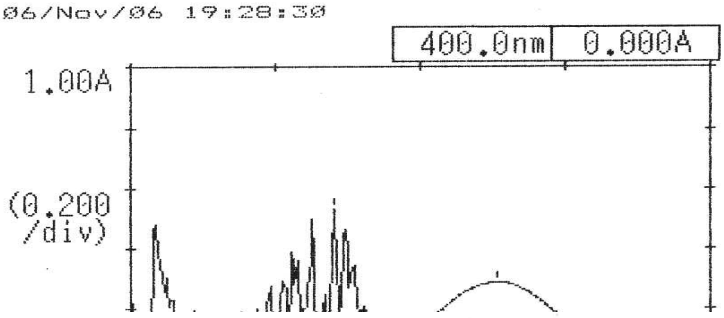
Fig. 2.1 UV-Visible spectra of L_1



Peak detection

λ	ABS
327.0	0.602
270.5	0.595
225.0	0.396

Fig. 2.2 UV-Visible spectra of L_2



Peak detection

λ	ABS
327.0	0.602
270.5	0.595
225.0	0.215

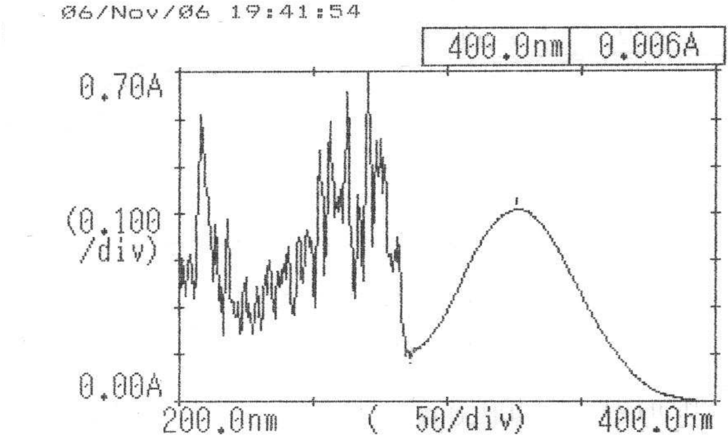
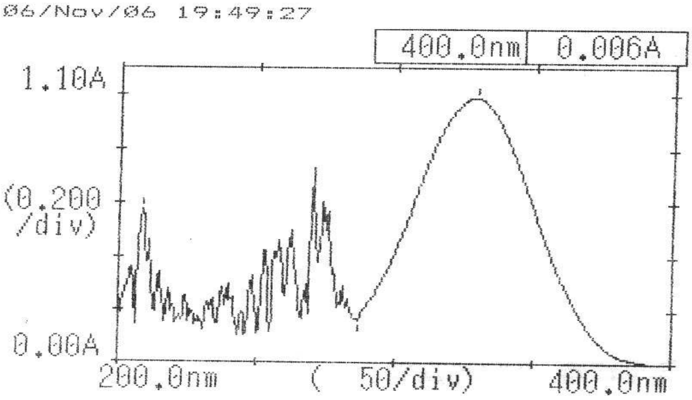


Fig. 2.3 UV-Visible spectra of L_3

Peak detection

λ	ABS
326.5	0.408
274.0	0.378
225.0	0.368

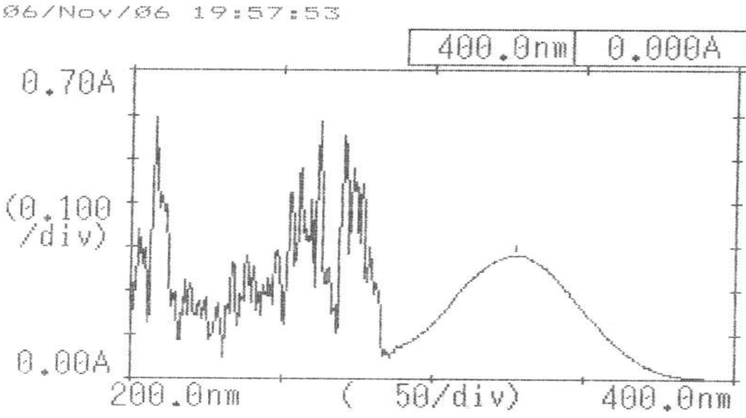
Fig. 2.4 UV-Visible spectra of L_4



Peak detection

λ	ABS
329.0	0.992
246.0	0.643
225.0	0.345
209.0	0.574

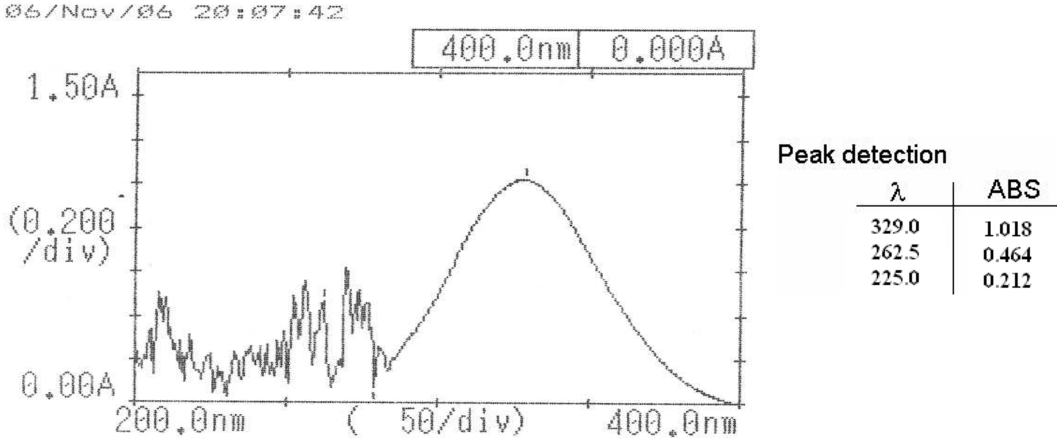
Fig. 2.5 UV-Visible spectra of L_5



Peak detection

λ	ABS
327.5	0.282
275.0	0.485
225.0	0.210

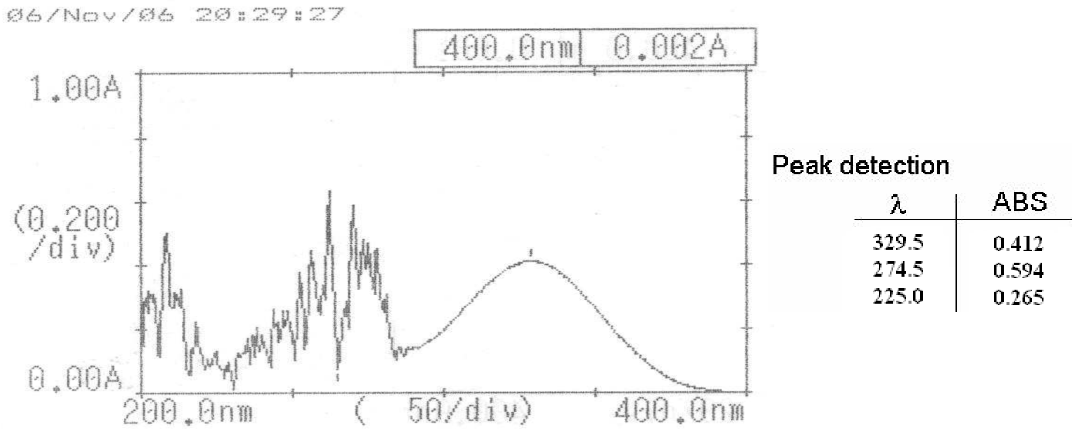
Fig. 2.6 UV-Visible spectra of L_6



Peak detection

λ	ABS
329.0	1.018
262.5	0.464
225.0	0.212

Fig. 2.7 UV-Visible spectra of L_7



Peak detection

λ	ABS
329.5	0.412
274.5	0.594
225.0	0.265

Fig. 2.8 UV-Visible spectra of L_8

Table 2.2 Electronic Spectral data a Schiff base ligands.

Sr. no.	Ligand	Symbol	λmax for >C=0 in nm.	λmax > C=N in nm.
1	3-[3-Chloro-Phenylimino-ethyl]-6-methyl-pyrane-2,4dion.	L_1	328.5	225
2	3-[3-Hydroxy -Phenylimino-ethyl]-6-methyl-pyrane-2,4dion.	L_2	327.0	225
3	3-[3-Methoxy -Phenylimino-ethyl]-6-methyl-pyrane-2,4dion.	L_3	327.0	225
4	3-[3-Tolylimino-ethyl]-6-methyl-pyrane-2,4dion.	L_4	326.5	225
5	3-[3-Bromo -Phenylimino-ethyl]-6-methyl-pyrane-2,4dion	L_5	329.0	225
6	3-[1-(3,4-dihydro-6-methyl-2,4dioxo-2Hpyran-3-yl)ethylideneamino]-benzoic acid.	L_6	327.0	225
7	3-[2-Ethoxy-Phenylimino-ethyl]-6-methyl-pyrane-2,4dion.	L_7	329.0	225
8	3-[3,4-dichloro-Phenylimino-ethyl]-6-methyl-pyrane-2,4dion.	L_8	329.0	225

b) PROTON NUCLEAR MAGNETIC RESONANCE SPECTRAL STUDY OF LIGAND: -

General discussion:

Nuclear Magnetic Resonance Spectroscopy can detect the different nuclei under the influence of different environment in a molecule. In the analysis of organic compound Proton Nuclear Magnetic Resonance Spectra plays very important role. It is a most valuable technique in structural investigations[6]. NMR spectroscopy is possible due to absorption of energy at particular frequencies by atomic nuclei that are placed in a magnetic field. As any spinning charge body generates magnetic field, the proton behaves like tiny spinning bar magnet, as it possesses both electrical charge and mechanical spin. Like all bar magnet, proton orients itself under the influence of external magnetic field.

The frequency of group of nuclei can be measured with respect to some reference like tetra methyl silane (TMS). The chemical shift (δ) of protons is obtained by

$$\delta = \frac{\Delta \upsilon}{\upsilon_0}$$

Where δ= chemical shift in ppm

Δ υ=Absorption frequency difference in hertz (Hz)

υ_o=Operating frequency of the instrument in mega heartz (MHz)

Factors like electronegativity, density of electron causes to appear different chemical shift for particular nuclei.

In the present Schiff bases, the aromatic amine condenses with 3-acetyl carbonyl of dehydroacetic acid (DHA). This was confirmed by ^{1}H NMR spectral study.

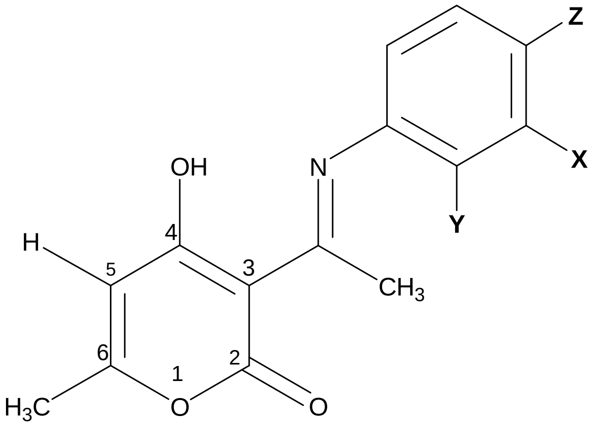
The ^{1}H NMR spectra of ligands were recorded using $CDCl_3$ as solvent.

Discussion of spectral data of Ligands:-

The formation of Schiff base ligands and their structures are confirmed by NMR spectral study of ligands. The NMR spectra of ligands are presented in Fig. 2.9 to Fig. 2.16; where as the characterisation of particular protons are presented in Table. 2.3.

The general structure of ligand is given below, the position of common H in given structure is indicated by letters and shift by particular protons is presented in Table 2.3.

The structure of ligand in general can be represented as-



Where for ligand L1 to L6, **Y** and **Z** are H and

For ligand L1 **X**= -Cl For ligand L2 **X**= -OH
For ligand L3 **X**= - OCH_3 For ligand L4 **X**= -CH_3
For ligand L5 **X**= -Br For ligand L6 **X**= -COOH.
For ligand L7, **X** =**Z** = H and **Y**=-O-CH_2-CH_3
For ligand L8, **Y**=H and **X**=**Z**=Cl

The structure of DHA has H at C-3, which may be in enolic with oxygen of nearest carbonyl, the H at C-5, 3H of methyl group of C-6 position and 3H of methyl at acetyl group.

The base value for chemical shift of 3H of –CH_3 of azomethine carbon is 2.0. The aromatic ring is bonded to Nitrogen and the π electron cloud of aromatic ring may dishield the methyl proton and thus δ value is shifted downfield to 2.17 to 2.45

The H of C-3 of DHA is expected to have shift at 2.1[7,8]. However, due to shielding of this proton by carbonyl and azomethine, it is shifted up field by 1.40 to 1.96. The same proton can also be represented in enolic form and gives δ at 15.47 to 15.94.

The base value δ for the system 3H of methyl bonded to C-6 have singlet 2.1[9,10]. The H of C-5 of DHA have singlet at δ=5.7

The chemical shift of protons of aromatic ring and substituted to aromatic ring are reported in Table 2.3 and are in good agreement with reported values[11] in literature.

Table 2.3 Chemical Shift for different Protons of ligand L1 to L8

Ligand	Chemical shift δ in ppm (splitting)						
	H For aromatic Hydrogen.	3H CH_3 bonded to Carbon of azomethine	3H $CH_3$of C_6 DHA moiety.	1H Shielded C_3 H of DHA moiety.	1H C_5 Hydrogen of DHA moiety.	Proton on X if any.	1H Enolic Proton on DHA moiety.

L1	7.16 to 7.5 (t, d, d , s)	2.17(s)	2.60(s)	1.75(s)	5.77(s)	-	15.94(s)
L2	7.00 to 7.40 (t, d, d, s)	2.45(s)	2.58(s)	1.60(s)	5.80(s)	4.38(s) 1H of OH	15.47
L3	6.98 to 7.36 (t, d, d, s)	2.19(s)	2.56(s)	1.40(s)s	5.78(s)	3.81(s) 3H of CH_3	15.47(s)
L4	7.00 to 7.34 (t, d, d, s)	2.17(s)	2.40(s)	1.66(s)	5.77(s)	2.60(s) 3H of CH_3	15.74(s)
L5	7.10 to 7.38 (t, d, d, s)	2.17(s)	2.61(s)	1.72(s)	5.77(s)	-	15.94(s)
L6	7.23 to 8.08 (t, d, d, s)	2.17(s)	2.60(s)	1.96(s)	5.77(s)	10.51(s) 1H of COOH	15.92(s)
L7	6.95 to 7.33 (t, t, d, d)	2.16(s)	2.55(s)	1.40(s)	5.81(s)	3.18, 1.39 (q), (t) for 2H,3Hof CH_2, CH_3 resp.	15.47(s)
L8	6.98 to 7.56 (d, d, s)	2.16(s)	2.59(s)	1.57(s)	5.78(s)	-	15.47(s)

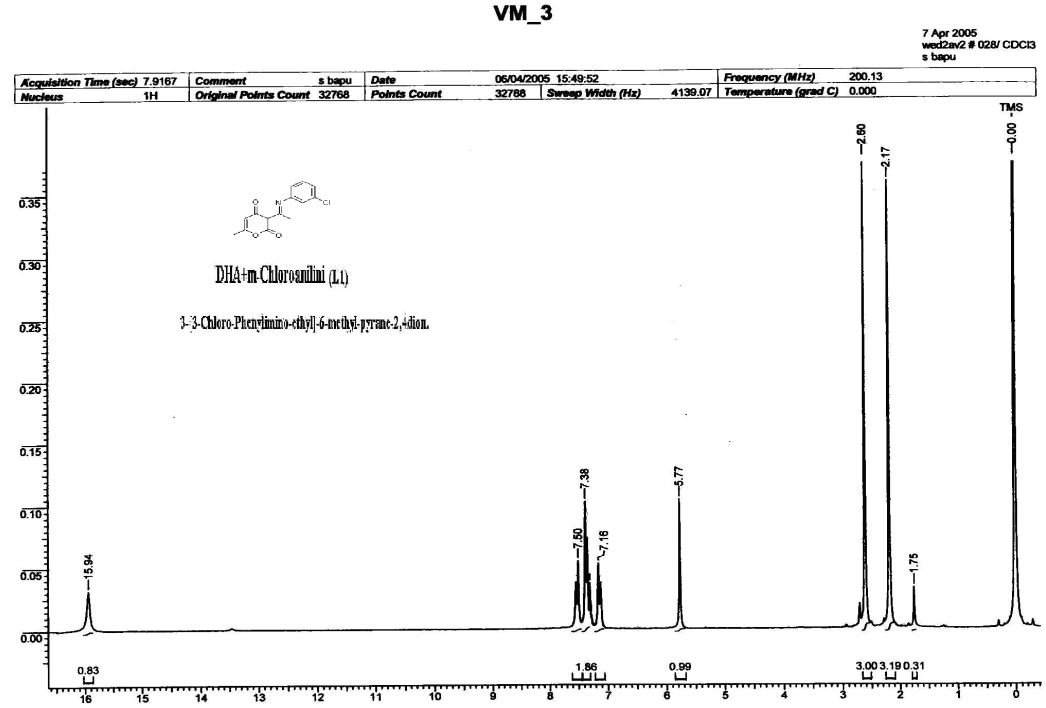


Fig 2.9 NMR Spectra of Ligand L1.

ML-2

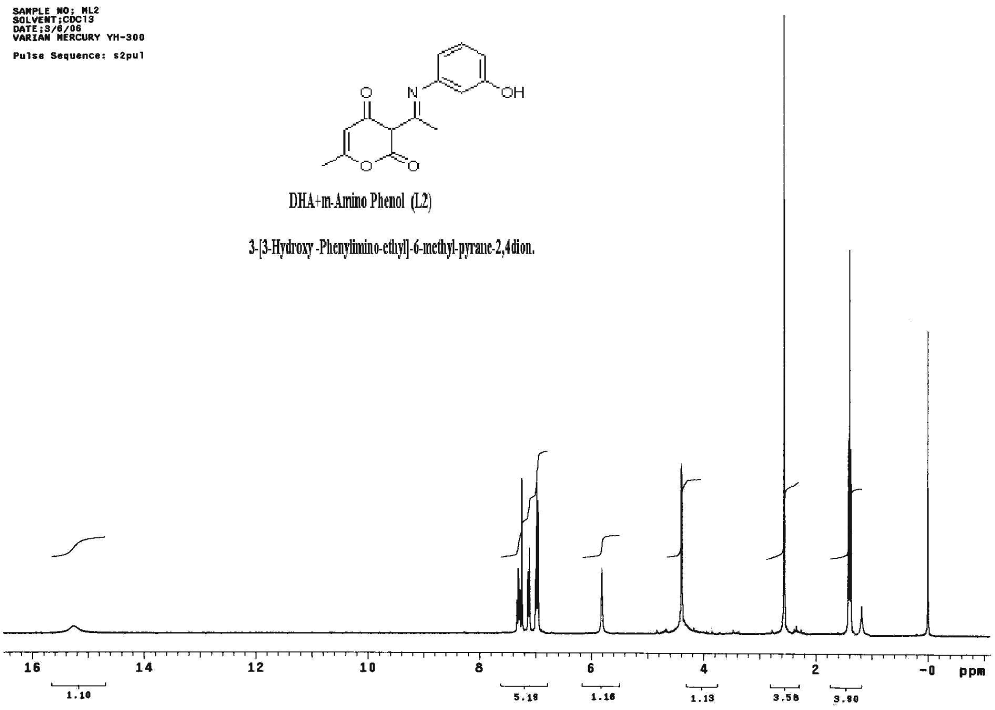


Fig 2.10 NMR Spectra of Ligand L2

ML-3

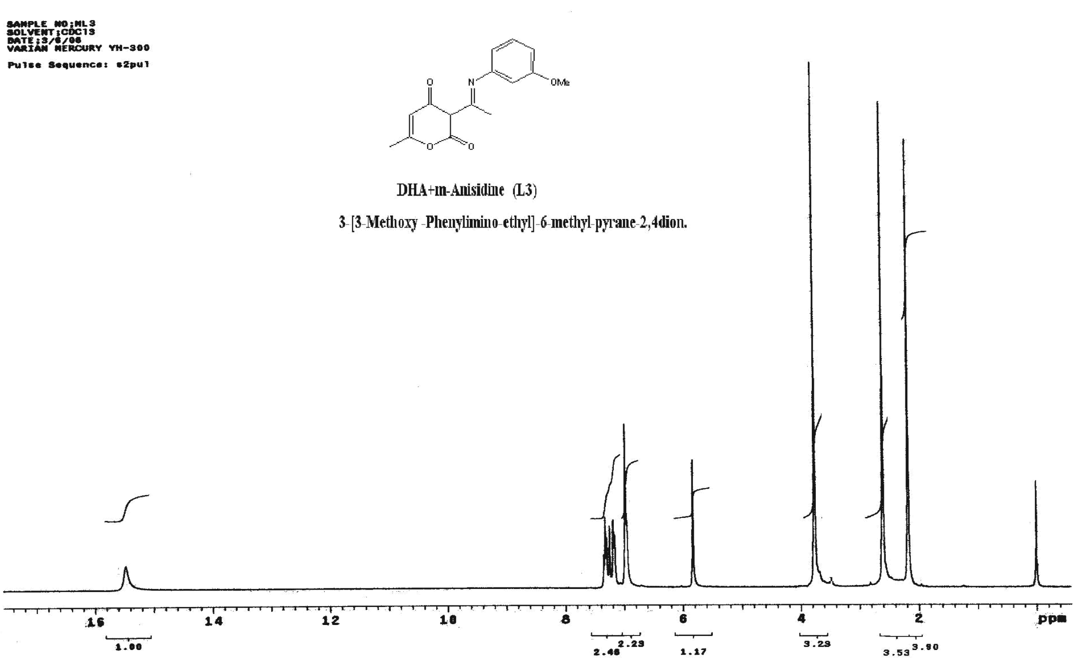


Fig 2.11 NMR Spectra of Ligand L3

VM-2

SB of m-toludine.

7 Feb 2005
mon2av2#011/CDCL3
Bapu

Acquisition Time (sec)	7.9167	Comment	Bapu	Date	07/02/2005 12:58:34	Frequency (MHz)	200.13
Nucleus	1H	Original Points Count	32768	Points Count	32768	Sweep Width (Hz)	4139.07
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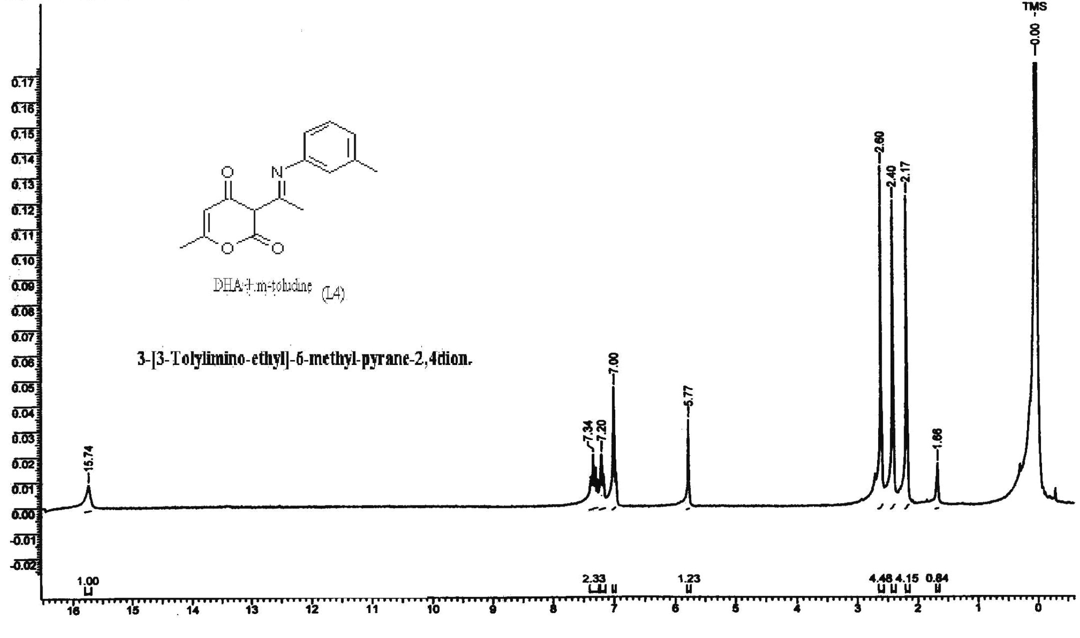


Fig 2.12 NMR Spectra of Ligand L4

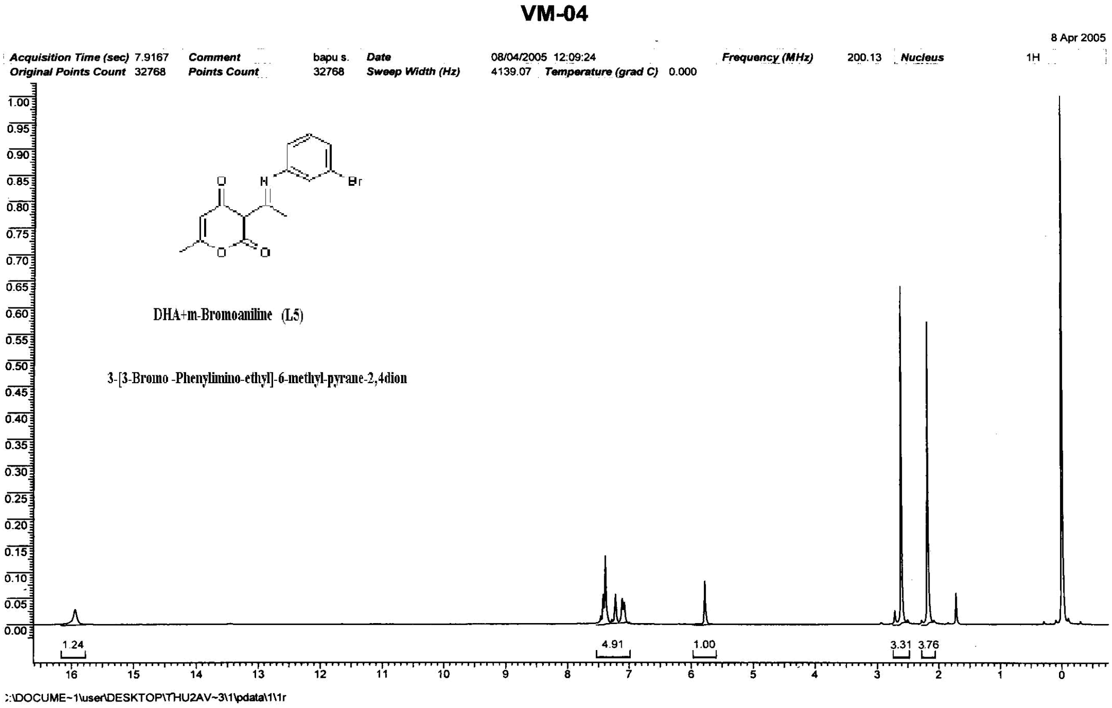


Fig 2.13 NMR Spectra of Ligand L5

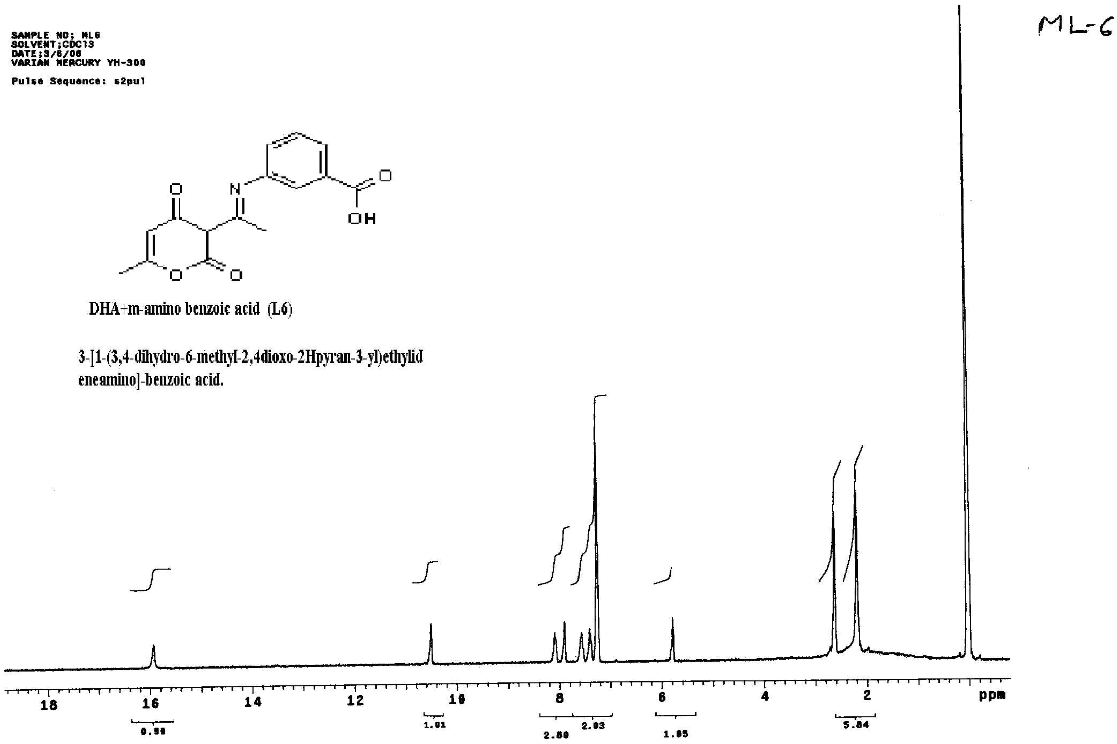
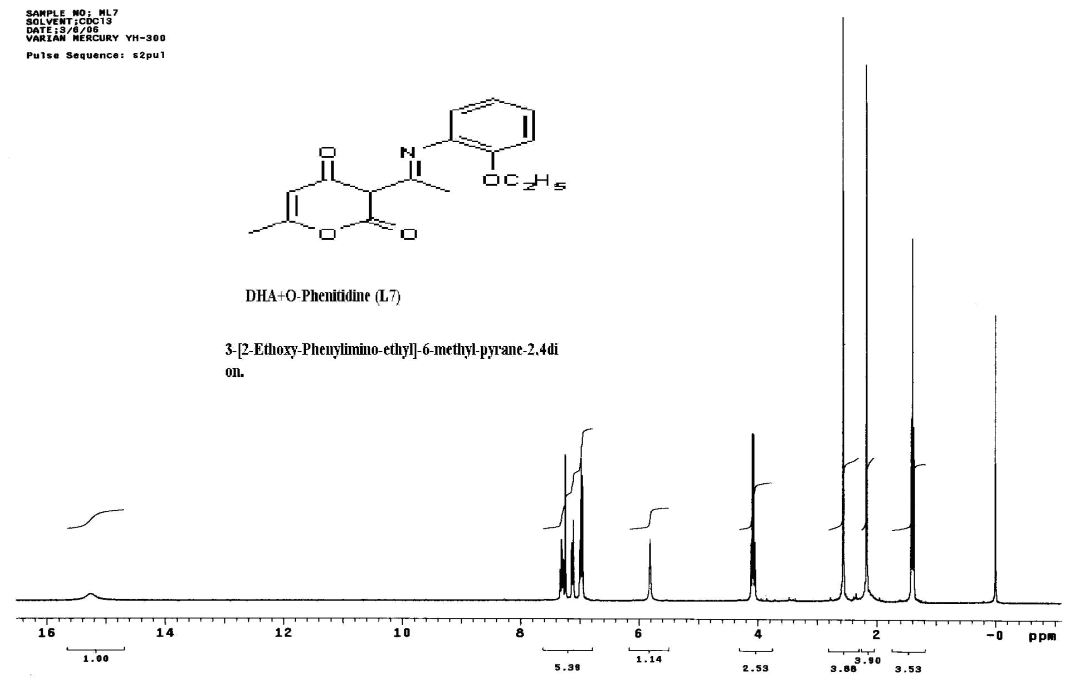


Fig 2.14 NMR Spectra of Ligand L6

ML-7



15·17 ppm

Fig 2.15 NMR Spectra of Ligand L7

ML-8

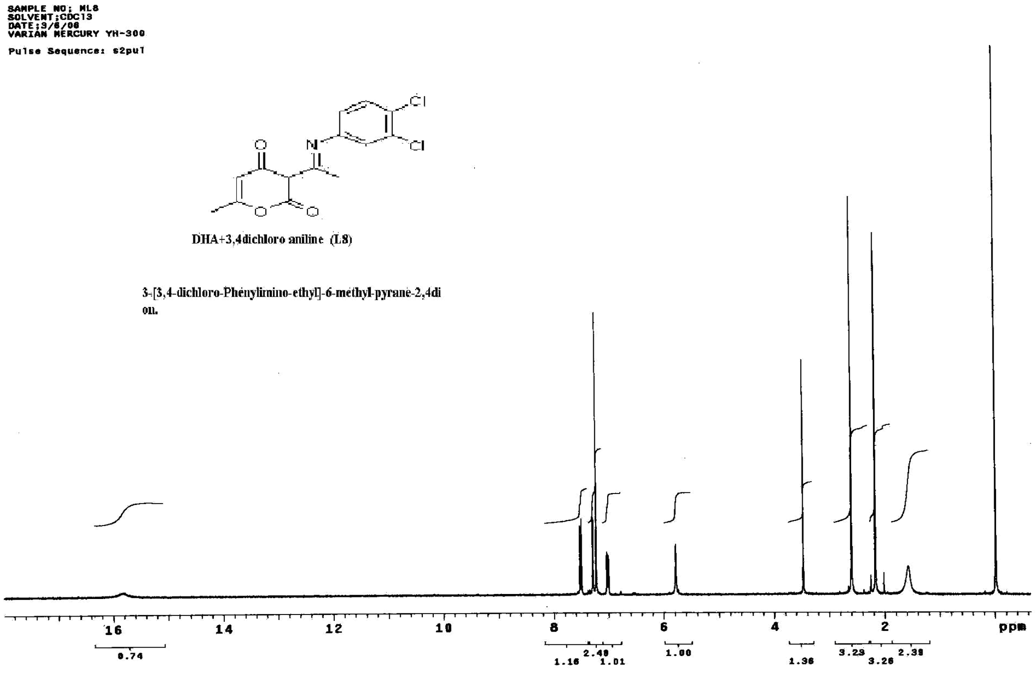


Fig 2.16 NMR Spectra of Ligand L8

2.4 SYNTHESIS OF METAL COMPLEXES:

The metal complexes are synthesised by various methods, in the present work, the transition metal complexes of Schiff bases are synthesized by refluxing the methanolic solutions of ligand (For L6 equivolume mixture of chloroform and methanol) and metal chloride in 2:1 molar ratio. The complexes were precipitated by the addition of methanolic ammonia.

Procedure:

0.02 mole of ligand in slight excess was taken in round bottomed flask containing 30 ml. of anhydrous methanol (For L_6 15 ml chloroform + 15 ml. methanol) so as to dissolve completely. A solution of 0.01 mole of metal chloride in 20 ml. of anhydrous methanol was then added drop-wise to the solution of the ligand. The contents were refluxed for two hours and then cooled to observe the occurrence of precipitation which rarely found in the cold reaction mixture, a ten percent methanolic solution of ammonia was added drop wise to increase the P^H till the metal complex precipitates out completely. The complexes of different metals were precipitated at different P^H range. This P^H range was definite for a given complex and found to be characteristic of that complex. The precipitate was digested for one hour. Any subsequent change in the P^H if observed was readjusted and contents digested again for one hour. The solid metal complex separated out was then filtered in hot condition. It was washed with portions of hot methanol, followed by petroleum ether ($40\text{-}60^0$ C) and dried in vacuum desiccator over anhydrous granular calcium chloride.

The P^H range of precipitation, colours and melting points for all the synthesised metal complexes are presented in Tables 2.4 to 2.8.

2.5 CHARACTERISATION OF METAL COMPLEXES:

All the metal chelates prepared are stable to air and moisture. These are insoluble in water and in different polar and non polar organic solvents at room temperature. Some complexes are easily soluble and some are sparingly soluble or insoluble in dimethyl sulfoxide (DMSO) and dimethyl formamide (DMF).

Table 2.4 P^H range of precipitation, colour, melting point/ decomposition temperature and solution conductivity of COPPER II complexes.

Copper (II) complexes of	P^H range of precipitation	Colour	Melting point Decomposition temp. ^0C	λm Mho cm^2mol^{-1}
L_1	7.5-8	Violet	>270	04.5
L_2	7.5-8	Ash	>270	10.5
L_3	7.5-8	Violet	>270	04.4
L_4	7.5-8	Violet	>270	04.9
L_5	7.5-8	Ash	260	01.6
L_6	7.5-8	Dark green	220	16.2
L_7	7.5-8	Violet	>270	07.5
L_8	7.5-8	Green	242	07.3

Table 2.5 P^H range of precipitation, colour, melting point/ decomposition temperature and solution conductivity of COBALT II complexes.

Cobalt (II) complexes of	P^H range of precipitation	Colour	Melting point Decomposition temp. ^0C	λm Mho cm^2mol^{-1}
L_1	7.5-8	Pink	>270	09.3
L_2	7.5-8	Light green	269	14.9
L_3	7.5-8	Light pink	>270	09.6
L_4	7.5-8	Pink	224	19.1
L_5	7.5-8	Pink	240	17.5
L_6	7.5-8	Light pink	>270	04.4
L_7	7.5-8	Light brown	130	04.4
L_8	7.5-8	pink	242	04.8

Table 2.6 P^{H} range of precipitation, colour, melting point/ decomposition temperature and solution conductivity of NICKLE II complexes.

Nickel (II) complexes of	P^{H} range of precipitation	Colour	Melting point Decomposition temp. ^{0}C	λm Mho cm^{2}mol^{-1}
L_1	6.5-7.00	Light pink	>270	01.8
L_2	6.5-7.00	Pink	>270	01.5
L_3	6.5-7.00	pink	>270	00.5
L_4	6.5-7.00	pink	>270	00.8
L_5	6.5-7.00	Pink	250	00.8
L_6	6.5-7.00	Light pink	>270	01.6
L_7	6.5-7.00	Light pink	>270	00.9
L_8	6.5-7.00	Light pink	>270	00.7

Table 2.7 P^{H} range of precipitation, colour, melting point/ decomposition temperature and solution conductivity of MANGANESE II complexes.

Manganese (II) complexes of	P^{H} range of precipitation	Colour	Melting point Decomposition temp. ^{0}C	λm Mho cm^{2}mol^{-1}
L_1	8.5-9	Dark brown	>270	16.2
L_2	8.5-9	Dark brown	>270	26.4
L_3	8.5-9	Dark brown	>270	19.5
L_4	8.5-9	Dark brown	>270	13.4
L_5	8.5-9	Dark brown	>270	13.4
L_6	8.5-9	Light brown	>270	02.2
L_7	8.5-9	Brown	140	23.4
L_8	8.5-9	Brown	>270	11.2

Table 2.8 P^H range of precipitation, colour, melting point/ decomposition temperature and solution conductivity of IRON II complexes.

Iron(III) complexes of	P^H range of precipitation	Colour	Melting point Decomposition temp. ^0C	λm Mho cm^2mol^{-1}
L_1	7.5-8	Brown	>270	03.8
L_2	7.5-8	Brown	>270	15.2
L_3	7.5-8	Brown	>270	14.4
L_4	7.5-8	Brown	>270	02.4
L_5	7.5-8	Light Brown	260	02.1
L_6	7.5-8	Brown	220	10.5
L_7	7.5-8	Brown	>270	04.6
L_8	7.5-8	Brown	242	07.3

The synthesized metal complexes are characterized by elemental analysis, solution conductivity, magnetic susceptibility, electronic and infrared absorption spectroscopy. They are also screened for thermogravimetric analysis and X- ray powder diffraction analysis.

2.5.1 Colour and melting point/decomposition temperatures of complexes: -

The melting point / decomposition temperatures of the complexes were determined by melting apparatus. The observed values of melting point / decomposition temperatures and colour of complexes are tabulated in Tables 2.4 to 2.8.

2.5.2 Solution conductivity of complexes: -

The solution conductivities of 10^{-4} M solutions of all metal complexes in DMF were measured on "EQUIPTRONICS" digital conductivity meter EQ-660 with range 20 μΩ to 20 mΩ at 298 ^0K temperature. A simple conductivity meter with dip type cell having platinised platinum electrodes with cell constant 1.001 was used. The values are represented in Tables 2.4 to 2.8

2.5.3 Elemental Analysis of Metal Complexes:-

a) Analysis of Carbon, Hydrogen and Nitrogen: -

The C, H and N content of metal complexes were performed using Elemental Analyzer 'PERKINELMER' model no. 2400. The percentage of C, H and N found in metal complexes and those calculated theoretically are tabulated in Table 2.9 to 2.13. The molecular stoichiometry of each compound is established on the basis of elemental analysis[12].

b) Analysis of Metal ions: -

The metal ions were estimated by means of complexometric titrations using ethylene diamine tetra acetic acid (EDTA) under optimum conditions of P^H using suitable metal ion indicators[12, 13]. The metal content data is used to decide the stoichiometric ratio of metal to ligand in the complexes.

i) Preparation and standardization of EDTA solution: -

The dry, pure A.R. grade disodium salt of EDTA was weighed accurately (3.7224 gm.) and dissolved in deionised glass distilled water and diluted to 1 liter to obtain 0.01 M. solution. It is standardized with Zn^{+2} solution prepared from A.R. zinc pellets, titrating against using buffer of 10 P^H and erichrome black-T indicator. The exact molarity of EDTA was determined.

ii) Preparation of metal solution of complexes: -

The sample of each metal complex weighed between 20-30 mg. taken in beaker, was decomposed by repeated heat treatment with small amount of concentrated hydrochloric acid. It was evaporated carefully to dryness at least twice. Then it was treated with few drops of perchloric acid and evaporated carefully to dryness. It was then extracted with small volume of deionised glass distilled water. The contents were transferred to 100 ml standard flask and diluted to mark.

1) Estimation of Copper (II):-

To the diluted solution of Cu(II), about 10 ml of 1 M ammonium chloride solution was added to prevent increase of P^H subsequently. The acidic solution of Cu (II) ions was neutralized with ammonia and P^H rose to about 8, freshly prepared 3 to 4 drops of supernants portion of muroxide indicator was then added and the solution was titrated against 0.01M EDTA solution with constant stirring until the colour changes from orange yellow to violet. A mean of three close readings was taken for the estimation of copper using conversion factor.

1 ml 0.01M EDTA = 0.6354 mg of Cu (II).

The amount of Cu (II) in the respective complexes was calculated.

2) Estimation of Cobalt (II):-

To the solution of Co(II) contained in conical flask, 4-5 drops of freshly prepared indicator solution (0.5% aqueous solution) of xylenol orange was added. Then granules of powdered hexamine were added with continuous stirring until the yellow colour of the solution changed to deep red ($P^H = 6$), 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. A mean of three readings was taken and the amount of metal can be estimated by the conversion factor,

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

3) Estimation of Nickel (II):-

The solution of Ni(II), from each complex was treated with 50 mg of solid muroxide indicator (1% mixture of it in potassium nitrate, followed by 10 ml of 1M ammonium solution), the P^H of the solution was raised to about 7 by adding ammonia solution drop wise, till the solution attains yellow colour. This solution was titrated against 0.01M EDTA solutions until the end point was approached. Near the end point 10 ml of ammonia solution were added to make it strongly alkaline. The titration was continued with constant shaking until the colour changed from yellow to bluish violet. From the mean of three burette readings, the amount of Ni(II) in respective complexes was calculated using the conversion factor.

1 ml 0.01 ml EDTA = 0.5871 mg of Ni (II).

4) Estimation of Manganese (II):-

To the diluted solution of Mn(II) complex, 0.3 g hydroxyl ammonium chloride was added to prevent its oxidation. The solution was warmed and neutralized with a dilute solution of sodium hydroxide. About 3 ml of triethanol amine was added to keep the manganese in solution and was made alkaline with aqueous ammonia. Then 2 ml of P^H 10 buffer solution was, followed by 4-5 drops of Eriochrome black T indicator solution.

The solution was then titrated against 0.01M EDTA until the colour changed from red to blue. The mean of three close readings was taken. The percentages of Mn(II) in respective complexes were determined by conversion factor.

1 ml 0.01M EDTA = 0.5493 mg of Mn (II).

5) Estimation of Iron (III):-

From the diluted solution the 25 ml solution of Fe(III) in conical flask was made acidic with 10-15 ml concentrated hydrochloric acid and heated the liquid to boiling. To the hot solution, an acidic solution of $SnCl_2$ was added drop by drop with constant shaking until the yellow colour just disappears. Then 1 or 2 drops of $SnCl_2$ were added in excess so that Fe(III) is completely reduced to Fe(II). The contents were cooled under tap water and 5 ml of 10% aqueous mercuric chloride ($HgCl_2$) was added to remove the excess of $SnCl_2$, resulting in the formation of silky white precipitate. The 10 ml phosphoric-sulfuric acid mixture (2.5% 200 ml H_2SO_4 + 85% 2.5 ml H_3PO_4) and 5 drops of 0.2% aqueous solution of sodium diphenylamine sulphate were added.

The Fe(III) obtained was slowly titrated against 0.01N $K_2Cr_2O_7$ (Potassium dichromate) solution until a grey blue tint colour appear near the end point. The titration was continued until the addition of one drop gives violet blue coloration even vigorous shaking. The mean of three such burette readings was used to calculate the percentage of Fe (III) in the complex by conversion factor.

1 ml 0.01M $K_2Cr_2O_7$ = 0.5585 mg of Fe(III).

6) Estimation of Metal Ions by Atomic Absorption Spectrophotometer:- The known weight (10 mg.) of respective complex was decomposed with concentrated hydrochloric acid by heating carefully to dryness. Few ml of concentrated perchloric acid was then added in it and again heated to dryness. The process was repeated twice. The residue was cooled and dissolved in glass distilled water. The concentration of acid in finally diluted solution was adjusted (not exceed than 1% v/v). The metal chloride solution formed was diluted to 250 ml solutions; the AAS analysis was carried out on the instrument Parkin Elimer Atomic Spectrophotometer-PE 300.

The complexes $[Cu(L_4)_2]$, $[Co(L_2)_2]$, $[Ni(L_1)_2]$, $[Mn(L_6)_2]$, and $[Fe(L_7)_2]$, were selected for the above purpose. From the diluted solution, the percentage of metal ion was calculated using atomic absorption spectrophotometer.

$$\text{Grams of metal in V ml of solution} = \frac{X \times V}{10^6}$$

$$\text{Percentage of Metal} = \frac{X \times V \times 100}{10^6 \times W}$$

Where, V – Volume of solution.

W – Weight of complex

X – AAS recording.

The complex were analyzed and found that there was no significant difference between the results of two methods.

7) Determination of Chlorides: -

The determination of chlorides in the metal complexes was carried out by Volhard's method[9]. 100 mg of metal complex was dissolved in DMSO solvent and diluted to 50 ml in a standard volumetric flask. 10 ml of this solution was used for analysis. 5 ml of 6M nitric acid was added 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 colouration appears. A blank titration was performed without the sample solution by following same procedure under similar experimental conditions. The difference in the two readings was used to find out the volume of 0.01M silver nitrate consumed by chloride ion. The percentage of chloride in respective metal complex was determined from conversion factor.

$$1\ \text{ml}\ 0.01\text{M}\ AgNO_3 = 0.3545\ \text{mg of}\ Cl^-$$

8) Estimation of Bromides: -

The estimation of bromide was carried out by Volhard's method. 100 mg of test sample of metal complexes L5 were dissolved in DMSO and diluted to 50 ml in a standard volumetric flask. To a 10 ml of this solution in a conical flask, 50 ml distilled water, 5ml glacial acetic acid and 5 drops of eosin were added. The whole mixture titrated against standard 0.01M silver nitrate solution with continuous shaking in a diffused light, till end point pink to violet appears. Process was repeated thrice and mean of these close readings was taken. Finally the percentage of bromide in respective metal complexes was determined from conversion factor,

$$1\ \text{ml}\ 0.01\ \text{M}\ AgNO_3 = 0.7990\ \text{mg of}\ Br$$

The characterization data of all the metal complexes of Schiff bases are given Table 2.9 to 2.13.

Table 2.9 Analytical data of Cu(II) complexes.

Complex of ligand	Molecular formula	Found (Calculated)					Mol.Wt
		C	H	N	Cl	M	
L1	$[C_{28}H_{24}Cl_4N_2O_6Cu]$	47.86 (48.75)	3.40 (3.51)	4.01 (4.06)	19.11 (20.56)	8.94 (9.21)	689.87
L2	$[C_{28}H_{26}Cl_2N_2O_8Cu]$	51.01 (51.50)	3.48 (4.01)	3.94 (4.29)	10.02 (10.86)	9.12 (9.73)	652.97
L3	$[C_{30}H_{30}Cl_2N_2O_8Cu]$	51.77 (52.91)	3.65 (4.44)	3.47 (4.11)	9.89 (10.41)	8.69 (9.33)	681.02
L4	$[C_{30}H30Cl_2N_2O_6Cu]$	54.71 (55.52)	3.80 (4.66)	4.02 (4.32)	9.91 (10.93)	8.93 (9.79)	649.02
L5	$[C_{28}H_{24}Br_2Cl_2N_2O_6Cu]$	42.54 (43.18)	2.79 (3.11)	3.11 (3.60)	8.54 (9.10)	7.64 (8.16)	778.78
L6	$[C_{30}H_{26}Cl_2N_2O_{10}Cu]$	49.78 (50.82)	3.55 (3.70)	3.45 (3.95)	9.65 (10.00)	7.89 (8.96)	708.99
L7	$[C_{32}H_{24}Cl_2N_2O_8Cu]$	53.51 (54.20)	3.59 (4.83)	2.66 (3.19)	9.65 (10.00)	7.94 (8.20)	709
L8	$[C_{28}H_{22}Cl_6N_2O_6Cu]$	43.88 (44.32)	2.49 (2.92)	3.21 (3.69)	27.25 (28.04)	7.94 (8.38)	758

Table 2.10 Analytical data of Co(II) complexes.

Complex of ligand	Molecular formula	Found (Calculated)					Mol.Wt
		C	H	N	Cl	M	
L1	$[C_{28}H_{24}Cl_4N_2O_6Co]$	48.57 (49.08)	3.42 (3.53)	4.01 (4.09)	19.87 (20.70)	7.44 (8.60)	685.25
L2	$[C_{28}H_{26}Cl_2N_2O_8Co]$	51.18 (51.87)	3.48 (4.04)	4.05 (4.32)	9.56 (10.94)	8.94 (9.09)	648.35
L3	$[C_{30}H_{30}Cl_2N_2O_8Co]$	52.77 (53.27)	3.55 (4.47)	3.94 (4.14)	10.00 (10.48)	7.86 (8.71)	674.41
L4	$[C_{30}H30Cl_2N_2O_6Co]$	55.81 (55.92)	4.40 (4.69)	4.27 (4.35)	10.85 (11.00)	8.73 (9.15)	644.41
L5	$[C_{28}H_{24}Br_2Cl_2N_2O_6Co]$	43.01 (43.44)	2.90 (3.12)	3.21 (3.62)	8.85 (9.16)	7.25 (7.61)	774.15
L6	$[C_{30}H_{26}Cl_2N_2O_{10}Co]$	50.85 (51.15)	3.45 (3.72)	3.54 (3.98)	9.65 (10.07)	8.01 (8.37)	704.37
L7	$[C_{32}H_{24}Cl_2N_2O_8Co]$	53.89 (54.56)	3.85 (4.86)	3.29 (3.98)	9.73 (10.07)	7.94 (8.37)	704.46
L8	$[C_{28}H_{22}Cl_6N_2O_6Co]$	44.23 (44.59)	2.48 (2.94)	3.25 (3.71)	27.68 (28.21)	7.44 (7.81)	754.14

Table 2.11 Analytical data of Ni(II) complexes.

Complex of ligand	Molecular formula	Found (Calculated)					Mol.Wt
		C	H	N	Cl	M	
L1	$[C_{28}H_{22}Cl_2N_2O_6Ni]$	54.10 (54.94)	3.24 (3.62)	4.05 (4.58)	11.05 (11.58)	9.04 (9.59)	614.1
L2	$[C_{28}H_{24}N_2O_8Ni]$	57.85 (58.47)	3.65 (4.21)	4.01 (4.87)	-	9.65 (10.20)	575.19
L3	$[C_{30}H_{28}N_2O_8Ni]$	58.77 (59.73)	4.12 (4.68)	3.94 (4.64)	-	8.86 (9.73)	602.25
L4	$[C_{30}H_{28}N_2O_6Ni]$	62.81 (63.08)	4.42 (4.94)	4.02 (4.90)	-	9.73 (10.27)	571.25
L5	$[C_{28}H_{22}Br_2N_2O_6Ni]$	47.12 (47.98)	2.91 (3.16)	3.79 (4.00)	22.25 (22.80)	8.12 (8.37)	700.99
L6	$[C_{30}H_{24}N_2O_{10}Ni]$	56.95 (57.08)	3.45 (3.83)	4.00 (4.44)	-	9.07 (9.30)	631.21
L7	$[C_{32}H_{32}N_2O_8Ni]$	60.32 (60.88)	4.49 (5.11)	4.01 (4.44)	-	8.94 (9.30)	631.3
L8	$[C_{28}H_{20}Cl_6N_2O_6Ni]$	48.95 (49.39)	2.49 (2.96)	3.98 (4.11)	19.87 (20.82)	7.944 (8.62)	680.17

Table 2.12 Analytical data of Mn(II) complexes.

Complex of ligand	Molecular formula	Found (Calculated)					Mol.Wt
		C	H	N	Cl	M	
L1	$[C_{28}H_{24}Cl_4N_2O_6Mn]$	48.98 (49.37)	3.08 (3.55)	3.87 (4.11)	19.95 (20.82)	7.74 (8.06)	681.25
L2	$[C_{28}H_{26}Cl_2N_2O_8Mn]$	51.85 (52.19)	3.49 (4.07)	4.01 (4.35)	10.65 (11.00)	7.94 (8.53)	644.36
L3	$[C_{30}H_{30}Cl_2N_2O_8Mn]$	52.77 (53.59)	3.63 (4.50)	3.47 (4.17)	10.01 (10.55)	7.86 (8.17)	672.40
L4	$[C_{30}H30Cl_2N_2O_6Mn]$	55.81 (56.26)	3.47 (4.72)	4.02 (4.37)	10.87 (11.07)	8.04 (8.58)	640.41
L5	$[C_{28}H_{24}Br_2Cl_2N_2O_6Mn]$	42.98 (43.67)	2.79 (3.14)	3.12 (3.64)	8.94 (9.21)	6.85 (7.13)	770.15
L6	$[C_{30}H_{26}Cl_2N_2O_{10}Mn]$	50.64 (51.45)	3.25 (3.74)	3.78 (4.00)	9.85 (10.12)	7.07 (7.84)	700.38
L7	$[C_{32}H_{24}Cl_2N_2O_8Mn]$	54.25 (54.87)	3.48 (4.84)	3.81 (4.00)	9.88 (10.12)	7.14 (7.84)	700.14
L8	$[C_{28}H_{22}Cl_6N_2O_6Mn]$	44.21 (44.83)	2.63 (2.96)	3.25 (3.73)	27.89 (28.36)	7.00 (7.32)	750.14

Table 2.13 Analytical data of Fe(III) complexes.

Complex of ligand	Molecular formula	Found (Calculated)					Mol.Wt
		C	H	N	Cl	M	
L1	$[C_{28}H_{24}Cl_4N_2O_6Fe]Cl$	46.21 (46.86)	3.14 (3.37)	3.51 (3.90)	24.00 (24.70)	7. 44 (7.78)	717.61
L2	$[C_{28}H_{26}Cl_2N_2O_8Fe]Cl$	49.01 (49.40)	3.49 (3.85)	3.91 (4.12)	15.01 (15.62)	7.94 (8.20)	680.72
L3	$[C_{30}H_{30}Cl_2N_2O_8Fe]Cl$	50.77 (50.84)	3.12 (4.27)	3.94 (3.95)	14.85 (15.01)	7.69 (7.88)	708
L4	$[C_{30}H30Cl_2N_2O_6Fe]Cl$	52.89 (53.24)	4.08 (4.47)	4.02 (4.14)	14.54 (15.72)	8.03 (8.25)	676.77
L5	$[C_{28}H_{24}Br_2Cl_2N_2O_6Fe]Cl$	41.12 (41.70)	2.79 (3.00)	3.02 (3.47)	12.83 (13.19)	6.42 (6.92)	806.51
L6	$[C_{30}H_{26}Cl_2N_2O_{10}Fe]Cl$	48.46 (48.91)	3.13 (3.56)	3.21 (3.80)	14.00 (14.44)	7.07 (7.58)	736.74
L7	$[C_{32}H_{24}Cl_2N_2O_8Fe]Cl$	52.01 (52.16)	4.14 (4.65)	3.25 (3.80)	13.98 (14.43)	7.14 (7.58)	736.82
L8	$[C_{28}H_{22}Cl_6N_2O_6Fe]Cl$	42.11 (42.76)	2.48 (2.82)	3.05 (3.56)	31.02 (31.35)	6.94 (7.10)	786.5

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CHAPTER III

EXPERIMENTAL TECHNIQUES

3.1 MAGNETIC SUSCEPTIBILITY.

3.2 SOLUTION CONDUCTIVITY.

3.3 ELECTRONIC ABSORPTION SPECTROSCOPY.

3.4 INFRARED SPECTROSCOPY.

3.5 THERMAL ANALYSIS.

3.6 X-RAY POWDER DIFFRACTION.

3.7 REFERANCES.

CHAPTER -3

EXPERIMENTAL TECHNIQUES

The different techniques have used to analysis the metal complexes. By the use of all such techniques the exact structure of metal chelates has been ascertained.

3.1MAGNETIC SUSCEPTIBILITY:-

3.1.1 Introduction to Magnetic Susceptibility: -

Magnetochemistry is one of the most valuable techniques in the investigation of transition metal complexes[1-3]. The measurement of magnetic properties can provide information of the electronic structure, oxidation state of metal ion, and in some cases stereochemistry and nature of bonding in metal complexes.

The magnetic moment can be calculated by determining the magnetic susceptibility. This is a most useful quantity in establishment of number of unpaired electrons, their distribution in orbitals around the central metal atom. The number of unpaired electrons and electronic configuration of the central metal ion decides the geometry of the metal complexes. The proper interpretation of observed magnetic data on the basis of valence bond and crystal field theories, valuable information about oxidation state of the metal, type of bonding and structure of transition metal complex can be obtained. The magneto chemistry of the metal complexes shows whether inner or outer d-orbitals are used and whether d-electrons are paired or unpaired in the complexes. This is useful to distinguishing the high spin and low spin complexes.

The ratio of intensity of magnetization induced due to the applied magnetic field is called as magnetic susceptibility. The intensity of magnetic field induced in the substance depends on paired or unpaired electrons present in orbitals of metal ion, from which the substances are classified as diamagnetic and paramagnetic. The induced magnetization in diamagnetic substance is always opposite in direction to the lines of forces of the external field, which results in a negative susceptibility of the diamagnetic material from -10^{-6} to -10^{-5} CGS units. Paramagnetism arises in substances containing unpaired electrons and induced magnetic field is parallel to the lines of force of external field. They have positive susceptibility in the order of 10^{-5} to 10^{-3} CGS units. The diamagnetic susceptibility is independent of the temperature while paramagnetic susceptibility varies inversely with the absolute temperature.

3.1.2 Experimental Method:-

The determination of magnetic susceptibility involves measurement of the force exerted by a homogeneous magnetic field on the sample under study. If the force acting on the sample under investigation is known, the magnetic susceptibility of the compound can be determined, and from this the value of the magnetic moment, can be calculated.

Gouy's method was used for the measurement of magnetic susceptibility of the compounds at room temperature. Gouy's balance consists of an electromagnet with a suitable power supply and a single pan-semi microbalance, E-Mettler-Zurich, Swiss-make-H-1640 with maximum capacity 80 mg and a precision ± 0.01 mg.

The electromagnets consists of cylindrical poles, 15 cm in diameter tapering at ends at an angle of 45^0 and ending in circular faces 3.5 cm in diameter. A gap of 4 cm is maintained between the two poles. The magnetic assembly having an electromagnet with capacity up to 7000 orresteds was placed around the tube, with a current of 6 amps fed by a suitable power supply.

The specimen tube made up of Pyrex glass, 14 cm in length and 3.5 mm in diameter, with a teflon stopper was used to hold the sample. The tube was supported and suspended freely in the magnetic field with the help of clean silver chain in such a way that its lower end was located at the center of the pole gap. The empty clean and dry tube was weighed successively when current is off and on with 4 amps and 6 amps. The field strength of the magnet and position of tube with respect to poles remain unchanged during every measurement. The mean of five readings gave the value W g for the empty tube.

3.1.3 Calibration of the Specimen Tube: -

For accurate measurement of the magnetic moments, the tube constant was determined, using substance of known magnetic susceptibility at room temperature. The standard substance used was mercury tetra thiocyanato cobalt (II), which was prepared by the standard method given in the literature[1]. The measurement of the force developed on the specimen tube was recorded with two independent fillings of the substance. The compound under investigation was filled in glass tube and packed to eliminate any air pockets. The gram susceptibility of the sample was taken as 16.44 x 10^{-6} CGS units. The tube constant (β) was determined at room temperature. This value was used for the calculation of magnetic susceptibility of metal complexes.

A typical data of the calibration is as follows –

Weight of empty tube	= 13.94215 gm.
Weight of empty tube in presence of magnetic field	= 13.9371gm
Force on the empty tube in presence of magnetic field	= 0.00505gm

Weight of $Hg[Co(NCS)_4]$, (gm)	Temperature, ^0K	Force on the sample, (gm)	β x 10^6
0.22990	299	0.0158	181.27

3.1.4 Sources of Error:-

The main source of error in the Gouy's method for solids arises from the improper packing of the sample. This can be reduced by repeating the measurements on homogeneously repacked samples until relatively constant values of gram susceptibility (χ_g) are obtained. Agreement within 1% is to be considered good.

3.1.5 Measurement of Magnetic Susceptibilities of Metal Complexes:-

The finely powdered metal complex was filled in the experimental tube up to reference mark. The precaution was taken to ensure tight and uniform packing without any air gap in the sample tube. The teflon stopper was tightly fixed on the tube and the tube was suspended between the poles with the help of silver chain suspension from the pan of the balance. Similar measurements were recorded which described earlier.

From the experimental data, the magnetic susceptibility (χ_g) of metal complexes was calculated from the following expression.

$$\chi_g = \frac{\beta \Delta\omega}{W}$$

Where,

χ_g = susceptibility per gram of the substance.

β = constant characteristic of the tube.

$\Delta\omega$ = force exerted by W gm of substance.

W = weight of the substance.

The molar susceptibilities (χ_M) of complexes were then calculated by the expression.

χ_M = χ_g x Molecular weight.

The magnetic moments (μ_{eff}) of complexes were calculated from the value of χ_M by the equation.

$$\mu_{eff} = 2.84 \sqrt{\chi_A T}$$

Where,

μ_{eff} = Magnetic Moment of the metal ion in Bohr magnetons (B. M.)

T = Temperature in Kelvin scale.

χ_A = χcorr. = Magnetic Susceptibilities obtained by subtracting from molar susceptibilities of metal complex from the diamagnetic susceptibility of ligand molecule calculated by using Pascal's constant.

That is, $\chi_{corr.} = \chi_{M.} - \chi_{dimagnetic(L)}$

Where;

$$\chi_{\text{diamagnetic (L)}} = \sum \chi_{\text{(atomic correction)}} + \sum \chi_{\text{(multiple bonds)}}$$

The reproducibility of magnetic susceptibility measurements of the complexes was within ± 2%. The diamagnetic susceptibility $\chi_{\text{diamagnetic (L)}}$ of ligand molecules are calculated from Pascal's constant [3,4]. These are used for calculation of $\chi_{\text{corr.}}$ are given in Table 3.1

Table 3.1: Diamagnetic susceptibilities [χ diamagnetic of ligand] Molecules computed from Pascal's constant.

Sr.No.	Name of Ligand	Symbols	χ-diamagnetic of ligand $\times 10^{-6}$/gm mole CGS.
1	DHA +3 chloroaniline	L_1	293.0
2	DHA +3 Amino phenol	L_2	250.5
3	DHA +3 methoxy aniline	L_3	291.5
4	DHA + 3 methyl aniline	L_4	218.7
5	DHA +3 Bromo aniline	L_5	313.4
6	DHA +3 amino benzoic acid	L_6	269.0
7	DHA +2 ethoxy aniline	L_7	298.0
8	DHA +3 dichloro aniline	L_8	312.5

3.2 SOLUTION CONDUCTIVITY:-

3.2.1 Introduction of Solution Conductivity:-

It is one of the recent methods for studying the complexes. The solution conductivity depends on the concentration of solute and the number of charges on ions, which are formed on dissociation in an ionic material[5]. The solution of an electrolyte conducts electric current by migration of ions under the influence of electric field. Hence the ability of any ion to transport charge depends on mobility of ions. Therefore by measuring the solution conductivity one can decide the electrolytic or non-electrolytic nature of the metal complexes, which helps in ascertaining its ionic and covalent nature.

The molar conductivity μ_v of a solution of solute is a measure of the number and rate of migration of anions and cations in one mole of the solute. By comparison of molar conductivities of complexes with that of known simple ionic materials, the total number of charges on the species formed, when the complex dissolve can be deduced, this decides the composition of complexes by cryoscopy measurement together[6].

3.2.2 Measurement of solution Conductivity:-

The solution conductivities of 10^{-4}M solution of all metal complexes in DMF were measured on “EQUIPTRONICS” digital conductivity meter EQ-660 with range 20μΩ to 20 mΩ at 298 K temperature. As the conductivity of solution rises by about 2 percent per degree, the temperature must be controlled. A simple conductivity meter with dip type cell electrodes with cell constant 1.001 was used for this purpose. The instrument and conductivity cell were calibrated using 0.005M KCL, solution at room temperature.

In practice the observed conductance (x) of solution was measured and specific conductivity K_v was calculated by multiplying the cell constant with observed conductance. Finally from specific conductivity and molarity (M) of solution, the molar conductivity μv was calculated by equation[7].

$$\mu_v = \frac{K_v \times 1000}{M}$$

Where, M- is molarity of a solution of solute.

The molar conductivity has the unit S cm^2 mol^{-1} or ohm^{-1} cm^2 mol^{-1}. The molar conductance values were interpreted with the help of literature data [8,9,10].

3.3 ELECTRONIC ABSORPTION SPECTRA:-

3.3.1 Introduction of Electronic Absorption Spectra:-

The absorption of ultraviolet (UV) or visible light results in a change in the energy of electrons of the absorbing molecule. The electronic spectrum consists of bands containing several absorption lines. Each band corresponds to a definite change in the electronic energy, and individual lines within the band are due to definite transitions.

The structure of metal complexes can be predicted from interpretation of their electronic absorption spectra and comparing them with the electronic absorption spectra of corresponding ligands. The complexes can be identified by their characteristic absorption, which is based on the position of maxima and minima in the absorption spectra along with the molar extinction coefficient value. In the spectra of transition metal ions, bands corresponding basically are of three types,

I) Bands due to d-d transitions.

II) Charge transfer bands.

III) Bands due to electron transfer within the ligand.

In the transition metal complexes, visible spectra arises when an electron is excited between t_{2g} and e_g orbital with different energy levels. Charge transfer bands may arise from the transition of an electron from an orbital of ligand to the central metal atom. The molar extinction coefficient of a charge transfer band is about hundred times than that of d-d transition bands.

By recording absorption spectra of known molecule, the wavelength of radiation absorbed is correlated with the characteristic structural feature. This information is then used in determining the structure of unknown molecules from their spectra[11,12]. In more stable complexes, the change in the spectrum of the ligand will depend on the degree of covalency of the metal ligand bond. The magnitude of the shift depends on the coordination number of the central atom and its ionic radius. In complexes, stability increases back coordination and charge transfer bands also appear besides the bands of the ligands. The UV/Vis spectroscopy is, therefore a powerful tool, for structure elucidation.

The correct interpretation of the absorption bands gives an insight into the energy of orbital, mode of bonding in the complexes and their geometries. By this means, it is possible to distinguish tetrahedral, octahedral, and square planar complexes and whether the shape is distorted or regular. Both the intensity and wavelength of absorption band is associated with resonance states of molecule as will as with energy difference between the ground and excited state of molecule. In general there is an increase in intensity as the length of conjugation chain increases[13].

Most organic molecules absorb in the near UV region (200-400 nm) in which the atmosphere is transparent where as transition metal complexes absorb in the visible region (400-800 nm) because of coloured solutions.

3.3.2 Scanning of UV/Vis. Spectra: -

The synthesized Schiff base metal complexes of Cu(II), Co(II), Ni(II), Mn(II) and Fe(III) were soluble in DMF. Therefore solution spectra were recorded on SHIMADZU-UV-1601 UV/Vis. double beam spectrophotometer in the region 190-1100 nm using quartz optic tubes of 2 cm path length.

3.4 INFRARED SPECTROSCOPY: -

3.4.1 Introduction of Infrared Spectra: -

Infrared radiation refers to that part of electromagnetic spectrum, which is in between visible, and microwave region. An infrared radiation occurs when the frequency of alternating field associated with the incident radiations matches a possible change in the vibration or rotational frequency of the absorbing molecule. It is suggested that when metal ion combines with the ligands to form complex, its vibrational spectrum is expected to change. The change in the vibration can be related to molecular symmetry or with the change in the individual frequency. A molecule can undergo two types of vibrational-stretching (υ) and bending (δ-deform), and stretching vibrations have higher frequencies than deformation.

Some of the important applications of IR spectroscopy are the identification of major types of bonds, various functional groups, hydrogen bonding in metal complexes and cis-trans isomers. One of the best features of IR spectroscopy in qualitative analysis is that, the absorption or lack of absorption in the specific frequency region can be corrected with specific stretching and bending modes and in some cases, with the relationship of these groups to rest of the molecule.

IR absorption occurs not only with organic molecules but also with covalently bonded metal complexes, which are generally active in the longer wavelength IR region. The inorganic complexes derived from organic chelating groups have a tendency to absorb in the IR region 400-660 cm^{-1} which is of greatest practical value in the study of metal complexes[14].

IR studies have thus provided much useful information about metal complexes.

3.4.2 Scanning of IR Spectra:-

The infrared spectra of Schiff base ligands and metal complexes were recorded on a Perkin Elmer Spectrum 1b No.-75430 Nujol spectrophotometer over the range 4000 cm^{-1} to 450 cm^{-1} using KBr pellet technique.

3.5 THERMAL ANALYSIS: -

3.5.1 Introduction of thermo analytical Techniques:-

The majority of compounds, including complexes suffer physical and chemical changes when subjected to heat. Under defined experimental conditions these changes are characteristic of the substance examined and can be used for its qualitative and quantitative analysis.

The sample to be analyzed is heated, various physicochemical changes like thermal decomposition, oxidation, dipole moment, electrical potential, magnetic susceptibility, crystal structure, electrical conductivity, water evaporation, sublimation may take place with a consequent change in the weight of the sample. The study of thermal decomposition of the substance is very useful in predicting the thermal stability of the substance. Chemical changes in the substance can be studied with the help of Thermogravimetric Analysis (TGA), and Differential Thermal Analysis (DTA), and therefore thermal properties are among the important properties of any substance.

3.5.2 Thermogravimetric Analysis (TGA):-

Thermogravimetry is a technique in which the change in the weight of a substance when heated or cooled at a controlled rate is recorded as a function of temperature and/or time. A plot of sample weight change as a function of temperature provides both qualitative and quantitative information of sample. It directly records the loss in weight as a function of temperature for transitions that involve dehydration or decomposition. Thermogravimetric curves are characteristic of a given compound or a material due to the unique sequence of physical transition and chemical reactions that occur over definite temperature ranges. Changes in weights are the results of breaking or formation of various bonds and evolution of volatile or heavier reaction products[15]. Kinetic studies of thermal decomposition reactions of a substance are of great importance in calculating various parameters like energy of activation (Ea), free energy change (ΔF), pre-exponential factor (Z), order of reaction (n), and entropy of activation (ΔS), which directly govern the factors of thermal stability of any substance.

The course and character of the TG curves are influenced by several experimental factors such as rate of heating, the atmosphere of the furnace, the geometry of the furnace and sample holder, particle size, heat of reaction and compactness of the sample.

3.5.3 Differential Thermal Analysis: -

It may be stated that a single thermal property is not sufficient to characterize a chemical reaction or system, but that as many thermal methods as possible be employed.

Differential thermal analysis (DTA) is a thermal technique in which the heat effects, associated with physical or chemical changes, are recorded as a function of temperature or time as the substance is heated at a uniform rate. Heats of enthalpy changes, either exothermic or endothermic are caused by phase transitions. Generally phase transitions, dehydration reactions, and some decomposition reactions produce endothermic effect, whereas crystallization, oxidation and some decomposition reaction produce exothermic effects. The heat effects occurring during these chemical and physical changes are measured by differential thermal analysis. Each substance will give a DTA curve whose number, size; shape and position of various endothermic and exothermic features serve as a means of qualitative information of the sample. The endotherms or exotherms can be used to calculate the heat of reaction or heat of phase transition. The area (A) of DTA peak is given by

$$A = \pm \frac{Gm\Delta H}{K}$$

Where, G= sample geometry,

m= sample mass,

K= constant,

ΔH (enthalpy change) = - ve →exothermic

= + ve→ endothermic

DTA is used to study the thermal stability of large number of metal complexes and organic ligands.

The thermogravimetric studies of metal complexes find extensive applications in determining the purity, metal-ligand bond strength, and melting points[16,17]. The simultaneous use of TGA and DTA for the study of metal complexes provides the benefits. The TG is most useful when it complements DTA. The similarity in the values of thermodynamic and kinetic parameters indicates the basic steps involved in the thermal degradation of chelates are same[18]. The simultaneous use of TGA and DTA plays an important role in the study of thermal behaviour of the inorganic substances.

3.5.4 Scanning of TGA-DTA Curves:-

The simultaneous thermo gravimetric, differential thermal analyses of representative metal complexes were performed on universal – V_2SH, JA-Instruments, USA, in an inert nitrogen atmosphere. The heating rate was 10 ^{0}K min^{-1} and flow rate 50.00 ml/min. over a temperature range of 0^0C to 1000^0C. The reference substance used was α-Al_2O_3 in platinum crucible and samples weighed in the range 3 to 6 mg.

3.6 X-RAY DIFFRACTION:-

3.6.1 Introduction of X-Ray Diffraction:-

The X–ray diffraction is a powerful method to understand the structure of the compound[19]. X–ray method, can determine the structure and symmetry properties of complexes. It gives information of inter atomic distance, bond angles and electronic arrangement in a complex.

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[20] gives the relation between inter planar distance and the diffraction angle.

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

Where,

n = order of reflection.

λ = Wavelength of X-rays.

d = inter planar distance and

θ = Angle of incident.

Constructive interference of the radiation from successive planes occurs when the path difference is an integral multiple number (n) of wavelength. This is the Bragg's law. All crystals of a substance possess the same elements of symmetry. Bragg pictured the diffraction effect or a reflection of X-rays from the lattice planes of the crystal. The atoms in the plane are being responsible for scattering of the X-rays to an extent, dependent upon the number of its electrons. This made a new and significant tool available to the crystallographers and as a result, an extensive amount of work on single crystal was carried out to reveal the internal structure of the compound and is a convenient and practical means for qualitative identification of crystalline compounds. Now a day, XRD is a well established and powerful technique to understand the structure of solids.

The procedure in analyzing the powder diffractogram of an unknown sample is consisting of measuring the intensities of the peaks, the diffraction angles θ or 2θ. Once θ is determined it is used for calculating the inter planer spacing d of reflection planes from the values of λ of X-rays used, and then the dimensions of unit cell are determined. Powder diffraction technique is very important method for the identification of unknown compound and applicable to all crystalline substances.

3.6.2 Scanning of X-ray Powder Diffraction and Indexing of the Data:-

The X-ray powder diffraction of representative metal complexes was scanned on Philips 50-70 PW –3710. Diffractometer attached to a digital computer along with graphical assembly in which Cu-K radiation source connected with the tube Cu-Ni-40 Kv/40 mA producing 1.543 A^0 wavelength radiation was used with scanning rate 2^0/min. Each test sample of 200-300 mesh size weighing minimum amount 10 mg was spread in the form of film and spectra were scanned in the range of $2\theta = 5$ to 100^0.

The data obtained was deduced using computer program (PDP-Burn). The preliminary data in the form of 2θ and intensity ratio were fed to the computer and corresponding h, k, l values were assigned to each peak. The programme calculates the lattice parameters a, b, c (A^0) and α, β, γ (degree) along with standard deviation in each. The crystal volume is also obtained from the unit cell data.

The pyknometric densities of each of the complexes were determined using specific gravity bottle by the principle of Archimedes[21]. The density is related to the formula factor as follows

$$D = \frac{ZxFxM}{V}$$

Where, Z – Number of formula units in the cell.
F – Formula weight of compound.
M – Mass of hydrogen atom in amu.
V – Crystal volume.

The calculated densities were correlated with the experimentally obtained densities. The observed densities were used to fix the value of Z to the nearest whole number. By using literature values for definite crystal system, probable space group was assigned to each of the complexes[22].

Once the dimension of the unit cell, the density and the chemical composition of crystals are known, the number of atoms per unit cell can be established. From the space group, number of atoms in equivalent position contained by the unit cell can be deduced. In this way the unit cell represents the lattice structure of a crystal.

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CHAPTER- IV

RESULTS AND DISCUSSION

PART – A

ELEMENTAL ANALYSIS, SOLUTION CONDUCTIVITY, MAGNETIC SUSCEPTIBILITY AND ELECTRONIC ABSORPTION SPECTRAL STUDIES OF

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PART – B

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CHAPTER- 4

RESULTS AND DISCUSSION

PART – A

ELEMENTAL ANALYSIS, SOLUTION CONDUCTIVITY, MAGNETIC SUSCEPTIBILITY AND ELECTRONIC ABSORPTION SPECTRAL STUDIES OF METAL COMPLEXES:-

4.1 COPPER (II) COMPLEXES–

4.1.1 Theoretical Considerations

The Copper (II) ion with d^9 configuration has both octahedral and tetrahedral environment and is most susceptible to Jahn-Teller Distortion[1-2]. In addition to the square merging into tetragonally distorted octahedral complexes, some other stereochemistry of Cu(II) are known, of which the most important is distorted tetrahedral. X – Ray studies have shown that many of the hexa coordinated octahedral complexes tend severally towards tetragonal distorted geometry[3].

Most of the square planar complexes have weakly coordinating groups in axial positions[4] and many of the copper (II) complexes with less bulky N-alky1 group or N-substitiuents are planar[5-6]. A wide range of penta-coordinated Cu(II) complexes of both trigonal bipyramidal and square pyramidal types have been reported[7].

The magnetic moments in Cu(II) complexes are not very informative with respect to stereochemistry and in such cases spectral studies are more reliable. The observed magnetic moment values of octahedral Cu(II) complexes fall in the range 1.8 to 2.1 B.M.[8]. The tetrahedral Cu(II) complexes shows magnetic moment values in the range 1.9-2.0 B.M.[9]

The magnetic moment is expected to be around 1.9 B.M. at room temperature for octahedral or tetrahedral Cu(II) complexes due to larger separation of interaction term i.e. spin orbital coupling constant. The theoretically expected magnetic moment value is 2.2 for ^2T_2g ground term in Cu(II) complexes[10]. Normal μ_{eff} value is greater than 1.9 B.M. for tetrahedral and less than 1.9 B.M. for square planar or pseudo octahedral Cu(II) complexes.

The copper (II) complexes can be broadly classified on the basis of magnetic properties into two categories. The one having temperature independent magnetic moment in the range 1.75 to 2.2 B.M. and the other has substantially low magnetic moment values than spin only value and are temperature dependent. The first category of Cu(II) complexes are essentially mononuclear without any interaction of the unpaired electrons on different Cu(II) ions. The second category of Cu(II) complexes has low magnetic moment values due to coupling of the spin when pair of copper (II) ions is held together[12,13].

The magnetic behavior of Cu(II) complexes is the spin exchange between copper atoms in seemingly magnetically dilute compounds. As expected, Cu(II) complexes have a doublet ground state; and the values of magnetic moment correspond to one unpaired electron and are usually a little bit above the spin only value of 1.73 B.M.

Most of the Cu(II) complexes are blue or green because of single broad absorption band in the region 10000-16000 cm^{-1}. A detailed interpretation of the electronic absorption spectra of Cu(II) complexes is rather complicated because of distorted octahedral or square planar geometry. Octahedral complexes without any distortion are expected to have only one transition $^2E_g \rightarrow ^2T_{2g}$. Due to Jahn-Teller Effect, the system becomes unstable resulting into distortion (D_{2h}). This leads to further splitting of E_g and T_{2g} levels into B_{1g}, A_{1g} and B_{2g} levels respectively. A broad band with several components is observed at 16000 cm^{-1} in the visible region and often a broad tail into the near infrared region[14]. This is due to Jahn-Teller distortion of regular octahedral to tetrahedral gemoetry[8]. As the distortion of tetrahedral geometry towards square planar continues, the band moves towards higher energy[15]. Regular tetrahedral Cu(II) complexes give a single band in near Infrared region without any absorption in the region 10000 to 20000 cm^{-1} corresponding to $^2T_{2g} \rightarrow ^2E_g$. However, low energy bands are observed in the visible region at 14700 cm^{-1} ($^2B_{1g} \rightarrow {}^2A_{1g}$) and 17900 cm^{-1} ($^2B_{1g} \rightarrow {}^2E_g$)[16].

Tetragonal distortion results into splitting of E_g and T_{2g} levels, so that more than one d-d transitions are to be expected for Cu(II) complexes. Three possible energy level sequences are suggested in order of increasing distortions.

i) $^2B_{1g} < {}^2A_{1g} < {}^2B_{2g} < {}^2E_g$

ii) $^2B_{1g} < {}^2A_{2g} < {}^2A_{1g} < {}^2E_g$

iii) $^2B_{1g} < {}^2B_{2g} < {}^2E_g < {}^2A_{1g}$

Copper (II) being a one-positron case; the following transitions are possible. [4,17,18]

For weakly distorted.

$d(x^2-y^2) \rightarrow d(xy)$ $^2A_{1g} \rightarrow {}^1A_{1g}$

$d(x^2-y^2) \rightarrow d(z^2)$ $^2B_{1g} \rightarrow {}^2B_{2g}$

$d(x^2-y^2) \rightarrow d(yz, xz)$ $^2B_{1g} \rightarrow {}^2E_g$

For strongly distorted

$d(x^2-y^2) \rightarrow d(z^2)$ $^2B_{1g} \rightarrow {}^2B_{2g}$

$d(x^2-y^2) \rightarrow d\ (yz, xz)$ $^2B_{1g} \rightarrow {}^2E_g$

$d(x^2-y^2) \rightarrow d(xy)$ $^2B_{1g} \rightarrow {}^2A_{1g}$

Thus, the three bands due to these transitions are expected to appear in the visible and near IR region and are very close together. Octahedral coordination around metal ions is also supported by the number and position of electronic spectral bands[19-20].

4.1.2 Elemental Analysis and Solution Conductivity:-

All the Cu(II) complexes synthesized from Schiff bases are coloured and stable to air and moisture. They are insoluble in polar solvent but sparingly soluble in methanol, ethanol, dimethylformamide and dimethy1sulphoxide. Most of them decompose at high temperature without melting.

The observed solution conductivities of Cu(II) complexes are presented in Table 2.4. The low conductivity values in DMF reveal their non-electrolytic nature. The elemental analysis (Table 2.9) shows that the metal to ligand ratio in all Cu(II) complexes is 1:2

4.1.3 Magnetic Susceptibility and Absorption Spectral Studies:–

The observed magnetic moment values of the Cu(II) complexes in the present investigation were found to be in the range 1.81–1.98 B.M. at room temperature corresponding to one unpaired electron. The magnetic moment values of Cu(II) complexes are slightly higher than spin only valve (1.73 B.M.) for one unpaired electron can be attributed to spin–orbit coupling[21] indicative of distorted or pseudo-octahedral gemoetry[22]

The electronic absorption spectra of Cu(II) complexes showed a broad band at 15106-16313 cm^{-1} and at 27855-28902 cm^{-1}. These values fall within the range of mainly pseudo octahedral complexes reported earlier[23-27].

The electronic absorption spectral data of Cu(II) complexes are presented in Fig. 4.1 to 4.8. The ligand field parameter values (Dq and LFSE) observed in the range 1510-1631cm^{-1} and 44.10-46.81 Kcal mol^{-1} respectively (Table 4.6) are in good agreement with the pseudo octahedral Cu(II) complexes. The magnetic moments and electronic absorption spectral data of Cu(II) complexes are presented in Table 4.1.

Upadhyaya, et.al.[22] studied Cu(II) complexes of 2-amino-4-methyl, 2-amino-4-ethyl benzothiazoles. The complexes showed magnetic moment values in the range 1.53-1.83 B.M. and suggested octahedral structure for these complexes.

Mishra, et.al.[28] reported Cu(II) complexes of Schiff bases derived from benzyl – 2, 4-dinitro phenyl hydrazones and observed the magnetic moment values in the range 1.78-1.84 B.M. All complexes exhibit one broad band at 14800-15500 cm^{-1} region indicating distorted octahedral geometry.

Sharada, et.al.[29] synthesized Cu(II) complexes of 6-chloro-4-hydroxy cumarin. They observed the magnetic moment 1.85 B.M. Some of the complexes exhibit an intense broad band at 15385 cm^{-1} attributed to $^2Eg \rightarrow {}^2T_2g$ transition and suggested distorted octahedral geometry. Macrocyclic Cu(II) complexes of Schiff Base ligands have been synthesized and analyzed by Reddy, et.al.[30]. The magnetic moment of Cu(II) complexes was reported to be in between 1.69 and 1.73 B.M., corresponding to one unpaired electron. Electronic spectra in DMF showed broad band maxima at to 16230 cm^{-1} and 17479 cm^{-1} respectively with a shoulder on the low energy side at 13650-15620 cm^{-1} and additional band at 24000 cm^{-1} assignable to charge transfer transitions suggesting distorted octahedral structure to these complexes.

Table 4.1 MAGNETIC AND ELECTRONIC ABSORPTION SPECTRAL DATA OF Cu(II) COMPLEXES.

Cu(II) complex of	μ_{eff}**(B.M.)**	**Absorption Maxima cm^{-1} (nm)**	
		$^2Eg \rightarrow {}^2T_2g$	**Charge transfer**
L1	1.87	15699 (637)	27933 (358)
L2	1.81	15798 (633)	28490 (351)
L3	1.95	15106 (662)	27933 (358)
L4	1.85	15129 (661)	28329 (353)
L5	2.09	16234 (616)	28090 (356)
L6	1.82	15385 (650)	28329 (353)
L7	1.93	15552 (643)	27855 (359)
L8	1.91	16313 (613)	28653 (349)

Khare, et.al.[31] studied some Schiff base Cu(II) complexes and observed the magnetic moment values in the range 1.89-1.95 B.M. and electronic absorption band in the range 12658-16393 cm^{-1} assigned to $^2Eg \rightarrow {}^2T_2g$ transitions. They reported the values of 10Dq and LFSE as 1548 cm^{-1} and 108.89 KJmol^{-1} respectively, favouring an octahedral geometry for these complexes.

Hiremath et.al.[32] synthesized and characterized Cu(II) complexes of Schiff Bases. The light green coloured Cu(II) complexes showed magnetic moment of 1.81 B.M. and a broad asymmetric band in the region 15380-16670 cm^{-1} in their electronic spectra assignable to $^2Eg \rightarrow {}^2T_2g$ transition associated with a distorted octahedral geometry.

Schiff bases of thiophenealdehyde derivatives of o- and m-phenylenediamine and their complexes with Cu(II) were reported by Satpathy et.al.[33] They observed the magnetic moment values in the range 1.89-1.95 B.M. and the electronic spectral bands in all the complexes around 16666cm^{-1} indicating their distorted octahedral geometry.

Synthesis and characterization of Schiff base Cu(II) complexes was done by Souza et.al.[34]. They observed magnetic moment values in the range 1.86-1.92 B.M. The electronic spectra of these complexes showed a very broad band in the region 14000-16000 cm^{-1}, with a shoulder at 12500 cm^{-1}, these absorption maxima were consistent with tetragonally distorted octahedral geometries for Cu(II) of approximate D_{4h} symmetry. The high intensity band observed at 20830 cm^{-1} and 21740 cm^{-1} were assigned to a charge transfer transitions.

4.1.3 Conclusion:-

In the present investigation, on the basis of solution conductivity, elemental analysis, magnetic moment, electronic absorption spectral data, 10Dq and LFSE values, a distorted octahedral geometry to mononuclear Cu(II) complexes may be suggested. The higher LFSE values of Cu(II) complexes shows that the complexes are more stabilized than Co(II), Ni(II), Mn(II) and Fe(III) complexes of Schiff bases derived from DHA and aromatic amine.

4.2 COBALT (II) COMPLEXES–

4.2.1 Theoretical Consideration: –

The Co(II) ion having d^7 configuration, forms number of complexes in various stereochemical types. Most of them were found to have either octahedral or tetrahedral geometry. However quite a good number of complexes of Co(II) with low spin, square planar and five coordinated geometries were reported. Co(II) complexes with three unpaired electrons may be either octahedral or tetrahedral[35].

Co(II) forms tetrahedral complexes than any other transition metal ion particularly with large ligands. This is in accordance with respect to d^7 configuration, which favours tetrahedral configuration relative to octahedral one. Due to the small stability difference between octahedral and tetrahedral Co(II) complexes, the complexes of both types with same ligand may be in equilibrium. The d^7 Co(II) is less satisfactory to Jahn-Teller distortion unless there is a sufficient strong field to induce spins pairing. In octahedral configuration, the ground state for Co(II) is t_{2g}^5, e_g^2 or t_{2g}^6, e_g^1 out of these, the latter one is rare because the high ligand field energy is required owing to Jahn-Teller distortion.

Numbers of cobalt (II) complexes having 1:2 (metal to ligand) stoichiometries are very well known and have been studied for different physicochemical properties.[36-37]. Some Co(II) complexes of 1:1 stoichiometry are also known, where the extra ionic charge on the central metal ion is neutralized by the anions like halide, sulphate, acetate etc.[38] Sindhwani and Singh[39] reported some Co(II) complexes with 1:3 metal to ligand stoichiometry. In octahedral field, the ground state $^4T_{1g}$ is three-fold orbitally degenerate state and causes an orbital contribution to the magnetic moment. The high spin octahedral complexes show the magnetic moment up to 5.2 B.M. at room temperature, the spin only value being 3.8 B.M. only for three unpaired electrons. For low spin octahedral Co(II) complexes possessing ^2E_g ground term, the observed magnetic moments are in the range of 1.8 – 1.9 B.M. which is very close to the spin only value (1.73 B.M.) and is temperature dependent[10]. Low spin octahedral complexes are expected only with the ligands of strong fields at the far end of the spectrochemical series. True octahedral complexes may not be expected due to a large Jahn-Teller distortion for t_{2g}^6, e_g^1 configuration. The very few known five coordinated Co(II) complexes show magnetic moment equivalent to one unpaired electron, Earnshaw and coworkers[40] have reviewed the chemistry of five coordinated complexes of Co(II).

The low spin tetrahedral Co(II) complexes exhibit magnetic moment values 1.92-2.47 B.M. at room temperature, which varies with temperature. The high spin Co(II) complexes with $^4A_2$ ground state are tetrahedral assumed to have angular moments leading to verification in the observed magnetic moment values in the range 4.2-4.8 B.M. The expected spin only value for three unpaired electrons is 3.88 B.M.

The rarely occurring square planer complexes of Co(II) are low spin with magnetic moment values in the range 2.2 to 2.9 B.M. at room temperature. The entire study of the spectral and magnetic properties of these complexes is not well known.

Magnetic exchange has been observed in a number of Co(II) complexes which leads to the lower values of magnetic moments[41]. Binuclear Co(II) complexes have been prepared and it is shown that there is antiferromagnetic spin exchange interaction between two metal atoms[42]. As the Co(II) complexes occur in variety of geometries, the spectral and magnetic properties of the ion are extremely varied.

In octahedral Co(II) complexes $^4T_{2g}$ and ^2E_g are the spin-free and spin-paired ground states arising from t_{2g}^5, e_g^2 (high-spin) and t_{2g}^6, e_g^1(low-spin) configurations respectively. A band near 8000-10000 cm^{-1} may be assigned to the $^4T_{1g}$ (F) → $^4T_{2g}$ (υ_1) to the lowest transition and a multiple band observed around 20000 cm^{-1} to the $^4T_{1g}$ (F) → T_{1g} (P) (υ_3) to the highest transition. The asymmetric visible band is typical of octahedral Co(II) complexes. The existence of distortion from a regular octahedral symmetry is indicated by an appreciable enhancement of intensity of electronic absorption spectra. For low-spin octahedral Co(II) complexes, with ^2E ground state arises from t_{2g}^6, e_g^1 configuration, Jahn-Teller distortion would be expected.

The spectra of tetrahedral Co(II) complexes with $^4A_2$ ground term expected three transitions appearing as multiple absorption in the, far IR, near IR and visible regions.

$^4A_2 \rightarrow {}^4T_2$	3000 – 5000cm^{-1}
$^4A_2 \rightarrow {}^4T_1$ (F)	Near IR region
$^4A_2 \rightarrow {}^4T_1$ (P)	15000 – 20000cm^{-1}

The intensities are higher than those of octahedral complexes and allow a clear cut distinction between the two stereochemistries[43]. The absorption bands are located around 20,000 cm^{-1} in both the geometries and although the tetrahedral compounds frequently exhibit absorption maxima near 15000 cm^{-1}[,44]. The spectral properties of square planar complexes of Co(II) are of well established. All the square planar complexes studied[45] are low-spin configuration with a ground state $^2E_{2g}$ or $^2A_{1g}$. The electronic spectra of these compounds are complex and neither magnetic nor spectral properties have been studied in detail. The planar complexes indicate one or two absorption maxima in the visible region and one band around 8100–8600 cm^{-1}. Many square planar complexes exhibit one band near 20000 cm^{-1}, some workers have reviewed the spectra of five coordinate Co(II) complexes. Both high-spin and low –spin trigonal bipyramidal and square pyramidal Co(II) compounds have been found.

4.2.2 Elemental Analysis and Solution Conductivity:-

In the present investigation, all the Co(II) complexes are pinkish, brown coloured, stable to air and moisture but decompose at high temperature rather than showing sharp melting points. They are insoluble in water and soluble in DMSO, DMF and dioxane. The low conductivity values in DMF solution (1 x10^{-4} M) are given in Table 2.5 indicates non-electrolyte nature.

Elemental analysis data reveals that the observed values of percentage of C, H, N, halogen and metal ion are in good agreement with values predicted and calculated for Co(II) complexes with 1:2 metal to ligand ratio (Table 2.10).

4.2.3 Magnetic Susceptibility and Electronic Absorption Spectral Studies of Co(II) complexes: –

The magnetic moments of the Co(II) complexes are in the range 4.72 to 5.01 B.M. which are in agreement with the values reported in the range 4.7-5.20 B.M., expected for high spin octahedral complexes of which the spin only value is 5.20 B.M.[46]. The electronic absorption spectra of Co(II) complexes are presented in fig. 4.9 to 4.16. The observed magnetic moments and their electronic absorption spectral data are given in Table 4.2.

The electronic spectra of Co(II) complexes showed three bands at 10131-10224 cm^{-1}, 18868-21186 cm^{-1} and 27027-29240 cm^{-1} which are assignable to $^4T_{1g} \rightarrow {}^4T_{2g}(F)$, $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ and charge transfer transition respectively and are summarized in Table 4.2. The ligand field parameters for these complexes have been calculated following standard equation[7]. The calculated values of ligand field splitting energy (10Dq), Racha inter electronic repulsion parameter (B), covalent factor (β), ratio υ_2/υ_1 and ligand field stabilization energy (LFSE) support the octahedral geometry for Co(II) complexes. The nephelauxetic ratios (υ2/υ1) are found to be less than 2 indicating partial covalent character in the metal ligand bond[48,49,50]. These values are falling in the range of octahedral Co(II) complexes[51,52].

Thimmaiah et.al.[53] have observed the magnetic moment 4.77 B.M., for Co(II) complexes synthesized from vanillin thiosemicarbazone, and the electronic spectrum exhibit two bands at 9500 cm $^{-1}$ and 17250 cm^{-1} assigned to the transitions $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ and $^2T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ respectively, the transition is consistent with the assignment of a distorted six coordinated geometry.

Table 4.2 MAGNETIC AND ELECTRONIC ABSORPTION DATA OF Co(II) COMPLEXES.

Co(II) complex of	μ_{eff}(B.M.)	Absorption Maxima cm^{-1} (nm)		
		$^4T_{1g} \rightarrow {}^4T_{2g}(F)$	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	Charge transfer
L1	4.36	10162(984)	19305 (518)	28011 (357)
L2	4.50	10214(979)	19342 (517)	29240 (342)
L3	4.16	10204(980)	19569 (511)	28571 (350)
L4	4.46	10204(980)	21097 (474)	27933 (358)
L5	4.32	10224(978)	20920 (478)	28409 (352)
L6	4.69	10152(985)	18868 (530)	28169 (355)

L7	4.58	10172(983)	19305 (518)	28011 (357)
L8	4.72	10131(987)	19342 (517)	29240 (342)

Syamal et.al.[54] synthesized new Schiff bases derived from salicyladehyde and 5-methyl pyrazole-3-carbohydrazide and its Co(II) complexes. The complexes exhibits magnetic moment value 4.82 B.M. for high spin and pseudo-octahedral structure. The electronic spectral parameters of the Co(II) complexes are Dq = 977 cm^{-1}, B^1= 705 cm^{-1}, β= 0.72 and showed that the racha parameter B^1 is lower than the free ion value (971 cm^{-1}) indicating the orbital overlap and delocalization of d-orbitals.

Rao el.al.[55] studied the mixed ligand complexes of Co(II) with dehydroacetic acid as a primary ligand and heterocyclic bases as secondary ligands. The complexes possessed magnetic moment values in the range 4.40 – 4.71 B.M. which are characteristic of high spin octahedral complexes. The electronic spectra of these complexes displayed two main bands in the region 19500-21500cm $^{-1}$ and 8550-8930 cm^{-1} which are assigned to $^4T_{1g} \rightarrow {}^4T_{1g}$ (P) and $^4T_{1g}(F) \rightarrow {}^4T_{2g}$ transition respectively.

Panda et.al.[56] synthesized and characterized Co(II) complexes of Schiff bases of isonicotinic acid and hydrazide. They observed the magnetic moment in the range 4.78-4.79 B.M. and electronic absorption bands at 9000 cm^{-1}, 16200 cm^{-1} and 18900 cm^{-1} assigned to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$ respectively. The ratio of υ_2/υ_1 being less than 2 as required for octahedral complexes which supports the distorted octahedral geometry.

On the basis of elemental analysis, conductivity, magnetic moment and electronic absorption spectral measurement, the Co(II) complexes in present work may be suggested as monomeric structures with distorted octahedral geometry.

4.3 NICKEL (II) COMPLEXES–

4.3.1 Theoretical Considerations –

The Ni(II) has $3d^8$ configuration and extensively studied in coordination complexes. The main structural types of Ni(II) are octahedral, tetrahedral and square planar. Strong ligand fields pair up the unpaired electrons of Ni(II) complexes giving rise to formation of diamagnetic square planar or trigonal bipyramidal complexes. Weak ligands give rise to outer octahedral complexes, paramagnetic in nature, which are generally blue or green coloured. A considerable number of Nickel (II) complexes have been described as anomalous because they do not behave either entirely or under all conditions as per the expectations. With the knowledge of ligand field theory and advent of powerful physicochemical methods, most of the anomalies have been satisfactorily explained[43]. The magnetic moment values of octahedral Ni(II) complexes fall in the range 2.9-3.4 B.M. depending on the magnitude of the orbital contribution and a small temperature independent contribution. These values of magnetic moments are slightly higher than expected from spin only values of 2.83 B.M. due to spin orbit coupling and contribution from the $^3A_{2g}$ and the next higher $^3T_{2g}$ state. The magnetic moments are still higher (3.4 to 3.5 B.M.) in some tetragonally distorted complexes[57]. The diamagnetic pseudo octahedral Ni(II) complexes are also known[58]. The observed magnetic moments of tetrahedral geometries are in the range of 3.5-4.0 B.M. indicating higher orbital contribution due to an orbitally degenerate $^3T_1(P)$ term of tetrahedral ligand fields of Ni(II) complexes.

Square planar Ni(II) complexes are essentially diamagnetic with a small contribution from temperature independent paramagnetism. These complexes are mainly obtained with ligands capable of forming a highly covalent bond with a strong π bonding character.

The electronic spectra of Ni(II) complexes along with magnetic data provide a better insight into the stereochemistry. The colour of the complexes themselves gives an indication of the geometry in many instances, octahedral Ni(II) complexes and some times tetrahedral complexes are blue purple and green where as square planar complexes are red, yellow or brown.

In octahedral field, the triplet T_{2g} lies lower in energy than doublet e_g and the electronic configuration of the ground state may be written as T_{2g}^6, e_g^2. Spectra of octahedral Ni(II) usually consists of three bands which are assigned as [15].

$^3A_{2g}$ (F) → $^3T_{2g}$ (F) = 10Dq, 7000 – 13000 cm^{-1}

$^3A_{2g}$ (F) → $^3T_{1g}$ (F) = 10000 – 20000 cm^{-1}

$^3A_{2g}$ (F) →$^3T_{1g}$ (P) = 19000 – 27000 cm^{-1}

υ_1 gives the value of Δ or 10 Dq directly. In addition to above two weak spin forbidden transitions $^3A_{2g} \rightarrow {}^1E_g$ and $^3A_{2g} \rightarrow {}^1T_{2g}$ are also observed [59].

The tetrahedral complexes of Ni(II) have intense blue colour due to the presence of an absorption band in the red part of the visible region (~ 15000 cm^{-1}). The electronic spectra of paramagnetic tetrahedral Ni(II) complexes with $^3T_1$ (F) ground term show more intense bands when compared to octahedral complexes. The three spin allowed transitions in tetrahedral Ni(II) complexes are,

$\upsilon_1 = {}^3T_1(F) \rightarrow {}^3T_2$ (<7000 cm^{-1})

$\upsilon_2 = {}^3T_1(F) \rightarrow {}^3A_2$ (<7000 - 8000cm^{-1}) and

$\upsilon_3 = {}^3T_1(F) \rightarrow {}^3T_1(P)$ (15000 cm^{-1})

and two spin forbidden transitions are,

$^3T_1(F) \rightarrow {}^1T_2$ and $^3T_1(F) \rightarrow {}^1E$.

However, only four bands corresponding to the following transitions are observed [60-61]

$^3T_1$ (F) → $^1T_2$ (~7000 cm^{-1})

$^3T_1$ (F) → $^3T_1$(P) (~11000 cm^{-1})

$^3T_1$ (F) → ^1E (~15000 cm^{-1})

$^3T_1$ (F) → $^3A_2$ (~20000 cm^{-1})

The $^3T_1$ (F) → $^3T_1$(P) band is strong one with high intensity when compared to other bands[17].

Ni(II) complexes with square planar geometry do not show any absorption below 10000 cm^{-1} due to large crystal field splitting and hence can be distinguished from octahedral and tetrahedral complexes. These show strong absorption band in the range of 15000-25000 cm^{-1} and in many cases a second more intense band 23000 to 30000 cm^{-1}. Certain square planer complexes exhibit a low energy band near 11000 cm^{-1} which is very weak and is probably a spin forbidden transition[62]. The square planar Ni(II) complexes are frequently red, yellow or brown in colour.

4.3.2 Elemental Analysis, Solution Conductivity:-

The newly synthesized Ni(II) complexes in the present investigation are pink in colour. They are stable to air and moisture. The complexes decompose at a high temperature. In order to check solubility of Ni(II) complexes, different polar and non-polar solvents have been tried. It is observed that these complexes are insoluble in water but moderately soluble in DMSO, DMF, dioxane and chloroform. The solution conductivity values of these complexes in DMF (1.0×10^{-4} M) show that they are non-electrolyte in nature. The observed conductivity values of Ni(II) complexes are presented in Table 2.6.

The elemental analysis data (Table 2.11) indicate that the observed values of percentage of C, H, N, halide and metal ion are in good agreement with the values predicted and calculated assuming 1:2 metal to ligand ratio corresponding to monomeric nature of these Ni(II) complexes.

4.3.3 Magnetic susceptibility and electronic absorption spectral studies for Ni(II) complexes-

All the Ni(II) complexes in present investigation are diamagnetic in nature. This indicates the square planer geometry of complexes[63]. The electronic spectra of Ni(II) complexes studied in the present investigation exhibit absorption bands around 17100 cm^{-1} and 26600 cm^{-1} which also supports the square planer geometry[63]. The electronic spectra of these complexes are given in fig. 4.17 to 4.24 and their spectral data are presented in Table 4.3.

In the complexes of Ni(II) the bands appeared in the region 17006-17543 cm^{-1} and 25773-27778 cm^{-1} transition are assigned to $^1A_{1g} \rightarrow {}^1T_{2g}$ transition and charge transfer transition. The absence of band below 10,000 cm^{-1} indicates square planer geometry[64].

Rao et.al.[65] reported Ni(II) complexes of Schiff bases derived from 1-tyrosin hydrazide and o-hydroxy acetophenone. The diamagnetic nature for the complexes suggest square planer geometry and bands observed at 1600 cm^{-1} and 21050 cm^{-1} in electronic spectra was assigned to the $^1A_{1g} \rightarrow {}^1T_{2g}$ and $^1A_{1g} \rightarrow {}^1B_{1g}$ transitions respectively.

Bahad et.al.[66] synthesized Ni(II) complexes with Schiff base ligands bis-(2-hydroxy-5methyl acetophenone)-1,3diamino propane and bis-(2-hydroxy-5chloro acetophenone)-1,3diamino propane. The dimagnetic chelates show two bands at 17750-18000 cm^{-1} and 23950-24000 cm^{-1} which were assigned to the transition $^1A_{1g}$ to $^1T_{2g}$ and $^1B_{1g}$ respectively indicates square planer geometry.

Venkateshwar Rao et.al.[67] have synthesized Ni(II) complexes from tetradentate Schiff base derived from dehydroacetic acid and thiocarbohydrazide. The diamagnetic complexes shows electronic spectral bands at 15267 and 22989cm^{-1} were assigned to $^1A_{1g} \rightarrow {}^1T_{2g}$ and $^1A_{1g} \rightarrow {}^1B_{1g}$ transitions in square planer geometry.

Table 4.3 MAGNETIC AND ELECTRONIC ABSORPTION SPECTRAL DATA OF Ni(II) COMPLEXES.

Ni (II) complex of	**Magnetic Nature**	**Absorption Maxima cm^{-1} (nm)**	
		$^1A_{1g} \rightarrow {}^1T_{2g}$	Charge transfer
L1	Diamagnetic	17006(588)	25773(388)
L2	Diamagnetic	17035(587)	26455(378)
L3	Diamagnetic	17006(588)	26525(377)
L4	Diamagnetic	17006(588)	27778(360)

L5	Diamagnetic	-	26954(371)
L6	Diamagnetic	17182(582)	26110(383)
L7	Diamagnetic	17152(583)	25773(388)
L8	Diamagnetic	17543(570)	26316(380)

Abdula et.al.[68] have reported electronic transition for square planer Ni(II) complexes at 370nm (27027cm^{-1}) is due to charge transfer and at 460-510nm (21739-19607cm^{-1}) is due to d-d transition for the diamagnetic Ni(II) complexes of Schiff bases derived from dehydroacetic acid and thiosemicarbazide.

4.4 MANGANESE (II) COMPLEXES:-

4.4.1 Theoretical Consideration:-

The Mn(II) has d^5 configuration. The divalent state of manganese is the most stable and important oxidation state. It forms an extensive series of salt with all common anions. The most common stereochemical state of Mn(II) in its complex is octahedral. However, the complexes of other geometries such as tetrahedral, square planer, 5-coordinate and 7-coordinate have been reported. Tetrahedral complexes of Mn(II) are not stable in contact with water or other donor solvents, but they exist as crystals in solvents of low or moderate polarity such as nitrobenzene, chloroform, methylnitrile etc. Polynuclear complexes of Mn(II) show high spin behavior and hence low ligand field stabilization energy. The high spin (weak field) complexes are expected to have the spin only magnetic moment of ~5.92 B.M. because the crystal field or spin orbit coupling alone is unable to lift the six fold degeneracy of the $^6A_{1g}$ state and five unpaired electrons. The expected magnetic moments thus are close to 5.92 B.M.

However, in many Schiff base complexes the observed magnetic moment fall in the range 4.7 to 5.7 B.M. at room temperature[8].

The octahedral low-spin complexes with $^2T_{2g}$ ground term and spin orbit coupling constant λ = -300 cm^{-1} gave magnetic moment of 2.5 B.M. which decreases with temperaure[8]. The magnetic moments of tetrahedral complexes have been found to close to the spin only value. Since $^6A_{lg}$ ground state persists in all symmetries, the moments of octahedral and tetrahedral high-spin complexes are close to each other i.e. 5.92 B.M. The square planar complexes of phthalocyanine with Mn(II) has a $^4A_{lg}$ ground state and does not obey Curie-Weiss law.

In tetrahedral environment, Mn(II) has intense green yellow colour, compared to the pink colour of the octahedrally coordinated ion. In the case of tetrahedral complexes, values are in the range 1.02 to 4.0 B.M. The greater intensity in tetrahedral complexes is due to the greater overlap of metal orbitals with ligand orbitals.

Many high spin octahedral Mn(II) complexes are very light coloured and intensities of transitions are extremely low. However, four lowest energy bands are observed in the visible region corresponding to different transitions having octahedral geometry[69].

$$^6A_{lg} \rightarrow {}^4T_{lg}$$

$$^6A_{lg} \rightarrow {}^4T_{2g}$$

$$^6A_{lg} \rightarrow {}^4E_g \text{ and } {}^4A_{lg}$$

Mn(II) ions in tetrahedral environment have a noticeable pale yellow-green colour and have transition about 10 times stronger than octahedral environment. This may be due to greater overlap of metal 3d orbitals with ligand orbitals.

4.4.2 Elemental Analysis, Solution Conductivity:-

The Mn(II) complexes are dark brown in colour. They are stable to air and moisture at room temperature. The complexes decompose at high temperature, rather than showing sharp melting point. They are insoluble in common polar solvents but partially soluble in DMSO, DMF. The observed conductivity of Mn(II) complexes are reported in Table 2.7. The low solution conductivity of 10^{-4} M solutions of Mn(II) complexes in DMF are suggestive of their non-electrolytic nature.

The elemental analysis data given in (Table 2.12) of Mn(II) complexes suggest 1:2 metal to ligand stoichiometry in a monomeric structure.

4.4.3 Magnetic susceptibility and electronic absorption spectral studies for Mn(II) complexes:-

The magnetic moment of Mn(II) complexes in the present investigation are in the range 5.7 to 6.00 B.M., which are almost close to the spin only value of 5.92 B.M. However, these values are fairly in good agreement with the moments reported for mononuclear high spin octahedral Mn(II) complexes by earlier workers[70-72].

The observed magnetic moments of Mn(II) complexes are given in Table 4.4. The electronic absorption spectra of Mn(II) complexes and their band positions are presented in Fig. 4.25 to 4.32 respectively (Table 4.4).

Table 4.4 MAGNETIC AND ELECTRONIC ABSORPTION SPECTRAL DATA OF Mn(II) COMPLEXES.

Mn(II) complex of	**μ_{eff}(B.M.)**	**Absorption Maxima cm^{-1} (nm)**		
		$^6A_{1g}\rightarrow{}^4T_{1g}(G)$	$^6A_{1g}\rightarrow{}^4T_{2g}(G)$	Charge transfer
L1	5.85	14706(680)	24272(412)	31949(313)
L2	5.98	14793(676)	24752(404)	31746(315)
L3	5.53	15152(660)	24691(405)	31546(317)
L4	6.00	14599(685)	24096(415)	31847(314)
L5	5.89	15106(662)	23981(417)	32258(310)
L6	5.70	14925(670)	24038(416)	32154(311)
L7	5.91	15151(660)	24876(402)	32467(308)

L8	5.87	14706(680)	24814(403)	32258(310)

The electronic absorption spectra of Mn(II) complexes were showed three bands at 14599 to 14948 cm^{-1}, 24876 to 24331 cm^{-1} and 31948 to 30581 cm^{-1} assignable to $^6A_{lg}\rightarrow{}^4A_{lg}(G)\rightarrow{}^4T_{lg}(G)$, $^6A_{lg}\rightarrow{}^4T_{2g}(G)$ and $^6A_{lg}\rightarrow{}^6A_{lg}(G)$/Charge transfer indicating octahedral geometry around the metal ion[73-75]. Thimmaiah et.al.[76] synthesized vanillin thio-semicarbazone and prepared Mn(II) complexes. The magnetic moment reported for the same was 5.90 B.M. The electronic spectra showed bands at 15000 cm^{-1}, 24800 cm^{-1} and 34300 cm^{-1}. On he basis of magnetic susceptibility and electronic spectra, the geometry assigned by them to Mn(II) complexes was octahedral.

Mn(II) norfloxacin complexes have been prepared and studied by Choubey et.al.[73]. The electronic spectral bands at 13800, 16300 and 19200 cm^{-1} were assigned to transitions $^6A_{lg}\rightarrow{}^4T_{lg}$ (^4G), $^4T_{1g}$ (^4G) and $^4A_{1g}$ (^4G) respectively. The observed magnetic moments of 5.8 B.M. suggested octahedral environment around Mn(II) ion.

Shrivastav et.al.[77] reported Mn(II) complexes and observed weak bands at 12658, 21276, and 24390 cm^{-1}. Since Mn(II) has d^5 electronic configuration, the same type of energy level diagram applies for metal ions surrounded by octahedral environment.

Complexation of 6-chloro-4-hydroxy-3-acetyl cumarin with Mn(II) was studied by Sharada et.al.[78]. The magnetic moment of the complex is 5.6 B.M. and the electronic absorption at 17241, 21217, and 24290 cm^{-1} suggest the octahedral geometry. The transitions assigned above band were $^6A_{lg}\rightarrow{}^4T_{lg}(4D)$, $^6A_{lg}\rightarrow{}^4T_{2g}$ and $^6A_{lg}\rightarrow{}^4E_g$ respectively.

It is reported that the electronic spectra alone cannot prove tetrahedral or octahedral geometry. Since for Mn(II) with d^5 configuration, the same type of energy level diagram applies whether the metal ion is surrounded by tetrahedral or octahedral environment.

Various ligand field parameters such as (10Dq), ligand field splitting energy, Racah interelectronic repulsion parameter (B) , covalent factor (β) , ratio υ_2/υ_1 and ligand field stabilization energy (LFSE) for Mn(II) complexes have been calculated following standard equations[7,46-48] and are presented in Table 4.6.

The reduction of Racah parameter to 718.83-809.85cm^{-1} for all the complexes from the free ion value of 960cm^{-1} indicates complex formation, thereby favouring the overlap and delocalization of d-orbital. The covalent factor (β) in each case is less than unity (0.74-0.84) indicates partial covalent character in metal ligand bond[49-50]. The LFSE values (41-43 Kcal mol^{-1}) suggest sufficient stability of the complexes. The Dq values (1470-1515 cm^{-1}) and the energy ratio υ_2/υ_1 values (1.58-1.68) being less than 2 also support the octahedral geometry of all Mn(II) complexes.

Based on the inferences drawn from the literature on analogous compounds and the interpretations on the conductivity, elemental and metal analysis, magnetic moment and electronic spectral data of complexes, a mononuclear structure with octahedral geometry may be suggested to Mn(II) complexes in the present work.

4.5 IRON (III) COMPLEXES-

4.5.1 Theoretical consideration-

Iron (III) with d^6 configuration forms a large number of complexes mostly octahedral. Depending on the ligand field, generally three types of Fe(III) complexes can be expected. The high spin (S=5/2), low spin (S=1/2) and intermediate spin (S=3/2), crossover complexes are very well characterized by Kanungo et.al.[79]. The cross over of ferric has ligand field strength near the crossover point of low spin and high spin. These are very well known for six coordinated iron (III) complexes. Literature survey reveals the formation of few tetrahedral and square planar Fe(III) complexes[80]. Fe(III) is isoelectronic with Mn(II) and magnetically it favors high spin complexes except with strong field ligands like CN^-, bipyridyl and phenanthroline. The high spin octahedral Fe(III) complexes with d^5 configuration give rise to ground term $^6A_{1g}$ and low spin complexes with ground term ^2T_g. The high spin complexes of Fe(III) show magnetic moments very close to spin only value of 5.92 B.M. The low spin complexes show higher magnetic moment values than spin only value of 1.73B.M. due to considerable orbital contribution to their magnetic moments at room temperature[10] . Some sulphur donor atoms in ligands forming Fe(III) complexes show anomalous magnetic moments between 3.8 to 4.05 at room temperature. These values lies between the values of high spin and low spin complexes. Polymeric complexes without Fe-O-Fe bridges have been reported to possess subnormal magnetic moments[81].

The electronic absorption spectra of octahedral Fe(III) complexes show multiple and very weak bands due to spin and multiplicity forbidden transitions. In octahedral Fe(III) complexes $^6A_{1g}$ and $^2T_{2g}$ are the high spin and low-spin ground terms derived from t_{2g}^3, e_g^2 (spin free) and t_{2g}^5 e_g^0 (spin paired) configurations respectively.

Electronic absorption spectra of octahedral iron (III) complexes show multiple and very weak bands due to spin and multiplicity forbidden transitions similar to Mn(II) complexes. However, Fe(III) carries an additional positive charge and consequently its greater ability to polarize coordinated ligands, produces intense charge transfer band at much lower energies than those of Mn(II) complexes.

Following transitions are expected to occur in Fe(III) octahedral complexes[85-86].

$^6A_{1g} \rightarrow {}^4T_{1g}(G)$

$^6A_{1g} \rightarrow {}^4T_{2g}(G)$

$^6A_{1g} \rightarrow {}^4A_1 \rightarrow {}^4E(G)$

$^6A_{1g} \rightarrow {}^4T_{2g}(D)$

$^6A_{1g} \rightarrow {}^4E(D)$.

These assignments are not certain due to charge transfer bands in the visible region and near ultraviolet region in Fe(III) complexes and which almost completely mask the very weak d-d bands.

Low spin octahedral Fe(III) complexes have been theoretically explained with regard to their magnetic and spectral behaviour[82].

The electronic spectra of octahedral Fe(III) complexes have not been satisfactorily interpreted owing to the very much greater tendency of the trivalent ion to give charge transfer bands in near ultraviolet region with its sufficiently strong low energy wings in the visible region[68]. The spectral features of Fe(III) ions in octahedral surroundings are in accordance with theoretical considerations.

The tetrahedral high-spin Fe(III) complexes reported to give a well defined spectrum with fairly narrow bands, but the assignments of various bands have not been made satisfactorily[83].

4.5.2 Elemental Analysis, Solution Conductivity -

In the present investigation, all the Fe(III) complexes synthesized are dark brown in colour and are stable to air and moisture at room temperature. They decompose at high temperature without melting. All of them are insoluble in water but partly soluble in DMSO, DMF, dioxane.

The low solution conductivity values in (10^{-4}M) solution indicate their non-electrolyte nature. Elemental analysis reveals that the Fe(III) complexes have 1:2 metal to ligand ratio in monomeric structure. The data is represented in Table 2.8 and 2.13 respectively.

4.5.3 Magnetic Susceptibility and Electronic Absorption Spectra:-

In the present investigation, all the Fe(III) complexes have magnetic moments values in the range 5.67-5.97 B.M. which are almost close to that of required for octahedral geometry. However, these values are slightly lower than the normal values for high-spin monomeric octahedral Fe(III) complexes reported earlier[84-85].

The observed magnetic moments of the complexes are presented in Table 4.5. The electronic absorption spectra of these complexes and their positions are shown in Fig. 4.33 to 4.40 and presented in Table 4.5 respectively.

The spectrum shows three bands at 15297-16181, 22936-24630 and 30769-32778cm^{-1}, which may be, assigned to high spin octahedral complexes, for transitions $^6A_{1g}\rightarrow{}^4T_1(D)$, $^6A_{1g}\rightarrow{}^4T_1$ and $^6A_{1g}\rightarrow{}^4T_{2g}$ respectively[86] corresponds to octahedral symmetry.

The last d-d band assigned to transition $^6A_{1g}\rightarrow{}^4T_{2g}$ in the present case may be associated with the charge transfer bands traveling into visible region of spectra[87].

The solid complexes of Fe(III) with N,N,-diphenyl benzamide have been synthesised and characterised on the basis of elemental analysis, magnetic, thermal and infrared spectra by Verma et.al.[86]. The magnetic moment value ~5.75 B.M. shows the presence of 5 unpaired electrons in Fe(III) complexes. The electronic spectra showed only two bands at 12195 and 18181 cm^{-1}. The complexes of Fe(III) with thiazoline thiones were studied by Sengupta et.al.[83]. The complexes were synthesized and characterized by elemental analysis, magnetic moment, infrared and electronic spectra. They reported 1:2 metal to ligand ratio for the complexes. The electronic spectra showed bands in the region 15000-15500, 16000-18000 and 23000-23500 cm^{-1} attributed to $^6A_{1g}\rightarrow{}^4T_{2g}(^4D)$, $^6A_{1g}\rightarrow{}^1T_{1g}$ and $^6A_{1g}\rightarrow{}^4T_{2g}(G)$ transitions respectively assigned pseudo-octahedral geometry. This was also supported by the magnetic moment values (4.2-4.5B.M.) for the complexes.

Fe(III) complexes of bidentate Schiff base ligands of dehydroacetic acid with some aromatic amines were synthesised and characterised by Shirodkar[87], the results of physicochemical analysis, shows 1:2 metal to ligand stoichiometric ratio. The magnetic moment of the complexes was reported in the range 4.52-5.8 B.M. The electronic spectra showed bands in the region 16666-17000, 22985-25000 and 26660-27777cm^{-1} assigned to $^6A_{1g}\rightarrow{}^4T_2(D)$, $^6A_{1g}\rightarrow{}^4T_{1g}$ and $^6A_{1g}\rightarrow{}^4T_{2g}$ respectively. He suggested monomeric structure with high spin octahedral geometry for Fe(III) complexes.

Table 4.5 MAGNETIC AND ELECTRONIC ABSORPTION SPECTRAL DATA OF Fe(III) COMPLEXES.

Fe(III) complex of	**μ_{eff}(B.M.)**	**Absorption Maxima cm^{-1} (nm)**		
		$^6A_{1g}\rightarrow{}^4T_{2g}(^4D)$	$^6A_{1g}\rightarrow{}^4T_1$	Charge transfer
L1	5.67	15873(630)	24390(410)	30769(325)
L2	5.81	15674(638)	24038(416)	32787(305)

L3	6.05	15924(628)	24630(406)	32154(311)
L4	6.07	15552(643)	25189(397)	31746(315)
L5	5.73	16181(618)	23696(422)	32573(307)
L6	5.38	15504(645)	24510(408)	31153(321)
L7	5.54	15267(655)	22936(436)	31645(316)
L8	6.03	15625(640)	23148(432)	31847(314)

The magnetic moment of Fe(III) complexes of monothio-β-diketones were reported at 5.15-5.2 B.M. by Saini, et.al.[88].

The ligand field parameters such as ligand field splitting energy (10Dq), Racah interelectronic repulsion parameter (B), covalent factor (β), (υ_2/υ_1) and ligand field stabilization energy for Fe(III) complexes have been calculated following standard equations[7] and values are presented in Table 4.10.

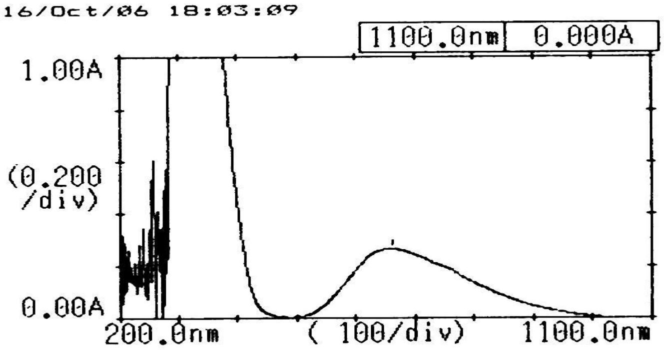
The reduction of Racah parameter to 502-685cm^{-1} for all the complexes from the free ion 1015cm^{-1} indicates complex formation, there by favouring the orbital overlap and delocalization of d-orbitals. The β-values obtained are less than one (0.49-0.67) in each case reveals the presence of considerable amount of covalent character of the metal ligand bond. The LFSE (43-46) indicate considerable stability of the Fe(III) complexes. The υ_2/υ_1 ratio (1.46-1.61) being close to reported values, and the 10Dq value found (1526-1618) indicate that all Fe(III) complexes are in octahedral geometry.

On the basis of inferences drawn from the literature on Schiff bases metal complexes and interpretation of data on the conductivity, elemental and metal analysis, magnetic and electronic absorption spectral measurements of complexes, a monomeric structure with octahedral geometry may be proposed to Fe(III) complexes in the present study.

Table 4.10 Ligand field parameter of Cu(II), Co(II), Ni(II), Mn(II) and Fe(III) Complexes.

Complexes	10Dq (cm^{-1})	B' (cm^{-1})	$\beta = B/B'$	$\nu 2/\nu 1$	LFSE (Kcal mol^{-1})
Cu-L1	1569.859			1.193	45.054
Cu-L2	1579.779			1.194	45.339
Cu-L3	1510.574			1.119	43.353
Cu-L4	1512.859			1.158	43.419

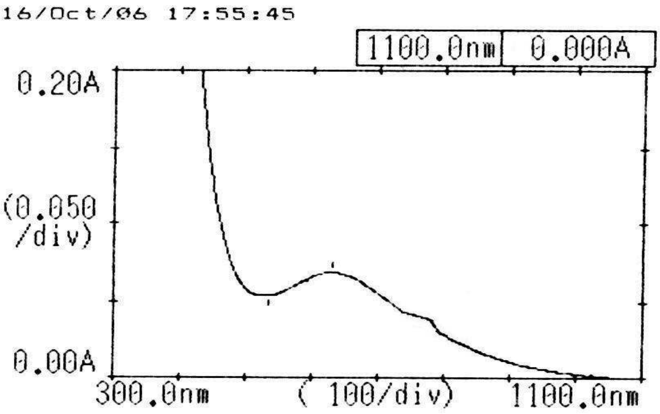
Cu-L5	1623.377			1.246	46.590
Cu-L6	1538.462			1.184	44.153
Cu-L7	1555.210			1.185	44.634
Cu-L8	1631.321			1.171	46.818
Co-L1	1165.501	823.412	0.848005	1.656	33.298
Co-L2	1162.791	913.227	0.940502	1.663	33.220
Co-L3	1179.245	850.902	0.876316	1.659	33.691
Co-L4	1201.923	864.821	0.890650	1.755	34.338
Co-L5	1173.709	941.221	0.969332	1.782	33.532
Co-L6	1176.471	782.854	0.806236	1.603	33.611
Co-L7	1183.432	707.202	0.728324	1.612	33.810
Co-L8	1203.369	873.104	0.899180	1.760	34.380
Mn-L1	1470.588	806.872	0.840492	1.650	42.014
Mn-L2	1479.290	807.987	0.841653	1.673	42.263
Mn-L3	1515.152	718.836	0.748788	1.629	43.287
Mn-L4	1459.854	809.859	0.843604	1.650	41.708
Mn-L5	1510.574	728.110	0.758449	1.587	43.157
Mn-L6	1492.537	761.112	0.792825	1.610	42.641
Mn-L7	1515.152	792.573	0.825598	1.641	43.287
Mn-L8	1470.588	863.620	0.899605	1.687	42.014
Fe-L1	1587.302	502.695	0.495266	1.536	45.349
Fe-L2	1567.398	653.560	0.643902	1.533	44.780
Fe-L3	1592.357	600.945	0.592065	1.546	45.493
Fe-L4	1555.210	685.243	0.675117	1.619	44.432
Fe-L5	1618.123	515.085	0.507473	1.464	46.229
Fe-L6	1550.388	610.054	0.601039	1.580	44.294
Fe-L7	1526.718	585.321	0.576671	1.502	43.618
Fe-L8	1562.500	541.352	0.533352	1.481	44.640



Peak detection

λ	ABS
760	0.186
637	0.214
358	4.000

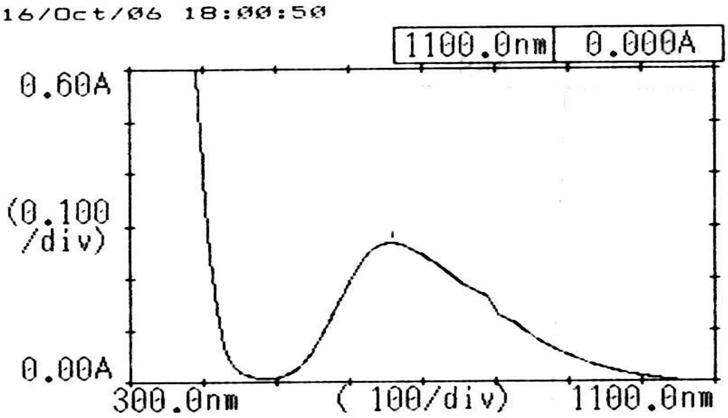
Fig. 4.1 ELECTRONIC ABSORPTION SPECTRA OF $Cu(L1)_2$ COMPLEXE.



Peak detection

λ	ABS
756	0.041
633	0.069
351	4.000

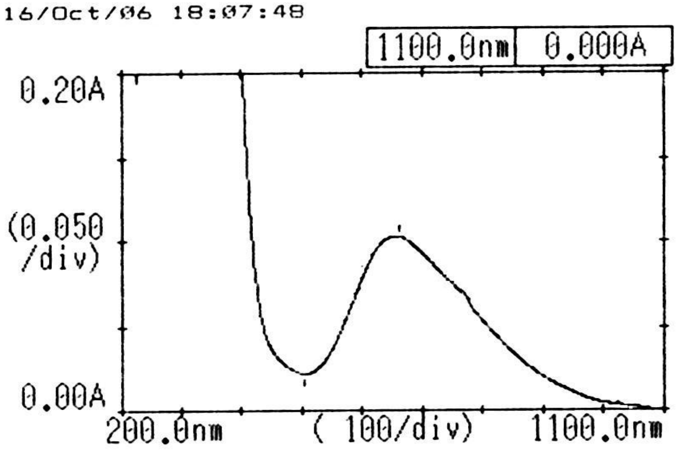
Fig. 4.2 ELECTRONIC ABSORPTION SPECTRA OF $Cu(L2)_2$ COMPLEXE.



Peak detection

λ	ABS
741	0.163
662	0.264
351	4.000

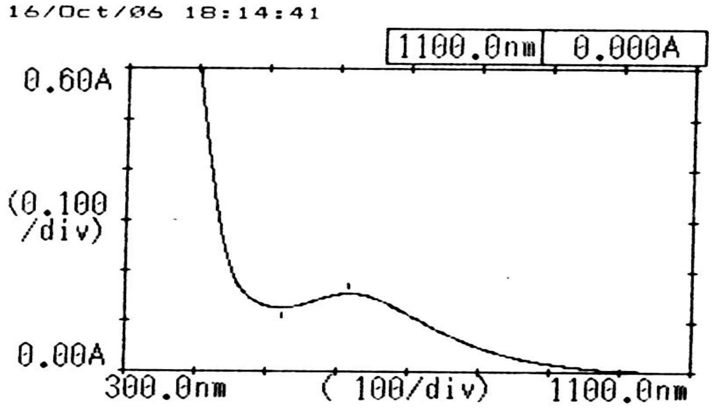
Fig. 4.3 ELECTRONIC ABSORPTION SPECTRA OF $Cu(L3)_2$ COMPLEXE.



Peak detection

λ	ABS
766	0.068
661	0.103
353	4.000

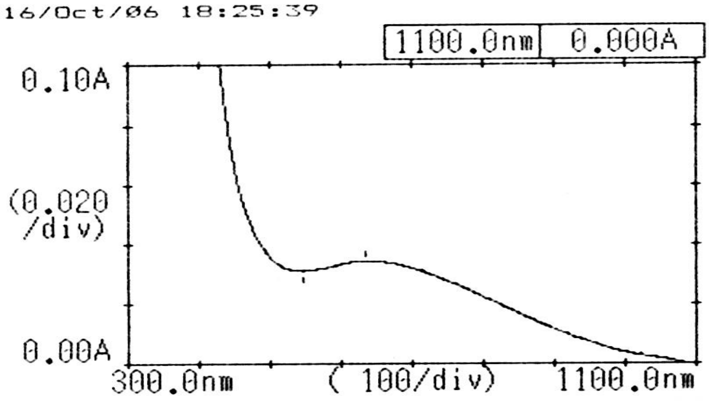
Fig. 4.4 ELECTRONIC ABSORPTION SPECTRA OF $Cu(L4)_2$ COMPLEXE.



Peak detection

λ	ABS
768	0.081
616	0.155
356	4.000

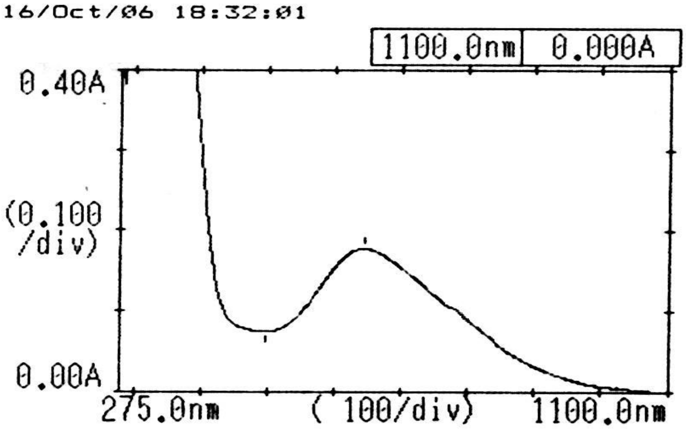
Fig. 4.5 ELECTRONIC ABSORPTION SPECTRA OF $Cu(L5)_2$ COMPLEXE.



Peak detection

λ	ABS
770	0.022
650	0.034
353	4.000

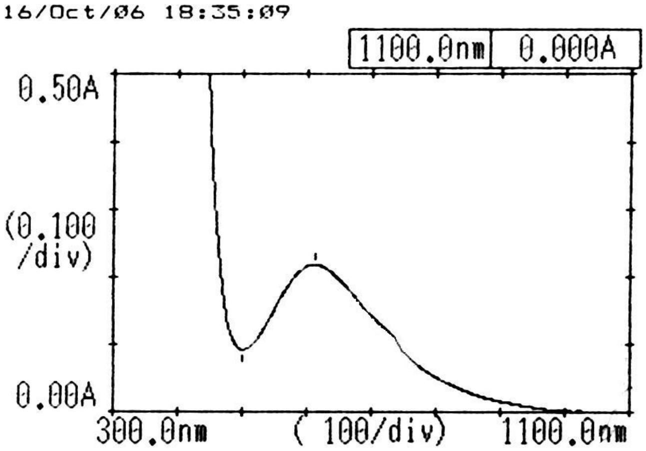
Fig. 4.6 ELECTRONIC ABSORPTION SPECTRA OF $Cu(L6)_2$ COMPLEXE.



Peak detection

λ	ABS
762	0.101
643	0.178
359	4.000

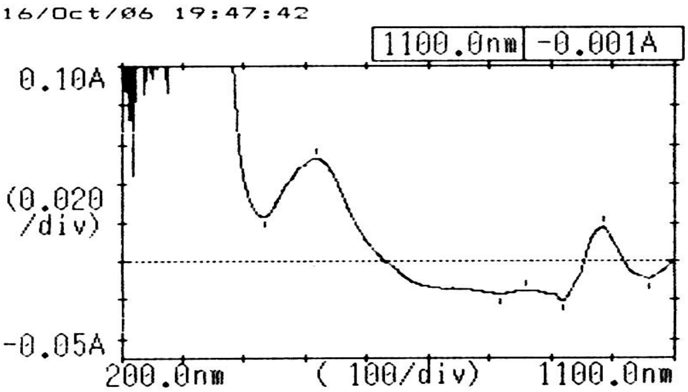
Fig. 4.7 ELECTRONIC ABSORPTION SPECTRA OF $Cu(L7)_2$ COMPLEXE.



Peak detection

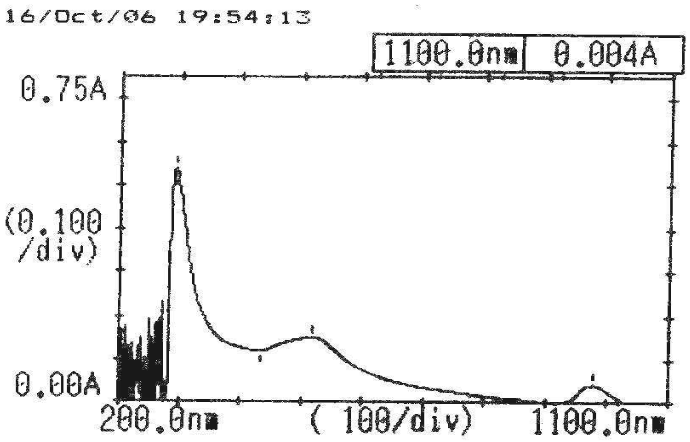
λ	ABS
718	0.108
613	0.218
349	4.000

Fig. 4.8 ELECTRONIC ABSORPTION SPECTRA OF $Cu(L8)_2$ COMPLEXE.



Peak detection

λ	ABS
984	0.017
858	0.015
518	0.053
357	4.000

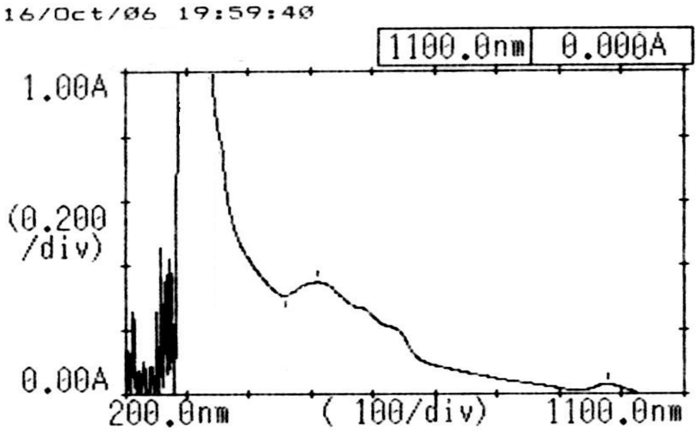


Peak detection

λ	ABS
979	0.043
860	0.011
517	0.152
342	0.541

Fig. 4.9 ELECTRONIC ABSORPTION SPECTRA OF $Co(L1)_2$ COMPLEXE.

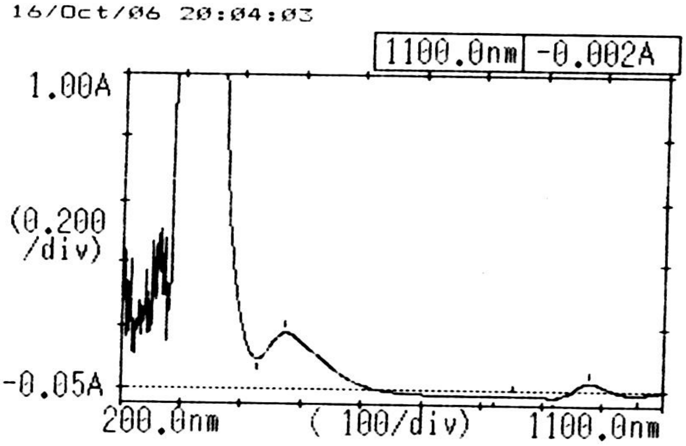
Fig. 4.10 ELECTRONIC ABSORPTION SPECTRA OF $Co(L2)_2$ COMPLEXE.



Peak detection

λ	ABS
980	0.310
848	0.230
511	0.347
350	2.870

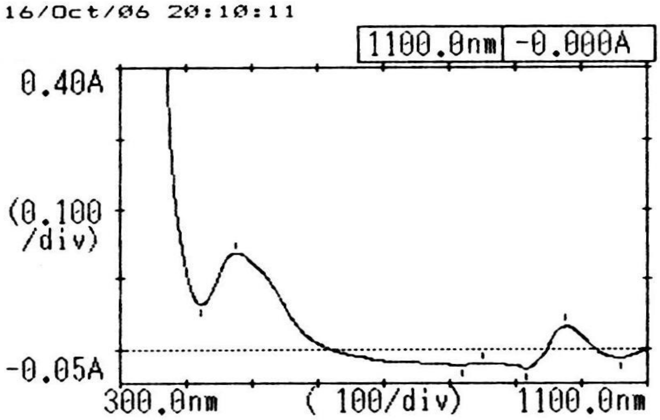
Fig. 4.11 ELECTRONIC ABSORPTION SPECTRA OF $Co(L3)_2$ COMPLEXE.



Peak detection

λ	ABS
980	0.026
832	0.016
474	0.179
358	4.000

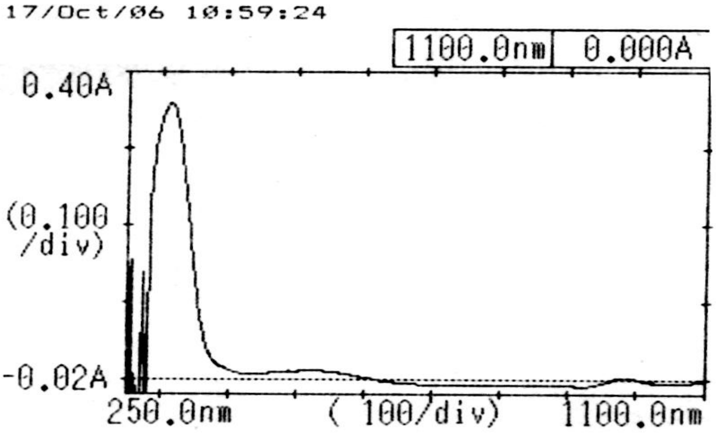
Fig. 4.12 ELECTRONIC ABSORPTION SPECTRA OF Co(L4)$_2$ COMPLEXE.



Peak detection

λ	ABS
978	0.033
852	0.020
478	0.136
352	2.664

Fig. 4.13 ELECTRONIC ABSORPTION SPECTRA OF Co(L5)$_2$ COMPLEXE.



Peak detection

λ	ABS
985	0.004
850	0.015
530	0.012
355	0.360

Fig. 4.14 ELECTRONIC ABSORPTION SPECTRA OF Co(L6)$_2$ COMPLEXE.

Peak detection

λ	ABS
983	0.007
845	0.018
524	0.160
370	0.739

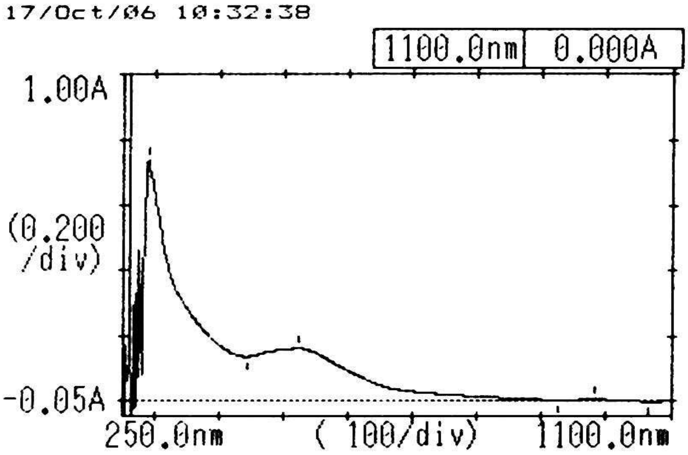
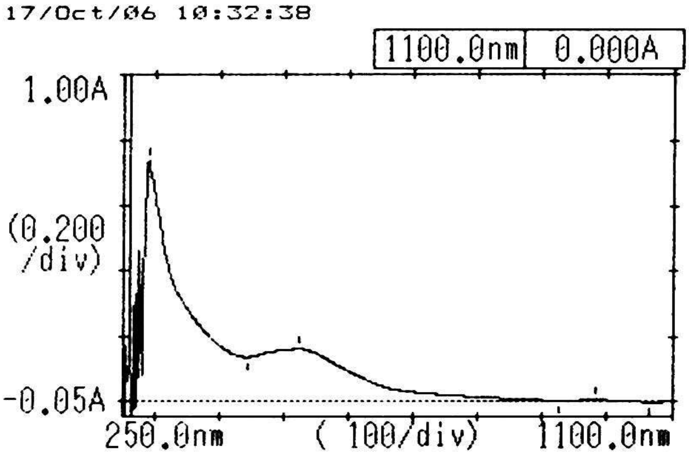


Fig. 4.15 ELECTRONIC ABSORPTION SPECTRA OF Co(L7)$_2$



Peak detection

λ	ABS
987	0.001
831	0.016
472	0.096
357	3.806

COMPLEXE.

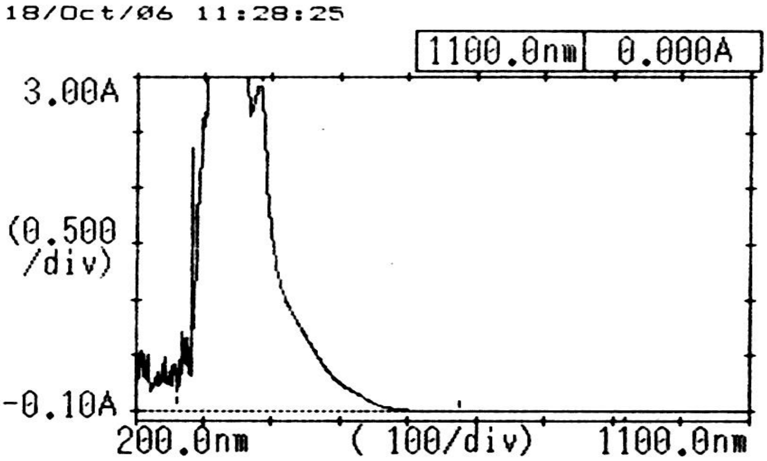
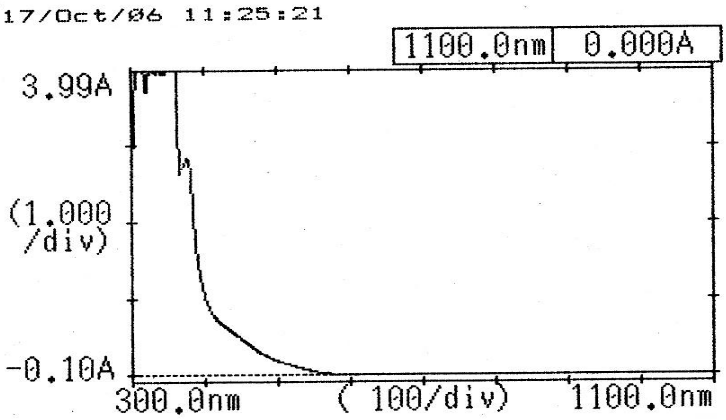


Fig. 4.16 ELECTRONIC ABSORPTION SPECTRA OF Co(L8)$_2$ COMPLEXE.

Peak detection

λ	ABS
588	0.001
388	2.914

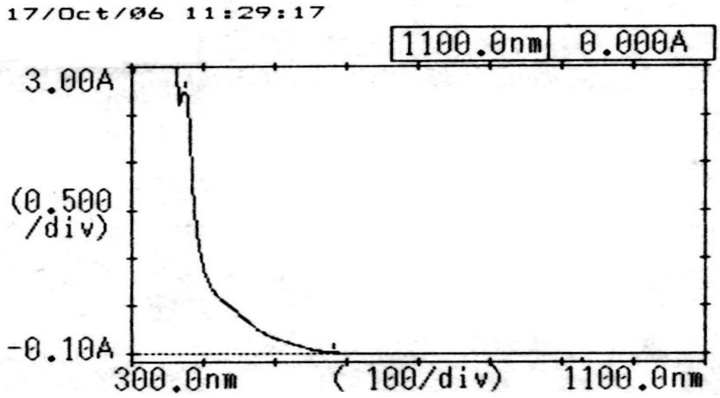
Fig. 4.17 ELECTRONIC ABSORPTION SPECTRA OF Ni(L1)$_2$ COMPLEXE.



Peak detection

λ	ABS
587	0.001
378	2.834

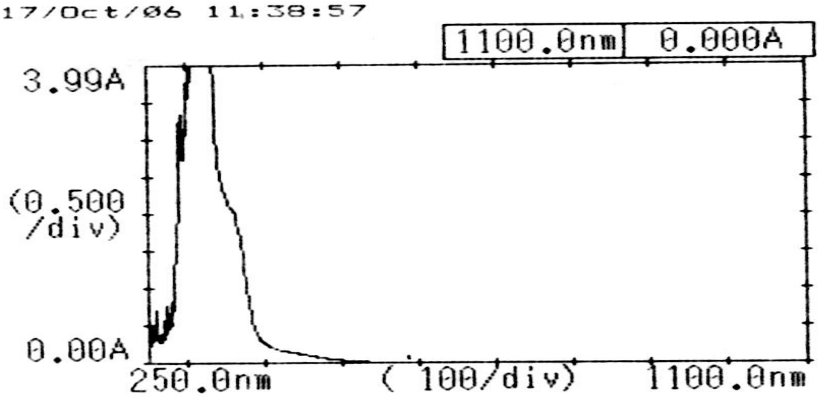
Fig. 4.18 ELECTRONIC ABSORPTION SPECTRA OF Ni(L2)$_2$ COMPLEXE.

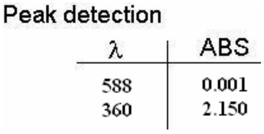


Peak detection

λ	ABS
588	0.001
377	2.752

Fig. 4.19 ELECTRONIC ABSORPTION SPECTRA OF Ni(L3)$_2$ COMPLEXE.

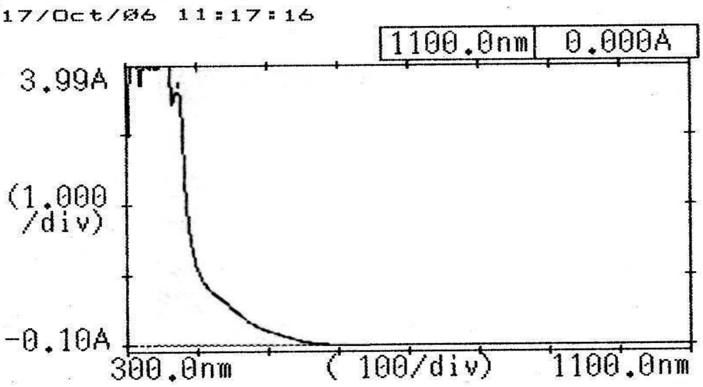


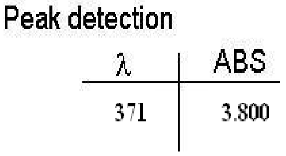


Peak detection

λ	ABS
588	0.001
360	2.150

Fig. 4.20 ELECTRONIC ABSORPTION SPECTRA OF Ni(L4)$_2$ COMPLEXE.

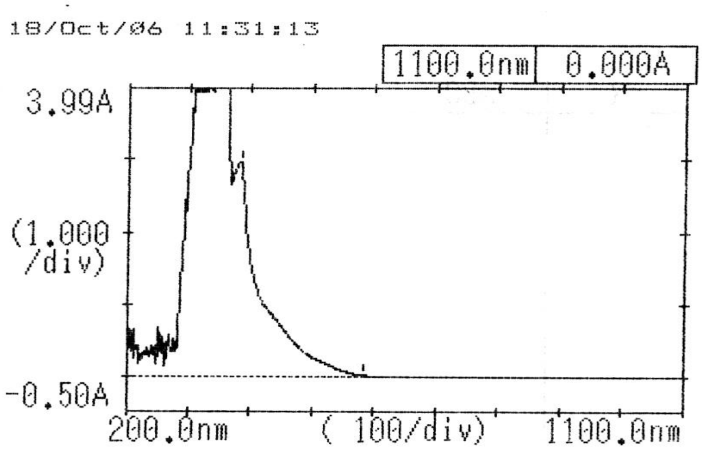


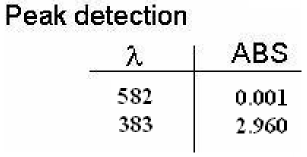


Peak detection

λ	ABS
371	3.800

Fig. 4.21 ELECTRONIC ABSORPTION SPECTRA OF Ni(L5)$_2$ COMPLEXE.

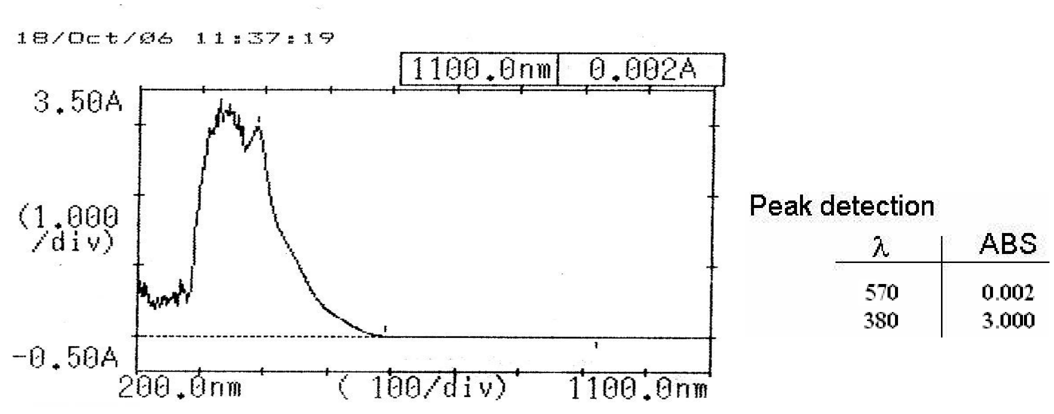




Peak detection

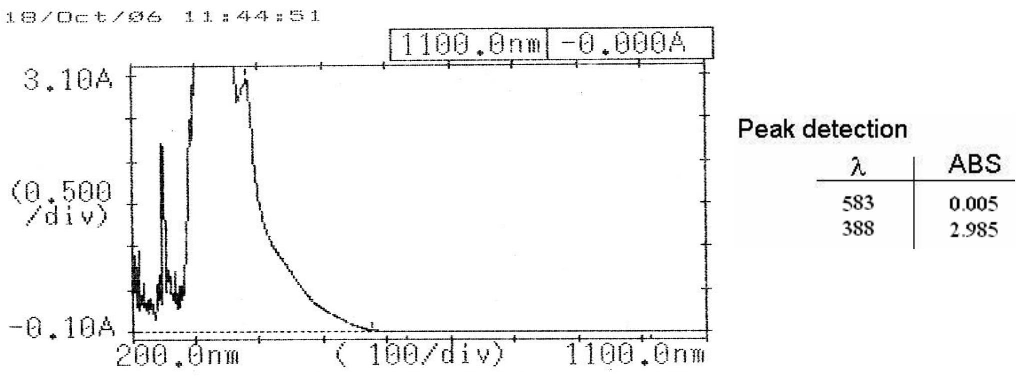
λ	ABS
582	0.001
383	2.960

Fig. 4.22 ELECTRONIC ABSORPTION SPECTRA OF Ni(L6)$_2$ COMPLEXE.



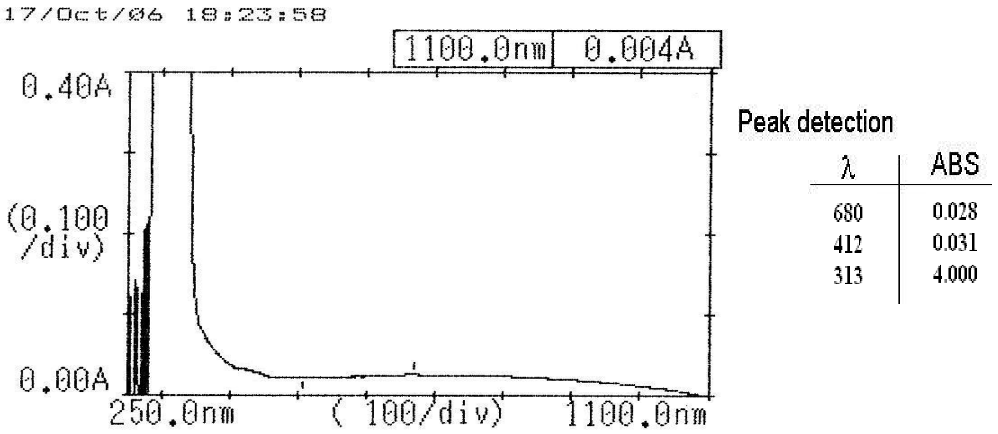
λ	ABS
570	0.002
380	3.000

Fig. 4.23 ELECTRONIC ABSORPTION SPECTRA OF $Ni(L7)_2$ COMPLEXE.



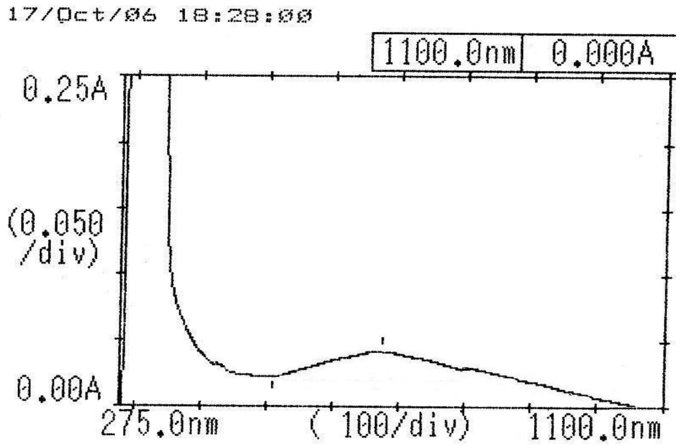
λ	ABS
583	0.005
388	2.985

Fig. 4.24 ELECTRONIC ABSORPTION SPECTRA OF $Ni(L8)_2$ COMPLEXE.



λ	ABS
680	0.028
412	0.031
313	4.000

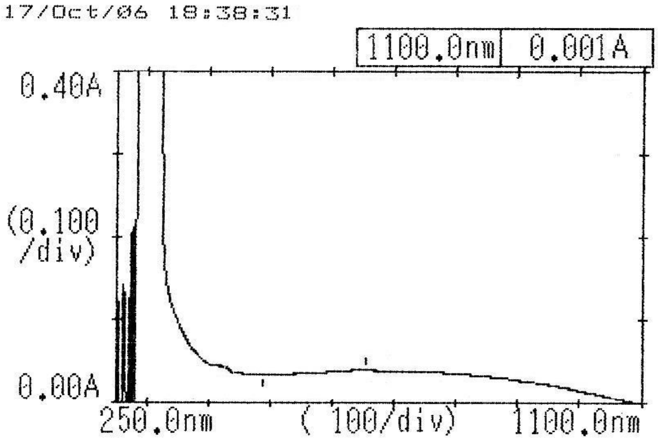
Fig. 4.25 ELECTRONIC ABSORPTION SPECTRA OF $Mn(L1)_2$ COMPLEXE.



Peak detection

λ	ABS
676	0.045
404	0.028
315	3.210

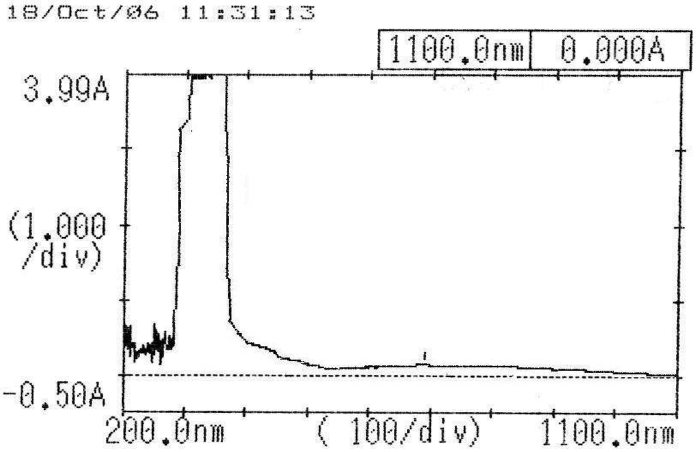
Fig. 4.26 ELECTRONIC ABSORPTION SPECTRA OF Mn(L2)$_2$ COMPLEXE.



Peak detection

λ	ABS
660	0.022
405	0.200
317	3.431

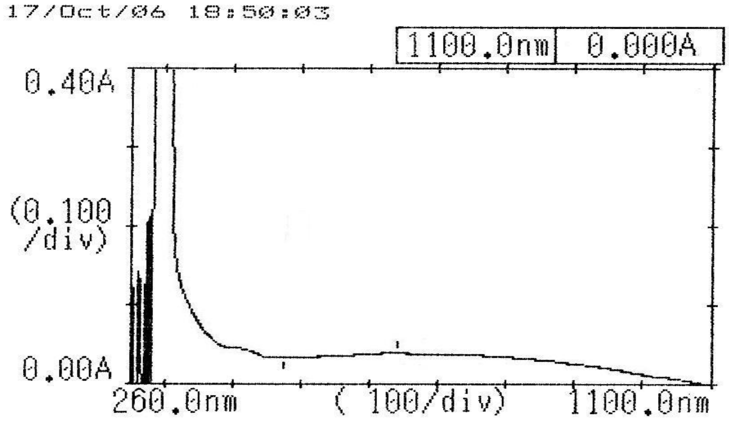
Fig. 4.27 ELECTRONIC ABSORPTION SPECTRA OF Mn(L3)$_2$ COMPLEXE.



Peak detection

λ	ABS
685	0.025
415	0.031
314	4.000

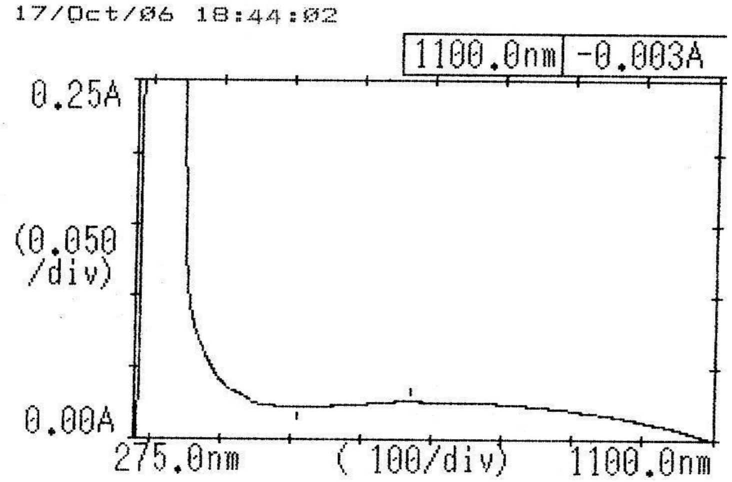
Fig. 4.28 ELECTRONIC ABSORPTION SPECTRA OF $Mn(L4)_2$ COMPLEXE.



Peak detection

λ	ABS
662	0.046
417	0.040
310	4.000

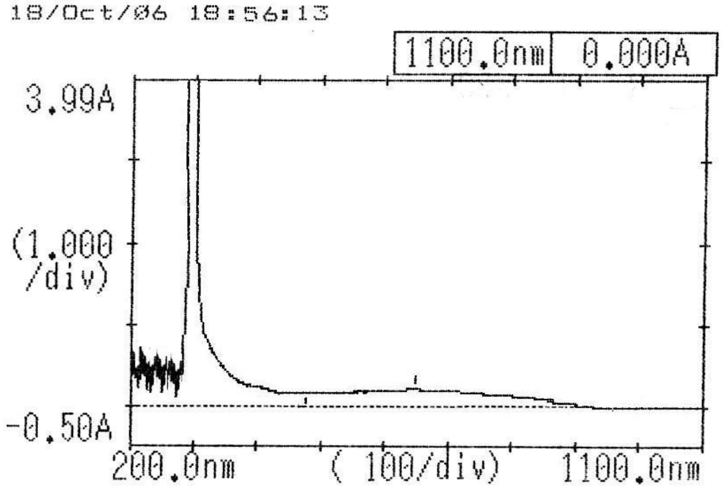
Fig. 4.29 ELECTRONIC ABSORPTION SPECTRA OF $Mn(L5)_2$ COMPLEXE.



Peak detection

λ	ABS
670	0.038
416	0.035
311	2.947

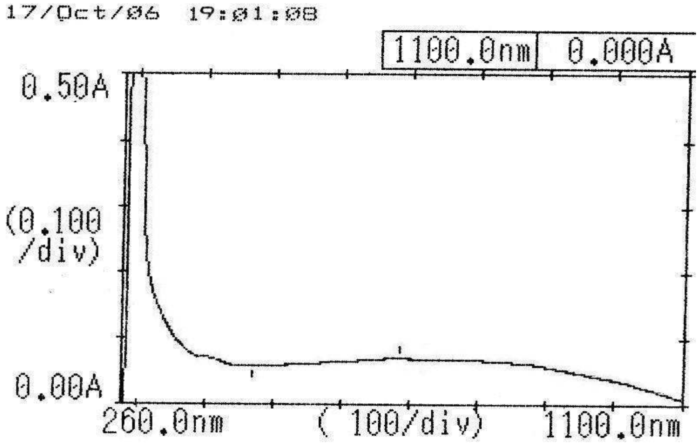
Fig. 4.30 ELECTRONIC ABSORPTION SPECTRA OF $Mn(L6)_2$ COMPLEXE.



Peak detection

λ	ABS
660	0.027
402	0.022
308	4.000

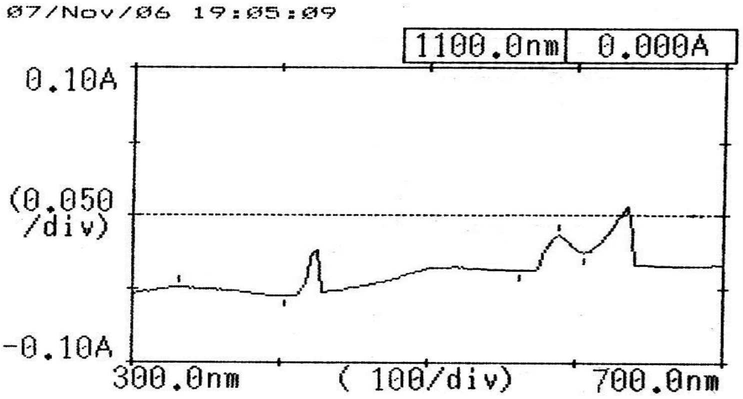
Fig. 4.31 ELECTRONIC ABSORPTION SPECTRA OF Mn(L7)$_2$ COMPLEXE.



Peak detection

λ	ABS
680	0.081
403	0.076
310	4.000

Fig. 4.32 ELECTRONIC ABSORPTION SPECTRA OF Mn(L8)$_2$ COMPLEXE.



Peak detection

λ	ABS
630	0.001
410	-0.040
325	-0.051

Peak detection

λ	ABS
638	-0.023
416	-0.030
305	-0.016

Fig. 4.33 ELECTRONIC ABSORPTION SPECTRA OF Fe(L1)$_2$ COMPLEXE.

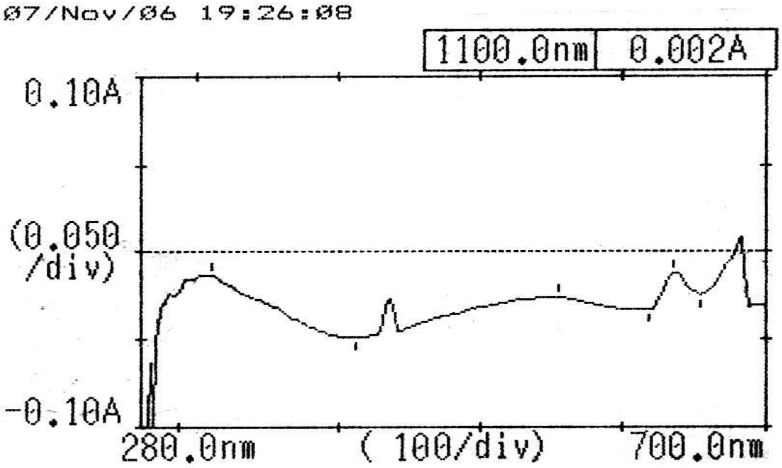
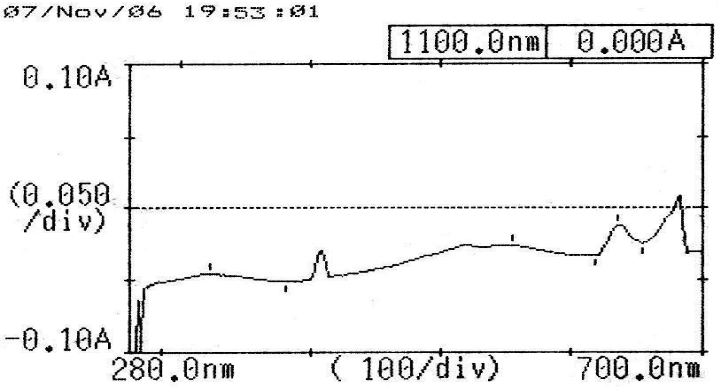


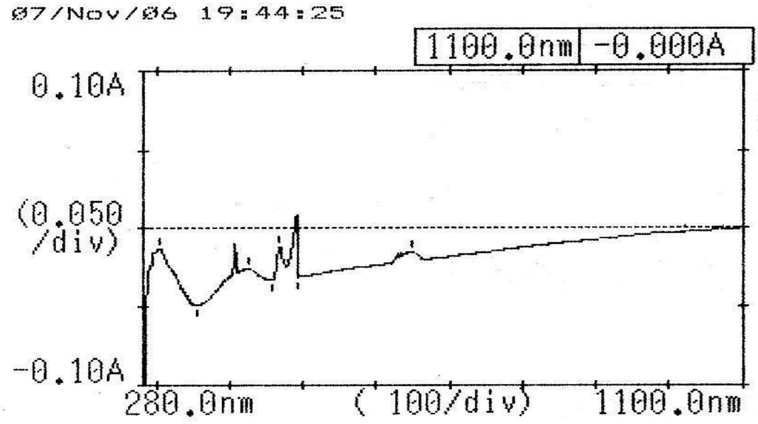
Fig. 4.34 ELECTRONIC ABSORPTION SPECTRA OF $Fe(L2)_2$ COMPLEXE.



Peak detection

λ	ABS
628	-0.017
406	-0.034
311	-0.046

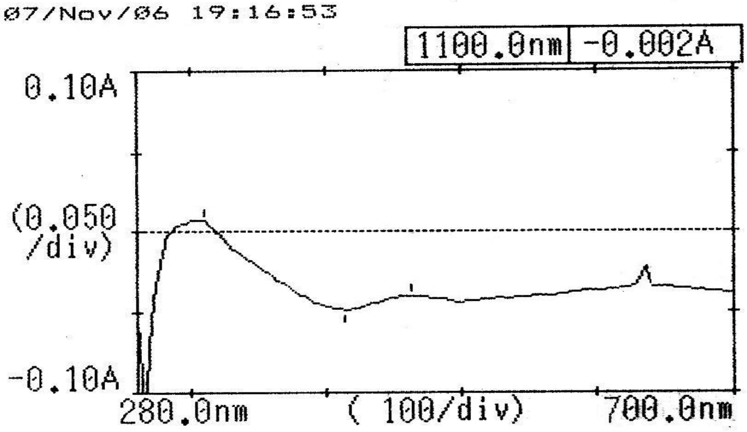
Fig. 4.35 ELECTRONIC ABSORPTION SPECTRA OF $Fe(L3)_2$ COMPLEXE.



Peak detection

λ	ABS
643	0.020
397	0.025
315	0.018

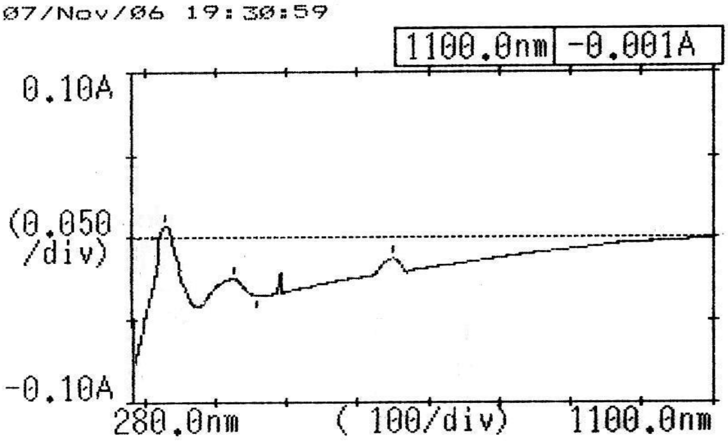
Fig. 4.36 ELECTRONIC ABSORPTION SPECTRA OF $Fe(L4)_2$ COMPLEXE.



Peak detection

λ	ABS
618	-0.026
422	-0.042
307	0.014

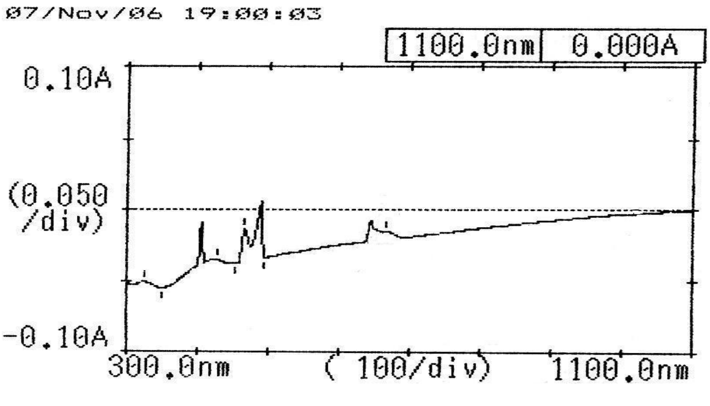
Fig. 4.37 ELECTRONIC ABSORPTION SPECTRA OF $Fe(L5)_2$ COMPLEXE.



eak detection

λ	ABS
645	-0.018
408	-0.023
321	0.016

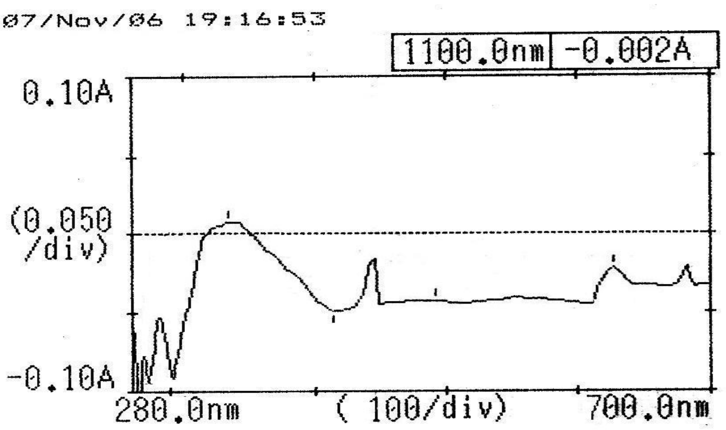
Fig. 4.38 ELECTRONIC ABSORPTION SPECTRA OF $Fe(L6)_2$ COMPLEXE.



Peak detection

λ	ABS
655	0.013
436	0.038
316	0.050

Fig. 4.39 ELECTRONIC ABSORPTION SPECTRA OF Fe(L7)$_2$ COMPLEXE.



Peak detection

λ	ABS
640	-0.020
432	-0.043
314	0.013

Fig. 4.40 ELECTRONIC ABSORPTION SPECTRA OF Fe(L8)$_2$ COMPLEXE.

PART-B

4.6 THERMAL STUDEIS OF METAL COMPLEXES:-

4.6.1 Theoretical considerations: -

Thermal analyses including mainly thermogravimetric (TG) and differential thermal analysis (DTA) are widely used techniques in qualitative evaluation of various compounds. In view of the possibilities offered by such methods in the investigation of both physical phenomena (melting point, sublimation, adsorption, change in crystallographic properties etc.) and chemical phenomena (dehydration, decomposition, oxidation, etc.) method of thermal analysis have found application in almost all the natural sciences.

Thermal properties are important for kinetic studies of thermal decomposition, energy of activation (Ea), free energy changes (ΔF), order of reaction (n), pre-exponential factor (Z), and entropy of activation (ΔS), which directly govern the factors of thermal stability of any substance.

Two alternative methods have been used in kinetic investigation of thermal decomposition of solids. In the first approach, weight loss-time/ temperature measurements are made and in the second approach the sample is subjected to a controlled rising temperature. The first method is called isothermal / static method and the second one is called non-isothermal / dynamic method.

In static methods determination of isobaric weight change isothermal weight change is carried where as in dynamic methods, thermogravimetric (TG), differential thermogravimetric (DTA) and more recently inverted thermogravimetric techniques are being used. In non-isothermal TG analysis, more information is extracted from a single TG-curve compared to many curved and hence non-isothermal TG-analysis is preferred over isothermal TG analysis.

The simultaneous use of TG and DTA is made in the present study of metal complexes with a view to understand stoichiometry, thermal stability, the presence and nature of water molecules. The water in inorganic compounds may be classified as lattice and coordinated water. There is no definite border line between the two. The former term denotes water molecule trapped in the crystalline lattice, either by weak bonds to the anion or by weak ionic bonds to the metal or both, where as the latter denotes water molecules bonded to the metal through partial covalent bonds or coordinate bonds. According to Freeman and Carrol[89] the water eliminated below 150°C can be considered as lattice water and above 150°C as water coordinated to metal ion[90]. Two coordinated water molecules in Cu(II) complexes of bis-(5-methyl dithio carbazate res-diacetophenone) has been reported on the basis of 6% weight loss at 150-210°C[91].

The technique also finds out the thermal stability, decomposition pattern, particularly decomposition temperature of Schiff bases over other polychelates are due to molecular weight, sterric effects and resonance energy along the back bone of the chain[92]. In the present study, a dynamic/ non-isothermal TGA-DTA technique is used. Considering percentage loss in weight, the thermal decomposition behaviour of Cu(II), Co(II), Ni(II) and Mn(II) complexes of some selected ligands are discussed on the basis of their simultaneous TGA-DTA curves as follows.

4.6.2 Thermal study of Cu(II) complexes:-

A close look at TG curve (Fig. 4.41, 4.42) of $[Cu(L3)_2]$ and $[Cu(L5)_2]$ complexes shows that there is no weight loss up to 287°C and 235°C respectively indicating absence of lattice as well as coordinated water in the complex. The Cu(II) complexes of ligand L3 and L5 exhibits high thermal stability and decomposes at > 270°C. It follows two step decomposition. In first step the decomposition begins at 250°C and continues up to 325°C shown by a sudden weight loss in TG curve, which is supported by exotherm at ~290°C in DTA curve. The percentage decomposition in first step is about 82% in complex of L3 and 62% in complex of L5. It may be due to decomposition of organic ligand part of complex and its subsequent oxidation[93]. In second step decomposition start at about 325°C and 300°C in complexes of L3 and L5 respectively and continues up to 600 °C. The decomposition is complete at ~600°C leading to the formation of stable residue as indicated by attainment of constant weight beyond this temperature.

Dash et.al.[27] in their thermal studies of Cu(II) complexes of 2-(o-anisylidine monoamine), 4-(p-bromophenyl) thiazole reported that, the complex did not form any stable residue and decomposition continued beyond 620°C. The thermogram reveals stability up to 220-290°C indicating the absence of water molecules. Beyond this range, the complex showed rapid decomposition denoting loss of ligand moiety.

4.6.3 Thermal study of Co(II) complexes:-

The thermogram of Co(II) complex $[Co(L7)_2]$ reveals that the weight loss occurs at 225°C. About 10% weight loss takes place up to temperature 250°C, which indicate loss of two coordinated chlorine atoms (10.07%). The rapid decomposition starts after 250°C which is due to the decomposition of organic ligand and subsequent oxidation which is indicated by large exotherm at ~295°C The TG thermogram of $[Co(L7)_2]$ is shown in Fig. 4.43. Its decomposition continues up to 860°C. After this, weight remains almost stable up to 1000°C indicates the formation of stables residue.

In the thermograms of Co(II) complexes of 2-hydroxy-3-bromo-4-methoxy-5-methyl chalkone oxime, Bhave and Kharat[94] reported loss of water molecules below 200°C on the basis of endothermic curves. Revankar and Mahale[95] made the similar observations. The constant weight region after decompositions is of cobalt oxide in the TGA curve. Finally CoO is obtained as the end procuct[96].

4.6.4 Thermal study of Ni(II) complexes:-

The two complexes $[Ni(L3)_2]$ and $[Ni(L5)_2]$ were screened for thermal study. The TG curve of $[Ni(L3)_2]$ complex (Fig.4.44) shows that the first exothermic peak occurs at 286°C and second at 556°C. The complex shows high thermal stability and absence of lattice or coordinated water as its decomposition starts at 300°C. It follows double step decomposition. In the first step the complexes undergo steady weight loss of 67% from 300-400°C temperature which may be due to the reaction interval corresponding to the decomposition of organic ligand part. The second step decomposition of chelate starts from 400°C and continue up to 600°C as indicated by horizontal line. Beyond this point a stable end product remains.

The TG curves of [$Ni(L5)_2$] complexes (Fig.4.45) reveals that there is no weight loss up to 300°C. It appears to decompose in two steps. The first step decomposition begins at ~300°C and continues up to 400°C shown by sudden weight loss of 65% in TG curve which is supported by sharp endotherm at 330°C. It may be due to decomposition of large part of organic ligand and its subsequent oxidation. In second step the decomposition of chelate appears to be start above 400°C complete at 600°C as indicated by horizontal line beyond this point-giving rise to a stable end product.

The thermal studies of Ni(II) complexes of 4,4'-dihydroxy-3,3'-dipropionyl biphenyl-(3,4-diamino anisole) performed by Ashwini Kumar[97] indicated a weight loss in the temperature range 170 - 190 °C equivalent to two coordinated water molecules. The TG curve shows continues mass loss upto 590 °C indicating the decomposition of the organic part of the chelate. Above 590°C, TG curve attains a constant level corresponding to their metal oxide.

4.6.5 Thermal study of Mn(II) complexes:-

The thermogram of [$Mn(L6)_2$] complex (Fig.4.46) shows no weight loss up to 325°C. The ligand starts to decompose at 325°C and shows about 10% weight loss up to 375°C which may be due to loss of two coordinated chlorine (cal. 10.12%). The first step decomposition takes place in the range 375-525 °C as shown by DTA curve.

Thermogravimetric studies indicate that the metal complexes of Mn(II) do not contain coordinated water or lattice water, and are thermally quit stable. The first step covering the reaction interval 325-525°C shows sharp exotherm at 347°C.

The second step decomposition is in the range of 525-900°C. After which a stable residue remains.

The Makode et.al.[89] characterised the Mn(II) complexes and reported negligible weight loss up to 210°C indicating absence of any water molecule. The decomposition of the complex involved two steps, out of which the first step is due to the fact that, the non-coordinated part of the ligand decomposes first (120-249°C) while the actually coordinated part decomposes later (250-690°C) leading to completion by formation of metal oxide.

The thermal behavior of transition metal complexes in the present study indicates that the metal complexes are thermally quite stable. Decomposition of all the complexes are started at relatively higher temperature (~250^oC), finally giving a metal oxide residue. Thermograms of all the complexes indicated the absence of coordinated as well as lattice water and exhibit higher thermal stability.

4.7 THERMAL DECOMPOSITION AND KINETIC PARAMETERS OF Cu(II), Co(II), Ni(II) and Mn(II) COMPLEXES:-

Kinetics of thermal decomposition reactions is useful for their industrial and analytical importance. The metal complexes of aryl-thiourea and thiazole derived from heterocyclic compounds have been a center of attraction for many workers in recent years[98]. Johri et.al.[99] reported extensive thermoanalytical investigations that have been under taken on complex compounds involving the two heterocyclic thiol ligands 2-amino-mercaptobenzothiazole, 2-amino mercaptobezimidazole and their Co(II), Ni(II), Cu(II) and Zn(II) complexes. The activation energy calculated by Coats-Redfern method for Cu, Zn, Co, and Ni complexes of 2-amino-mercaptobenzothiazole are 651.8, 338.8, 429.9 and 366.1 KJ Mol^{-1} respectively.

Comparatively little attention has been given to the benzothiazoles derived form N-substituted thioureas and no attempt has been made to study the kinetics of thermal decomposition of their metal complexes in solid state. In the present study, the non-isothermal decomposition of the Cu(II), Co(II), Ni(II) and Mn(II) complexes has been carried out at a uniform heating rate of 10^oC per minute in nitrogen atmosphere and simultaneous differential thermal analysis (DTA) and thermogravimetric curves haves been recorded. The Kinetic and thermodynamic parameters for their non-isothermal decomposition have been evaluated.

4.7.1 Theoretical Consideration-

Thermal decomposition and kinetic studies of thermal reactions are useful in determining thermodynamic and kinetic parameters like free energy, entropy change, energy of activation, pre-exponential factor and frequency factor. This concept was first proposed by Akahira[100]. Since then so many methods and equations have been put forward for studying thermal decomposition kinetics of the reaction. Thermal decomposition studies of materials can be studied with the help of TGA, DTA, and DTG curves.

Thermal decomposition kinetics was studied by analytical data. Since then various methods have been proposed for kinetic analysis[101], some prominent methods are Horowitz-Metzger[102], Sharp-Wentworth[103]. Piloyan-Novikova[104], Fuoss, et.al.[105], Dharwadkar-Karkhanwala[106] and Coats-Redfern[107] .These methods have been applied depending upon the needs and conditions for kinetic analysis of thermal decomposition of solid substances on the basis of non-isothermal concept [108-110].

Horowitz-Metzger method gives reasonably good results while the other methods seem to be more accurate but time consuming[111]. Therefore, Horowitz-Metzger method has been used for finding the kinetic parameters for non-iso-thermal decomposition of Cu(II), Co(II), Ni(II), Mn(II) and Fe(III) complexes in the present work . By this method thermal decomposition reaction of many coordination complexes of transition metal has been reported[108, 112]

4.7.2 Horowitz-Metzger Method:-

The methold of Horowitz-Metzger is illustrative of the approximation methods. They derived the relation for such reactions by the following equation[111].

$$\log (\log W_c/W_r) = E_a\theta / 2.303RT_m^2 - \log 2.303$$

The energy of activation (Ea) was calculated from slope of plots of

$$\log (\log W_c/W_r) \text{ Vs } \theta$$

Where, $W_r = W_c - W$.

Wc - weight loss at completion of reaction and W-total weight loss upto time t.

The frequency factor (Z) was calculated by,

$$\text{Intercept} = \log (Z\, R/\beta\, E_a)$$

And the equation used for calculating entropy change (ΔS) is

$$\Delta S = 2.303\ R \log Zh / k\ Tm.$$

Where, k - Boltzman constant, h– Planks constant,

β – Rate of heating 10^0C, R- Molar gas constant and Tm- Peak temperature.

By using different value of order of reaction, straight line was fitted by regression. The highest value of correlation coefficient gave the correct value of 'n'. From the slope and intercept, Ea and Z values were calculated. Using Ea and Z values, the values of ΔS and ΔG were determined.

4.7.3 **Results and Discussion:–**

The non- isothermal kinetic parameter ΔF, ΔS, Ea and Z for thermal decomposition of complexes have been calculated by Horowitz-Metzger method from the TG curves Fig. (4.41 to 4.47) are presented in Table 4.7.

The TG-DTA curves reveal single stage decomposition of $[Co(L7)_2]$ complexes and two stage decomposition of $[Cu(L3)_2]$, $[Cu(L5)_2]$, $[Ni(L5)_2]$, $[Ni(L5)_2]$, $[Mn(L6)_2]$ complexes. Theoretically with decreasing value of Ea, the value of Z increases and the higher value of activation energy suggested the higher stability[113]. However, some other inherent physical and chemical factors may cause a change or deviation in this trend. The higher values of activation energy of copper (II) complexes indicate higher stability than other complexes. Higher values of activation energy (Ea) and lower values of frequency factor (Z), favour the reaction to proceed slower than normal. In present studies, the numerical values of activation energy, frequency factor and entropy of activation all together indicate about the smoothness of reaction rate of the initial stage compounds. The negative values for entropy of activation indicate that the activated complexes have a more rigid structure than the reactants or intermediate and the reactions are slower than normal[114], which is further supported by lower Z values.

The variation in the trend of the thermal stability of complexes might be due to some inter molecular interaction occurring in them, besides this there are several other experimental factors[115]. The values of thermodynamic and kinetic parameters, Ea, ΔS, ΔF and Z of the complexes determined are comparable with the values found for related compounds by the earlier workers[116-117].

Table 4.7 Thermal decomposition parameters of metal complexes by Horowitz-Metzger method.

Sr. No	Metal complex	Order of reaction (n)	Ea (KJ mol^{-1})	ΔS ($JK^{-1}Mol^{-1}$)	ΔF (KJ mol^{-1})	Z (S^{-1})
1	$[Cu(L3)_2]$	0.95	189.85	-063.08	184.78	257
		0.80	019.98	-224.45	036.76	246
2	$[Cu(L5)_2]$	1.05	192.14	-165.14	179.19	568
		0.80	011.39	-243.49	030.49	261
3	$[Co(L7)_2]$	1.20	020.02	-227.70	035.46	149
4	$[Ni(L3)_2]$	1.05	114.14	-067.34	078.00	962
		0.95	167.26	-016.51	166.00	215
5	$[Ni(L5)_2]$	1.10	152.35	-065.00	147.00	345
		0.95	040.68	-218.00	063.16	707
6	$[Mn(L6)_2]$	1.50	052.82	-157.00	064.55	759
		0.70	005.13	-258.00	024.36	416

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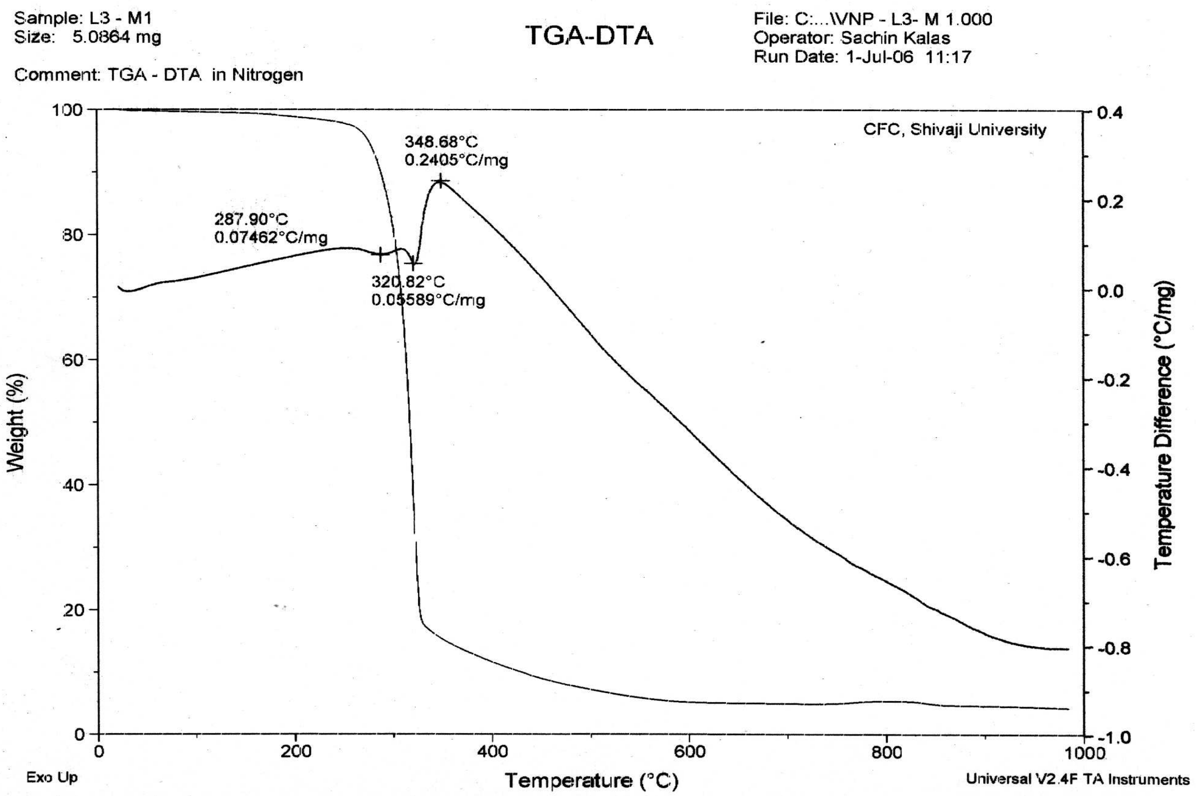


Fig. 4.41 Thermogravimetric Curve of Cu(II) Complex with L3.

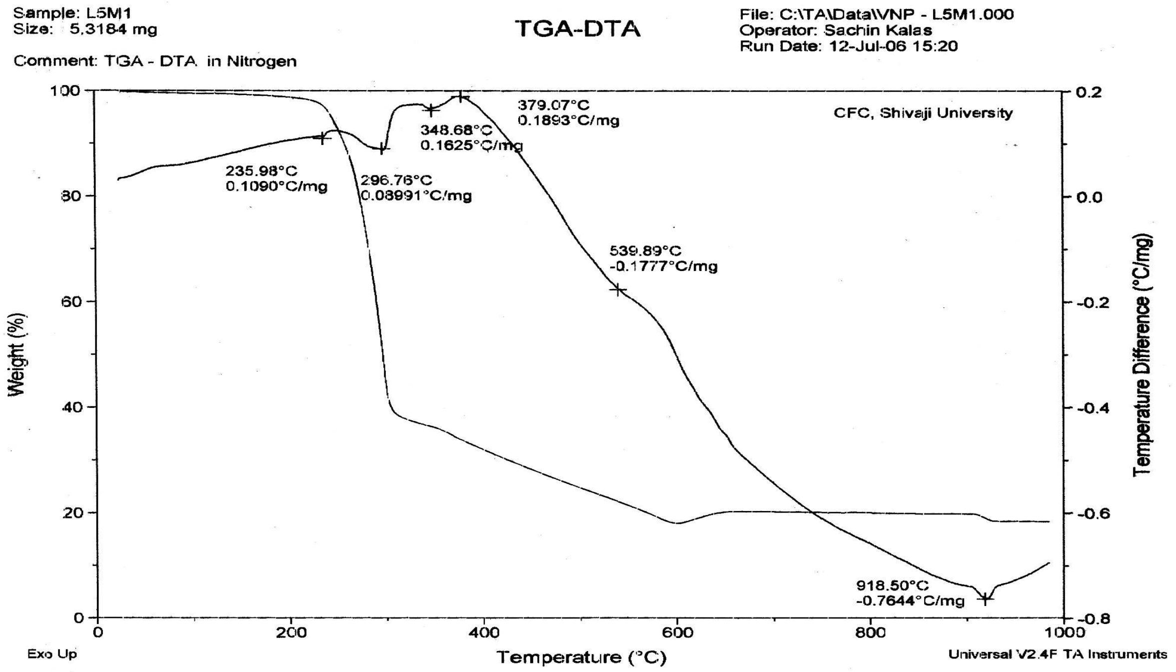


Fig. 4.42 Thermogravimetric Curve of Cu(II) Complex with L5.

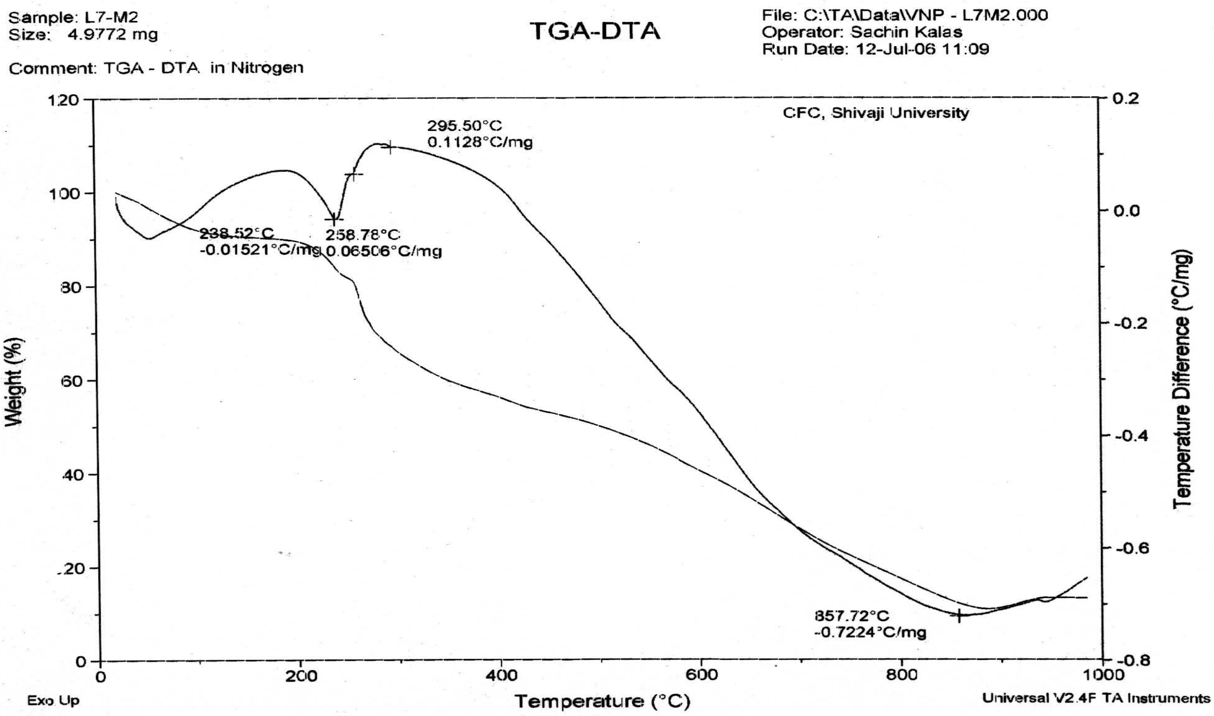


Fig. 4.43 Thermogravimetric Curve of Co(II) Complex with L7.

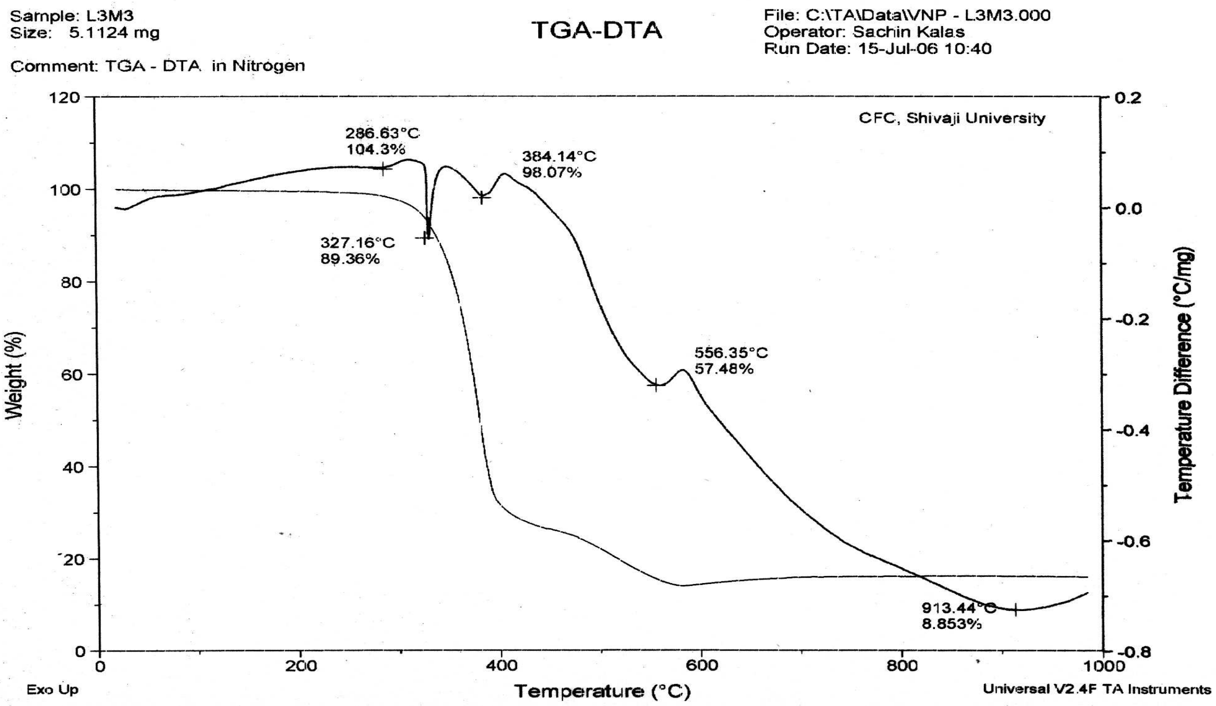


Fig. 4.44 Thermogravimetric Curve of Ni(II) Complex with L3.

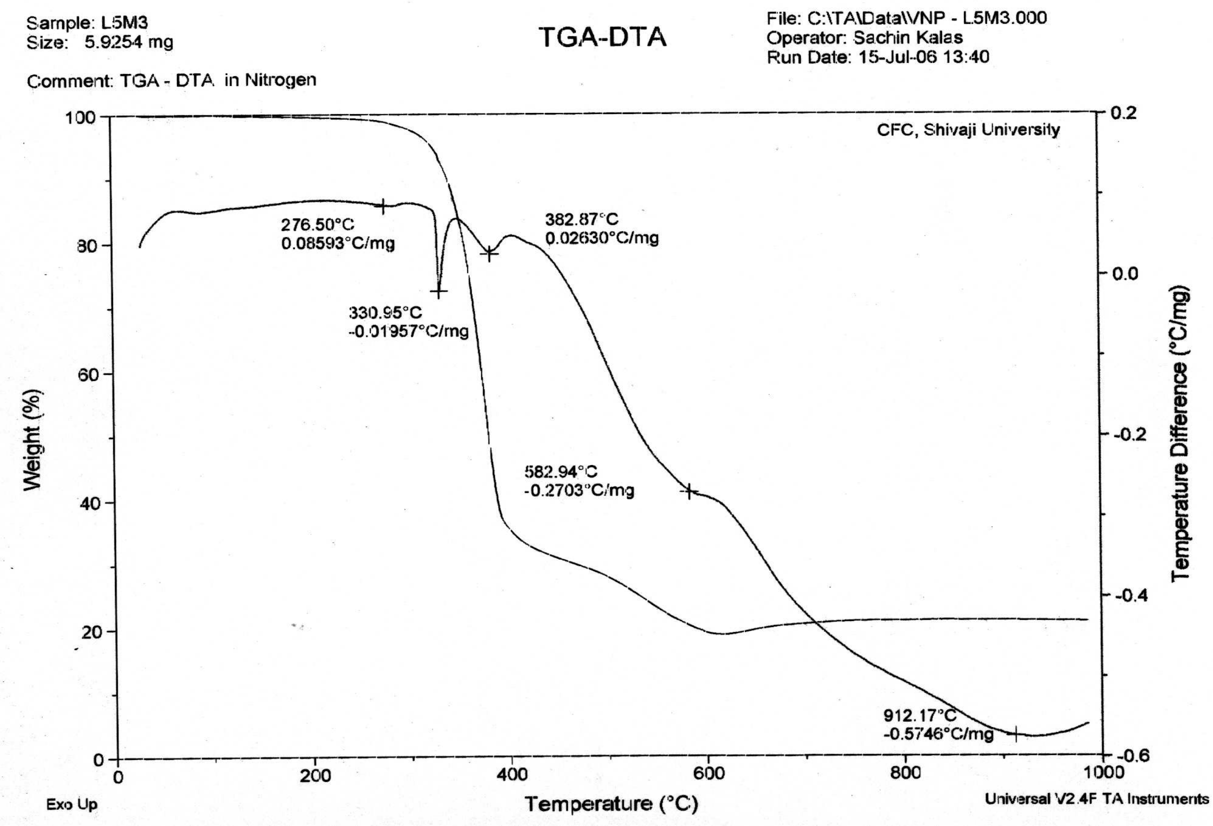


Fig. 4.45 Thermogravimetric Curve of Ni(II) Complex with L5.

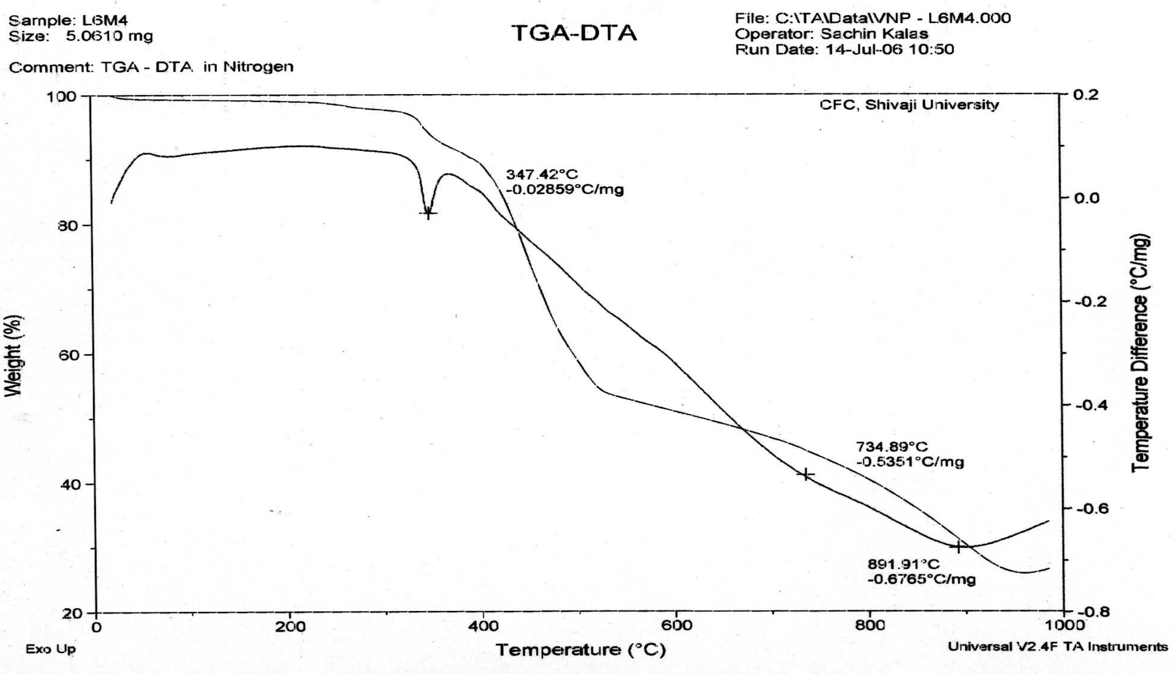


Fig. 4.46 Thermogravimetric Curve of Mn(II) Complex with L6.

Part C

4.8 X-ray Diffraction Spectral Studies of Metal Complexes-

4.8.1 Theoretical Considerations-

The X-rays interact with inner most electronic cloud in the atoms and suggest internal arrangement of the atoms in the crystal[118-119]. The intensity of diffracted beam is related to the structural factor. The cation distribution in the sample can be determined by interpreting the XRD patterns and it is a direct tool for assigning the crystal pattern for the complexes.

The X-ray diffractograms of representative metal complexes were scanned in the range 5-100^0 at λ=1.543 Å. The diffractograms and associated data depict the 2θ value for each peak, relative intensity and observed inter planar spacing (d-values). The information gathered from the diffractogram and associated data was used for indexing the pattern and to find out the unit dimensions and space group. The cell data of metal complexes along with the powder diffraction data are given in Table 4.8 to 4.14. The positions of each reflection with the intensity are recorded. Inter planar spacing d_{hkl} were calculated from 2θ values using the relation $d=n\lambda/\sin\theta$.

Programming used for indexing data was Powder-X. Then the preliminary data in the form of 2θ and intensities fed to the computer and all differences (d- obs.) are calculated as required. All the possible combinations of h. k. l. plane and d-observed values are arranged in the decreasing order.

In this programme all the essential features of X-ray programme are present and in addition, it calculates the deviation in lattice parameters a, b, c, in terms of Å unit and α, β and γ in terms of degree minutes. When the system of compound is unknown, the observed data is first tested with the isometric chart and Hul-Devy`s curve for tetragonal and hexagonal system. If these tests are proved to be negative then the data is subjected to programme bar and an attempt is made for the existence of lower symmetry and then data can be index in an orthorhombic system. The failure of all these tests is an indication for the existence of lower symmetry and then data can be indexed on either monoclinic or triclinic system. The precise lattice parameters and the deviation are obtained from Powder-X programme.

4.8.2 Density and Space Group Determination:-

To have perfection in indexing and assigning the space group to the given crystal system a density determination becomes essential. Therefore, densities of the metal complexes used for XRD study were determined using specific gravity bottle by the principle of Archimedes[120]. Using these observed values of densities and other data obtained from indexing of XRD pattern the formula factor Z was calculated.

The formula factor (Z) was rounded up to the nearest whole number and thus the density was recalculated and was taken as calculated density. The closeness of observed and calculated value of density on the basis of unit cell volume was used to judge the assignment. The percentage porosity was calculated from the observed and calculated densities. By using the literature value for definite crystal system, probable space group was assigned to each of the complexes[121].

The programme calculates the various parameter and standard deviation in the calculated lattice parameters a, b, c, in Å and α, β and γ in degrees and minutes. The refinement of the lattice parameters is continued with better combination of h, k, l values until the final deviation is within the permissible limit of 2%. The refined values also give the volume of unit cell.

The density ρ in gcm^{-3} of the compound is related to the formula factor Z and volume of the unit cell V in $Å^{-3}$ as per the following expression.

$$\rho = ZM/NV.$$

Where,

Z = number of formula units present within unit cell.
M = molecular formula weight of the compound.
V = volume of unit cell, and
N = Avogadro's constant / Number = 6.023×10^{23} $mole^{-1.}$

4.8.3 Results and Discussion-

The X-ray powder diffractogram of the metal complexes were used for the structural characterisation and determination of lattice dimensions. The observed data of complexes under investigation was compared with other literature data having analogous cell and subsequently indexed to similar geometry. The original diffraction patterns of complexes are reported in Fig. 4.47 to 4.53 respectively.

4.8.3.1 X-ray Diffraction Study of Cu(II) Complexes-

The Cu(II) complexes of ligand L1 and L4 were subjected to X-ray powder diffraction studies (Fig.4.47 and 4.48) X-ray powder data of all the main peaks have been indexed independently by trial and error method. The indexed powder diffraction data, the unit cell data, crystal lattice parameters of complexes are presented in Table 4.8 and 4.9. The data was indexed such that the standard deviation in the lattice parameter values reaches minimum value. The standard deviation observed for Cu(II) complexes is within permissible limit of 2%. The crystal volume is obtained from indexing of the diffraction pattern. The Z value was calculated and rounded up to the nearest whole number. The porosity percentage was calculated from the observed and calculated densities. The density calculated from diffraction data and the observed density was found to be very close to each other indicating perfection in indexing. The observed densities of $Cu(L1)_2$ and $Cu(L4)_2$ are 1.736, 1.789 gcm^{-3} and calculated densities are 1.815, 1.751 gcm^{-3} respectively. The porosity percentage is 1.142% and 1.432% respectively and complex crystallises in the monoclinic crystal system with 2 molecules per unit cell. The probable space group is P2/m

Panattoni et al[122] have determined the crystal structure of bis(N-ethyl salicyl aldiminato) Cu(II) complex by XRD and found to crystallize in monoclinic crystal system with space group $P2_1/C$. The observed and calculated densities were found to be 1.40 g cm^{-3} and 1.38 g cm^{-3} respectively. The lattice parameters reported are a = 9.824 Å, b = 8.432 Å, c = 20.989 Å, $\beta = 101^o$ and V = 1706 Å^3.

Djedouani[123] have determine the crystal structure of Bis[3-acetyl-6-methyl-2H-pyran-2,4(3H)dionato]bis(dimethyl sulfoxide)copper II by single crystal XRD and found to crystallize in monoclinic crystal system with space group $P2_1/n$. The lattice parameters were found to be a = 11.5880(5)Å, b = 6.320(5) Å, c = 16.424 (2)Å and β = 92.27(5)°, Z = 4.

Conclusively the X-ray powder diffractrograms suggest that the Cu(II) complexes under investigation crystallize with monoclinic crystal system and space group P2/m.

4.8.3.2 X-ray Diffraction Study of Co(II) Complexes-

The X-ray power diffractogram of $[Co(L4)_2]$ and $[Co(L6)_2]$ complexes were selected for the study and are reported in (Fig.4.49 and 4.50). The XRD data was fed to computer to get the values of h, k, l, d, for various refluxes using $1/d^2$ values. The indexing of data with respect to prominent peaks was done independently by trial and error method. The crystallographic data and the indexed powder diffraction data is listed in Table 4.10 and 4.11. The standard deviation in crystal parameter found is within permissible limit. The observed densities of $[Co(L4)_2]$ and $[Co(L6)_2]$ are 1.1235, 1.3214 gcm^{-3} and calculated densities are 1.4221, 1.4312 gcm^{-3} respectively. The porosity percentage was calculated from the observed and calculated density which is found to be 21.005% and 7.728% respectively. The crystallographic data of the complexes fit perfectly in monoclinic crystal system with 4 molecules per unit cell. The probable spaces group is P2/m.

Bruckner et al[124] reported cryatallographic study of N,N'-ethylene bis(salicylaldehyde iminato) Co(II) complex and found to crystallize in monoclinic system with probable space group C_2/c. The lattice parameters are found to be a = 26.52 ± 0.03, b = 7.05 ± 0.01, c = 14.36 ± 0.02 Å, β = 98.4 ± 0.3°, Z = 8, Dcal = 1.63 g cm^{-3} and Dobs = 1.60 g cm^{-3}.

The XRD of Co(II) complex of N,N'-(o-phenylene) bis (salicylaldehyde imine) was studied by Pahor et al[125] and reported that the crystals were monoclinic with space group P2/n and lattice parameters reported are a = 10.681Å, b = 8.354 Å, c = 18.185 Å, β = 105.3° , Dcal = 1.58 g cm^{-3} and Dobs = 1.62 g cm^{-3} having 4 molecules per unit cell.

Conclusively the X-ray powder diffractogram suggest that Co(II) complex under investigation crystallize with monoclinic crystal system having space group P2/m.

4.8.3.3 X-ray Diffraction study of Ni(II) Complexes-

The complexes of L6 and L8 were used to study the X-ray powder diffrractogram and are presented in Fig. 4.51 and Fig. 4.52. The indexing in the powder diffraction was done independently by trial and error method. The crystallographic data and the indexed powder diffraction data is presented in Table 4.12 and 4.13. The standard deviation observed is within the permissible limit. The observed density for $[Ni(L6)_2]$ and $[Ni(L8)_2]$ is 1.202 gcm^{-3} and 1.681 gcm^{-3} while calculated density from Z value and unit cell volume for complexes are 1.2695 gcm^{-3} and 1.8242 gcm^{-3} respectively. The porosity percentage calculated from the observed and calculated densities was found to be 5.321 and 7.832 respectively. The crystal system was found to be monoclinic with 4 molecules per unit cell having probable space group p2/m.

Frasson and Panattoni[126] reported monoclinic crystal system for Ni(II)-methyl glyoxime complex.

Salunke[127] have determined the crystal structure of Ni(II) complexes of azo Schiff bases of dehydroacetic acid and substituted anilines by XRD and found to crystallize in monoclinic crystal system with space group Pm with 2 molecules per unit cell. The observed and calculated densities were found to be 0.9872 g cm^{-3} and 1.2968 g cm^{-3} respectively. The lattice parameters reported are a = 12.044 Å, b = 6.4171 Å, c = 34.6572 Å, $\beta = 74^{o}53'$ and V = 2586.5 $Å^3$.

Conclusively, the X-ray powder diffractogram suggest that Ni(II) complexes under investigation crystallize with monoclinic crystal system with probable space group P2/m.

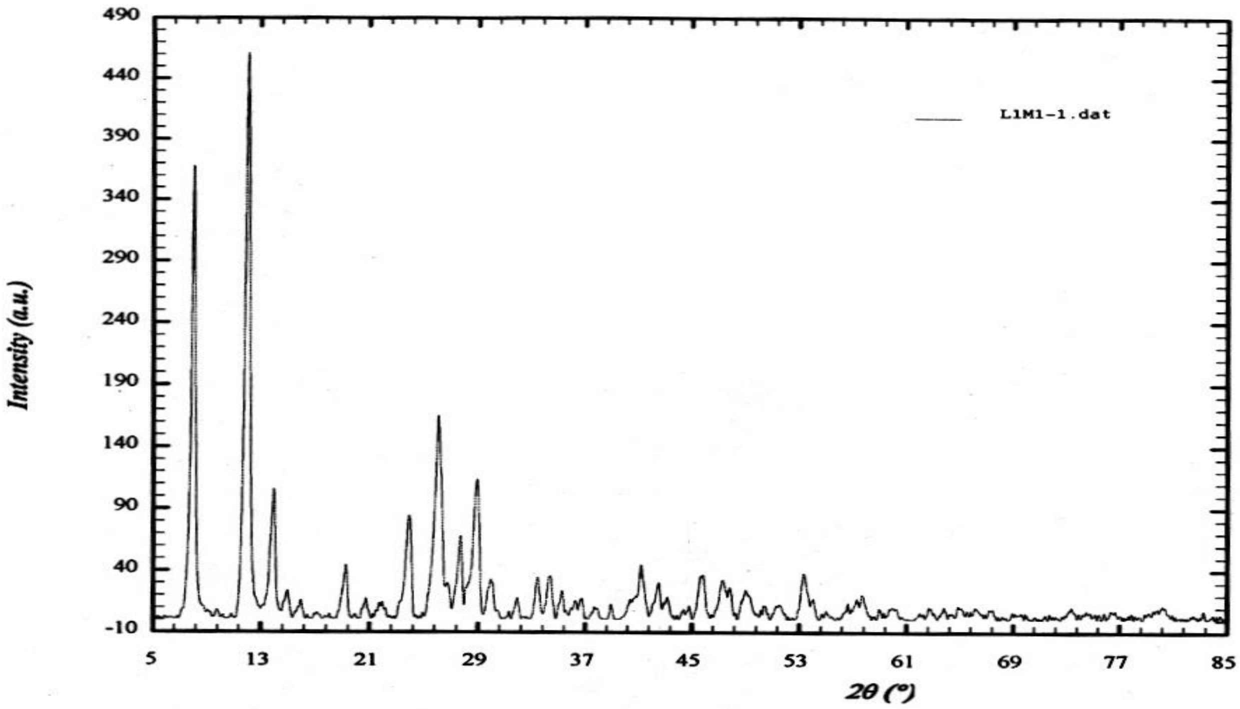
4.8.3.4 X-ray Diffraction Study of Mn (II) Complexes-

The Mn(II) complex of ligand L6 is subjected to X-ray powder diffraction studies. The X-ray diffraction pattern of the complex $[Mn(L6)_2]$ is shown in Fig. 4.53. The XRD data was fed to get the values of h, k, l, for various reflections using $1/d^2$ values. The indexing of data with respect to prominent peaks was done independently by trial and error method. The unit cell data crystal lattice parameters and the data obtained after indexing the powder data is presented in Table 4.14. The standard deviation observed is within the permissible range. The observed density for $[Mn(L6)_2]$ is 1.732 gcm^{-3} while calculated density from Z value and unit cell volume for complexes are 1.8021 gcm^{-3}. The porosity percentage calculated from the observed and calculated densities and found to be 4.017 %. The crystal system was found to be monoclinic with 2 molecules per unit cell having probable space group p2/m.

Aguiari et al[128] performed the X-ray diffraction study of Mn(II) complexes of ligands derived from 3-methoxy salicylaldehyde and 1,2-diaminoethane and 4-N-dodecyl diethylene triamine and the compound reported to crystallize in monoclinic crystal system with space group $P2_1/C$ having 4 molecules per unit cell. The lattice parameters reported are a = 10.910 Å, b = 12.382 Å, c = 21.196 Å, $\beta = 90.91^o$ and V = 1706 $Å^3$.

Rasam[129] characterized the Mn(II) complexes of N-Propanoyl-2-amino benzoates by XRD and lattice constants revealed the existence of crystals in monoclinic system containing 2 molecules per unit cell with probable space group $P2_1$. The observed densities found to match well with the calculated densities.

Conclusively the X-ray powder diffractograms suggest that Mn(II) complexes under investigation crystallize with monloclinic system having space group P2/m.



7.945	7.945	11.1190	11.119	0.004799	0.004799	-1	0	1	50.9
8.066	8.066	10.9532	10.952	0.004946	0.004946	0	0	1	70.5
12.085	12.085	7.3176	7.3175	0.011081	0.011081	1	0	1	100
14.010	14.017	6.3162	6.3129	0.014873	0.014889	0	1	1	8.7
26.065	26.065	3.4159	3.4158	0.050852	0.050852	1	2	1	19.3
26.300	26.298	3.3859	3.3861	0.051758	0.051748	2	2	0	9.5
28.905	28.894	3.0864	3.0875	0.062289	0.062244	-3	2	1	11.4

Fig. 4.47 X-ray Diffractogram of Cu(II) complex with Ligand L1.

Table 4.8 X-ray Powder diffraction data of Cu$(L1)_2$ Complex.

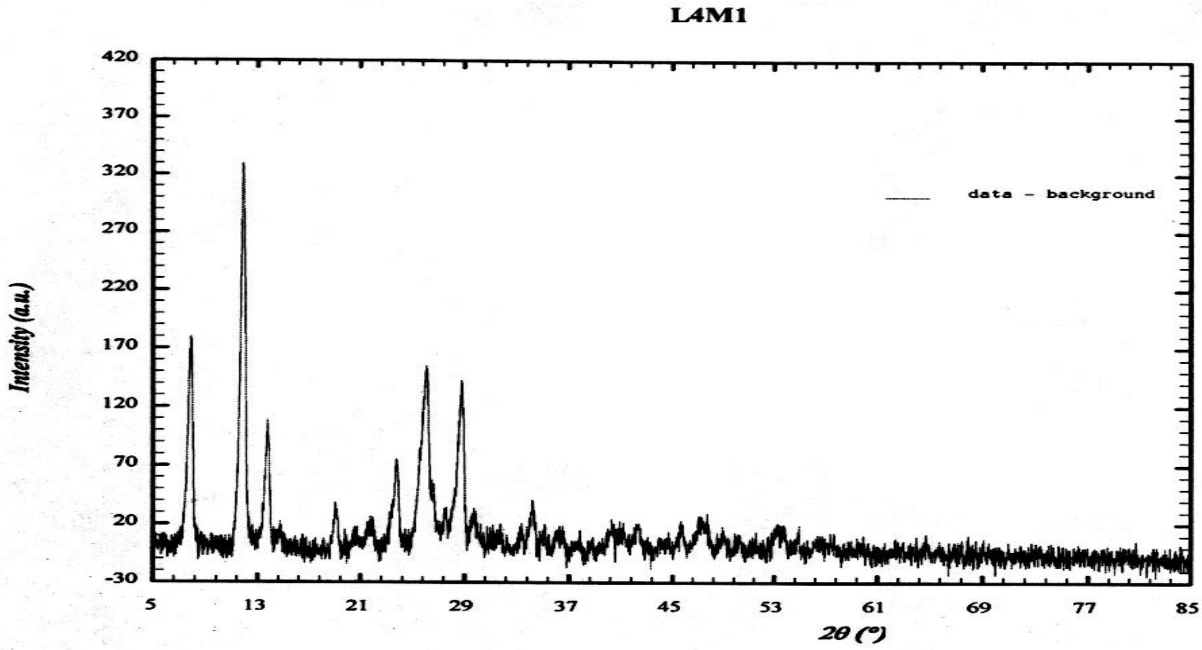
Unit cell data and crystal lattice parameter

A=15.41923 Å B=7.72515 Å C=11.99757 Å

$\alpha=90.00^0$ $\beta=114.084^0$ $\gamma=90.00^0$

Crystal system: - Monoclinic Space group: - P $_{2/m}$ Volume of cell = 1304.7 Å^3

Density (D_{obs}.):- 1.736506 g/cm^3 Density (D_{cal}.):- 1.751231 g/cm^3



$2\theta_{observed}$	$2\theta_{Calculated}$	d-observed (Å)	d-calcu. (Å)	$\sin^2\theta$ observed	$\sin^2\theta$ calculated	Miller Indicies			Relative intensity
						h	k	l	
7.785	7.759	11.3471	11.385	0.004608	0.004578	1	0	0	32.9
11.850	11.848	7.4622	7.4633	0.010656	0.010653	0	0	1	100
11.980	11.990	7.3815	7.3752	0.010890	0.010909	-1	1	1	68.5
13.762	13.754	6.4294	6.433	0.014354	0.014337	-1	2	1	17.1
23.750	23.750	3.7434	3.7433	0.042344	0.042344	3	1	0	9.7

Porocity: 1.1428% Particle size: 246.3716 Å Z=2

Fig. 4.48 X-ray Diffractogram of Cu(II) complex with Ligand L4.

26.154	26.110	3.4045	3.41	0.051192	0.051025	-3	0	2	25.9
28.796	28.796	3.0979	3.0978	0.061829	0.061830	1	6	1	24.6

Table 4.9 X-ray Powder diffraction data of $Cu(L4)_2$ Complex.

Unit cell data and crystal lattice parameter

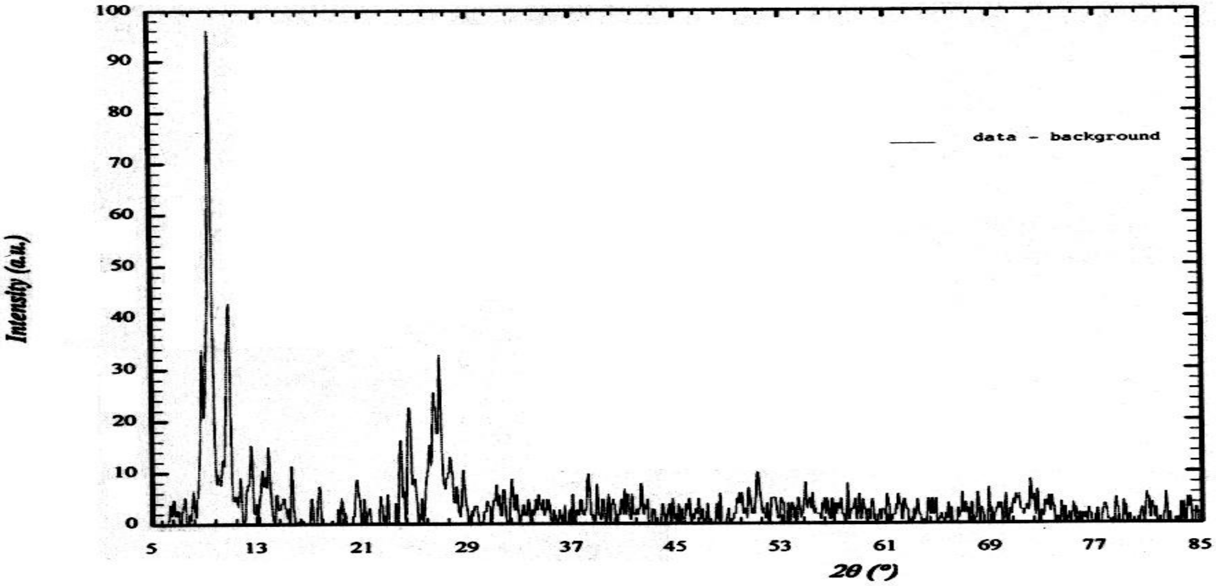
A=11.83926 Å B=22.69410 Å C=8.11671 Å

$\alpha=90.00^0$ $\beta=105.904^0$ $\gamma=90.00^0$

Crystal system: - Monoclinic Space group: - $P_{2/m}$ Volume of cell = 2097 $Å^3$

Density (D_{obs}.):- 1.789141 g/cm^3 Density (D_{cal}.):- 1.815466 g/cm^3

Porocity: 1.432% Particle size: 312.2541 Å Z=2



17.586	17.585	5.0392	5.0392	0.023367	0.023365	1	1	2	13.8
20.445	20.425	4.3404	4.3445	0.031496	0.031434	2	2	0	9.7
23.755	23.756	3.7426	3.7423	0.042362	0.042364	-4	1	2	15.2
26.786	26.779	3.3256	3.3263	0.053650	0.053623	4	1	2	21.0
28.536	28.534	3.1255	3.1256	0.060740	0.060732	-4	2	2	33.9

Fig. 4.49 X-ray Diffractogram of Co(II) complex with Ligand L4.

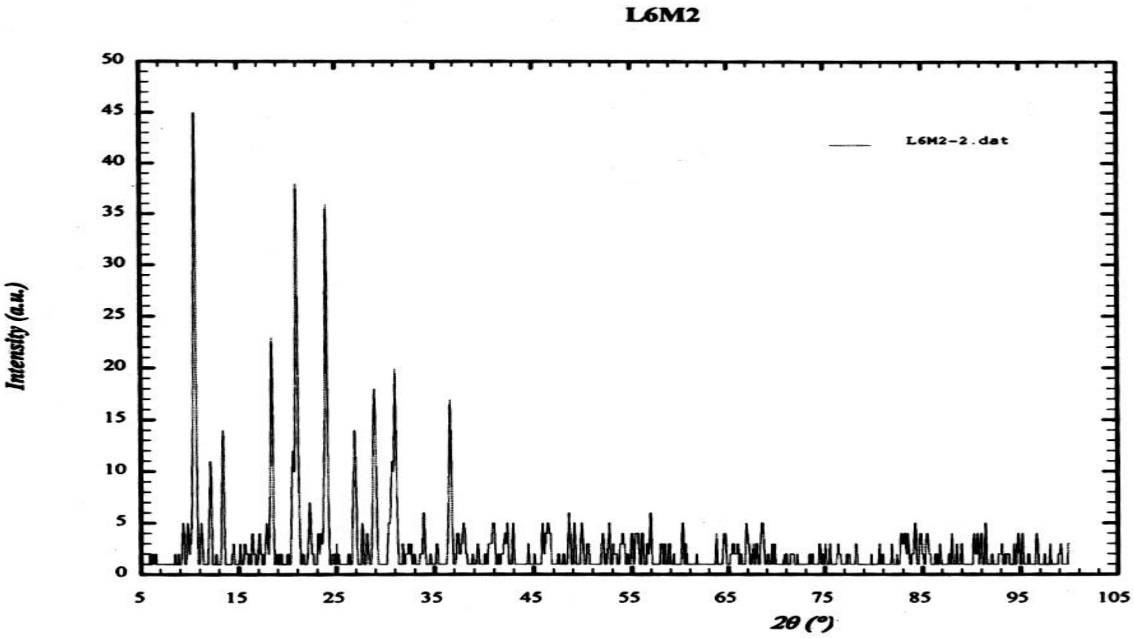
Table 4.10 X-ray Powder diffraction data of $Co(L4)_2$ Complex.

Unit cell data and crystal lattice parameter

A=18.67931 Å B=9.84437 Å C=13.10770 Å $\alpha=\gamma=90.00^0$ $\beta=98.178^0$

Crystal system: - Monoclinic Space group: - $P_{2/m}$ Volume of cell = 2385 $Å^3$

Density (D_{obs}.):- 1.12356 g/cm^3 Density (D_{cal}.):- 1.42215 g/cm^3



$2\theta_{observed}$	$2\theta_{Calculated}$	d-observed (Å)	d-calcu. (Å)	$\sin^2\theta$ observed	$\sin^2\theta$ calculated	Miller Indicies			Relative intensity
						h	k	l	
10.580	10.582	8.3547	8.3532	0.008501	0.008503	0	0	1	93.8

Porocity: 21.0058% Particle size: 246.37 Å Z=4

Fig. 4.50 X-ray Diffractogram of Co(II) complex with Ligand L6

12.115	12.104	7.2996	7.306	0.011136	0.011116	2	0	0	26.6
13.411	13.430	6.5970	6.5875	0.013634	0.013672	-2	0	1	32.0
18.406	18.402	4.8164	4.8173	0.025578	0.025566	2	0	1	66.8
20.531	20.523	4.3225	4.324	0.031758	0.031735	1	1	0	100
23.985	23.996	3.7072	3.7055	0.043175	0.043211	1	1	1	86.6
26.865	26.866	3.3160	3.3158	0.053964	0.053966	3	1	0	26.6
28.886	28.882	3.0885	3.0887	0.062207	0.062191	-2	1	2	36.5
30.990	30.994	2.8833	2.8829	0.071372	0.071390	3	1	1	57.0
36.585	36.569	2.4542	2.4552	0.098513	0.098430	5	1	0	39.6

Table 4.11 X-ray Powder diffraction data of Co(L6)$_2$Complex.

Unit cell data and crystal lattice parameter

A=15.34769 Å B=4.52683 Å C=8.7738 Å $\alpha=\gamma=90.00^0$ $\beta=107.81^0$

Crystal system: - Monoclinic Space group: - P $_{2/m}$ Volume of cell = 1580 Å^3

Density (D$_{obs}$.):- 1.32141 g/cm^3 Density (D$_{cal}$.):- 1.4312 g/cm^3

Porocity: 7.728% Particle size: 147.32 Å Z=4

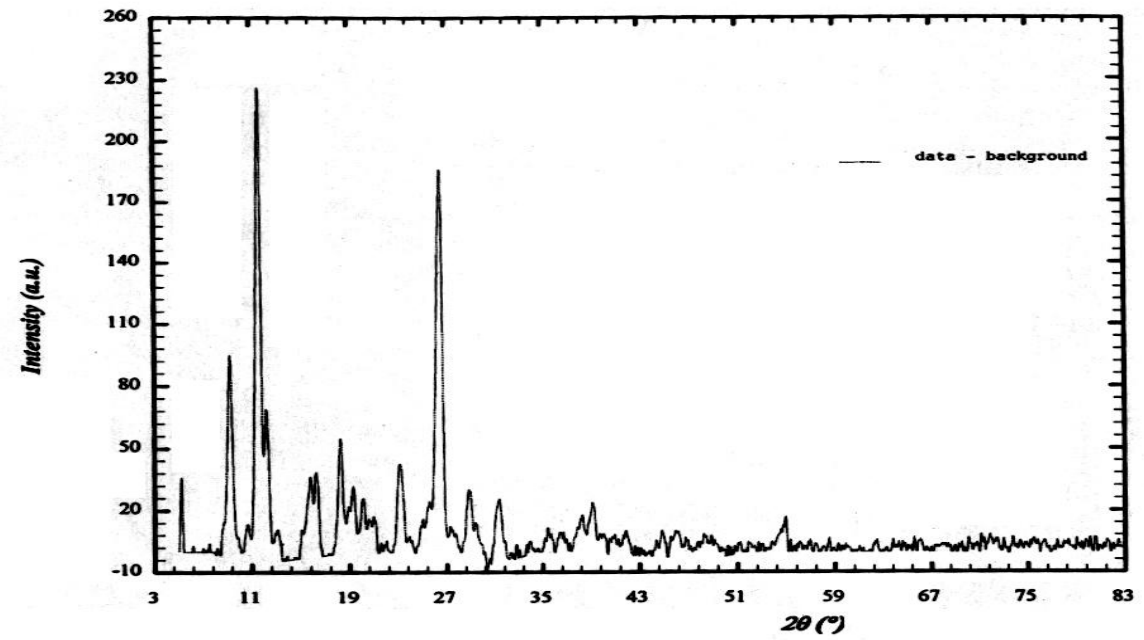


Fig. 4.51 X-ray Diffractogram of Ni(II) complex with Ligand L6.

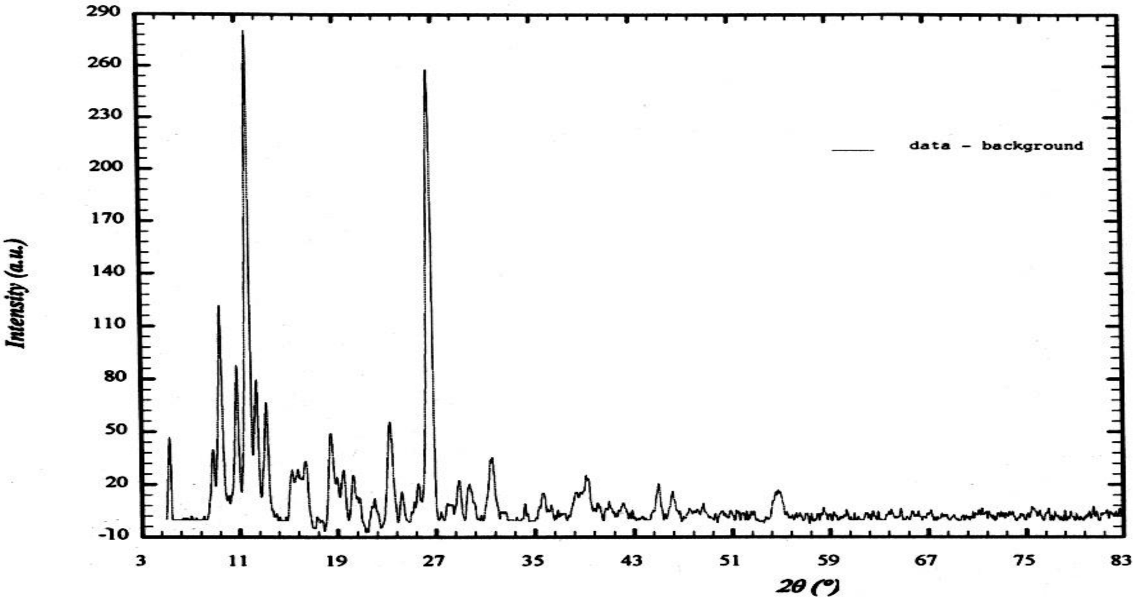
5.210	5.191	16.9482	17.01	0.002066	0.002050	0	2	0	23
9.241	9.247	9.5626	9.5559	0.006489	0.006497	1	1	0	27.5
12.196	12.191	7.2514	7.2541	0.011284	0.011276	-1	0	1	100
15.765	15.761	5.6168	5.6118	0.018808	0.018799	1	5	0	18.6
16.215	16.188	5.4619	5.4708	0.019890	0.019825	0	3	1	7.9
18.241	18.238	4.8597	4.8603	0.025125	0.025117	0	7	0	11.9
21.145	21.145	4.1983	4.1982	0.033665	0.033665	0	6	1	8.3
26.565	26.567	3.3527	3.3524	0.052787	0.052795	-1	9	1	68.5

Table 4.12 X-ray Powder diffraction data of Ni(L6)$_2$Complex.

Unit cell data and crystal lattice parameter

A=11.65607 Å B=34.02341 Å C=7.31117 Å $\alpha=\gamma=90.00^0$ $\beta=121.323^0$

Crystal system: - Monoclinic Space group: - P 2/m Volume of cell = 2476 Å^3



Density (D_{obs}.):- 1.202 g/cm^3 Density (D_{cal}.):- 1.2695 g/cm^3

Porocity: 5.321% Particle size: 115.657 Å Z=4

Fig. 4.52 X-ray Diffractogram of Ni(II) complex with Ligand L8.

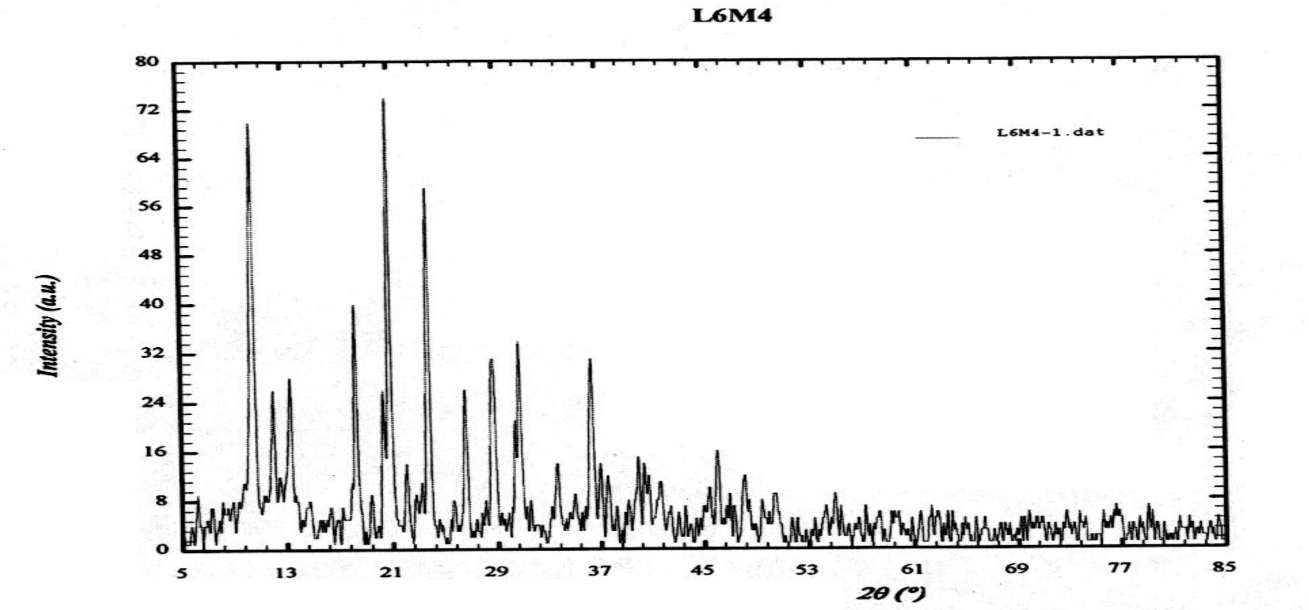
10.806	10.774	8.1806	8.2047	0.008867	0.008813	2	0	0	20.4
11.795	11.792	7.4967	7.4986	0.010558	0.010551	-1	1	1	100
12.426	12.411	7.1179	7.126	0.011712	0.011684	1	0	1	17.0
13.196	13.196	6.7040	6.7038	0.013202	0.013203	-2	1	1	11.8
18.441	18.440	4.8074	4.8075	0.025674	0.025673	-4	0	2	11.2
23.255	23.253	3.8219	3.8221	0.040623	0.040615	-3	2	1	13.7
26.571	26.571	3.3520	3.3519	0.052810	0.052812	-4	2	2	97.9
26.750	26.752	3.3299	3.3296	0.053512	0.053520	2	1	2	62.8
28.906	28.929	3.0863	3.0838	0.062292	0.062392	4	2	0	8.9

Table 4.13 X-ray Powder diffraction data of Ni(L8)Complex.

Unit cell data and crystal lattice parameter

A=19.92965 Å B=9.35182 Å C=12.58909 Å $\alpha = \gamma = 90.00^0$ $\beta = 124.572^0$

Crystal system: - Monoclinic Space group: - P $_{2/m}$ Volume of cell = 1932 Å^3



Density (D_{obs}.):- 1.6812 g/cm^3 Density (D_{cal}.):- 1.8242 g/cm^3

Porocity: 7.832 Particle size: 113.457 Å Z=4

Fig. 4.53 X-ray Diffractogram of Mn(II) complex with Ligand L6.

10.595	10.563	8.3431	8.3681	0.008524	0.008473	1	1	0	81.3
12.031	12.032	7.3504	7.3496	0.010982	0.010985	-2	0	1	24.2
13.346	13.282	6.6290	6.6606	0.013503	0.013374	-1	1	1	26.4
18.275	18.281	4.8506	4.8489	0.025219	0.025237	1	2	0	50.5
20.321	20.330	4.3667	4.3646	0.031118	0.031146	-2	0	2	26.9
20.835	20.839	4.2600	4.2591	0.032696	0.032710	0	2	1	100
23.740	23.739	3.7449	3.745	0.042310	0.042305	-3	2	1	7.4
26.541	26.541	3.3557	3.3556	0.052692	0.052694	3	0	1	31.7
28.661	28.664	3.1122	3.1117	0.061262	0.061276	-2	3	1	32.9
30.691	30.701	2.9108	2.9098	0.070032	0.070079	-3	0	3	36.8
36.330	36.330	2.4709	2.4708	0.097191	0.097193	-1	4	1	34.2

Table 4.14 X-ray Powder diffraction data of Mn$(L6)_2$Complex.

Unit cell data and crystal lattice parameter

A=16.54953 Å B=10.30473 Å C=8.73422 Å $\alpha = \gamma = 90.00^0$ $\beta = 119.940^0$

Crystal system: - Monoclinic Space group: - P 2/m Volume of cell = 1290 $Å^3$

Density (D_{obs}.):- 1. 732 g/cm^3 Density (D_{cal}.):- 1.8021 g/cm^3

Porocity: 4.017% Particle size: 231.342 Å Z=2

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CHAPTER V

RESULTS AND DISCUSSION

5.1 INTRODUCTION.

5.2 INFRARED SPECTRAL STUDIES OF LIGANDS.

5.3 INFRARED SPECTRAL STUDIES OF METAL COMPLEXES.

5.4 CONCLUSION.

5.5 REFERENCES.

CHAPTER-5

RESULTS AND DISCUSSION

5.1) INTRODUCTION:

Infrared spectroscopy is one of the important techniques in the study of metal complexes. This offers the possibility of chemical identification and provides useful information about the structure of molecule. The vibrational frequency of the bonds and functional groups of ligands are influenced by the neighboring bonded groups. The interaction of functional group with its surrounding can be identified by this technique. Infrared spectrum is useful to study the organic groups / bonds in the ligands and their bonding with metals in the complexes.

The infrared spectra of metal complexes are different than the corresponding free ligands to certain extent. The change in vibrational frequency can be related to change in molecular symmetry or group frequency or both. By correlating the spectra of ligands with that of their metal complexes, the bonding character in the metal complexes can be deduced.

The characterizations of metal chelates by their vibrational spectra are usually carried out by taking into account following consideration with respect to their free ligand spectra.

1) Change in the position of bands.
2) Appearances of new bands.
3) Splitting of bands into multipletes.
4) Change in relative intensities of bands.

The assignment of various stretching and bending vibrations for a molecule can be made by the selection rules given in the literature, the interaction of the functional group along with the surrounding ions is important and can be identified by absorption spectra of metal complexes in the IR region.

5.2) INFRARED SPECTRAL STUDIES OF LIGAND:-

(Results and discussion)

Schiff bases used for synthesis of complexes in the present study are derived from dehydroacetic acid and different aromatic amines. The IR spectral data of ligands are tabulated in Table 5.1 and their spectra are presented in fig. 5.1 to 5.8. The data presented in the Table 5.1 is discussed by assigning various bands in the spectra with respect to vibration caused by different functional groups of ligands. The absorption pattern in infrared spectra exhibits complex nature due to various vibrational modes. However, with limited objective only important band frequencies related to enolic –O-H, aromatic >C=C<, azomethine >C=N-, aryl azomethine >C-N=, lactone carbonyl C=O and enolic C-O / C=O groups of ligands that are involved in the complex formation are discussed.

5.2.1) Enolic O-H frequency (inter molecular H bonded):-

In all Schiff bases, the-O-H stretching frequencies were observed as broad weak bands at 3362 to 3371 cm^{-1}. The normal free-O-H stretching frequency ranges from 3600-3500 cm^{-1} to above value is accepted due to strong intermolecular hydrogen bonding between enolic-OH and the nitrogen of the azomethine group. (O-H……N).

Venkateshwar Rao. et.al.[1] have assigned a band at 3400 cm^{-1} to –OH (intermolecular H-bonded) vibrations of Schiff bases derived from Dehydroacetic acid and thiocarbohydrazide.

More et.al.[2] have assigned a broad weak band at 2900 cm^{-1} for the intermolecular hydrogen bonded –OH of Schiff bases derived from substituted 2-amino thiazoles and o-hydroxy aldehydes.

Mahapatra et.al.[3] was assigned the IR bands at 3000 and 3475-3380 cm^{-1} due to –O-H….N intermolecular hydrogen bonding. The absence of these bands in the metal chelates suggested coordination of the deprotonated dianionic ligands to the metal ions.

Bahed et.al.[4] assigned a band at 2935-2915 cm^{-1} to intermolecular hydrogen bonded phenolic -OH stretching of the Schiff base ligands derived from 2-hydroxy-5-methyl acetophenone and diamino propane. Its disappearance in the spectra of the chelates indicated deprotonation of –OH and subsequent coordination at oxygen with metal ion.

Thus the broad weak bands at 3362 to 3371 cm^{-1} in the present study were assigned to hydrogen bonded enolic –O-H…N stretching frequency. These bands disappeared in the spectra of their respective metal chelates owing to the deprotonation of –O-H and subsequent coordination of oxygen with metal ion.

5.2.2) Azomethine (C=N) stretching frequency:-

The Schiff bases exhibit azomethine (C=N) stretching vibrational bands at 1689-1471 cm^{-1} region.[5] Rao et.al.[6,7] reported C=N stretching band at 1665 cm^{-1} and 1650 cm^{-1} in the IR spectra of dehydroacetic acid-glycine anil and dehydroacetic acid-ethylene diamine anil respectively. Abdulla et.al.[8] assigned IR spectral bands at 1647-1625 cm^{-1} to C=N stretching vibration of schiff bases derived from hydrazine 5-methyl carbodithioate, thiosemicarbazide and dehydroacetic acid.

Kotwale et.al.[9] observed C=N frequencies in the heterocyclic Schiff bases derived from substituted salicylaldehyde, 2-hydroxy-1-napthaldehyde and amino pyridines at 1621-1608 cm^{-1}. Mane et.al.[10] assigned 1670-1660 cm^{-1} frequencies in the spectra of schiff bases of dehydroacetic acid and aromatic amines to C=N stretching vibrations.

The various vibrations are observed for azomethine group of conjugated system. In many schiff bases, C=N stretching frequency is dependent on the substitutent on it, mostly causing resonance interaction and hydrogen bonding. [11]

In the present work, the bands observed at 1646 to 1663 cm^{-1} are assigned to azomethine C=N stretching vibrations.

5.2.3) Lactone carbonyl (C=O) stretching frequency:-

The bands appeared at 1695 to 1715 cm^{-1} in the IR spectra of all ligands were assigned to C=O stretching vibrations of lactone carbonyl and the fact is supported by literature data. The carbonyl (C=O) stretching frequency of tri and tetradentate Schiff bases derived from diamines, amino acids, amino phenols/alcohols and dehydroacetic acid were observed at 1740-1685 cm^{-1} by Tan et.al.[12] and other workers[6,7].

5.2.4) Aromatic ring C=C stretching frequency:-

The IR bands due to aromatic ring C=C stretching vibrations are often seen around 1600-1585 cm^{-1} and 1500-1400 cm^{-1} region[5]. Tan et.al.[12] reported the appearance of IR bands at 1590-1545 cm^{-1} for the complexes of Schiff bases derived from anilines, diamines, amino acids, amino phenols, amino alcohols and dehydroacetic acid and assigned to C=C aromatic ring. In the present investigation the bands at 1571 to 1580 cm^{-1} are assigned to (C=C) aromatic ring stretching vibrations.

5.2.5) Aryl azomethine C-N stretching frequency:-

The IR bands at 1428 to 1455 cm^{-1} are due to aryl C-N vibrations. Percy and Thorton[13] studied N-aryl salicylaldehydeimines and suggested that the appearance of two IR bands in the region 1350-1375 cm^{-1} and 1470-1450 cm^{-1} attributable to aromatic azomethine C-N stretching vibrations. Maria et.al.[14] assigned the bands at 1330-1315 cm^{-1} in the IR spectra of Schiff base metal complexes derived from 4, 6 diamino 1, 2 dihydro-2 thiopyrimidine to C-N stretching vibrational mode. The bands at 1360–1350 cm^{-1} appeared in the IR spectra of transition metal complexes of Schiff bases derived from 4-amino phenol, 4-amino benzoic acid and dehydroacetic acid were assigned to stretching frequency of aryl azomethine C-N group by Shirodkar et.al.[15].

5.2.6) Enolic C-O / C=O stretching Frequency:-

The ligands in the present work are in tautomeric form. The carbonyl group may be in keto form or in enol form[16]. The C=O stretching frequency can be reported in lower value than lactones C=O. The bands appeared at 1622 to 1634 cm^{-1} in the present investigation of all ligands were assigned to enolic C=O stretching vibration mode.

The IR spectral bands due to enolic C-O stretching vibrational modes are expected to appear around[17,18] 1200 cm^{-1}. Rao et.al.[6,7] assigned the bands at 1245 - 1212 cm^{-1} and 1260 cm^{-1} for enolic C-O stretching vibrations, appeared in the IR spectra of Schiff bases derived by condensation of dehydroacetic acid with glycine, thioethanol amine and benzoyl hydrazide/semicarbazide respectively. Mane et.al.[19] has reported the enolic

C-O stretching frequency at 1250-1230 cm^{-1} for the Schiff bases derived from p-totuidine, p-bromoaniline, p-anisidine and dehydroacetic acid. On coordination shifting of these bands upwards by 20-30 cm^{-1} indicated that oxygen is involved in bonding.

In the present work weak strong bands observed at 1220 to 1247 cm^{-1} in the IR spectra of all ligands were assigned to enolic C-O stretching vibration mode.

5.3) INFRARED SPECTRAL STUDIES OF METAL COMPLEXES:-

Results and Discussion:-

Infrared spectral study is useful in the identification of functional and the effect of their surrounding groups and their bonding with metal in the complexes. The assignment for frequencies of different groups in metal complexes corresponding to those considered for ligands have been proposed on the basis of literature data of similar metal complexes.

The IR spectra of metal complexes are presented in the Fig. 5.9 to 5.48 and their spectral data along with their characteristic parameters are tabulated in Tables 5.2 to 5.6

5.3.1) Cu(II) Complexes:-

The IR spectra of Cu(II) complexes are presented in fig.5.9 to 5.16 and their group absorption frequencies are tabulated in Table 5.2.

i) Azomethine (C=N) and Aromatic(C=C) stretching Frequency:-

In the spectra of Cu(II) complexes, the medium to strong bands appeared in the region 1610-1651 cm^{-1} were assigned to C=N stretching vibrational mode. In the corresponding ligands, frequencies for same group are observed from 1646 to 1663 cm^{-1}. A downward shift of the band by 12 to 36 cm^{-1} in complexes indicate that the C=N group of the ligands is coordinated to the metal ion via its azomethine nitrogen[20].

Rao et.al.[6] observed similar bathochromic shift of the C=N band for Cu(II) complex derived from DHA-gly. anil. Symal et.al.[21] reported the lowering of C=N stretching frequency in dioxo Uranium (VI) complexes by 10-25 cm^{-1} in comparison of the free ligands. This lowering may be due to reduction in electron density in the azomethine link as the nitrogen coordinates to the metal ion.

The medium to strong band in the region 1560-1573cm^{-1} in the IR spectrum of Cu(II) complexes were assigned to aromatic C=C stretching vibration[22]. These bands in the corresponding free ligands appeared almost in the same region 1571-1580 cm^{-1}. However, the bands due to C=C aromatic ring vibrations may shift their position as a result of change in the distribution of electrons and molecular environment due to introduction of metal ion [23].

ii) Aryl C-N stretching frequency:-

The IR bands in the region 1428-1460 cm^{-1} attributed to aromatic C-N stretching vibrations in the free ligands spectra were appeared at higher frequency side in the region 1459 to 1463 cm^{-1} in the spectra of its Cu(II) complexes. The observed increase in magnitude of vibrational frequency of this group by about 3 to 27 cm^{-1} on complexation may be attributed to increase in double bond character of aryl azomethine C-N bond presumably due to π electron delocalization from the metal to the nitrogen atom and resonance interaction with the benzene ring[23]. Similar observations were made by earlier workers for the Cu(II) complexes of Schiff bases derived from dehydroacetic acid and aromatic amines.

iii) Enolic C=O Frequecy :-

The medium to strong bands observed at 1600 to 1626 cm^{-1} appeared in the spectra of copper complexes was assigned to enolic C=O stretching vibrations. These bands in the corresponding free ligands are at 1622 to 1634 cm^{-1}. The observed downward shift of this band on chelation indicates the participation of enolic carbonyl oxygen of DHA moiety of ligands in the complex formation. A similar shift of C=O band to lower frequency side by were observed by earlier worker[16].

iv) New bands and other changes observed:-

All the ligands exhibited a broad weak band at 3362-3371 cm^{-1} assigned to O-H……N stretching vibration. The absence of these bands in the spectra of complexes further confirms the subsequent coordination of enolic oxygen with metal forming M-O bond.

The new bands observed in the region 639 to 565 cm^{-1} and 509 to 541 cm^{-1}, in the IR spectra if complexes may be assigned to the stretching of M-O and M-N bonds respectively [6,7,12].

5.3.2) Co(II) Complexes :-

The group absorption frequencies of Co(II) complex are summarized in Table 5.3 and the original spectra of these complexes are presented in fig. 5.17 to 5.24.

i) Azomethine C=N and Aromatic C=C frequency :-

In the IR spectra of Co(II) complexes the strong bands appeared in the region 1638-1650 cm^{-1} were assigned to C=N stretching frequency. It is shifted towards lower frequency than corresponding ligands 1646 to 1663. The lowering in frequency indicate the coordination through nitrogen of azomethine C=N group[5, 26].

The bands due to aromatic C=C stretching frequency was observed in the same region 1562-1577 cm^{-1} as compared to its free ligand band similar to Cu(II) complexes

ii) Aryl azomethine C-N frequency :-

The bands in Co(II) complexes at 1460-1462 cm^{-1} are due to aryl azomethine. The increase in frequency than corresponding free ligands 1428 to 1460 cm^{-1} attributed to the region similar to Cu(II) complexes[10,14,15,24].

iii) Enolic C=O frequency :-

The bands observed at 1610-1628 cm^{-1} in the Co(II) complexes are assigned to enolic C=O. The frequency of this band is decreased to lower side than the corresponding free ligand 1622 to 1637 cm^{-1}. This decrease in the frequency indicate the formation of bond between oxygen of C=O and metal ion.

iv) New bands and other changes observed :-

The absence of band in the region 3362 due to hydrogen bonded enolic O-H….N stretching frequency, confirms the participation of enolic oxygen in coordination with metal [23,27,28] in Co(II) complexes.

The new bands in the region 580-619 cm^{-1} and 513-538 cm^{-1} in the spectra of Co(II) complex indicate the vibration of M-O and M-N bonds respectively [12,15,22].

5.3.3) Ni(II) complexes :-

The group absorption frequencies of Ni(II) complex and its corresponding ligands are tabulated in Table 5.4 and IR spectra are presented in Fig. 5.24 to 5.32.

i) Azomethine C=N and Aromatic C=C frequency :-

In the IR spectra of Ni(II) complexes, the bands appeared at 1631 to 1653 cm^{-1} are assigned due to C=N stretching vibration. The bands in the corresponding free ligands are found at 1646-1663 cm^{-1}. The shift of this band to lower frequency on chelation indicates the participation of azomethine nitrogen in bonding with the central Ni atom[29].

The bands due to aromatic C=C stretching frequency was observed in the same region 1581-1582 as compared to its free ligands, similar to Cu(II) complexes.

ii) Aryl azomethine C-N frequency :-

The bands observed in IR spectra of Ni(II) complexes at 1445-1475 cm^{-1} are attributed to aryl azomethine C-N stretching. The same bands in free corresponding ligands are observed at 1428 to 1460 cm^{-1}. The observed increase in the position may be attributed to the region similar to Cu(II) complex[10,14,15,24] .

iii) Enolic C-O frequency :-

The upward shift of C-O frequency in Ni(II) complex (1243-1325 cm^{-1}) than the corresponding free ligand (1220-1247 cm^{-1}) suggest the bonding of enolic oxygen with Ni(II) during complexation [7,10,15,19,30].

The higher frequency in the metal complexes may be described to delocalization of 6-electron density from the oxygen atom to the metal ion resulting in an increase in electronegativity of oxygen atom. This will lead to greater ionic character of the C-O bond and a consequent increase in the C-O vibration frequency on metal complexation.

iv) New bonds and other changes observed :-

The IR bands observed of ligands around 3370 cm^{-1} due to O-H…..N vibration are absent in the corresponding complex indicate the deprotonation of enolic –OH and subsequent bonding of its oxygen with Ni during complex formation.

The additional bands at 596-668 cm^{-1} and 511 to 520 cm^{-1} were assigned to Ni-O and Ni-N bonds respectively [7,12,15].

5.3.4) Mn(II) and Fe(III) complexes:-

The group absorption frequencies of Mn(II) and Fe(III) complexes are summarized in Table 5.5, 5.6 and the original spectra of these complexes are presented in fig.5.33 to 5.40 and 5.41 to 5.48 respectively.

i) Azomethine C=N and Aromatic C=C frequency :-

In the IR spectra of Mn(II) and Fe(III) complexes, the strong bands appeared in the region 1578-1650 cm^{-1} were assigned to C=N stretching frequency. It is shifted towards lower frequency than corresponding free ligands 1646-1663 cm^{-1}. The lowering in frequency indicate the coordination through nitrogen of azomethine C=N group[5,24].

The bands due to aromatic C=C stretching frequency was observed in the same region 1546-1582 cm^{-1} as compared to its free ligands, similar to Cu(II) complexes

ii) Aryl azomethine C-N frequency :-

The bands in Mn(II) and Fe(III)complexes at 1443-1477 cm^{-1} are due to aryl azomethine. The increase in frequency than corresponding free ligands 1428 to 1460 cm^{-1} attributed to the region similar to Mn(II) and Fe(III) complexes[10,14,15,23].

iii) Enolic C=O frequency :-

The bands observed at 1585-1635 cm^{-1} in the Mn(II) and Fe(III) complexes are assigned to enolic C=O. The frequency of this band is shifted to lower side than the corresponding free ligand 1622 to 1637 cm^{-1}. The decrease in the frequency indicate the formation of bond between oxygen of C=O and metal ion. The absence of C=O frequency in some complexes may be due to merges with C=N frequency.

iv) New bands and other changes observed :-

The absence of ligand bands in the region 3362 cm^{-1} due to hydrogen bonded enolic O-H….N stretching frequency in Mn(II) and Fe(III) complexes, confirms the enolic carbonyl oxygen coordinates with metal [22,25,26].

The new bands in the region 585-632 cm^{-1} and 490-540 cm^{-1} in the spectra of Mn(II) and Fe(III) complexes indicate the vibration of M-O and M-N bonds respectively [12,15,21].

Table 5.1 Salient features of IR spectral data of ligands.

Bond vibrational mode stretching (*v*)	Ligand band position (wave number cm^{-1})							
	L1	L2	L3	L4	L5	L6	L7	L8
O-H---N (bonded)	3364	3362	3371	3368	3370	3364	3364	3367
C=O lactone carbonyl	1702	1715	1714	1697	1714	1702	1702	1695
C=N Azomethine group	1650	1660	1663	1649	1663	1646	1661	1663
C=C Aromatic ring	1575	1580	1578	1574	1578	1575	1571	1575
C-N Aryl azomethine	1440	1436	1460	1428	1436	1439	1455	1448
C-O-C pyrane ring	1377	1377	1377	1377	1377	1377	1377	1377
C-O Enolic	1227	1220	1247	1220	1228	1228	1226	1220
C=O Enolic	1634	1629	1637	1629	1632	1622	1628	1628

Table 5.2 Salient features of IR spectral data of Cu(II) complexes.

Bond vibrational mode Stretching (*v*)		band position of Cu(II) complexes (wave number cm^{-1})							
		L1	L2	L3	L4	L5	L6	L7	L8
O-H---N (bonded)		-	-	-	-	-	-	-	-
C=O (lactone carbonyl)		1703	1714	1713	1701	1713	1681	1712	1684
C=N(Azomethine group)		1631	1650	1651	1642	1649	1610	1651	1650
C=C Aromatic ring		1573	1561	1567	1562	1562	1567	1567	1560
C-N(Aryl azomethine)		1461	1460	1460	1459	1462	1463	1462	1462
C=O (Enolic)		1611	1621	1625	1626	1622	1600	1624	1626
New bands	M-O	611	618	618	639	617	565	618	608
	M-N	512	541	541	541	509	533	541	536

Table 5.3 Salient features of IR spectral data of Co(II) complexes.

Bond vibrational mode Stretching (*v*)		band position of Co(II) complexes (wave number cm^{-1})							
		L1	L2	L3	L4	L5	L6	L7	L8
O-H---N (bonded)		-	-	-	-	-	-	-	-
C=O (lactone carbonyl)		1705	1713	1714	1693	1714	1715	1708	1695
C=N(Azomethine group)		1648	1648	1648	1640	1649	1638	1648	1650
C=C Aromatic ring		1562	1575	1575	1577	1577	1577	1576	1580
C-N(Aryl azomethine)		1461	1460	1461	1460	1462	1460	1461	1462
C=O (Enolic)		1610	1610	1628	1603	1625	1612	1617	1623
New bands	M-O	617	612	617	617	619	580	612	615
	M-N	513	540	538	518	538	530	534	540

Table 5.4 Salient features of IR spectral data of Ni(II) complexes.

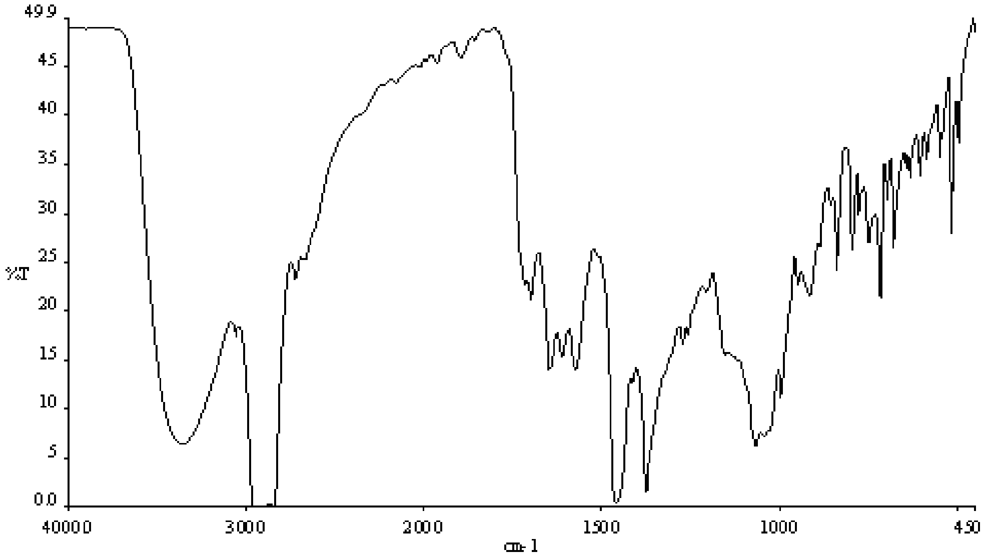
Bond vibrational mode Stretching (*v*)		band position of Ni(II) complexes (wave number cm^{-1})							
		L1	L2	L3	L4	L5	L6	L7	L8
O-H---N (bonded)		-	-	-	-	-	-	-	-
C=O (lactone carbonyl)		1703	1723	1712	1709	1739	1708	1712	1743
C=N(Azomethine group)		1633	1654	1654	1631	1645	1631	1651	1634
C=C Aromatic ring		1582	1582	1582	1582	1581	1581	1582	1582
C-N(Aryl azomethine)		1445	1475	1475	1452	1453	1452	1475	1445
C-O (Enolic)		1246	1244	1325	1243	1245	1246	1244	1256
New bands	M-O	615	617	668	606	600	596	620	620
	M-N	518	515	514	512	512	520	511	522

Table 5.5 Salient features of IR spectral data of Mn(II) complexes.

Bond vibrational mode Stretching (*v*)		band position of Mn(II) complexes (wave number cm^{-1})							
		L1	L2	L3	L4	L5	L6	L7	L8
O-H---N (bonded)		-	-	-	-	-	-	-	-
C=O (lactone carbonyl)		1720	1718	1711	1702	1718	1713	1714	1738
C=N(Azomethine group)		1641	1640	1640	1636	1650	1578	1642	1670
C=C Aromatic ring		1582	1578	1580	1578	1579	1546	1575	1579
C-N(Aryl azomethine)		1463	1459	1463	1461	1455	1443	1477	1455
C=O (Enolic)		1610	1617	1610	1600	1621	1619	1620	1621
New bands	M-O	618	608	595	610	623	585	625	636
	M-N	513	499	505	500	509	490	534	520

Table 5.6 Salient features of IR spectral data of Fe(III) complexes.

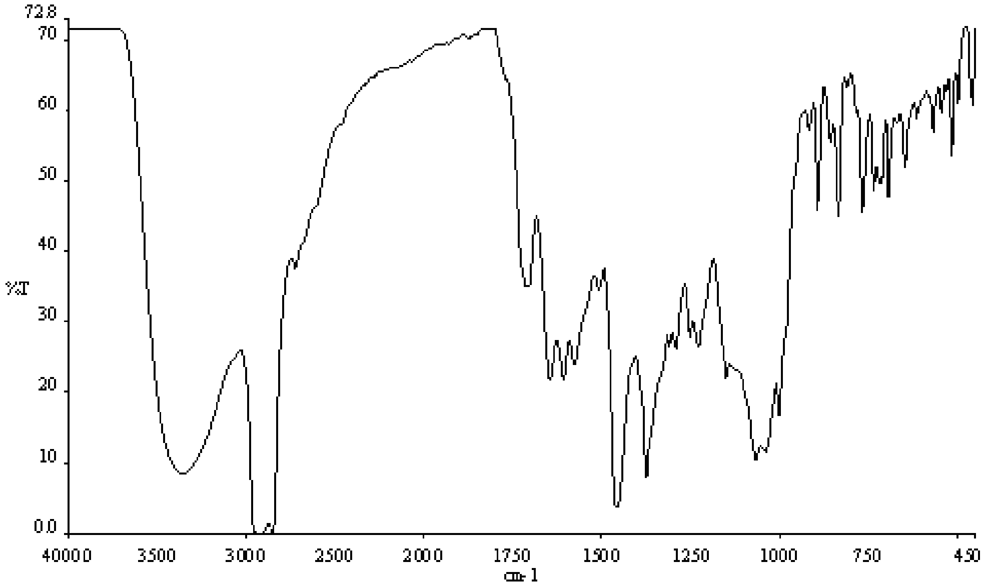
Bond vibrational mode Stretching (*v*)		band position of Fe(III) complexes (wave number cm^{-1})							
		L1	L2	L3	L4	L5	L6	L7	L8
O-H---N (bonded)		-	-	-	-	-	-	-	-
C=O (lactone carbonyl)		1708	1714	1714	1700	1711	1695	1712	1690
C=N(Azomethine group)		1648	1646	1648	1628	1649	1609	1643	1643
C=C Aromatic ring		1576	1574	1576	1576	1577	1568	1567	1574
C-N(Aryl azomethine)		1461	1462	1460	1461	1462	1459	1463	1459
C=O (Enolic)		-	-	1611	1600	1613	1585	-	-
New bands	M-O	620	616	601	630	618	632	580	611
	M-N	520	512	518	532	512	535	531	540



L1

Fig. 5.1 IR spectra of Ligand L1 (DHA+ m-Chloro Aniline).

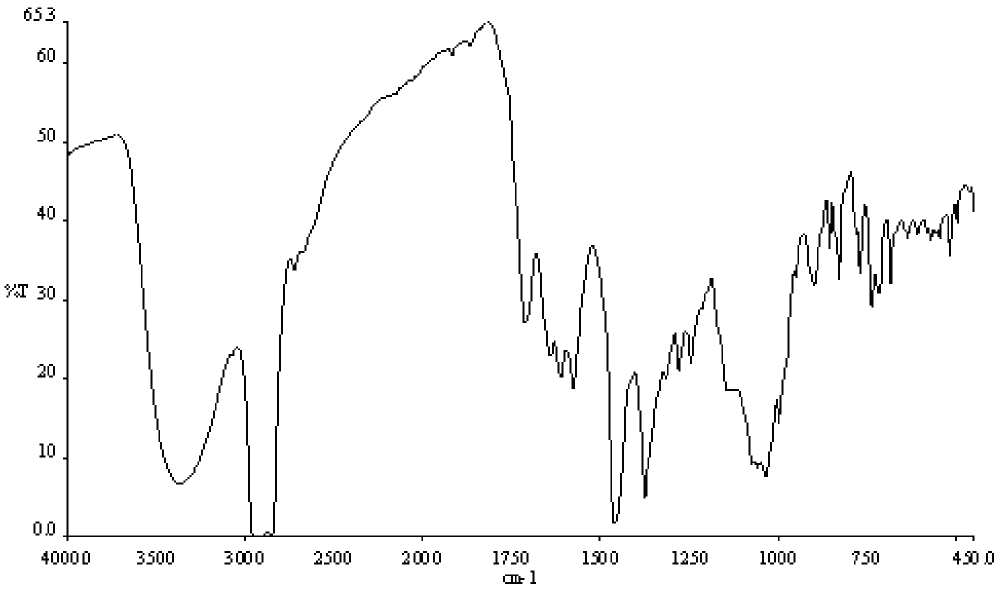
Peaks: 3364.18-6.36, 2930.42-0.00, 1702.39-21.10, 1650.88-13.94, 1634.44-15.25, 1575.11-13.94, 1440.88-0.34, 1377.48-1.53, 1069.29-6.12, 999.23-11.18, 918.61-21.43, 841.69-24.23, 799.20-26.22, 779.66-29.81, 752.91-26.94, 719.25-21.14, 700.66-31.26, 681.89-26.44, 636.31-33.59, 608.38-33.95, 589.88-35.53, 552.86-35.69, 519.88-27.99, 499.98-37.14.



L2

Fig. 5.2 IR spectra of Ligand L2 (DHA+ m-Amino Phenol).

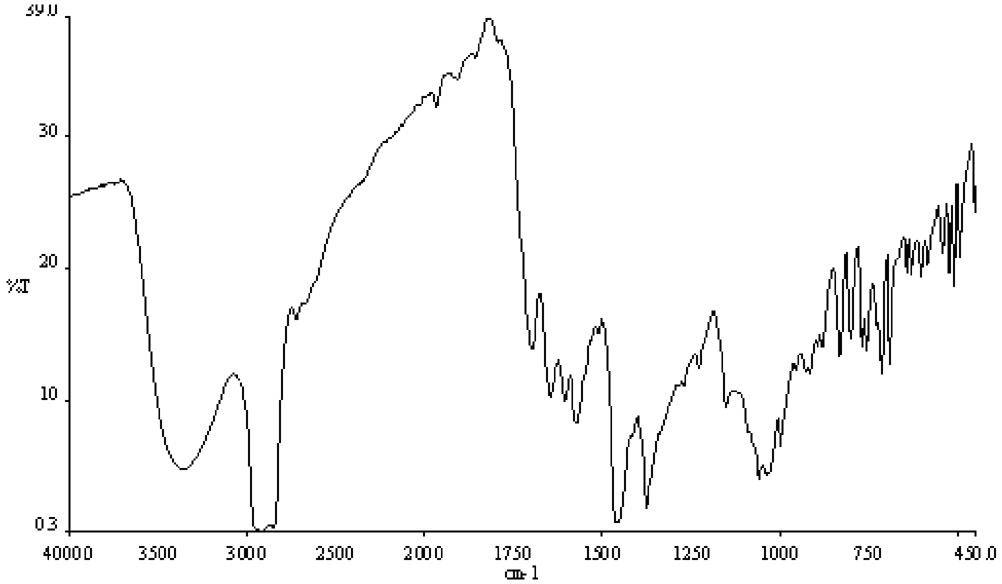
Peaks: 3362.93-8.56, 2924.76-0.03, 1715.59-35.00, 1660.55-21.78, 1629.33-21.62, 1580.05-23.89, 1510.41-34.53, 1459.40-3.70, 1377.15-7.84, 1295.22-26.23, 1254.53-27.86, 1230.77-26.36, 1069.83-10.41, 1004.87-16.66, 920.55-57.22, 896.39-45.82, 860.76-55.54, 837.08-44.79, 769.48-45.57, 738.68-48.39, 714.43-49.53 696.16-47.71, 650.02-51.93, 617.00-58.83, 571.65-56.55, 547.98-59.51, 518.57-53.50, 500.51-60.93, 459.97-60.88.



L3

Fig. 5.3 IR spectra of Ligand L3 (DHA+ m-Anisidine).

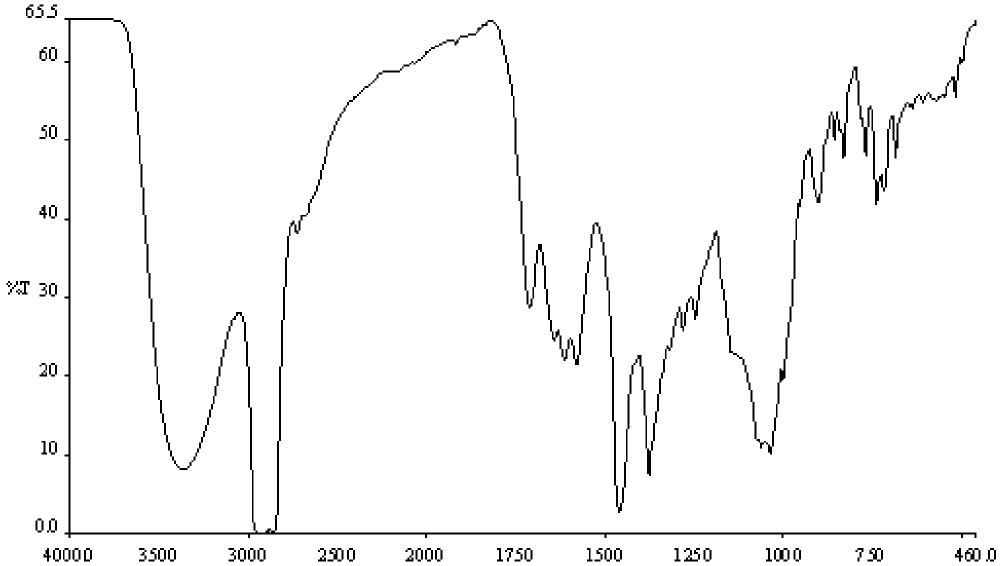
Peaks: 3371.64-6.64, 2918.30-0.00, 1714.97-27.16, 1663.22-20.29, 1637.14-19.78, 1578.19-18.82, 1460.93-1.57, 1377.23-4.93, 1283.53-20.91, 1247.97-21.83, 1037.69-7.48, 1001.00-14.20, 902.13-31.93, 858.41-36.47, 831.07-32.58, 772.65-33.23, 740.85-29.07, 720.90-30.88, 686.81-31.97, 639.24-37.94, 574.03-37.70, 519.97-35.59, 500.04-39.86.



L4

Fig. 5.4 IR spectra of Ligand L4 (DHA+ m-Toludine).

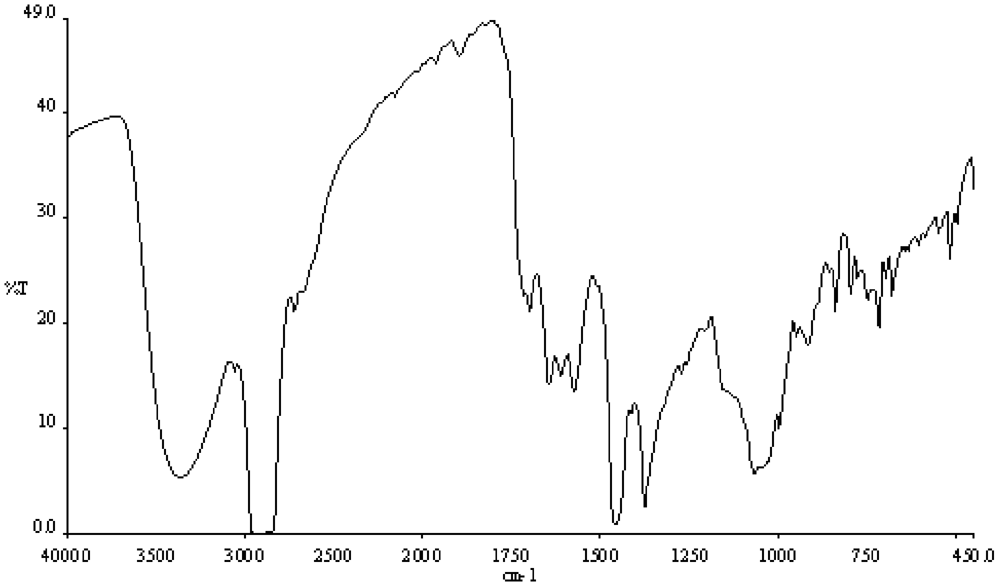
Peaks: 3368.00-4.91, 2923.61-0.27, 1697.38-14.00, 1649.07-10.42, 1629.24-9.11, 1574.60-8.43, 1428.33-0.91, 1377.92-2.02, 1063.66-4.25, 833.07-13.41, 804.15-14.68, 760.02-13.85, 716.34-12.01, 694.92-12.86, 648.52-19.71, 634.40-19.60, 607.67-19.45, 545.63-21.14, 527.14-19.66, 514.09-18.69, 498.11-20.89, 456.32-24.19.



L5

Fig. 5.5 IR spectra of Ligand L5 (DHA+ m-Bromo Aniline).

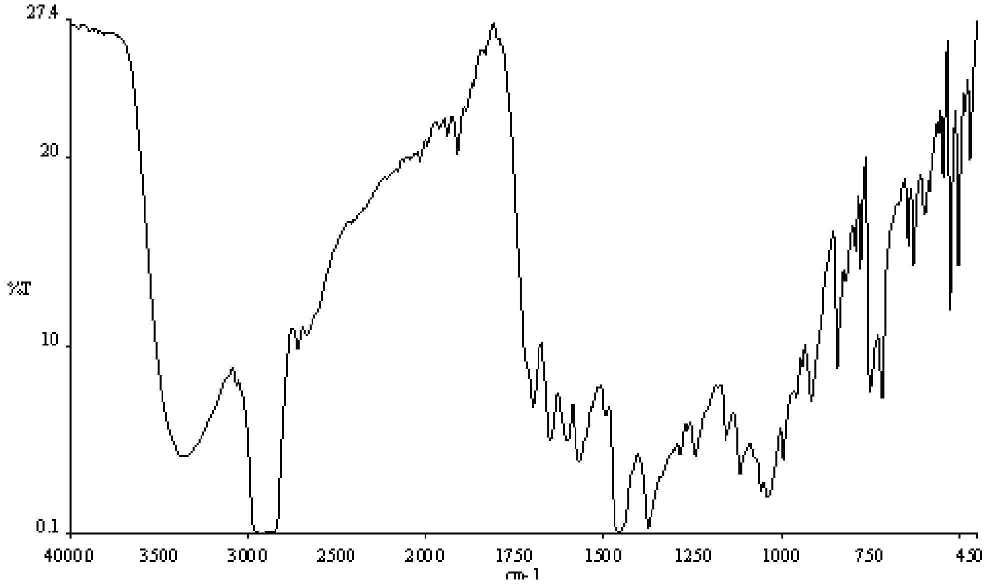
Peaks: 3370.97-8.14, 2919.28-0.00, 1714.72-28.80, 1663.16-24.99, 1630.28-21.18, 1578.66-21.39, 1436.09-2.76, 1377.21-7.33, 1283.52-25.75, 1228.06-27.25, 1038.17-10.22, 902.80-42.13, 858.49-50.00, 831.15-47.79, 772.44-48.08, 740.68-41.89, 686.92-47.83, 520.15-55.67.



L6

Fig. 5.6 IR spectra of Ligand L6 (DHA+ m-Amino Benzoic Acid).

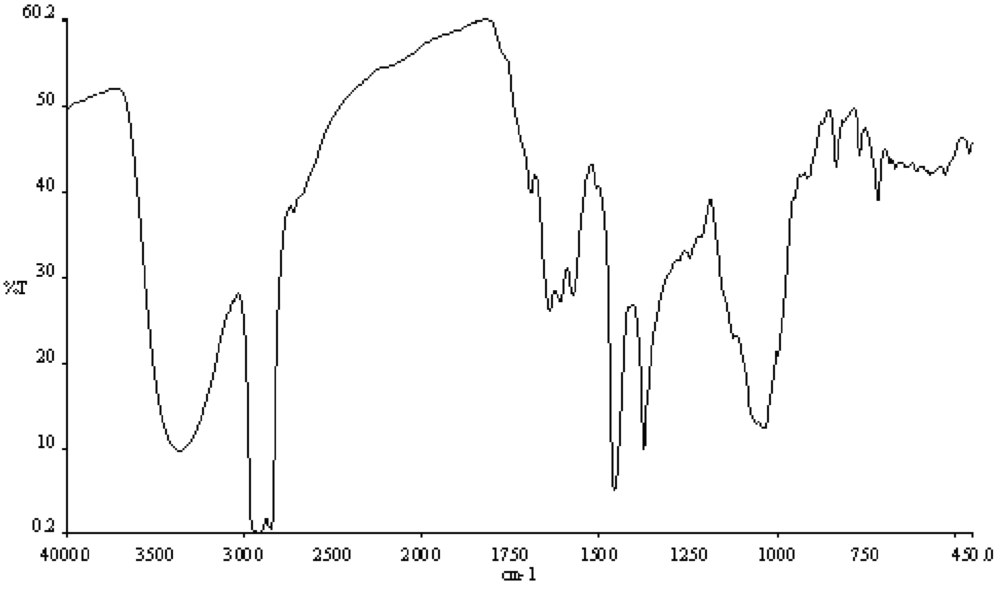
Peaks: 3364.55-5.39, 2930.32-0.00, 1702.21-21.07, 1646.20-14.28, 1622.46-15.08, 1575.14-13.59, 1439.70-0.86, 1377.44-2.38, 1069.04-5.59, 918.74-17.93, 841.69-21.18, 799.22-22.74, 719.32-19.52, 681.93-22.62, 519.87-26.11.



L7

Fig. 5.7 IR spectra of Ligand L7 (DHA+ o-Phenitidine).

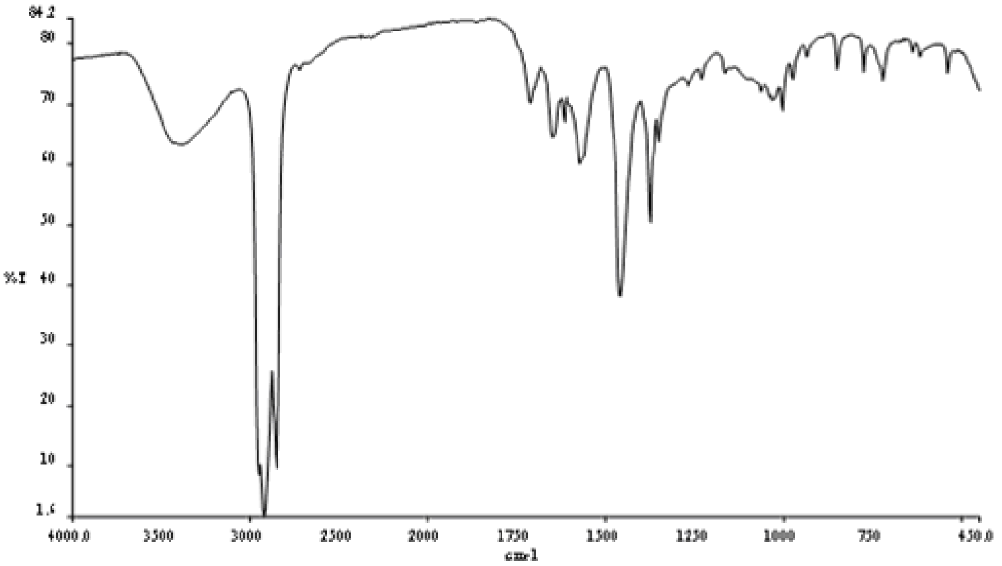
Peaks: 3364.25-4.17, 2929.59-0.10, 1914.39-20.16, 1702.92-6.78, 1661.59-5.03, 1628.18-4.83, 1571.64-3.90, 1455.18-0.24, 1377.11-0.39, 1040.40-1.99, 919.58-7.06, 846.24-8.83, 779.86-14.07, 756.27-7.62, 720.87-7.27, 648.79-15.32, 630.96-14.32, 598.07-17.01, 549.02-18.88, 529.64-11.87, 505.83-14.33, 472.42-19.84.



L8

Fig. 5.8 IR spectra of Ligand L8 (DHA+ 3,4-dichloro Aniline).

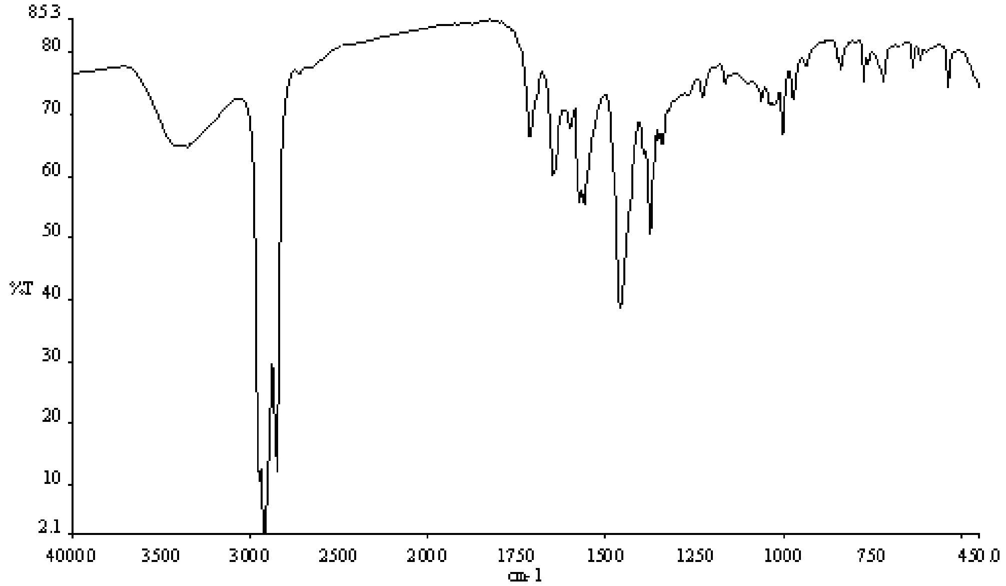
Peaks: 3367.70-9.72, 2923.70-0.23, 1695.14-39.86, 1663.02-25.96, 1628.42-26.15, 1575.90-27.89, 1448.13-5.14, 1377.43-9.92, 1034.83-12.50, 837.74-42.97, 771.70-44.11, 720.87-39.02, 532.07-41.



M1L1

Fig. 5.9 IR spectra of Cu(II) complex with Ligand L1.

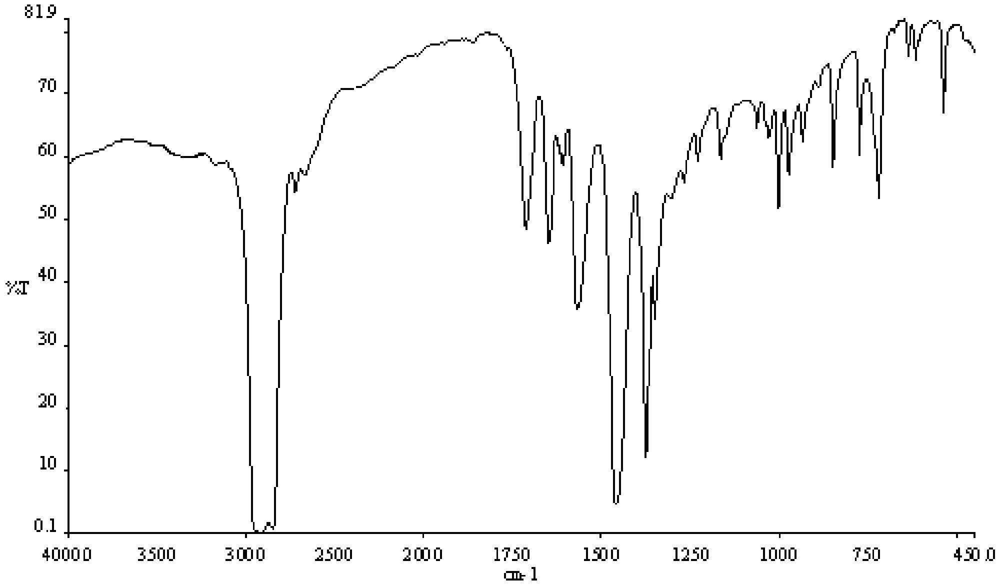
Peaks: 3396.08-63.39, 2924.42-1.55, 2854.36-9.57, 1703.83-70.17, 1631.92-64.54, 1611.34-68.87, 1573.87-60.27, 1461.19-38.16, 1377.50-50.22, 1352.78-63.70, 1280.23-75.34, 1032.69-70.57, 1005.22-68.96, 976.61-73.99, 936.95-77.82, 851.63-75.64, 776.98-75.27, 722.23-73.95, 611.28-77.85, 512.69-75.06.



M1L2

Fig. 5.10 IR spectra of Cu(II) complex with Ligand L2.

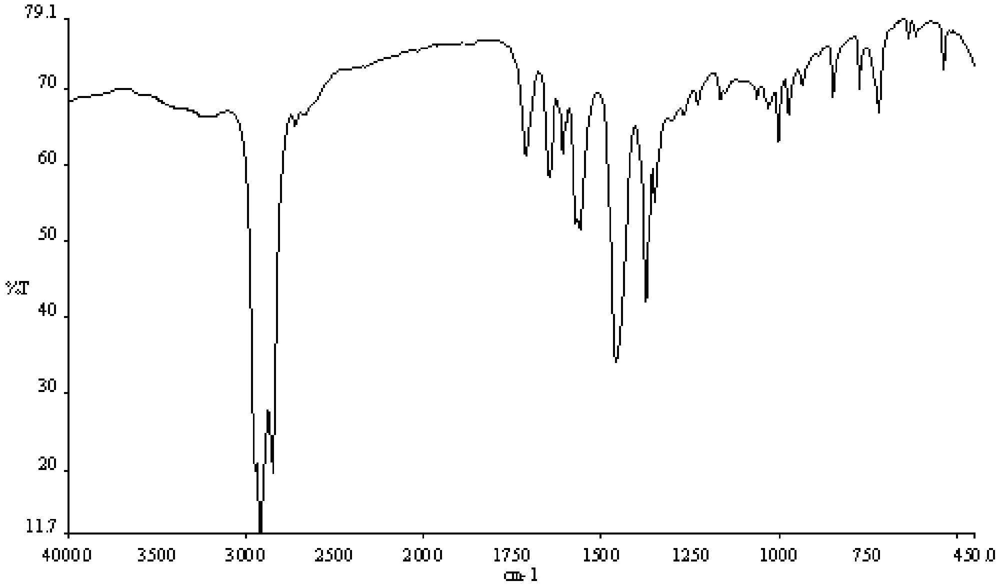
Peaks: 3356.35-64.45, 2924.69-2.13, 2854.45-12.18, 1714.70-66.28, 1650.81-60.20, 1621.24-69.13, 1561.24-55.28, 1460.77-38.76,1377.82-50.54, 1343.42-64.97, 1221.45-72.53, 1065.76-72.08, 1032.19-71.40, 1005.18-66.59, 975.71-72.19, 842.49-76.93, 777.39-75.34, 722.02-75.39, 640.32-77.51, 618.62-78.94, 541.62-74.32.



M1L3

Fig. 5.11 IR spectra of Cu(II) complex with Ligand L3.

Peaks: 2923.28-0.14, 2726.01-54.39, 1713.35-48.45, 1651.64-46.19, 1625.24-58.41, 1567.49-35.85, 1460.93-4.70, 1377.36-12.23, 1352.48-34.21, 1270.84-55.77, 1232.17-59.23, 1168.83-59.55, 1065.36-64.48, 1032.52-62.93, 1004.72-51.67, 976.06-56.97, 936.95-62.47, 851.17-58.44, 776.82-60.20, 722.22-53.38, 639.59-75.91, 618.86-75.57, 541.60-66.88.



M1L4

Fig. 5.12 IR spectra of Cu(II) complex with Ligand L4.

Peaks: 2924.30-11.71, 2854.32-19.64, 1701.98-61.24, 1642.46-58.45, 1626-63.44, 1562.06-51.51, 1459.06-34.05, 1377.44-41.93, 1352.55-54.87, 1232.37-67.78, 1168.81-68.53, 1032.54-67.49, 1004.92-62.94, 976.25-66.54, 937.39-70.29, 851.35-68.81, 776.98-69.90, 722.12-66.88, 639.45-76.49, 541.59-72.24.

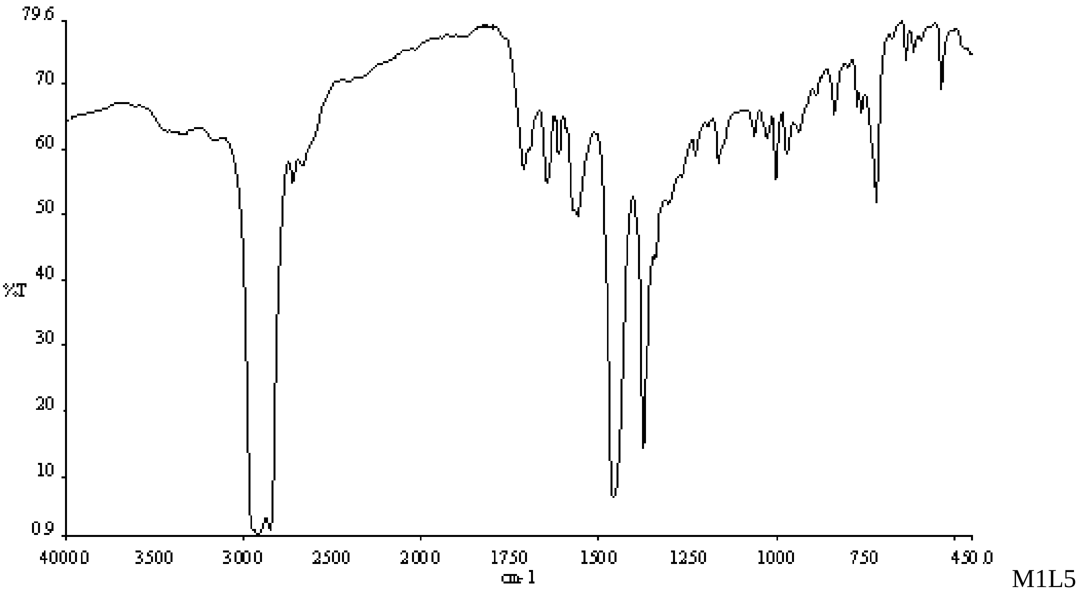


Fig. 5.13 IR spectra of Cu(II) complex with Ligand L5.

Peaks: 3355.38-61.06, 2923.79-0.88, 2853.48-1.74, 2725.80-54.83, 1713.78-57.01, 1649.61-54.98, 1622.13-61.32, 1562.87-49.91, 1462.85-6.64, 1377.31-14.16, 1231.91-59.22, 1167.30-57.81, 1065.42-62.11, 1031.44-61.68, 1005.10-55.49, 974.43-59.19, 840.93-65.51, 777.23-66.70, 765.04-65.72, 721.94-51.95, 639.85-73.68, 617.95-74.96, 509.99-69.24.

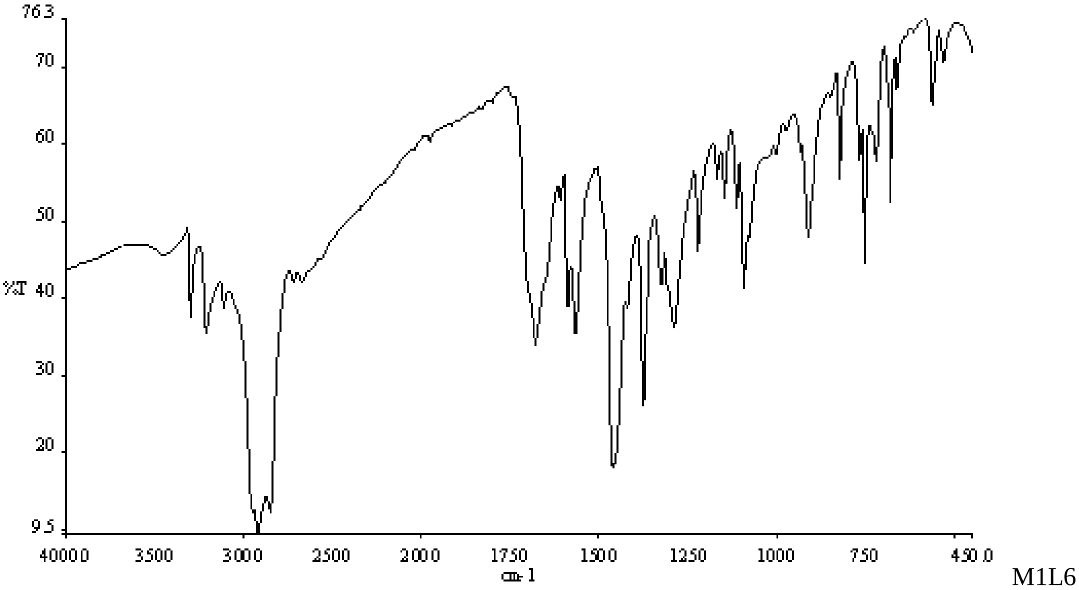


Fig. 5.14 IR spectra of Cu(II) complex with Ligand L6.

Peaks: 3304.99-37.51, 3216.58-35.51, 3117.59-38.71, 2923.15-9.53, 2853.51-12.11, 1681.84-34.09, 1610.62-52.70, 1600.28-41.35, 1591.84-38.90, 1567.91-35.35, 1463.05-18.10, 1377.52-26.19, 1327.84-41.66, 1291.25-36.22, 1223.54-46.11, 1170.57-55.50, 1149.64-52.99, 1115.73-51.67, 1094.96-41.45, 913.45-48.06, 825.64-55.31, 769.60-58.05, 755.91-44.6, 722.30-57.66, 682.95-52.50, 663.18-67.03, 565.53-65.02, 533.98-70.57.

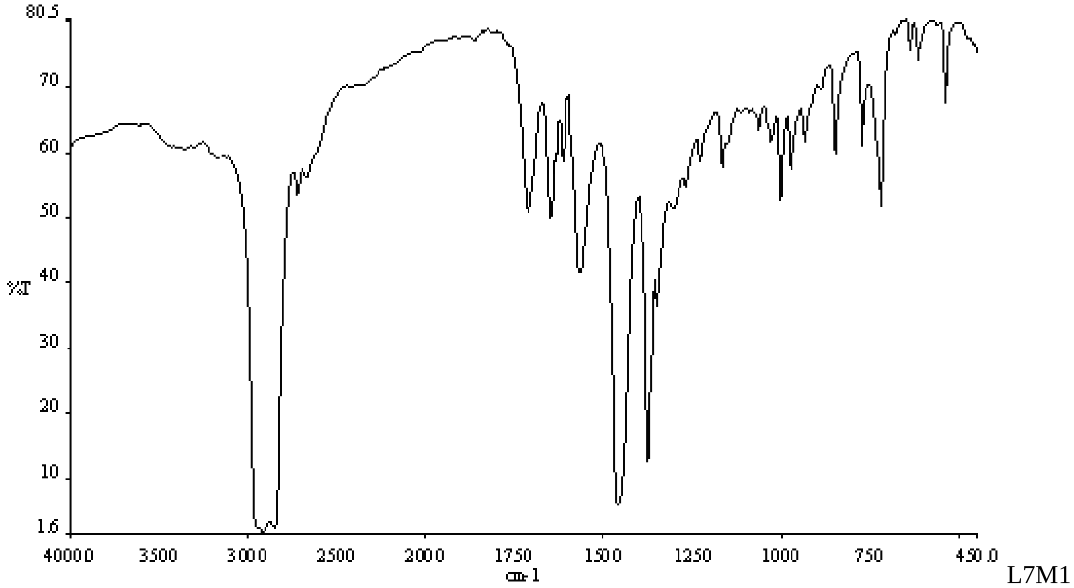


Fig. 5.15 IR spectra of Cu(II) complex with Ligand L7.

Peaks: 2923.35-1.54, 2725.83-53.62, 1712.84-50.84, 1651.08-49.87, 1624.57-58.36, 1567.08-41.40, 1462.81-5.83, 1377.34-12.43, 1352.56-36.34, 1232.03-58.63, 1168.72-57.80, 1065.35-63.23, 1032.31-61.59, 1004.69-52.62, 975.98-57.45, 936.79-61.71, 851.01-59.68, 776.67-61.08, 722.18-51.65, 639.96-75.76, 618.51-74.03, 541.52-67.53.

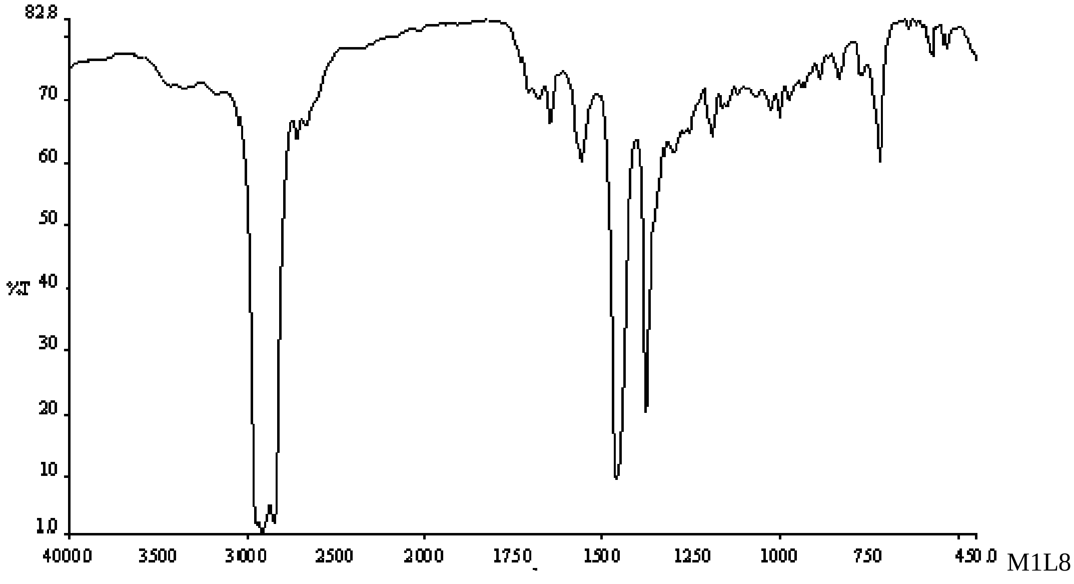


Fig. 5.16 IR spectra of Cu(II) complex with Ligand L8.

Peaks: 2923.86-0.95, 2853.71-2.34, 2725.73-63.78, 1684.13-69.97, 1650.54-68.24, 1626.37-66.51, 1560.48-60.14, 1462.92-9.50, 1377.40-20.20, 1230.14-64.45, 1168.46-68.47, 1028.45-68.24, 1002.47-67.51, 976.50-69.62, 893.42-73.29, 839.59-73.14, 721.98-60.12, 608.12-61.23, 536.22-78.11.

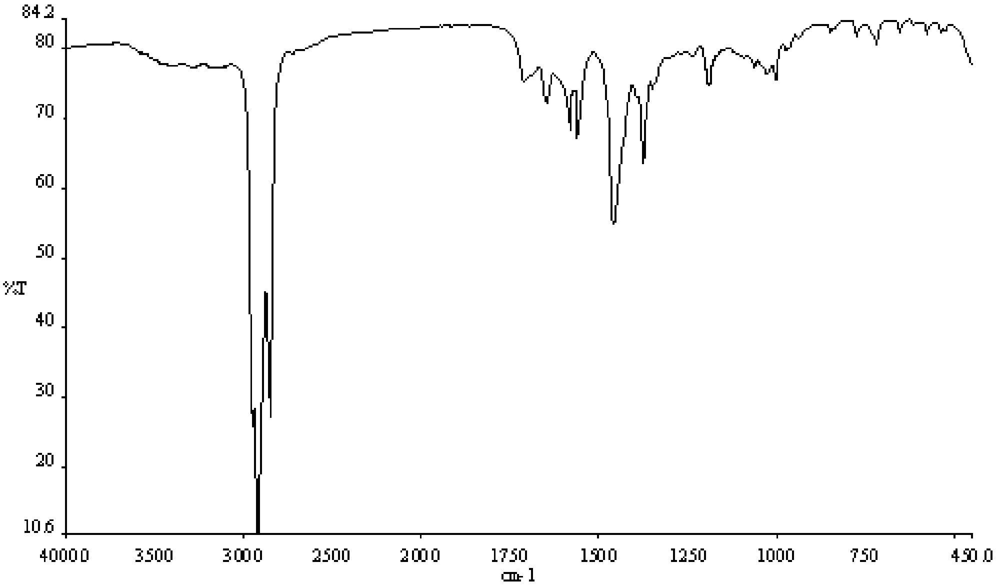


Fig. 5.17 IR spectra of Co(II) complex with Ligand L1.

Peaks: 2954.16-25.92, 2924.42-10.57, 2854.35-27.06, 1705.15-75.10, 1648.62-72.17, 1610.12-64.25, 1562.22-67.71, 1461.48-54.84, 1377.80-63.51, 1005.74-75.28, 722.06-80.72, 617.41-81.42, 513.36-82.42,.

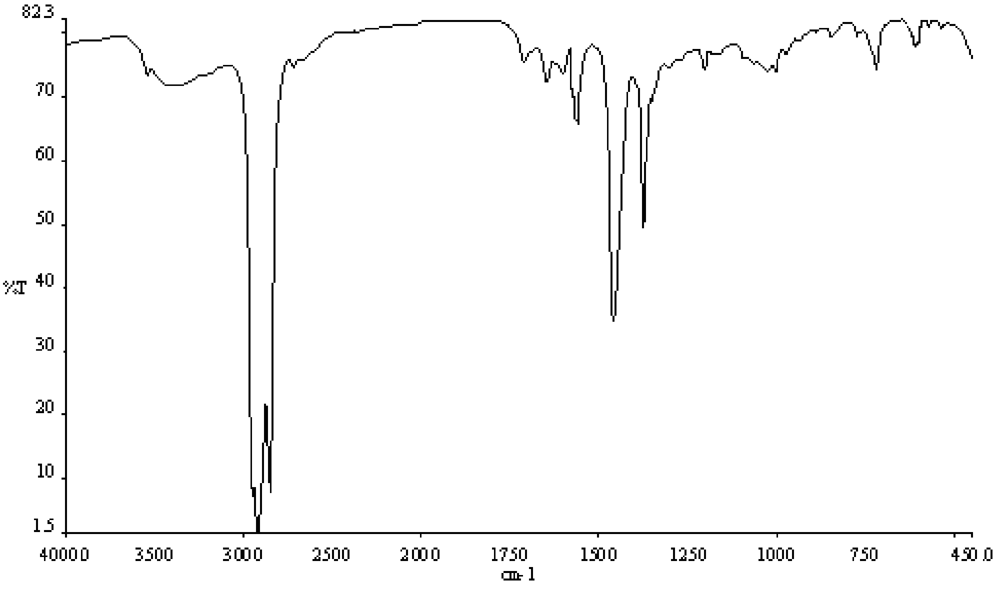
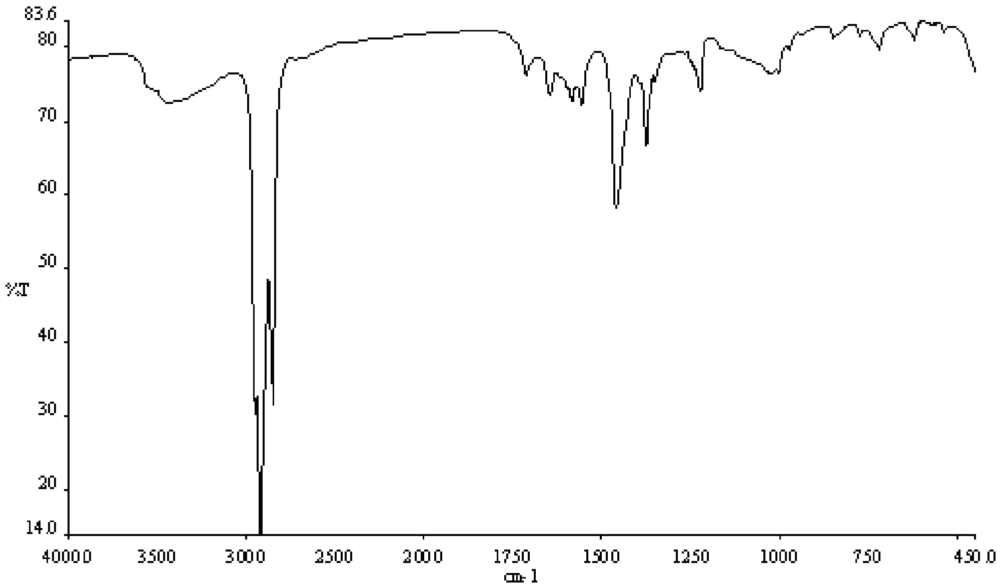


Fig. 5.18 IR spectra of Co(II) complex with Ligand L2.

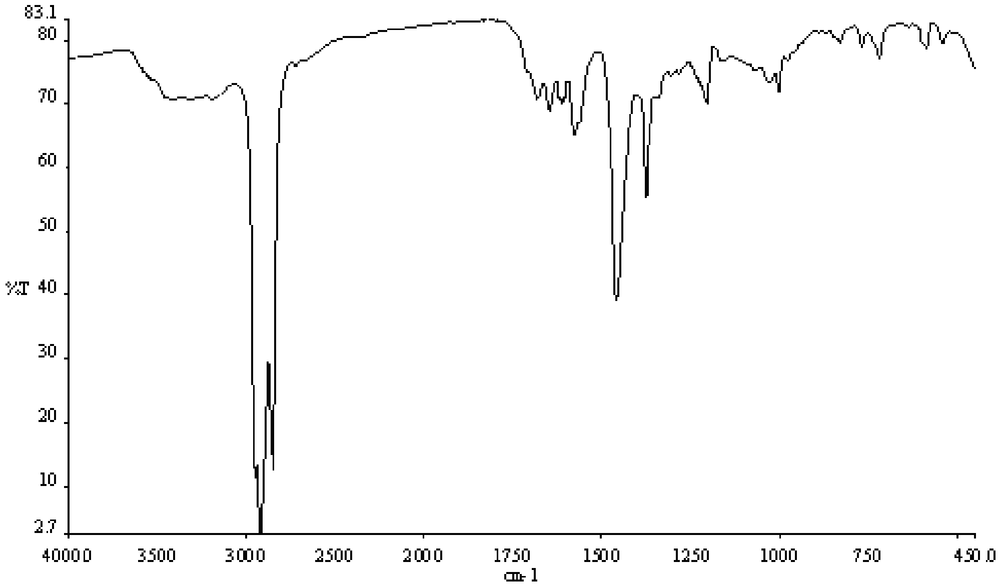
Peaks: 3438.43-71.81, 2924.39-1.49, 2854.36-7.72, 1713.84-75.41, 1648.25-72.40, 1610.21-72.38, 1575.99-64.90, 1460.07-34.85, 1377.39-49.48,1240.18-74.22, 1005.65-73.77, 722.10-74.37, 612.47-75.12, 540.23-75.35.



M2L3

Fig. 5.19 IR spectra of Co(II) complex with Ligand L3.

Peaks: 2954.18-30.27, 2924.47-13.98, 2854.37-31.44, 1714.52-76.23, 1648.51-73.50, 1628.34-73.11, 1575.75-70.44, 1461.87-58.28, 1377.74-66.43, 1260.45-66.54, 1026.04-76.34, 722.29-79.72, 617.44-78.43, 538.13-79.28.



M2L4

Fig. 5.20 IR spectra of Co(II) complex with Ligand L4.

Peaks: 2924.53-2.69, 2854.35-12.48, 1693.55-70.71, 1640.85-68.79, 1603.25-70.88, 1577.70-65.01, 1460.22-39.22, 1377.46-55.01, 1228.55-68.32, 1005.41-71.53, 832.73-79.41, 771.53-78.82, 722.01-76.97, 617.23-76.14, 518.18-77.14.

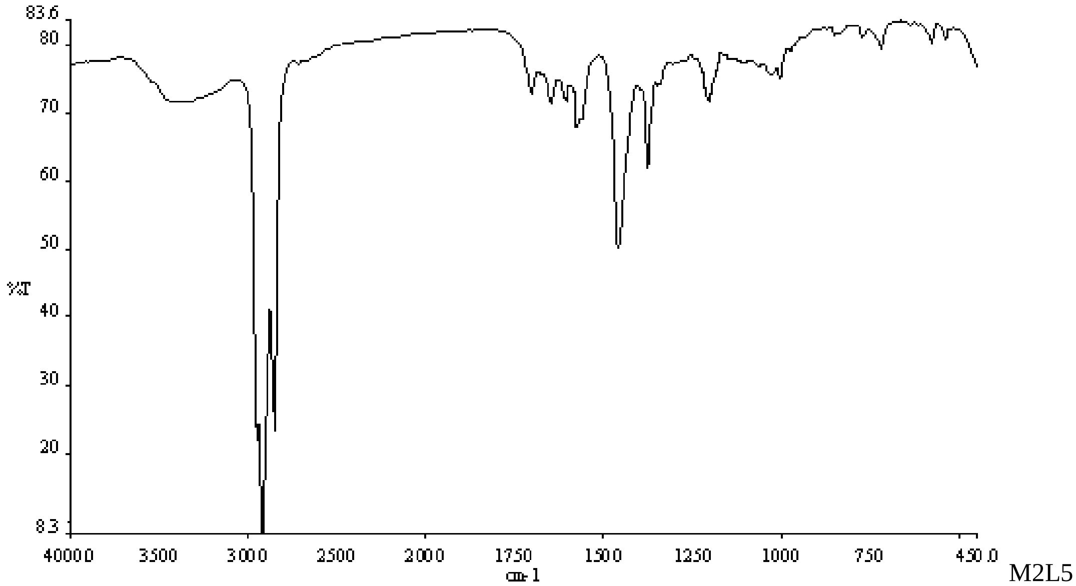


Fig. 5.21 IR spectra of Co(II) complex with Ligand L5.

Peaks: 2954.16-22.06, 2924.37-8.28, 2854.35-23.28, 1714.45-72.34, 1649.09-71.34, 1625.73-73.08, 1577.08-67.79, 1462.38-50.30, 1377.64-61.86, 1242.66-71.22, 1005.77-74.44, 722.03-79.37, 619.13-75.44, 538.47-76.10.

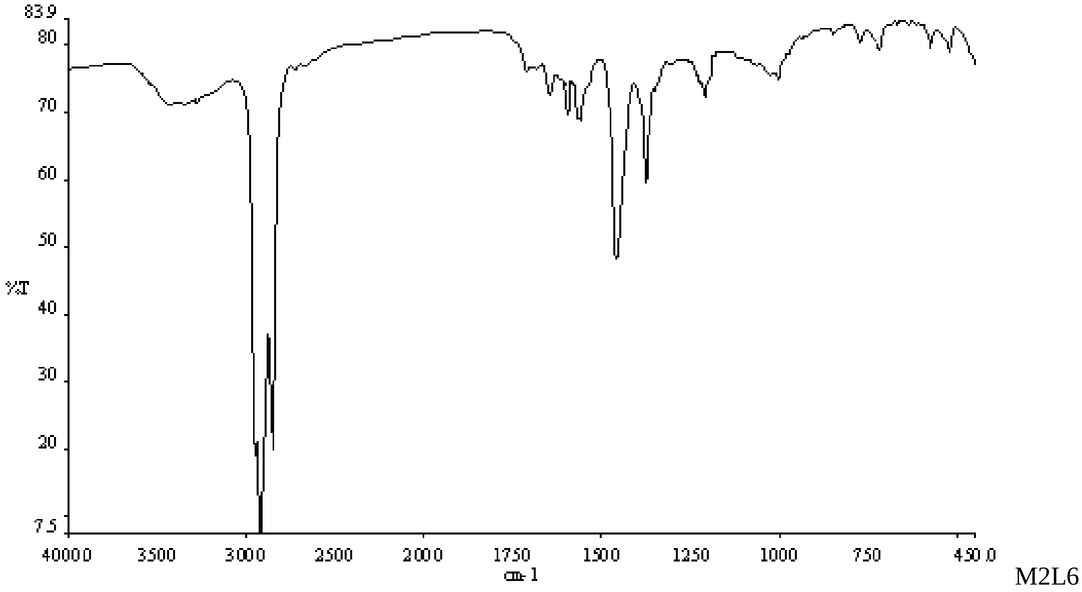
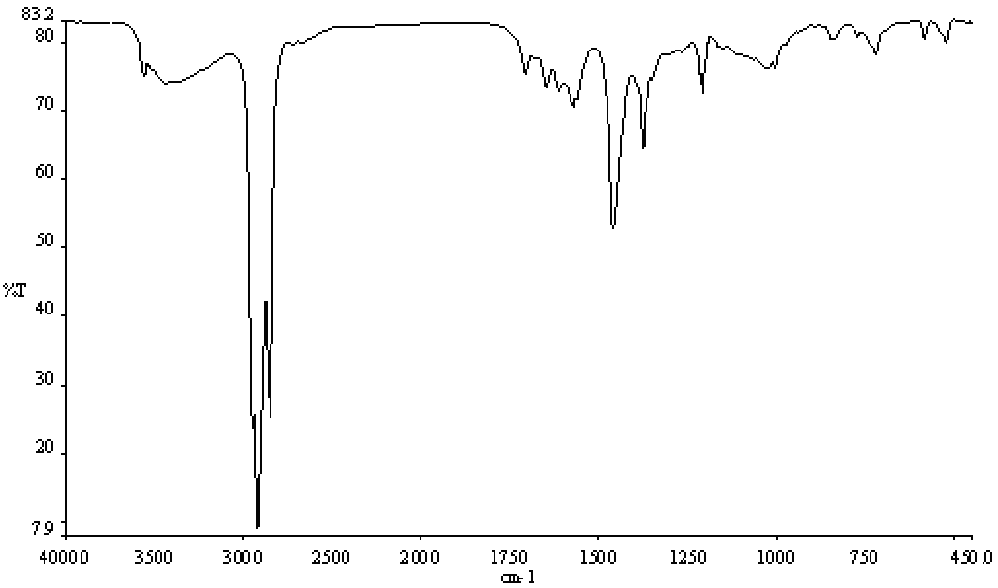


Fig. 5.22 IR spectra of Co(II) complex with Ligand L6.

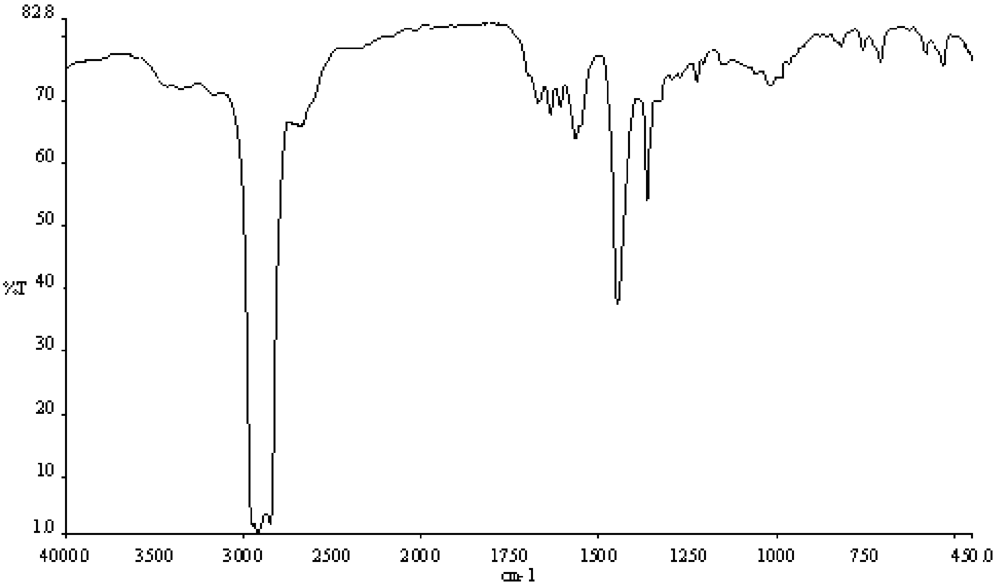
Peaks: 2954.13-19.16, 2924.52-7.48, 2854.35-19.93, 1715.24-74.66, 1648.49-72.65, 1612.17-68.70, 1577.20-69.00, 1460.13-48.14, 1377.56-59.35, 1232.44-71.86, 1005.95-74.78, 776.81-79.61, 722.06-79.01, 580.19-77.54, 530.34-77.24.



M2L7

Fig. 5.23 IR spectra of Co(II) complex with Ligand L7.

Peaks: 3550.07-73.06, 2924.39-9.00, 2854.40-25.14, 1708.44-76.23, 1648.48-73.63, 1617.48-74.29, 1576.83-71.04, 1461.37-53.08, 1377.61-64.46, 1248.25-73.51, 1032.09-76.34, 722.26-78.24, 612.60-80.23, 534.13-80.11.



M2L8

Fig. 5.24 IR spectra of Co(II) complex with Ligand L8.

Peaks: 2923.86-0.95, 2853.71-2.34, 1695.23-69.78, 1650.37-67.61, 1623.37-68.71, 1580.48-61.51, 1462.92-39.58, 1377.40-54.13, 1230.14-71.24, 1168.46-68.47, 1028.45-68.24, 1002.47-67.51, 721.98-70.12, 615.15-73.34, 540.22-73.01.

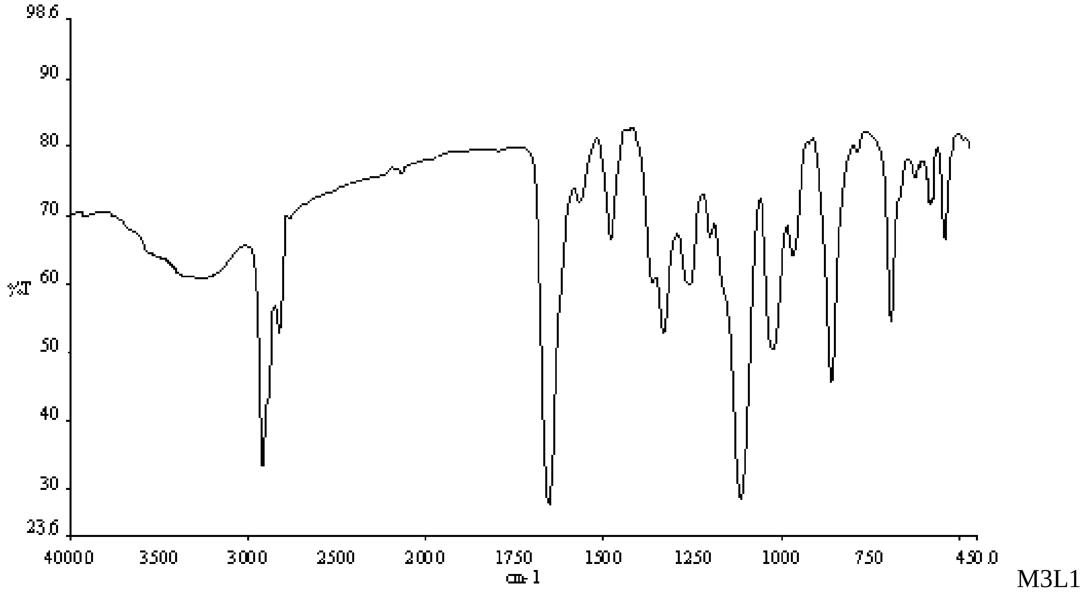


Fig. 5.25 IR spectra of Ni(II) complex with Ligand L1.

Peaks: 2968.95-30.18, 2882.35-49.87, 1703.22-25.62, 1633.09-68.67, 1582.55-63.21, 1445.41-49.56, 1375.37-56.74, 1246.39-25.55, 1161.85-47.33, 1110.17-60.86, 1010.34-42.46, 856.04-51.61, 793.38-72.43, 762.41-61.34, 615.32-69.54, 518.41-63.71.

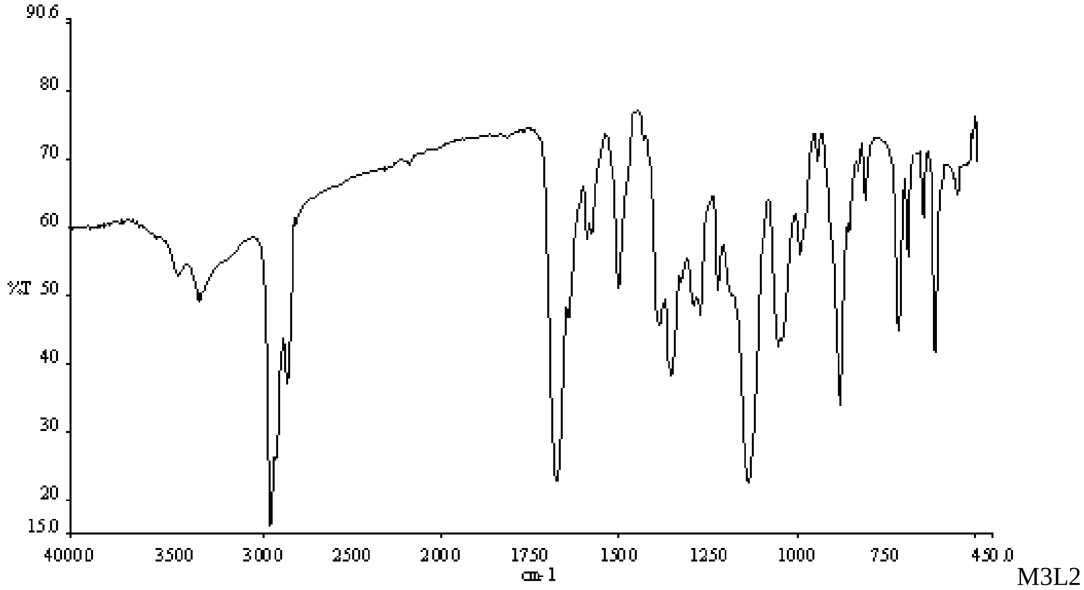


Fig. 5.26 IR spectra of Ni(II) complex with Ligand L2.

Peaks: 3334.59-49.08, 2967.09-16.03, 2880.19-37.01, 1723.52-22.65, 1654.35-58.35, 1638.21-58.73, 1582.17-50.97, 1475.03-45.63, 1444.49-38.00, 1370.19-47.13, 1325.39-50.65, 1244.98-22.35, 1169.42-42.47, 1111.48-55.99, 1066.96-69.92, 1008.40-33.71, 942.86-63.93, 856.01-44.80, 832.45-55.53, 792.67-61.35, 763.74-41.64, 668.03-71.33, 617.24-43.36, 515.46-61.23.

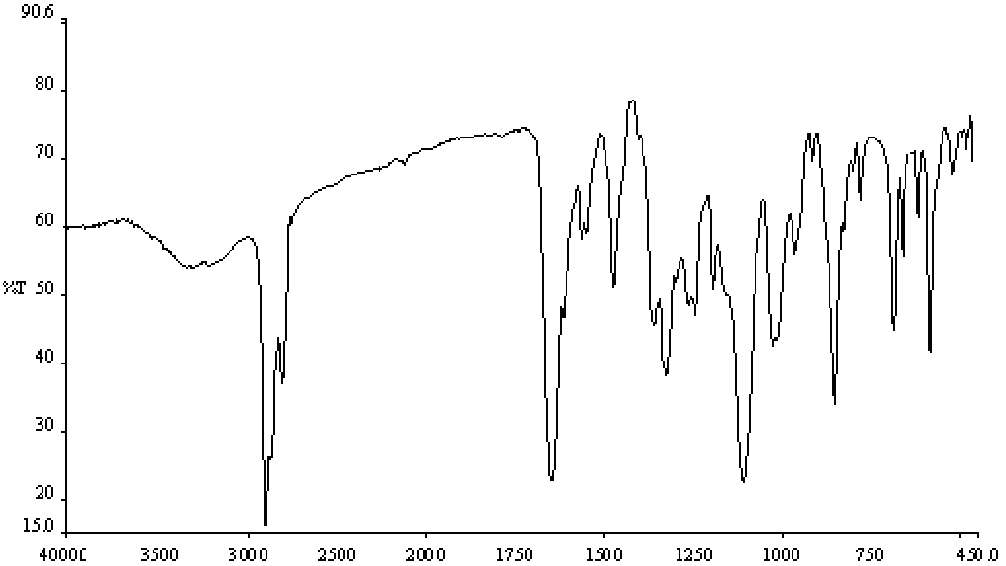


Fig. 5.27 IR spectra of Ni(II) complex with Ligand L3.

Peaks: 2967.14-19.75, 2880.32-45.33, 1743.16-23.35, 1712.24-48.46, 1654.98-62.43, 1582.83-53.83, 1475.01-49.57, 1444.88-42.08, 1370.46-51.20, 1325.84-55.35, 1245.54-23.40, 1169.75-45.57, 1111.40-58.88, 1067.58-74.91, 1008.90-35.95, 943.54-71.23, 856.00-46.82, 832.70-62.09, 792.96-67.69, 763.63-48.60, 668.06-76.78, 514.64-64.53.

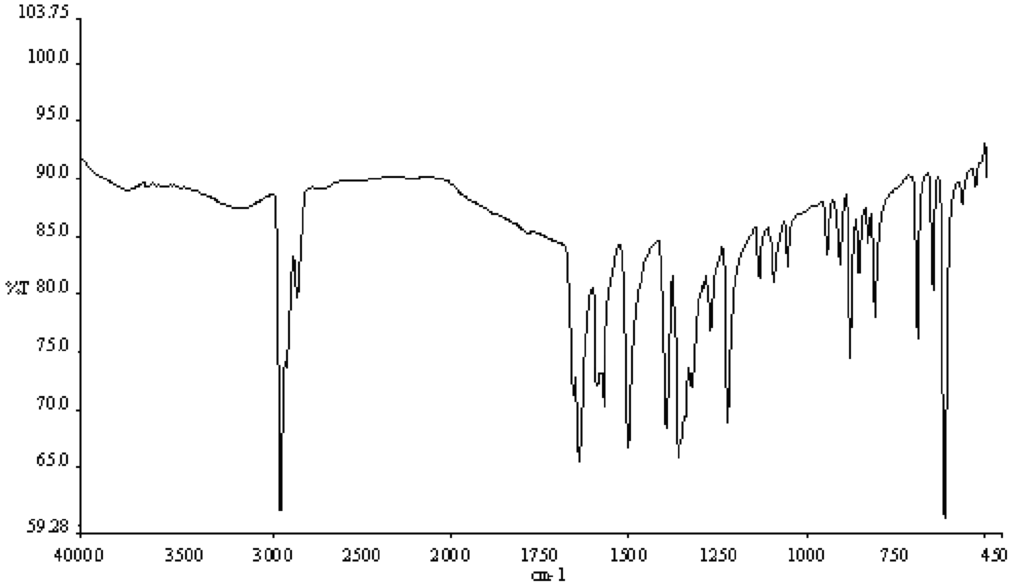


Fig. 5.28 IR spectra of Ni(II) complex with Ligand L4.

Peaks: 2902.22-62.63, 2792.92-75.29, 1709.78-65.40, 1631.96-71.71, 1582.12-66.62, 1483.52-68.23, 1452.80-65.82, 1369.47-76.65, 1324.96-68.88, 1243.09-81.32, 1205.07-81.11, 1169.74-82.30, 1066.93-83.34, 1033.45-82.51, 1007.30-74.32, 983.69-81.75, 960.77-84.42, 942.68-77.94, 832.59-76.00, 792.69-80.27, 763.72-60.51, 606.39-87.65, 512.75-89.11.

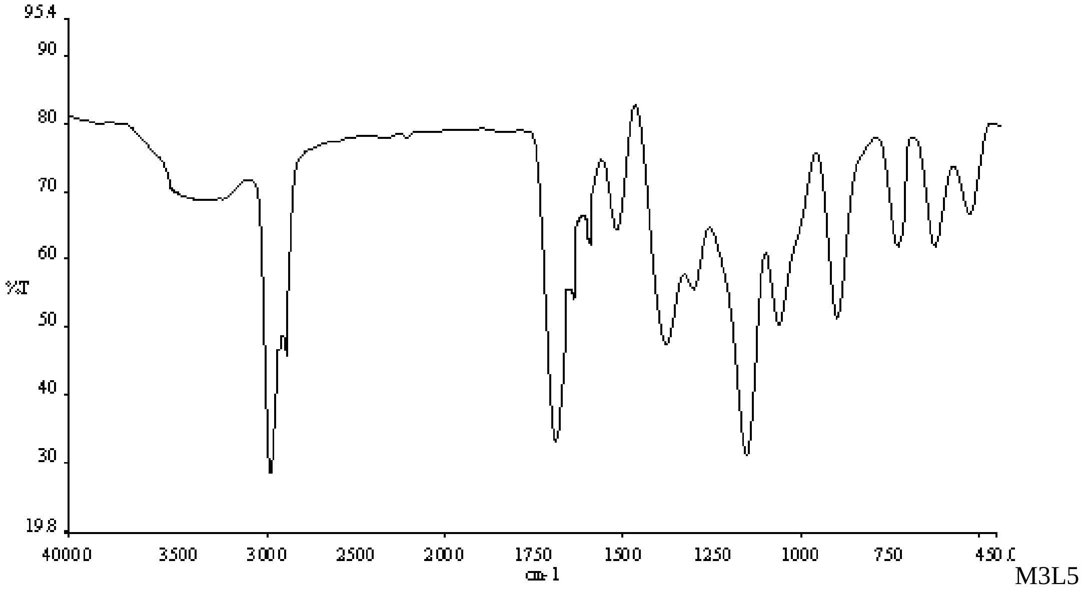


Fig. 5.29 IR spectra of Ni(II) complex with Ligand L5.

Peaks: 2960.02-28.55, 1739.94-33.17, 1645.18-44.36, 1581.72-64.39, 1453.35-47.60, 1384.32-55.73, 1245.68-31.15, 1161.49-50.43, 1010.51-51.34, 852.90-62.03, 763.01-66.65, 600.01-66.60, 512.48-68.55.

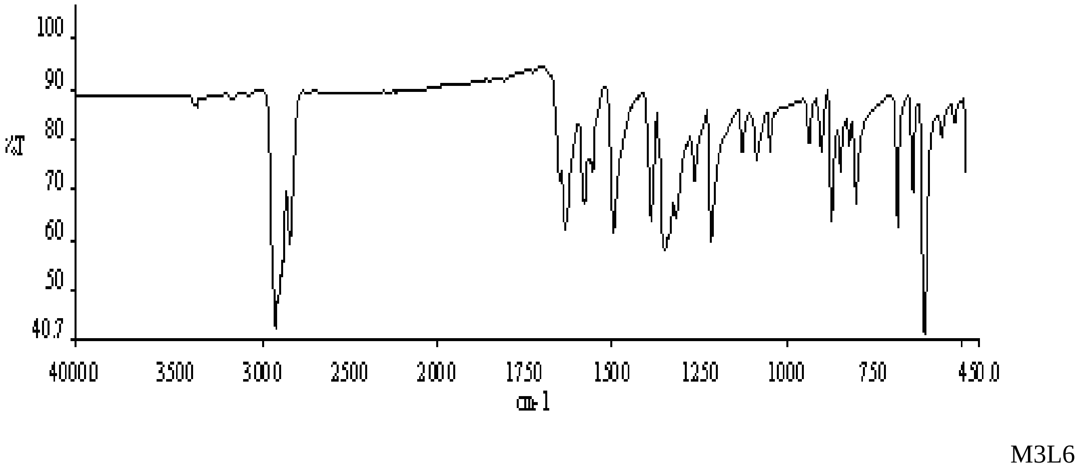


Fig. 5.30 IR spectra of Ni(II) complex with Ligand L6.

Peaks: 3346.75-85.60, 3334.16-85.75, 2902.17-42.26, 2563.22-88.94, 1724.21-71.69, 1708.96-62.19, 1631.96-68.11, 1581.38-61.76, 1483.16-63.83, 1452.05-59.16, 1418.29-64.35, 1368.89-71.55, 1324.45-59.93, 1246.57-77.37, 1204.58-76.05, 1169.45-77.70, 1066.42-78.94, 1033.39-77.47, 1006.71-63.42, 983.41-73.85, 960.62-78.47, 942.25-67.31, 832.34-62.74, 792.40-69.07, 760.03-60.73, 716.22-80.48, 682.85-40.96, 596.47-81.34, 520.44-82.41.

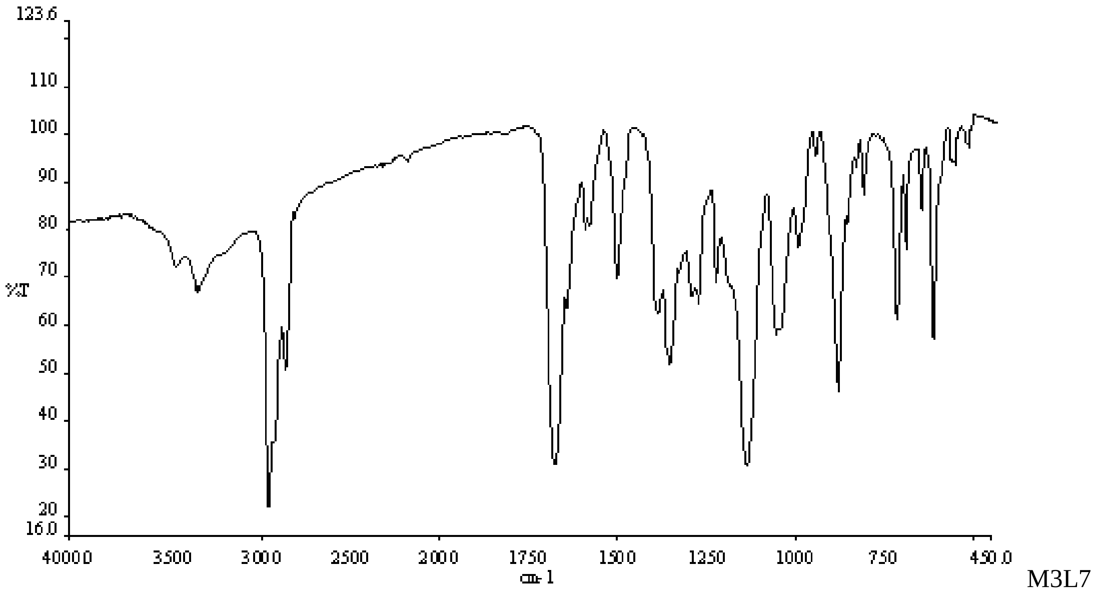


Fig. 5.31 IR spectra of Ni(II) complex with Ligand L7.

Peaks: 3447.67-72.16, 3334.59-66.96, 2967.09-21.87, 2880.19-50.49, 1743.52-30.90, 1712.40-63.49, 1664.35-79.61, 1651.05-80.50, 1582.17-69.53, 1475.03-62.24, 1444.49-51.83, 1370.19-64.30, 1325.39-69.10, 1244.98-30.49, 1169.42-57.94, 1111.48-76.39, 1066.96-95.39, 1008.40-45.99, 942.86-87.21, 856.01-61.12, 832.45-75.75, 792.67-83.69, 763.74-56.80, 620.74-91.39, 511.66-92.41.

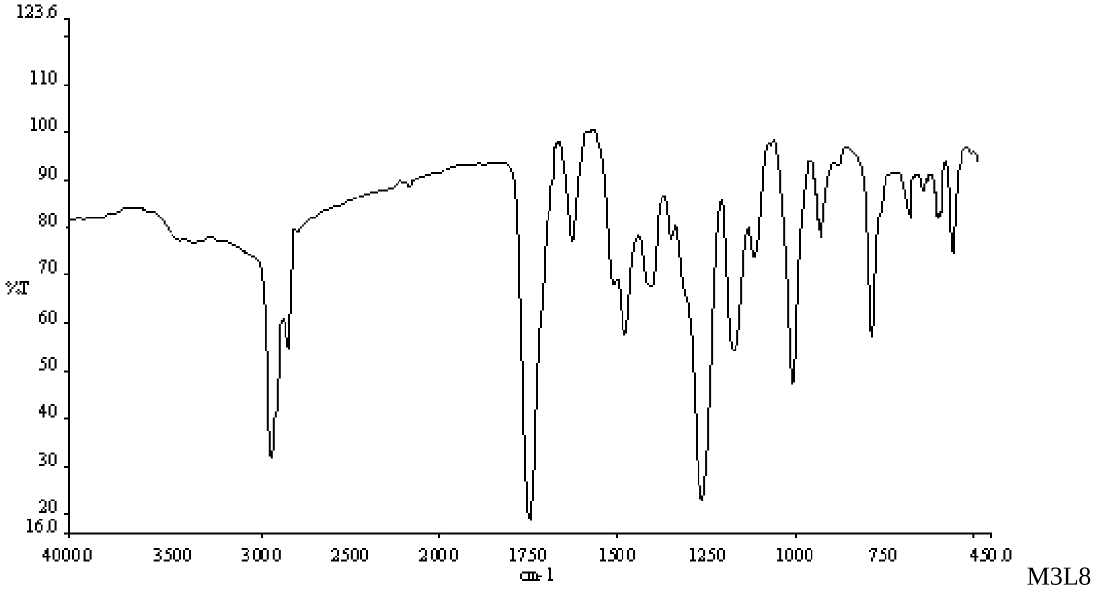


Fig. 5.32 IR spectra of Ni(II) complex with Ligand L8.

Peaks: 2969.85-32.15, 2880.33-52.24, 1743.21-20.12, 1634.09-73.84, 1582.55-68.11, 1500.12-54.67, 1445.54-64.37, 1375.37-56.74, 1256.39-25.55, 1161.85-47.33, 1110.17-46.29, 1010.34-42.46, 856.04-51.61, 793.38-72.43, 762.41-61.34, 620.32-79.84, 522.41-73.61.

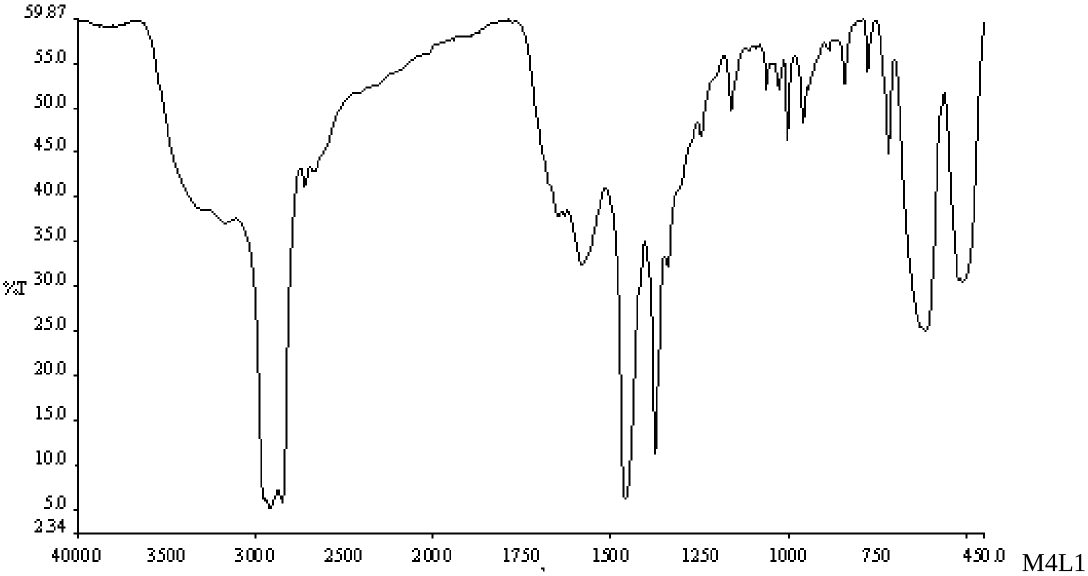


Fig. 5.33 IR spectra of Mn(II) complex with Ligand L1.

Peaks: 2923.11-5.01, 1720.13-37.43, 1641.13-37.25, 1610.78-35.27, 1582.85-32.42, 1463.14-6.17, 1377.37-11.14, 1255.42-32.54, 1164.08-49.46, 1064.98-52.07, 1031.55-52.02, 1006.76-46.32, 962.24-48.27, 845.31-52.48, 779.61-53.99, 721.62-44.77, 618.11-24.97, 513.28-30.53.

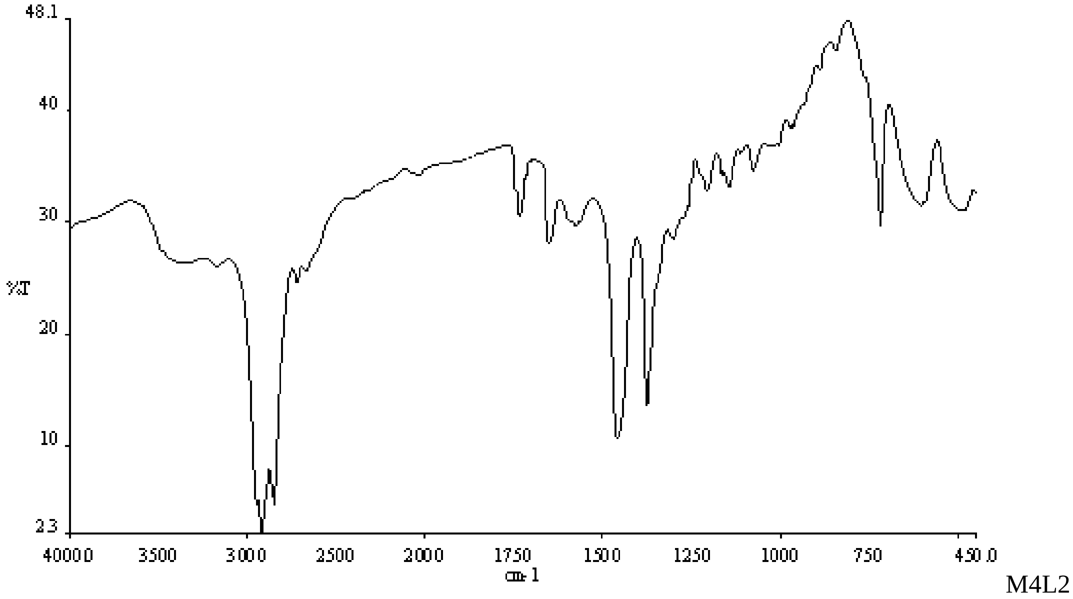


Fig. 5.34 IR spectra of Mn(II) complex with Ligand L2.

Peaks: 2924.21-2.24, 2854.05-4.81, 1718.46-30.87, 1640.56-27.41, 1617.92-28.44, 1578.46-29.65, 1459.86-10.72, 1377.22-13.55, 1247.51-32.84, 1147.77-33.09, 1078.52-34.62, 721.78-29.70, 608.26-31.47, 499.74-30.49.

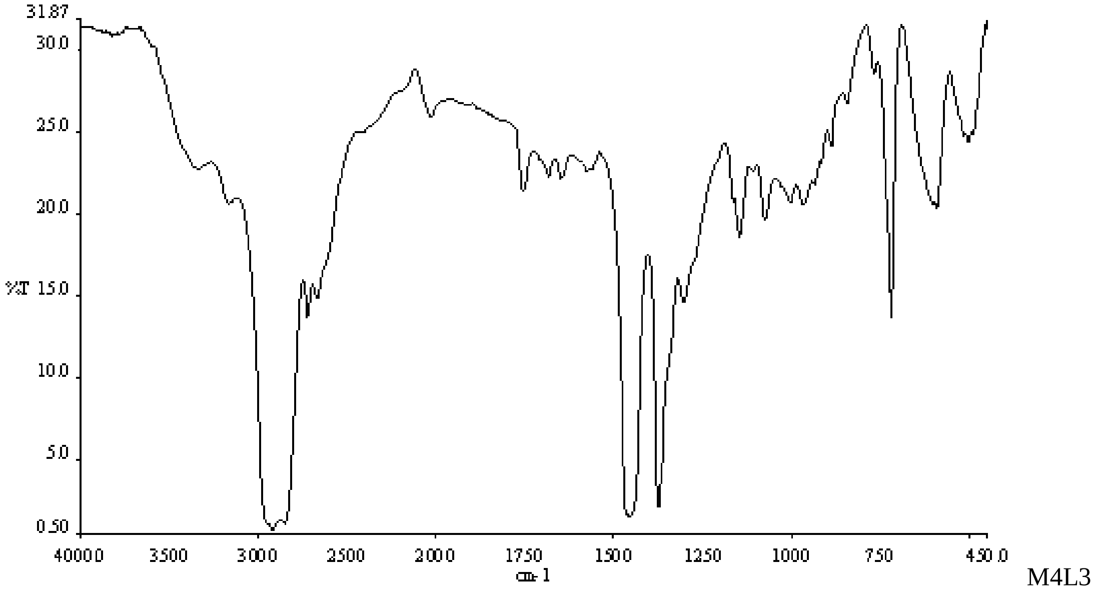


Fig. 5.35 IR spectra of Mn(II) complex with Ligand L3.

Peaks: 2923.19-0.68, 2725.02-13.69, 2032.03-25.92, 1711.57-21.54, 1640.31-23.14, 1610.61-23.44, 1580.49-24.54, 1463.63-1.58, 1377.28-2.07, 1148.52-18.62, 1076.82-19.66, 722.03-13.69, 595.08-20.37, 505.20-24.35.

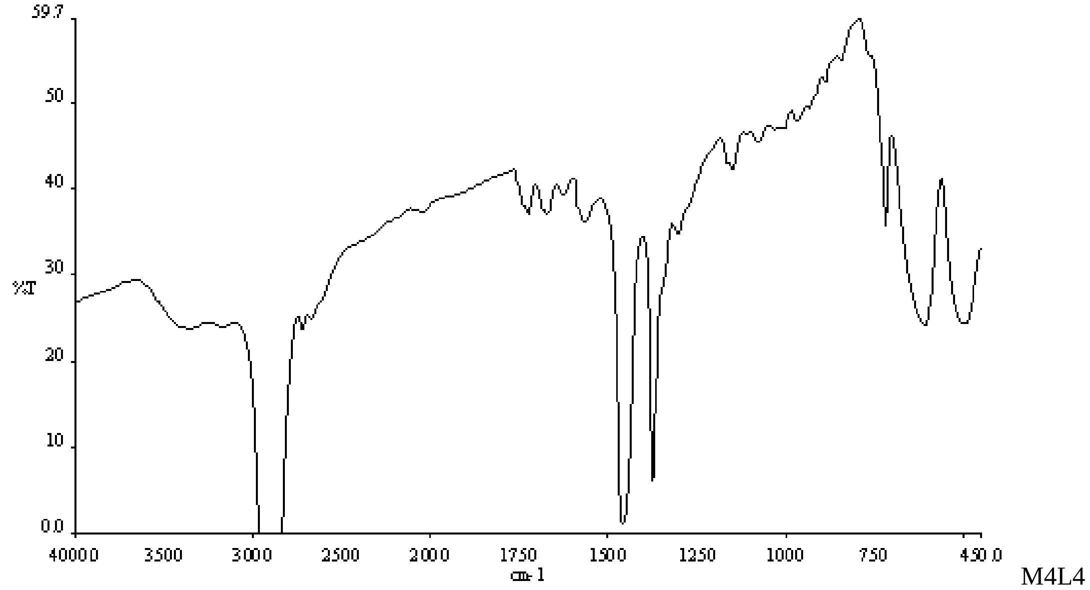
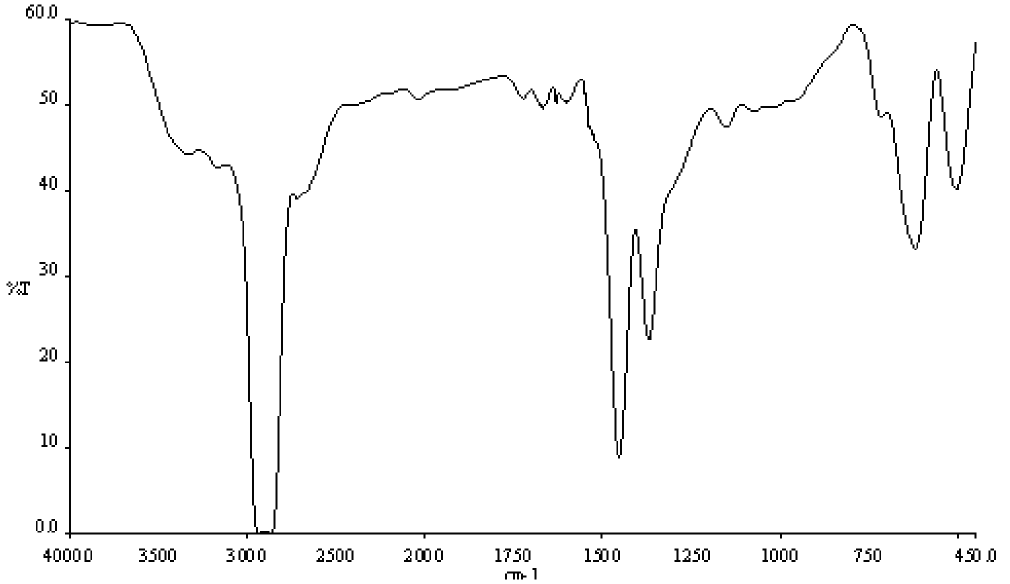


Fig. 5.36 IR spectra of Mn(II) complex with Ligand L4.

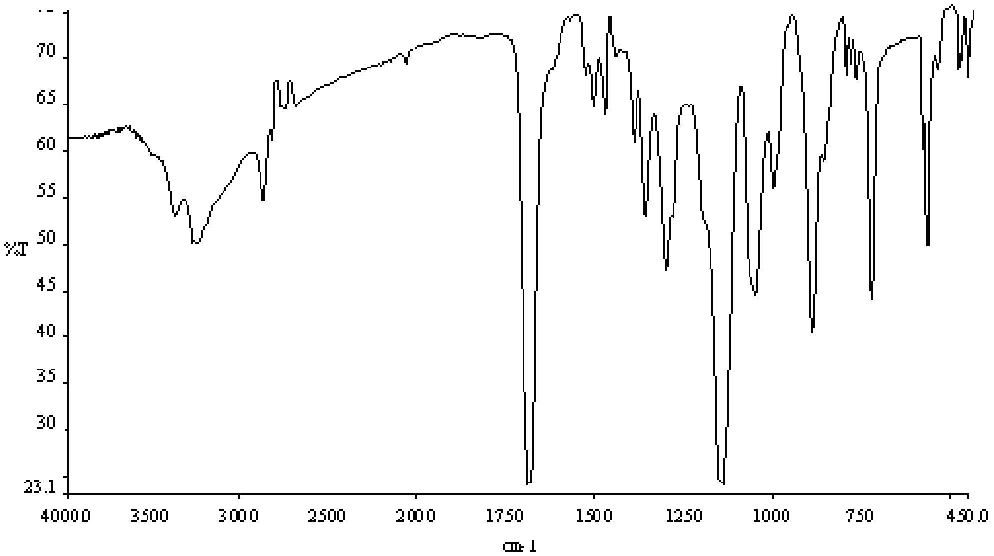
Peaks: 2924.42--0.03, 1702.64-36.41, 1636.54, 36.18, 1600.54-37.84, 1578.13-35.62, 1461.01-1.15, 1377.28-6.01, 1262.34-35.74, 1152.87-42.24, 721.68-35.76, 610.87-24.09, 500.75-24.25.



M4L5

Fig. 5.37 IR spectra of Mn(II) complex with Ligand L5.

Peaks: 2942.81--0.02, 1718.45-50.45, 1650.58-49.67, 1632.37-49.51, 1579.24-49.69, 1455.95-8.79, 1372.47-22.70, 1155.93-47.43, 623.25-33.32, 509.46-40.16.



M4L6

Fig. 5.38 IR spectra of Mn(II) complex with Ligand L6.

Peaks: 3356.34-50.06, 2988.12-54.67, 2877.86-64.42, 2819.61-64.91, 1713.71-23.08, 1578.35-65.39, 1546.59-64.63, 1472.87-61.73, 1443.25-53.63, 1390.31-47.71, 1246.65-23.18, 1158.06-45.15, 1111.41-56.58, 1011.08-41.15, 922.85-68.73, 911.43-69.96, 898.46-68.28, 855.93-44.63, 784.91-60.36, 774.24-46.88, 585.32-67.79, 490.46-68.66.

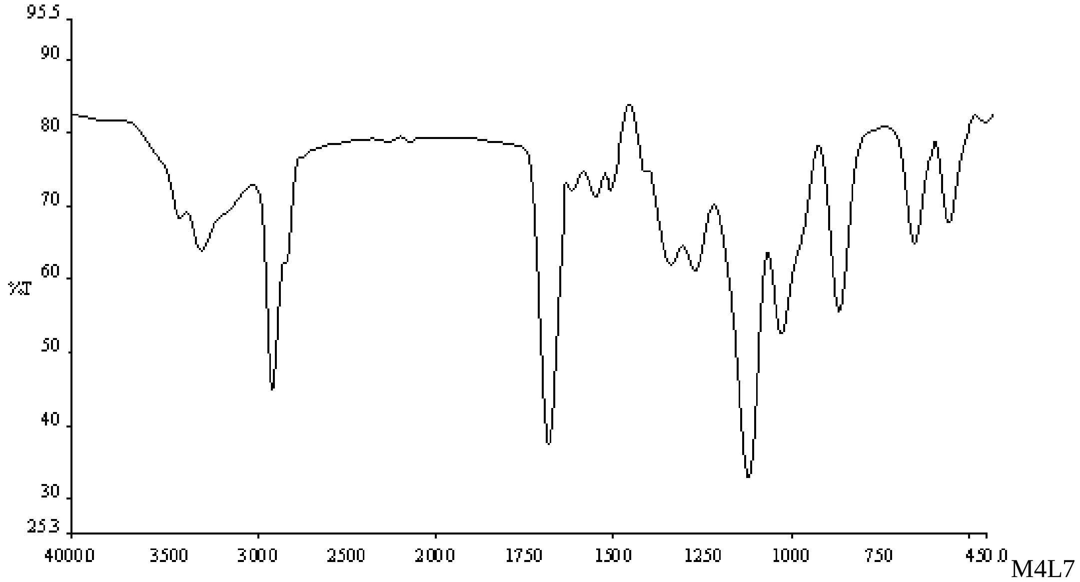


Fig. 5.39 IR spectra of Mn(II) complex with Ligand L7.

Peaks: 3331.19-63.96, 2962.89-44.90, 1714.15-37.41, 1642.42-71.28, 1620.54-70.84, 1575.61-73.90, 1477.78-61.97, 1384.11-61.27, 1245.88-32.92, 1160.80-52.48, 1010.74-55.74, 855.51-64.24, 625.19-65.39, 534.68-67.34.

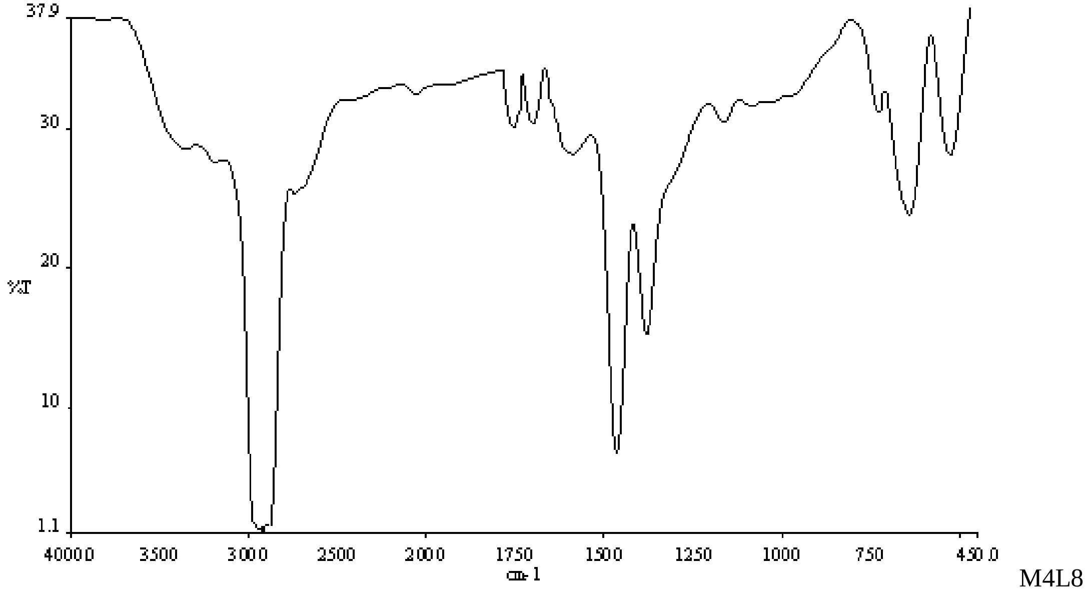
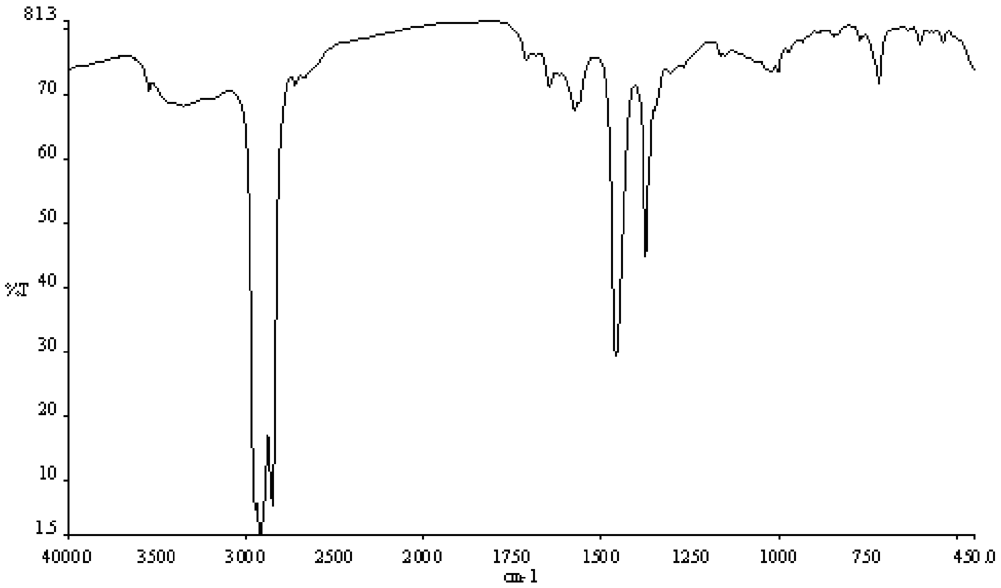


Fig. 5.40 IR spectra of Mn(II) complex with Ligand L8.

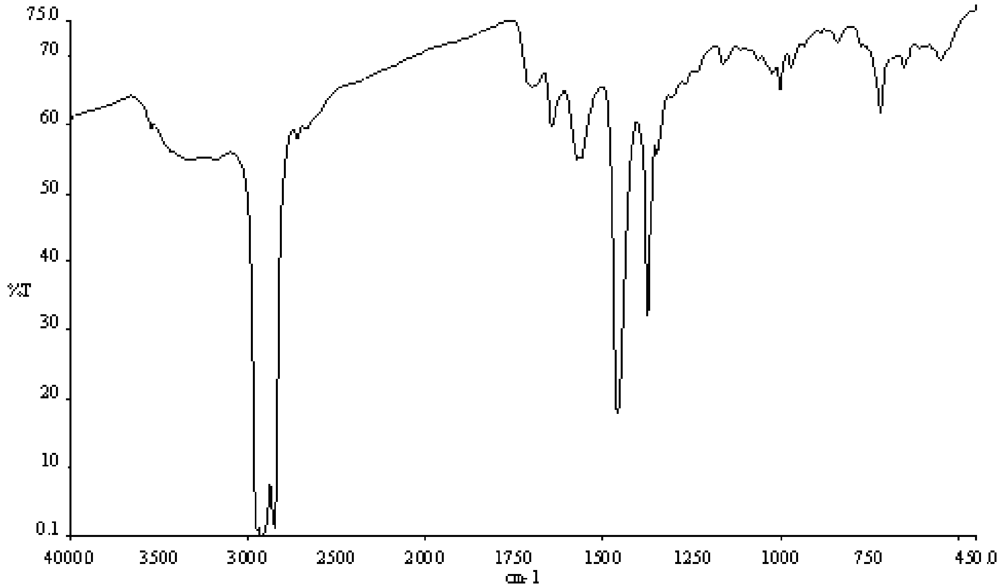
Peaks: 2942.81-1.02, 1738.45-30.45, 1670.58-31.67, 1621.37-29.51, 1579.24-27.69, 1455.95-8.79, 1372.47-16.70, 1155.93-31.43, 740.38-31.54, 636.22-23.91, 520.12-28.42.



M5L1

Fig. 5.41 IR spectra of Fe(III) complex with Ligand L1.

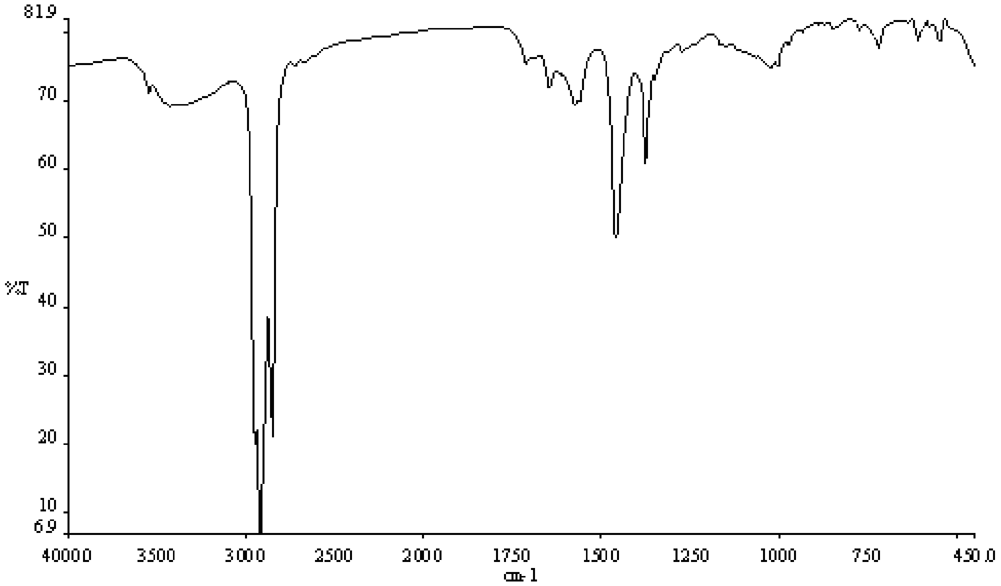
Peaks: 2924.32-1.52, 2854.34-5.87, 1708.84-75.41, 1648.50-68.12, 1576.92-69.59, 1461.19-29.27, 1377.36-44.60, 1005.71-73.33, 722.06-71.70, 620.81-77.79, 520.69-78.54.



M5L2

Fig. 5.42 IR spectra of Fe(III) complex with Ligand L2.

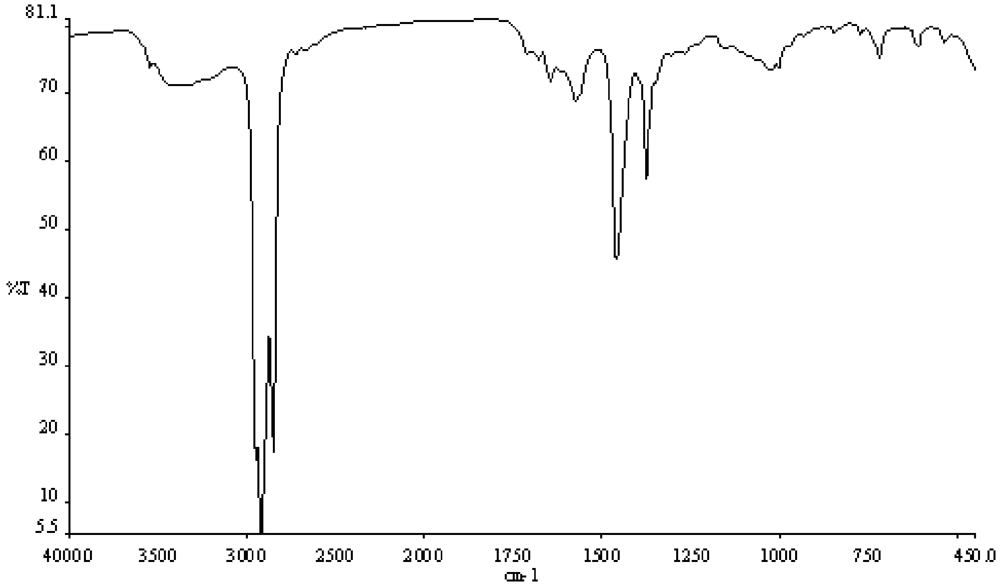
Peaks: 2924.94-0.06, 2854.43-1.04, 1714.58-64.29, 1646.72-59.78, 1574.99-55.05, 1462.75-17.79, 1377.42-32.03, 1168.06-68.77, 1004.62-64.90, 721.86-61.70, 616.84-67.49, 512.37-68.28.



M5L3

Fig. 5.43 IR spectra of Fe(III) complex with Ligand L3.

Peaks: 3438.97-69.24, 2954.16-19.90, 2924.59-6.93, 2854.35-21.02, 1714.28-73.22, 1648.39-71.98, 1611.41-71.21, 1576.67-69.25, 1460.81-50.05, 1377.53-60.91, 1268.59-75.49, 1028.42-74.86, 722.11-77.66, 601.54-78.32, 518.34-78.14.



M5L4

Fig. 5.44 IR spectra of Fe(III) complex with Ligand L4.

Peaks: 2954.18-16.29, 2924.46-5.45, 2854.36-17.25, 1700.42-74.89, 1628.37-71.63, 1600.27-71.14, 1576.78-68.93, 1461.84-45.72, 1377.50-57.41, 1027.08-73.58, 722.09-75.37, 630.46-76.29, 532.61-77.26.

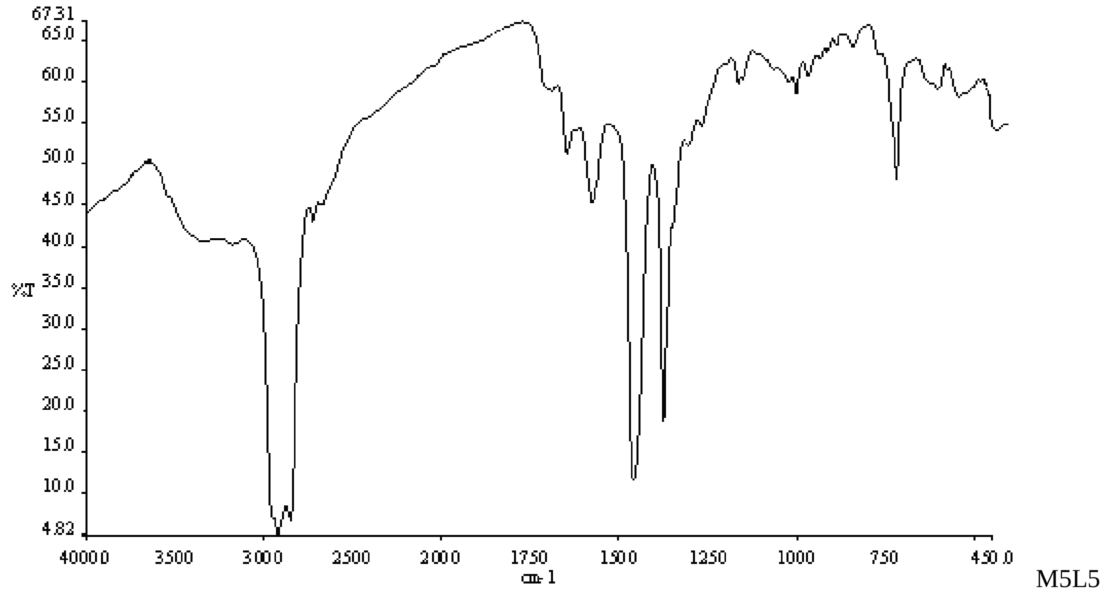


Fig. 5.45 IR spectra of Fe(III) complex with Ligand L5.

Peaks: 2923.87-4.81, 1711.64-55.34, 1649.03-51.25, 1613.24-44.32, 1577.38-45.31, 1462.87-11.70, 1377.35-18.59, 1281.54-53.49, 1168.57-59.83, 1004.50-58.32, 721.98-48.04, 618.57-57.69, 512.67-56.21.

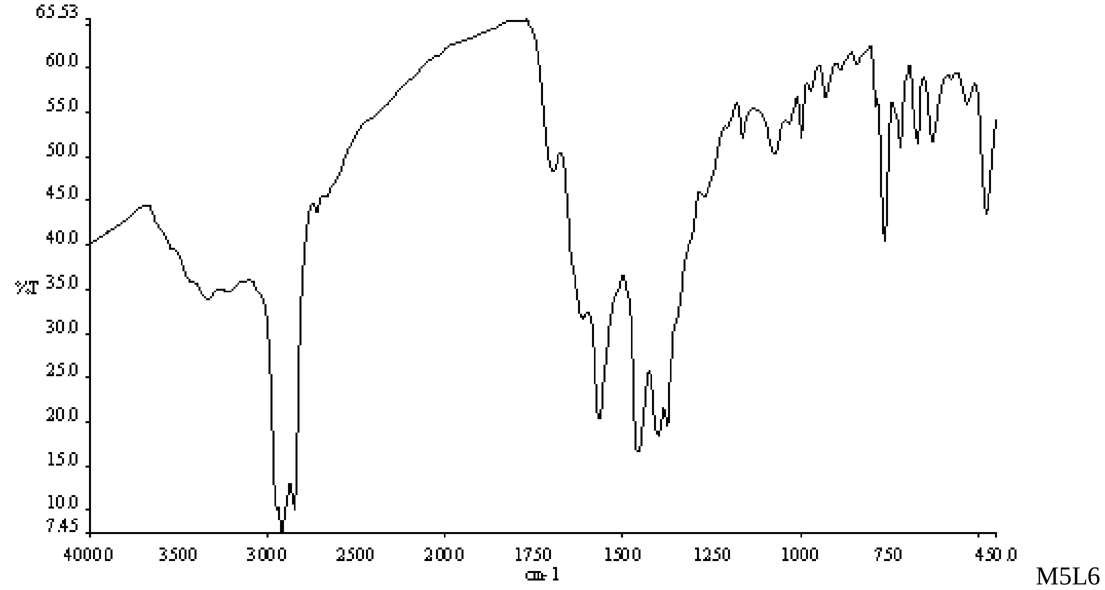


Fig. 5.46 IR spectra of Fe(III) complex with Ligand L6.

Peaks: 3342.25-33.81, 2923.94-7.44, 2853.83-10.05, 1711.49-56.28, 1695.92-48.36, 1609.42-31.81, 1585.42- 1568.11-20.29, 1459.86-16.56, 1403.43-18.54, 1166.52-52.22, 1077.80-50.31, 1000.75-51.96, 933.11-56.71, 767.20-40.58, 722.00-50.97, 673.37-51.38, 632.36-51.65, 535.46-55.89, 480.43-43.63.

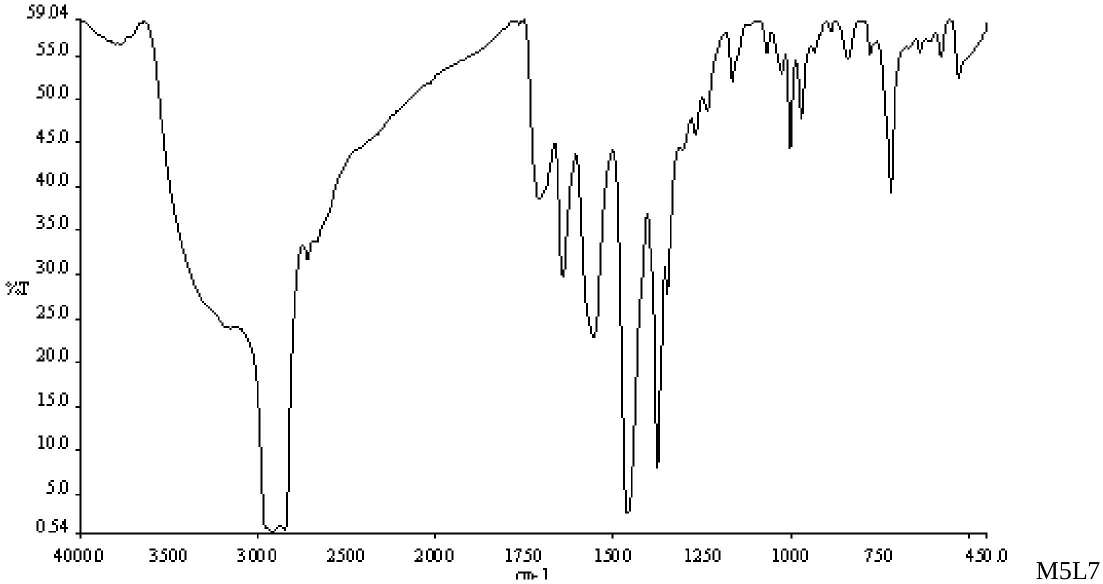


Fig. 5.47 IR spectra of Fe(III) complex with Ligand L7.

Peaks: 3788.31-56.12, 2924.61-0.79, 1712.25-38.50, 1643.55-29.79, 1567.95-22.80, 1463.82-2.82, 1377.51-7.98, 1351.13-27.75, 1168.06-52.02, 1069.69-55.18, 1029.06-52.94, 1004.34-44.25, 973.77-47.74, 842.98-54.63, 721.81-39.27, 580.52-54.76, 531.91-52.39

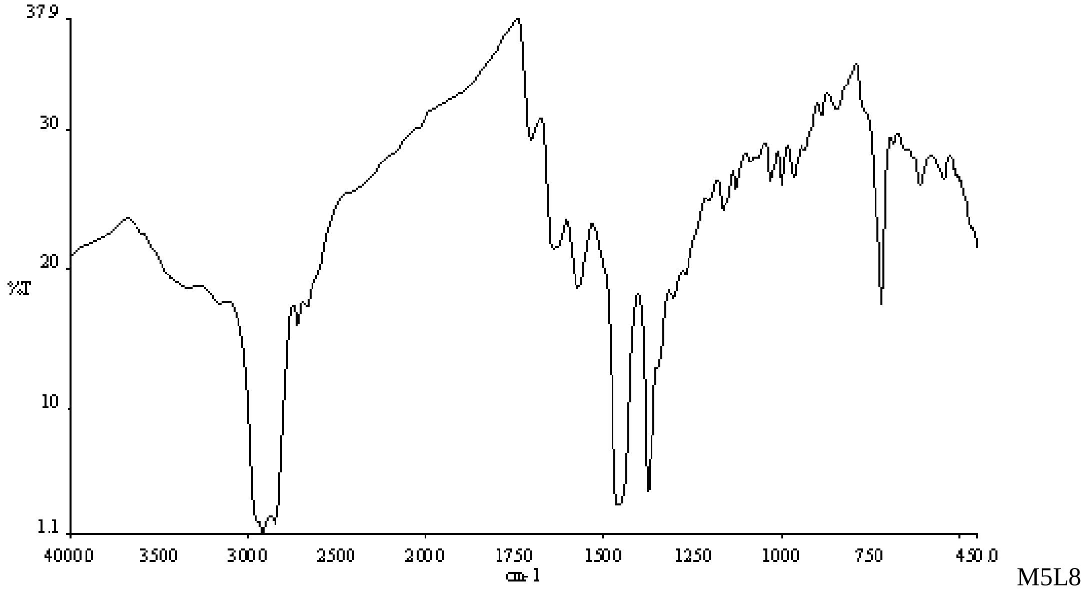


Fig. 5.48 IR spectra of Fe(III) complex with Ligand L8.

Peaks: 2924.06-1.08, 1690.19-28.34, 1643.85-21.38, 1574.97-18.66, 1459.89-3.10, 1377.31-4.03, 1168.69-24.25, 1033.74-26.33, 1002.10-26.13, 967.41-26.56, 721.76-17.41, 611.27-26.13, 540.62-27.34.

5.4) CONCLUSION:-

From the above discussion on IR spectral data of ligands and their metal chelates, the following conclusion may be drawn.

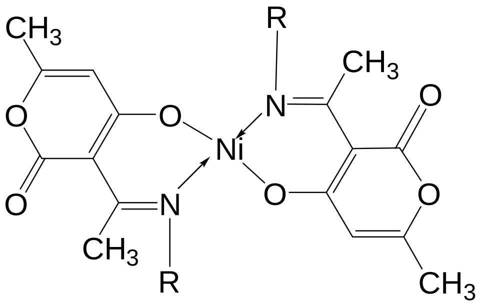
The absence of bands in the region more than 3300 cm^{-1} indicates the absence of coordination and lattice water in the present metal complexes.

The disappearance of ligand bands around 3364-3371 cm^{-1} due to hydrogen bonded enolic -O-H….N stretching frequency in the spectra of their respective metal chelates indicates the deprotonation of enolic O-H and subsequent coordination of enolic oxygen with metal ion forming M-O bond. A significant shift of the ligand bands due to enolic C-O stretching vibration to higher frequency side further confirms the participation of phenolic oxygen of the ligands in the bond formation with Nickel(II) ion, where as with other metal ions enolic carbonyl C=O forms bond.

The lowering of C=N frequency in the complexes than the corresponding ligands indicates that the coordination of ligand to the metal ion takes place through azomethine nitrogen. This observation is further supported by significant upward shift of the band due to aromatic C-N stretching vibration on chelation.

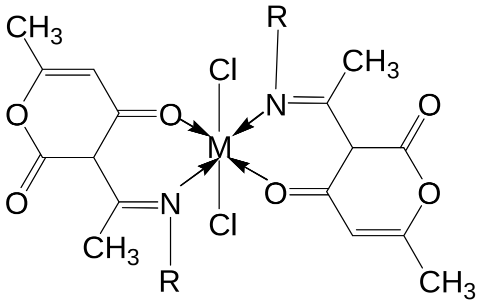
The appearance of new band in the region 580-638 cm^{-1} and 500-541 cm^{-1} in the IR spectra of complexes supports the formation of M-O and M-N bonds respectively in the complexes.

On the basis of results of elemental analysis, magnetic susceptibility, solution conductivity measurement, thermoanalytical, IR and electronic spectral data, X-ray diffraction, it may be concluded that, the complexes of Cu(II), Co(II), Mn(II) and Fe(II) have distorted octahedral structure and the complexes of Ni(II) have square planer structure.



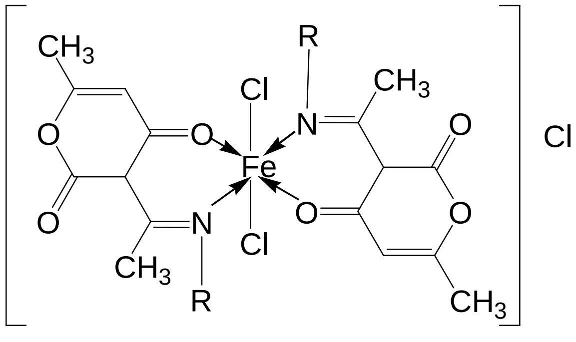
R= substituted aromatic ring.

Fig. 5.49 Expected structure of Ni(II) complex.



Where, M= Cu(II), Co(II), Mn(II).
R= substituted aromatic ring.

Fig.5.50 Expected structure of Metal complexes.



R= substituted aromatic ring.

Fig.5.51 Expected structure of Iron complex.

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CHAPTER VI

BIOLOGICAL STUDIES OF SCHIFF BASES AND THEIR METAL COMPLEXES

6.1 INTRODUCTION TO ANTIFUNGAL ACTIVITY

6.2 INTRODUCTION TO ANTIBACTRIAL ACTIVITY

6.3 PREVIOUS RELATED STUDY

6.4 EXPERIMENTAL TO ANTIFUNGAL ACTIVITY

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CHAPTER 6

BIOLOGICAL STUDIES OF SCHIFF BASES AND THEIR METAL COMPLEXES

6.1 INTRODUCTION TO ANTIFUNGAL ACTIVITY OF SCHIFF BASES AND THEIR METAL COMPLEXES:

The fungi represent one of the most important kingdoms of living organisms and constitute a very large and diverse group of living things. Mycological studies reveals that the fungi may be unicellular (Yeast) or multicellular with uni, bi or multinucleate cell. Fungi have eukaryotic cellular organization and possess heterotrophic mode of nutrition. They cannot synthesis their own organic food through photosynthesis or chemosynthesis and instead obtain it from other sources.

The cell wall composition is not similar in all the fungi. In some fungi, fungal cellulose is the chief cell wall constituent. The external factors such as the composition of the medium used for fungal cultivation, P^H value and temperature influence the composition of fungal cell walls[1].

The various common groups of fungi are called molds, rusts, smuts, mushrooms, toad stools, puff balls etc. These common fungi are classified as lower fungi that include Phycomycetes and higher fungi which include Ascomycetes, Basidiomycetes and Deuteromycetes.

The better we can utilize these organisms in agriculture, industry, medicine, food and nutrition and at the same time the greater will be our control over their harmful activities as pathogens of plants, animals and man; and as destroyers of timber, textile, food and leather. The physiological studies on fungal metabolism have helped in improving the industrial production of various substances such as citric acid, gluconic acid, enzymes and other metabolites by Aspergillus niger.

6.1.1 Aspergillus niger:

Aspergillus niger (A. niger) a kind of Ascomycetes has been selected for the present study because of its immense economic importance in industry, agriculture, medicine, food and nutrition.

Over 30 species of the genus Aspergillus have been recorded so far in India. Thom and Raper[2] recognised more than 78 species of Aspergillus. The black Aspergilli or Aspergillus niger group includes the fungi which are commonly called as black mold. The genus is widely distributed in nature. A huge number of spores (conidia) of these organisms are suspended in air and responsible for variety of allergies and respiratory disorders in human being. Aspergillus niger is a plant deleterious fungi and air borne ascomycetes to which A. niger belong are found on paddy crops. It is difficult to find a substance containing some organic matter and little moisture on which the Aspergilli cannot grow. Thus, the Aspergilli are responsible for our welfare in a variety of ways. They have both beneficial and harmful activities.

The fungus is always associated with food grains, fruits and vegetables during storage and cause spoilage to these stored products. Aspergillus niger and several other fungal species are often found on exposed food stuffs causing decay. The species like A. niger, A. flavus commonly grow on fruits, vegetables, pickles, jams, jellies and other food stuffs, and produce some toxic substances (aflatoxins) which are carcinogenic in nature. They are also common contaminants of culture in bacteriological and mycological laboratories. Several species grow on leather, timber, and cloth/fabrics and reduce their commercial value. Especially in tropical climates Aspergilli are troublesome as they impart musty odour to shoes and clothing.

A. niger is used in the study of many biological processes and can detect trace quantities of elements Mn, Fe, Cu, Zn and Mo, in the unknown sample.

Reulin[3] observed an increase in the growth of A. niger on addition of Fe and Zn to the basal medium and concluded that these elements are indispensable for the growth of these organisms. Brotel[4] found that Cu is essential for the perfection of the growth as well as for sporulation of A. niger.

6.1.2 Fungal Growth and Method of Measurement:

When microorganisms are inoculated in a suitable medium and incubated under appropriate conditions, a tremendous increase in the cell mass or number of cells occurs within a relatively short time. This is called microbial growth. With reference to fungi, the growth may be defined as irreversible increase in mass of the whole or part of living organism by the synthesis of macromolecules. Growth usually refers to changes in the culture of cells rather than to changes in an individual organism. It denotes the increase in number of microorganisms beyond that present already in the original inoculum.

Depending upon the situation in hand, different methods for measurement of growth are employed. The Dry Weight Method is probably the most widely used and applicable method for quantitative assessment of fungi. In this method, the spores produced after inoculation and subsequent incubation are filtered through preweighed Gooch crucible and collected as the culture medium. The cell mass is dried to a constant weight at 80^0C. The dried mycelium is then weighed on semi micro analytical balance and taken as Micelial Dry Weight (MDW).

6.1.3 Factors Affecting Fungal Growth:

The factors that affect the growth are:

1) Temperature: For any specific organism, there will be minimum and maximum temperature which refers to the temperature at which considerable growth occurs. The optimum temperature is the temperature at which the growth rate is high.

2) pH of the Medium: The activity of fungi secreted enzymes help fungi in assimilation of nutrients for growth is known to be conditioned by the P^H and composition of the medium. Different enzymes released from fungi have different P^H optima for their activity. The general favourable range lies between P^H 4 to 8.

3) Humidity: A relative humidity between 95 to 100% generally supports efficient growth of most fungi and that below 80-85% inhibits their growth.

4) Concentration: Raulin[3] has studied the effect of concentration of essential trace elements on the growth of fungi. He reported that different fungi require different trace concentration of elements for their optimum growth. Higher the concentration than that required for optimum growth have been found to be inhibitory for the growth of fungi.

To ward off the harmful effects of these friendly fungi and to search control measures for such effects and also to test the biological applications of the newly synthesized complexes, it was felt wiser to undertake the antifungal study of the prepared compounds.

6.2 INTRODUCTION TO ANTIBACTRIAL ACTIVITY OF SCHIFF BASES AND THEIR METAL COMPLEXES:

The microorganisms have minute body size and simple structure. They reproduce at rapid rate and produce physical and chemical changes in their environment and causes beneficial as well as harmful effect on human being. The microorganisms are the causes for any metabolic disturbance in humans. The diseases causing micrograms are called as pathogens. The growth of pathogens and other harmful bacteria is controlled by antibacterial agents which is essential for survival of the mankind. The antibacterial agents are natural as well as synthetic molecules. Those antibacterial agents which are obtained from natural sources are termed as antibiotics. The antibacterial agents may be biotic, just inhibiting the growth of bacteria or biocidal and kill the bacteria.

6.3 PREVIOUS RELATED STUDIES:-

Dehydroacetic acid (DHA) is biologically active compound. Literature survey reveals that, the compound has antibacterial and fungicidal effects[5]. In aqueous solutions at very low concentrations (0.02 to 0.2%), DHA shows a strong antiseptic effect[6]. The compound is widely used in food technology. It is used to enhance vitamin-C stability, protect vegetables from loss of nutrients during food processing[7] and as preservative in products such as fish and sausage[8]. It also shows very interesting biological, antibacterial[9] and fungicidal activities[10] and used by some workers to control pathogenic fungi[11]. Some Schiff bases of DHA have shown interesting biological properties such as antitumour, antibacterial and antiviral activities, in addition to a wide range of chemotherapeutic activities. Coordination of such Schiff bases with metal ions Fe(III), Co(II), Ni(II) and Cu(II) often enhance their activity as reported for the control of pathogenic fungi. The Schiff base complexes find many applications in food industry[12] and show fungicidal and agrochemical activity in crop science[13].

The coordination chemistry of Schiff bases has extended its tentacles in microbiological studies too. In view of the promising biological activities of Schiff bases of dehydroacetic acid and their metal complexes, the microbiological work on these compounds is documented in the literature. A brief resume of such work is summarised in the following paragraphs.

Suryarao et.al.[14] synthesised the Schiff bases of dehydroacetic acid with hydrazide, salicyl hadrazide and thiosemicarbazide and their transition metal complexes. They were screened for their biological activity in vitro against Sozacladium oryzae and Xanthomonas oryzae and found to be highly toxic. The activity of some of the chelates was found to be equivalent to the commercial pesticides. The Schiff bases exhibited toxicity in the range 800 to 1000 ppm. The toxicity of their respective chelates was found to be enhanced to a greater extent due to the synergistic effect of metal ions and ligands in the complex and the metal chelates showed toxicity in the range 50-500 ppm. The toxicity of the metal chelates followed the order Cu>Ni>Zn>Fe>Mn>Co.

The fungicidal activities of some mixed ligand complexes of DHA with Mn(II), Fe(II), Ni(II), Co(II), Cu(II) and Zn(II) ions have been studied by Rao et.al.[15], in vitro against Aspergillus niger. It was observed that at 10 and 500 ppm concentration levels, the ligands showed 6.8 and 74.6% inhibition respectively while their respective metal complexes exhibited enhanced inhibition 71.2 and 100% respectively. The order of inhibition of growth of A. niger by metal chelates was found to be Cu>Ni>Fe>Zn>Mn>Co. Ramarao et.al.[10] synthesised transition metal chelates of Schiff bases derived from dehydroacetic acid and 2-amino ethane thiol and screened their fungicidal activity. It was found that the metal complexes showed greater fungicidal effect than their respective free ligands and some chelates exhibited 100% inhibition at 500 ppm level.

The antifungal activity of 2-acetyl pyridine N-ethyl thiosemicarbazone and its Fe(III), Co(II), Ni(II) and Cu(II) complexes in vitro against A. niger was studied by

Douglas et.al.[16] and observed an effective inhibition of growth of organism. It was concluded that, the complexation may be responsible for the inhibition of growth of Aspergillus niger growth.

Mehta et.al.[17] synthesised Cu(II) complexes of Schiff base derived from 2-hydroxy-1-napthaldehyde and primary amines antharanilic acid, o, p-toluidine and aniline and studied their antimicrobial activity. It was concluded that, the copper chelates do not possess any appreciable antimicrobial activity.

Jeewoth et.al.[18] screened the antibacterial activity of Cu(II), Zn(II) and Ni(II) complexes of Schiff base derived from 2,3 diamino pyridine and selected aldehydes salicyladehyde, 4-hydroxy benzaldehyde and 4-nitro benzaldehyde. The metal complexes were found to display appreciable antibacterial properties.

The fungicidal activity of Cu(II), Ni(II), Co(II), Fe (III) and Mn(II) chelates of Schiff base of dehydroacetic acid and primary aromatic amines like p-toluidine, p-bromoaniline, p-anisidine, 2-napthyl amine and o-phenylene diamie were screened in vitro against A. niger by Chodhekar et.al.[19]. The results indicated that, at 500 ppm level, the ligands arrested the A. niger growth by 60 to 70% while their respective metal chelates exhibited enhanced inhibition of A. niger growth by 75 to 100% due to cumulative effect of metal and ligands. Restriction of the growth by metal complexes followed the order Cu > Ni > Fe > Mn > Co.

Salunke et.al.[20] synthesised aryl azo Schiff bases of dehydroacetic acid and primary aromatic amines and evaluated their antifungal activity against A. niger and antibacterial activity in vitro against E.coli, Staphylococcus Sp., Proteus Sp. and Candida albicans bacteria. It was found that the percentage inhibition against A. niger at 250 ppm. is 19-59 and at 500 ppm. it is 27-100. While as inhibition against all the species of bacteria is zero.

Pachling[21] reported the fungicidal activity of Fe(III), Cr(II), Cd(II), Hg(II) and Pb(II) chelates of Schift bases derived form DHA and semicarbazide, thiosemicarbazides, ethanol amine, thiothanol amine, 2-hydroxy benzoylhydrazide, 2-choloro benzoyl hydrazide and benzoyl hydrazide in vitro against A.niger. The cumulative fungicidal effect due to metal and ligand in the complexes followed the order Pb > Hg > Cd > Fe > Cr.

From the documented literature, it is evident that, dehydroacetic acid anils and their complexes having halogen and hydroxy phenyl group exhibited appreciable antifungal activity[22] and the activity varied with different amine moiety and metal ions in these complexes.

The numbers of compounds have been tried for their antibacterial activity. It was found that antibacterial activity of a compound depends in part upon its ability to form chelates[23]. The use of metal complexes as antibacterial agents and the chelates playing the role of certain drugs has been realised in recent decades.

Shlyakhov et.al.[24] synthesised Cu(II) and Ni(II) complexes of Schiff bases derived from furfurals and semicarbazides and studied their antimicrobial activity in vitro against staphylococci, Bacillus cerius, B. anthracis and E. coli and evaluated their minimum inhibitory concentrations.

Literature survey reveals that, the reported work[10,14,15,19,24] on biological activity of DHA anils and their complexes is related to fungicidal activity and not on antibacterial activity.

With reference to literature survey discussed the study of fungicidal and bacterial activity, an attempt is made to study the antifungal and antibacterial activity of Schiff bases of DHA and their transition metal complexes. The fungicidal activities were screened in vitro against Aspergillus niger, and bacterial activities were screened in vitro against E-Coli.

6.4 EXPERIMENTAL TO ANTIFUNGAL ACTIVITY OF SCHIFF BASES AND THEIR METAL COMPLEXES:

The fungi toxicity of Schiff bases and metal complexes in liquid medium was studied by the method followed by Bhist and Khulbe[29] in vitro against A. niger at 200 ppm and 400 ppm levels separately.

6.4.1 Preparation of Glucose – Nitrate Medium :

The Glucose-Nitrate (GN) medium required for the growth of A. niger was prepared by dissolving 10gm. of glucose, 2.5gm. of KNO_3, 1gm. of KH_2PO_4 and 0.5 gm. of $MgSO_4$ H_2O in one liter of sterile distilled water. The glucose and KNO_3 in the medium are the sources of carbohydrate and nitrogen respectively while KH_2PO_4 and $MgSO_4$ $7H_2O$ are the activators for growth.

6.4.2 Preparation of Sets of Test Sample and Control Flasks :

All the ligands and the complexes of each ligand with five different metal ions were used for testing their fungi toxicity separately at two different concentration levels 200ppm and 400ppm. For each concentration level six sets of flasks, one set each for a ligand and its five complexes were prepared. Each set comprised of flasks one each for control, free ligand and five complexes.

The narrow necked 100ml conical flasks were used for the purpose and the sets prepared in the following manner.

a) A flask with 25ml G.N. medium without test sample served as control.

b) A flask with 25ml G.N. medium without test sample and 5 ml DMSO served as control.

c) For free ligand, 25 ml G.N. medium and accurately weighed test ligands dissolved in 5 ml DMSO were taken in the flask.

d) 25 ml G.N. medium and accurately weighed test complexes dissolved in 5 ml DMSO was taken in the flask for screening fungi toxicity of the complex.

All the flasks were plugged with nonabsorbent cotton and then thoroughly mixed aseptically by autoclaving at 15 lbs pressure for 30 minutes. This ensured total sterilization.

6.4.3 Inoculation and Incubation:

The autoclaved flasks were transferred aseptically to the inoculation chamber where they were exposed to UV light. The stock culture of fungi A. niger were collected from the culture unit of the department of Botany itself where these tests were undertaken. The cell culture of test fungi in the form of spore suspension was prepared by adding 10 ml of sterile distilled water to a seven day old culture of A. niger. The inoculation was done in the ultraviolet chamber under aseptic conditions. The autoclaved media flasks of control, ligand and complexes were inoculated each with 5 drops of the spore suspension which contained $5X10^2$ spores of A. niger per microscopic field. The inoculated flasks were then incubated for 7 days at 25 ± 2^0C.

6.4.4 Harvesting of Microbial Biomass :

After desired incubation, the mycelial mat was harvested. The fungal biomass content filtered through previously dried and weighed Whatman No.42 filter paper. The mycelial biomass was then dried along with filter paper in an oven maintained at $65^0 \pm 5^0$ to constant weight, cooled and finally weighed on semi micro analytical balance. The mycelial dry weight (MDW) was obtained by subtracting the weight of mycelium free filter paper from final dry weight [16].

Three replicates of each treatment were prepared in all experiments. The MDW was corrected each time by subtracting the dry weight obtained from un inoculated flask under similar experimental conditions. The yield of MDW in mg at 200 ppm and 400 ppm are presented in Tables 6.1 and 6.2. The percent decrease in mycelial dry weight due to the test compound in each case was calculated and tabulated in terms of average percentage inhibition. (Table 6.3 and 6.4)

Table 6.1 Yield of Mycelial Dry Weight (MDW) in mg. at 200ppm for ligand and their metal complexes after 168hrs.

Ligand	MDW(mg) in Ligand	MDW(mg) Control	MDW (mg) in Complexes of				
			Cu	Co	Ni	Mn	Fe
L1	65	88	52	59	20	25	62
L2	67	88	49	57	23	28	59
L3	75	88	19	61	46	50	54
L4	70	88	43	58	44	52	52
L5	61	88	23	51	42	47	49
L6	54	88	41	44	46	54	53
L7	40	88	30	11	29	36	18
L8	58	88	12	40	57	43	48

Table 6.2 Yield of Mycelial Dry Weight (MDW) in mg. at 400ppm for ligand and their metal complexes after 168hrs.

Ligand	MDW(mg) in Ligand	MDW(mg) Control	MDW (mg) in Complexes of				
			Cu	Co	Ni	Mn	Fe
L1	30	88	20	17	23	25	28
L2	32	88	06	15	21	18	27
L3	36	88	18	21	24	13	16
L4	36	88	20	20	18	16	24
L5	28	88	20	19	00	00	18
L6	26	88	07	25	12	19	29
L7	19	88	00	12	08	06	16
L8	28	88	09	11	00	16	18

Table 6.3 Percentage inhibition after 168hrs for Aspergillus niger at 200ppm.

Average % inhibition after 168hrs for Aspergillus niger						
Ligand		In Complexes of				
		Cu	Co	Ni	Mn	Fe
L1	26.13	40.90	32.95	77.27	71.59	29.54
L2	23.86	44.31	35.22	73.86	68.18	32.95
L3	14.77	78.40	30.68	47.72	43.18	38.63
L4	20.45	51.13	34.09	50	40.90	40.90
L5	30.68	73.86	42.04	52.27	46.59	44.31
L6	38.63	53.40	50	47.72	38.63	39.77
L7	54.54	65.90	87.5	67.04	59.09	79.54
L8	34.09	86.36	54.54	35.22	51.13	45.45

Table 6.4 Percentage inhibition after 168hrs for Aspergillus niger at 400ppm.

Average % inhibition after 168hrs for Aspergillus niger						
Ligand		In Complexes of				
		Cu	Co	Ni	Mn	Fe
L1	65.90	77.27	80.68	73.86	71.59	68.18
L2	63.63	93.18	82.95	76.13	79.54	69.31
L3	59.09	79.54	76.13	72.72	85.22	81.81
L4	59.09	77.27	77.27	79.54	81.81	72.72
L5	68.18	77.27	78.40	100	100	79.54
L6	70.45	92.04	71.59	86.36	78.40	67.04
L7	78.40	100	86.36	90.90	93.18	81.81
L8	68.18	89.77	87.5	100	81.81	79.54

6.5 EXPERIMENTAL TO ANTIBACTRIAL ACTIVITY OF SCHIFF BASES AND THEIR METAL COMPLEXES:

6.5.1 Test Sample: The solution of test sample with requisite concentration were prepared in dimethyl sulfoxied (DMSO) and kept at 4^0C temperature.

6.5.2 Test organism: The culture of human pathogenic bacteria Escherichia coli was collected from department of Botany. Aseptic techniques[26] were employed to prepare the culture freshly, in which the culture of bacteria E. coli was maintained at 4^0C in nutrient agar medium.

6.5.3 Medium for Growth: The Nutrient Agar Medium was used for screening the antibacterial activity.

6.5.4 Inoculation and Incubation: Agar diffusion method (cup / well assay method), given by Kavanagh[31] was used to check antibacterial activity. When the media in disc get solidified, two wells of 5mm diameter were bored with an aseptic corck borer. Each of the well was filled with the test sample with the help of pasture pipette. Such plates were placed in uv chamber for 5 min. Then the strains of E. coli were seeded uniformly. The plates were then incubated at 28^0C for 24 hours and the inhibition zones were recorded in terms of diameter of zone of inhibition of growth of bacteria.

Table 6.5 Diameter of inhibition zone in an Antibacterial activity of ligands and their metal complexes.

Diameter of inhibition zone (mm) after 24 hrs.						
Ligand		in Complexes of				
		Cu	Co	Ni	Mn	Fe
L1	00	00	00	00	00	00
L2	00	00	00	00	00	00
L3	00	00	00	00	00	00
L4	00	00	00	00	00	00
L5	00	00	00	00	00	00
L6	00	00	00	00	00	00
L7	00	00	00	00	00	00
L8	00	00	00	00	00	00

6.6 RESULTS AND DISCUSSION:

Antifungal activity- The results of investigation indicates that all the ligands and their metal complexes arrested the growth of A. niger. A considerable increase in fungitoxicity of metal complexes as compared to their ligands is observed for both 200 ppm and 400 ppm levels.

At 200 ppm concentration, the percentage inhibition of A. niger growth due to ligands was found to be 14-54% while that due to their complexes enhanced to 29-86%. In all the cases, the chelates exhibited a higher toxicity as compared to their respective free ligands. The percentage inhibition of growth of A. niger increases with concentration of test samples.

At 400 ppm concentration the percentage inhibition of A. niger growth due to ligands was found to be 59-78 % while that due to their complexes enhanced to 67-100 %. In all cases, the chelates exhibited a higher toxicity as compared to their respective free ligands. The percentage inhibition of growth of A. niger increases with concentration of test samples.

The percentage decrease in mycelial dry weight for the ligands at 400ppm was found to be in the order L7>L6>L8>L5>L1>L2>L3>L4. In general on average the percentage decrease in mycelial dry weight for the metal complexes can be given in the order Cu(II)>Ni(II)>Mn(II)>Co(II)>Fe(III).

Antibacterial activity- The inhibitory zone data reveals that, both ligand as well as their complexes does not show any inhibition against E. coli.

The results obtained above are in good agreement with previous findings[10,15,20] with respect to comparative activity of free ligand and its complexes.

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