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SYNTHESIS AND BIOLOGICAL EVALUATION OF METAL CHELATES

THESIS
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FOR
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OF

Doctor of Philosophy

IN
CHEMISTRY
BY

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Under the supervision of
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OCTOBER-2009

Statement under O.Ph.D. 7 of Saurashtra University

The work included in the thesis is my own work under the supervision of **Dr. K. J. Ganatra** and leads to some contribution in the field of Chemistry and is supported by recent references.

Jignesh H. Pandya

CERTIFICATE

This is to certify that the present work submitted for the Ph.D. Degree of Saurashtra University by **Mr. Jignesh H. Pandya** has been the result of work carried out under my supervision and is a good contribution in field of Chemistry of “Metal Chelates” with a special emphasis on synthetic aspects.

Dr. K. J. Ganatra

Principal

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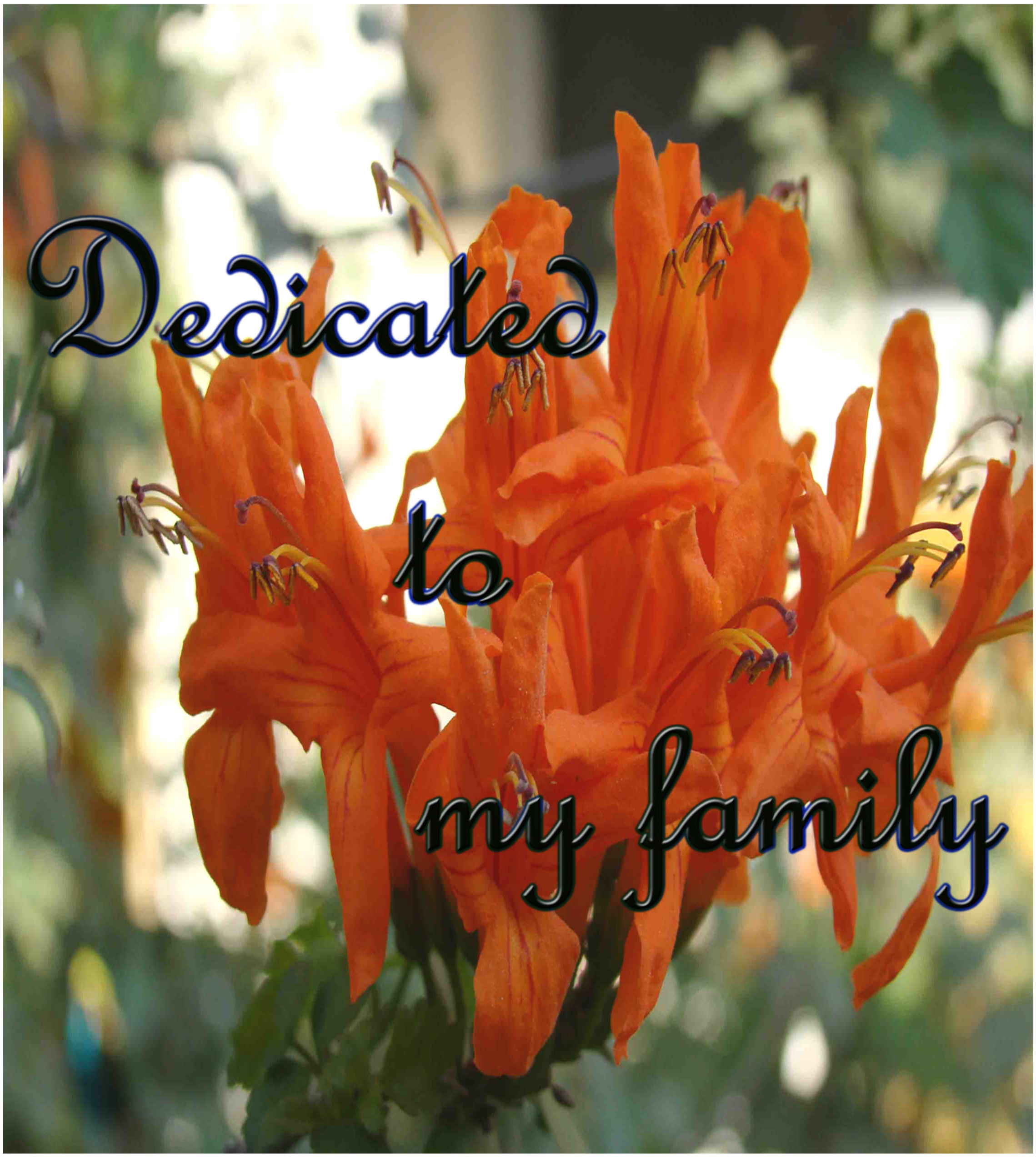

Dedicated

to

my family

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SYNOPSIS

SYNOPSIS

SYNTHESIS AND BIOLOGICAL EVALUATION OF METAL CHELATES

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SYNOPSIS of the thesis to be submitted to the Saurashtra University for the degree of **Doctor of Philosophy** in Chemistry.

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Summary of the work incorporated in the thesis with the title “SYNTHESIS AND BIOLOGICAL EVALUATION OF METAL CHELATES” has been described as under.

The present work divided into four chapters.

CHAPTER-1: Synthesis and characterization of ligand.
CHAPTER-2: Synthesis and characterization of metal chelates.
CHAPTER-3: Synthesis and characterization of mixed ligand metal complexes.
CHAPTER-4: Biological evaluation of ligands and metal chelates.

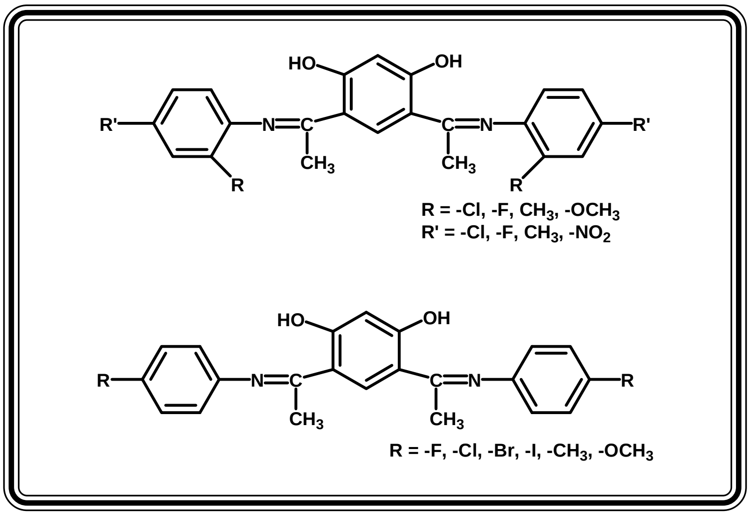
CHAPTER-1

SYNTHESIS AND CHARECTERIZATION OF LIGAND

Preparation of Schiff base ligand in two parts
Part-1: 4,6 Diacetyl resorcinol + p-substituted anilines
Part-2: 4,6 Diacetyl resorcinol + 2,4 di-substituted anilines

Compounds containing an azomethine group are known as imines (Schiff bases). Schiff base ligands are considered privileged ligands because they are easily prepared by the condensation between aldehydes/ketons and imines. Stereogenic centres or other elements of chirality (planes, axes) can be introduced in the synthetic design. Schiff base ligands are able to coordinate many different metals, and to stabilize them in various oxidation states, enabling the use of Schiff base metal complexes for a large variety of useful catalytic transformations. Schiff described the condensation between an aldehyde/ketone and an amine leading to a Schiff base in 1864. Schiff base ligands are able to coordinate metals through imine nitrogen and another group, usually linked to the aldehyde or ketone. Modern chemists still prepare Schiff bases, and nowadays active and well-designed Schiff base ligands are considered privileged ligands. In fact, Schiff bases are able to stabilize many different metals in various oxidation states, controlling the performance of metals in a large variety of useful catalytic transformations. Schiff bases are also able to transmit chiral information to produce non-racemic products through a catalytic process; chiral aldehydes or chiral amines can be used. From a practical point of view, the aspects involved in the preparation of Schiff base metal complexes are spread out in the literature.

The ligand characterized by IR, 1H NMR and MASS Spectra.



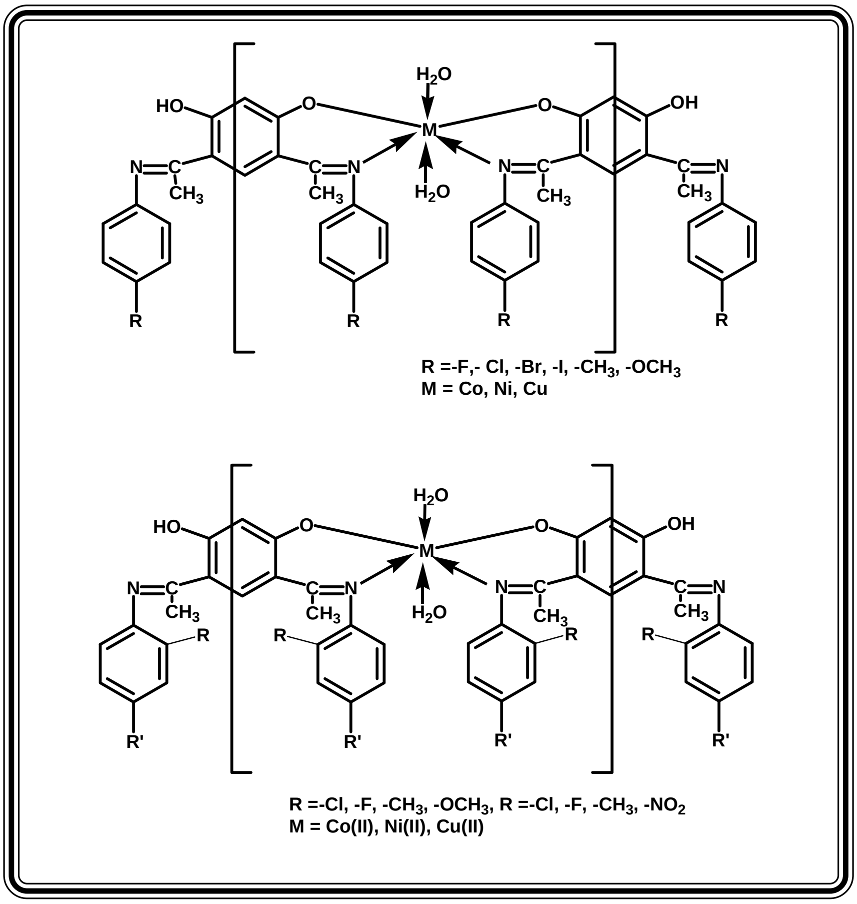
R = -Cl, -F, CH_3, $-OCH_3$
R' = -Cl, -F, CH_3, $-NO_2$

R = -F, -Cl, -Br, -I, $-CH_3$, $-OCH_3$

CHAPTER-2

SYNTHESIS AND CHARECTERIZATION OF METAL CHELATES

Numerous Schiff bases and their transition metal complexes have been investigated by various techniques for different purposes. Schiff-base metal complexes have been widely studied because they have industrial, antifungal and biological applications. They serve as models for biologically important species and find applications in biomimetic catalytic reactions. Chelating ligands containing O and N donor atoms show broad biological activity and are of special interest because of the variety of ways in which they are bonded to metal ions. Transition metals play a key role in biological systems such as cell division, respiration, nitrogen fixation and photosynthesis. Also Schiff bases and their complexes in aqueous solutions have been studied because of their interesting and important properties.



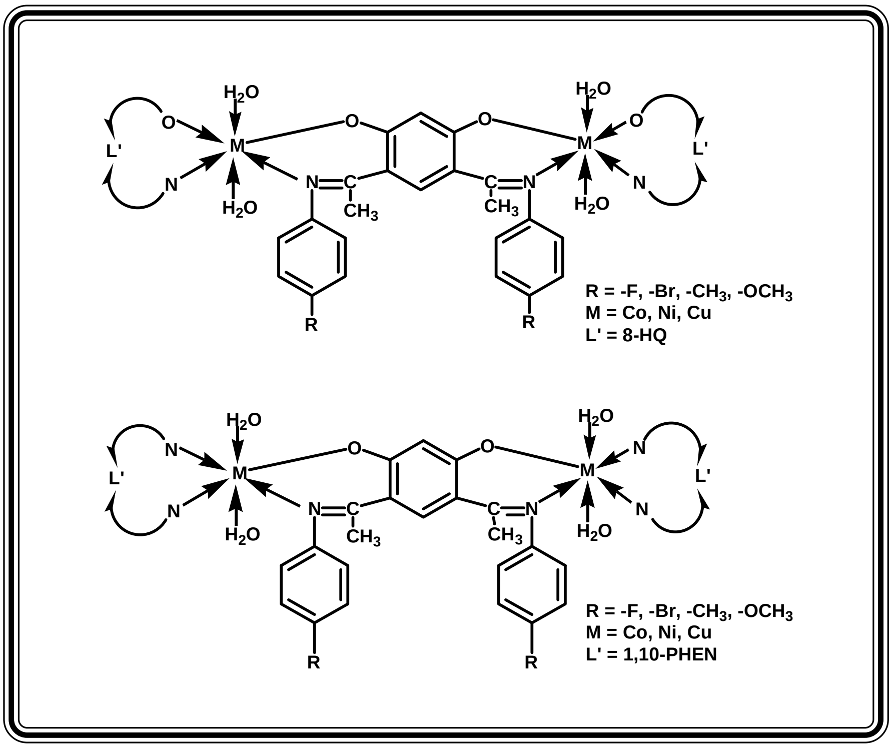
R =-F,- Cl, -Br, -I, -CH_3, -OCH_3
M = Co, Ni, Cu

R =-Cl, -F, -CH_3, -OCH_3, R =-Cl, -F, -CH_3, -NO_2
M = Co(II), Ni(II), Cu(II)

CHAPTER-3

SYNTHESIS AND CHARACTERIZATION OF MIXED LIGAND METAL COMPLEXES

Transition metal Schiff-base complexes are important stereochemical models in coordination chemistry due to their preparative accessibility and structural diversity. A comprehensive review on cyclic and acyclic Schiff-bases and related derivatives appeared recently, particularly dealing with the development of synthetic procedures for the preparation of mono-, di- and polynuclear Schiff-base complexes and their reduced analogues. Some Schiff-base complexes show catalytic properties, or act as oxygen carriers and antifungal agents increased by the presence of hydroxyl groups in the ligands.



R = -F, -Br, $-CH_3$, $-OCH_3$
M = Co, Ni, Cu
L' = 8-HQ

R = -F, -Br, $-CH_3$, $-OCH_3$
M = Co, Ni, Cu
L' = 1,10-PHEN

PART - I

INTRODUCTION

INTRODUCTION

Coordination chemistry has an old history originating in the discovery of $[Co(NH_3)_6]Cl_3$ by Tassaert in 1798[1]. But it was Werner who systematized the subject by propounding his coordination theory in 1893[2]. Werner's basic ideas on the stereochemistry of metal complexes, mechanisms of isomerization and racemization, etc. remain unchallenged even today despite all the monumental developments which have taken places since his days and during the last five decades in particular, owing to the advent of sophisticated physico-chemical techniques of high precision and capability[3,4]. These have considerably enriched our understanding of the nature of the metal-ligand bond, structure and stereochemistry of metal complexes, their stabilities and liabilities and other properties. Even metal which were earlier thought to be non-complex formers are now known to form quite stable complexes with special types of ligands, such as the alkali metal complexes formed by crown ethers and cryptates[5-8].

According to Werner[9] atoms possess two types of valency called primary or principal valency and secondary or residual or auxiliary valency. While ordinary molecules results from the satisfaction of primary valencies, utilization of the secondary valencies leads to the formation of coordination compounds[10]. The bidentate and other higher polydentate ligands form closed rings on binding to a metal ion and hence, were called **chelating ligands** by Morgan (chelate in Greek means **crab's claw**) and the closed ring formed was called a **chelate** ring[3,11].

Unambiguous evidence regarding the geometrical arrangement of the coordinated units around the cation, as required by his theory, was furnished by Werner through the preparation of quite a large number of geometrical isomers of six-coordinate (octahedral), and four co-ordinate (Planer) complexes, and by the resolution of several octahedral complexes into their optical enantiomers. Compounds of the types MA_4B_2 (octahedral) and MA_2B_2 (square planer) occur in two isomeric (geometrical) forms which are designated as *cis* and *trans* respectively, depending upon whether the two ligands B occur in adjacent or diagonally opposite coordination positions around the central metal atom (ion)[12-14].

A survey of the literature shows that besides investigating problems of electronic structure, bonding and stereochemistry of metal complexes and stabilities of metal complexes, during the last 50 years, an increasing number of studies have been devoted to the dynamics and mechanisms of reaction of metal complexes[15-20]. The classical application of complex formation in analysis and other laboratory practices have been refined and sophisticated to such a degree that it is now possible to monitor concentration of species at unbelievably low level, viz. in the range of a fraction of a microgram per milliliter of solution based on several physico-chemical characteristics, such as color, catalytic activity, etc. indeed, many such techniques are now extremely valuable in monitoring hazardous metal which are serious environmental pollutants[21].

According to the modern concept, even the organometallic compounds belong to the general class of coordination compounds, and a host of such compounds of a large majority of metal have been synthesized with wide variety of organic substrates. Apart from their academic importance, these are of great technological significance because of their useful catalytic properties[22,23]. Of course, the application of metal complexes too have an old history, and many complex formation reactions are in use since early days for the detection, separation and estimation of metals both in macro and micro scales. Some more recent and somewhat exciting application of metal complexes may be observed in the photolytic splitting of water producing hydrogen. This process has immense potential for generating a nonpolluting fuel which may be ultimate solution to save the world from a severe crisis in the future due to non-availability of fossil fuels. Another important development is the recognition of the vital role of metal complexes in biological systems[24,25]. A knowledge of the factor that govern the stabilities and reactivity of metal complexes can be of immense help in understanding the behavior of metal complexes both in biological systems and their applications in the laboratory and in technology. It is the knowledge of the nature of the metal-ligand bond which provides a fundamental basis for understanding the behavior of metal complexes. Another important use of metal complexes and of complex formers is in the field of therapy. The use of gold complexes in the treatment of tuberculosis dates back to 1917 and many complexes of gold are known to be useful in the treatment of arthritis since 1927[26]. However several significant developments have taken place during the last 30 years or so in the field of application of metal complexes in biology and medicine[27-29]. Many of the complexes and complex formers are known to be used as drugs in certain types of diseases as also for metal detoxification in the case of metal poisoning[30,31].

Studies on co-ordination compounds have become so very wide that it is not possible to describe this in few pages. Co-ordination compounds where the central metal ion is bounded to different Ligands exhibit different characteristics properties. The characteristics of such compounds are based on nature of metal as well as the type of ligands and their structures. Metal complexes containing organic molecule in the physiological systems play crucial role to the existence growth, maintenance and formation of entire living being and therefore the recent research activity phosphorus, nitrogen, oxygen and sulphur containing organic molecules are very essential components of physiological system and therefore complexation studies of organic compounds containing these atoms received particular attention by coordination chemists[32-34].

During the past two decades, considerable attention has been paid to the chemistry of the metal complexes of Schiff bases containing nitrogen and other donors[35-41]. Schiff bases offer a versatile and flexible series of ligands capable to bind with various metal ions to give complexes with suitable properties for theoretical and/or practical applications. Since the publication of Schiff base complexes, a large number of polydentate Schiff base compounds have been structurally characterized and extensively investigated. This may be attributed to their stability, biological activity and potential applications in many fields such as oxidation catalysis, electrochemistry, etc. Various studies have shown a relationship between the metal ions and their metal complexes as antitumor and antibacterial agents, which is a subject of great interest. The inorganic pharmacology started to be an important field with more than 25 inorganic compounds being used in therapy as antibacterial, antiviral and anticancer drugs[42-51].

SCHIFF BASE – LIGAND

With ever increasing knowledge of properties of functional groups and nature of donor atoms and the central metal ion, ligands with more selective chelating group called anils, imines and azomethines or best known as **Schiff bases** are being used for the complex formation studies. They have general structure RC=NR’ where R and R’ are alkyl, aryl or heterocyclic compounds.

Extensive investigation in the field of Schiff bases have been reported by Bayer[52]. Their preparation, chemical and physical properties have been described by Layer[53], Dwyer and Mellor[54]. It concern primarily with the stereochemistry of Schiff base complexes as well as aspect of behavior of such complexes in solution, has also been published[55].

Schiff[56] may be regarded as the first to have determined the composition of a metal complex with such ligands containing azomethine group by establishing the metal : ligand ratio 1 : 2 in copper complex derived from N-aryl salicyladimines. The systematic synthetic study of Schiff base complexes was initiated by Pfeiffer and coworker[57-60]. This work still serves as a source of preparative detail and structural interpretation for contemporary chemists and its importance may be judge by the relatively large number of citation in the modern literature[61-65]

Transition metal complexes derived from Schiff bases have occupied a central role in the development of coordination chemistry. The azomethine group > C=N of the Schiff base forming a stable metal complexes by coordinating through nitrogen atom. Large number of Schiff bases have been investigated by many workers as chelating agents. Most of them are prepared by the condensation of salicyldehyde with aromatic amines and aliphatic amines. Calvin and Berkelow[66] have synthesized nearly twelve anils by condensing salicyldehyde with substituted anilines and other aromatic amines.

Recently **J.H.Pandya** et al.[67] have reported binuclear transition metal complexes derived from 5-bromo salicyldehyde. Javed Iqbal et al.[68] synthesized Chloro-salicylidene aniline and their complexes.

Ligand having phenolic-OH group and nitrogen are very effective. This fact is very well illustrated by the use of 8-hydroxy quinoline, 8-hydroxy quinazoline, monodentate, bidentate and polydentate ligands have been studied and their Schiff bases are extensively used as a chelating agent. Several bidentate Schiff bases in which phenolic -OH and immino nitrogen are present in such a way that they form six membered ring, forms chelates with metal ions. K. Natarajan et al.[69] have introduced Ruthenium metal chelates containing bidentate Schiff base.

Recently Mehmet Tuncel and Selahattin Serin, [70] reported new azo-linked Schiff base metal chelates. Several tridentate ligands were also investigated and used as chelating agents by Tarek M. Ismail et al. [71], and M. Sivasankaran Nair et al. [72].

Compounds containing an azomethine group are known as imines (Schiff bases). Schiff base ligands are considered “privileged ligands” because they are easily prepared by the condensation between aldehydes/ketons and imines[17,73-76]. Stereogenic centres or other elements of chirality (planes, axes) can be introduced in the synthetic design. Schiff base ligands are able to coordinate many different metals, and to stabilize them in various oxidation states, enabling the use of Schiff base metal complexes for a large variety of useful catalytic transformations. Schiff described the condensation between an aldehyde/ketone and an amine leading to a Schiff base in 1864. Schiff base ligands are able to coordinate metals through imine nitrogen and another group, usually linked to the aldehyde or ketone[77-79]. Modern chemists still prepare Schiff bases, and nowadays active and well-designed Schiff base ligands are considered “privileged ligands”.

Recently **J.H.Pandya** et al. have reported binuclear metal complexes derived from schiff base[80]. In fact, Schiff bases are able to stabilize many different metals in various oxidation states, controlling the performance of metals in a large variety of useful catalytic transformations. Schiff bases are also able to transmit chiral information to produce non-racemic products through a catalytic process; chiral aldehydes or chiral amines can be used[81-83]. From a practical point of view, the aspects involved in the preparation of Schiff base metal complexes are spread out in the literature. We wish to summarize and introduce some practical guidelines for the preparation and use of Schiff base metal complexes in catalysis[84]. When two equivalents of salicylaldehyde are combined with a diamine, a particular chelating Schiff base is produced[85,86]. The so-called Salen ligands, with four coordinating sites and two axial sites open to ancillary ligands, are very much like porphyrins, but more easily prepared. Although the term Salen was used originally only to describe the tetradentate Schiff bases derived from ethylenediamine, the more general term Salen-type is used in the literature to describe the class of [O,N,N,O] tetradentate bis-Schiff base ligands[87]. Basic guidelines for the design, synthesis and application of metal Schiff base complexes in catalysis will thus be surveyed with the emphasis on the relevant problems in producing active and useful complexes[88-90].

In the last decade Schiff-base ligands have received more and more attention, mainly because of their wide application in the fields of synthesis and catalysis[91-93]. This attention is still growing, so that a considerable research effort is today devoted to the synthesis of new Schiff-base complexes with transition and main group metal ions, to further develop applications in both catalysis and material chemistry[94-96]. The salen ligand has also been used to activate redox chemistry for the selective recognition and modification of nucleic acids. Adducts formed between guanine and nickel complexes based on salen ligands strongly inhibit polynucleotide elongation, allowing sensitive detection through polymer extension assays[97].

Although the first chelate was recognized and described by Werner, the development of chelate chemistry has taken place almost entirely within recent years[9,10]. However, chelation is nothing more than a special form of complex formation, and what has been said concerning simple complexing applies equally well to chelate formation[98]. On the other hand the majority of chelate compounds result from the linking of metal atoms to organic molecules; consequently this branch of chemistry might be incorporated as well in the field of organic chemistry as in that of inorganic chemistry. Moreover the information relating to chelate chemistry has become so extensive that it is impossible to present more than an outline summary[11,12,28].

Nature of Ligand:

The stability of the chelate is mainly affected by the size and the number of chelate rings, the basic strength of ligand, the nature of donor atom and the steric effect of the substituents in the ligand molecule[1,3]. It has been established that five and six membered rings are most stable and the stability of the complexes increases in the number of rings. Schwarzenbach[99] showed the the stability of a metal chelate is considerably greater than that of an analogous compound with fewer chelate rings. He termed this effect as chelate effect. He emphasized the role of entropy as a fundamental factor in chelate effect. A linear correlationship has been established for the basic strength of the ligand and the stability of the metal complexes. The basic strength of the ligand is highly affected by the nature of the group or atom present in the ligand molecule[100]. Substituent such as methyl (σ and π donor) increases the basicity of the donor atom whereas substituents like nitro (σ and π acceptor) decreases it. Martell and Calvin[101] have reported the steric effect of the substituent in the ligand molecule in complex formation. The lowering in stability due to bulky group present on or near the donor atom has been reported by several authors[102-104]. The different types of steric effect have been discussed in detail in the literature[99]. Calvin et al.[101] have studied the significance of resonance effect in the stability of chelate rings and suggested that metal ion may be involved in the benzenoid resonance in the chelate ring through back donation of d-electrons.F.J.C. Rossotti et al.[105] and S.D. Christian[106] have reported the stability depends upon enthalpy and entropy of the system.

METAL AND METAL CHELATES

The element which constitute Group-IIIA to IB in the fourth, fifth and sixth periods of periodic table are classified as the ‘transition elements’. They are metals characterized by having atoms which, either in their neutral state, or in the case of the coinage metals, in their common oxidation states, have partly filled d or f shells[107,108].

Properties of the transition elements:

(1) Physical:

Nearly all the transition elements have the simple h.c.p., f.c.c., or b.c.c. lattices characteristic of the true metals and display typical metallic properties – high tensile strength, ductility, malleability, high thermal and electrical conductivity. Their m.p. and b.p. are high; in any period, these rise to a maximum value at the group

VIA metal and then, expect for Mn and Tc regularly fall again.

(2) Chemical:

Most of the metals dissolve easily in dilute acids. The froth period d-block metals, with the exception of copper, are readily soluble in non-oxidizing acids. Only the coinage metals and some that precede them in the fifth and sixth period show noble character. Because they have partly filled shells, many transition metals give compounds which are paramagnetic. The promotion of an electron from one d orbital to another usually requires a quantum of energy appropriate to absorption in the visible spectrum; thus many transition metal compounds are colored, but often only weakly, as d-d transition are 'forbidden' ones in the quantum-mechanical sense[11,12].

The most important chemical characteristic of the transition metals is that nearly all of them exhibit several oxidation states. The coordination number of the metal atom in a compound, the stereochemistry of the atom and the nature of the bonds it forms are all, to some extent, dependent on the particular oxidation state[109]. The structure of transition metal compounds may be rationalized by means of purely electrostatic models (**Crystal Field Theory**) or by means of covalent bond models (**Molecular Orbital Theory**) but the approaches made in the two models are complementary rather than contradictory and are effectively combined in **Ligand-Field theory**[110].

METAL	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
mp(^{0}C)	1668	1890	1875	1244	1537	1493	1453	1083
Properties	Hard, corrosion resistant	Hard, corrosion resistant	Brittle, corrosion resistant	White, brittle, reactive	Lustrous, reactive	Hard, bluish color	Quite corrosion resistant	Soft and ductile, reddish color
Density (g cm^{-3})	4.51	6.11	7.19	7.18	7.87	8.90	8.91	8.94
E^0 (V)	-	-1.19	-0.91	-1.18	-0.44	-0.28	-0.24	+0.34
Solubility in acids	Hot HCl, HF	HNO_3, HF concentrated H_2SO_4	Dilute HCl, H_2SO_4	Dilute HCl, H_2SO_4, and so on	Dilute HCl, H_2SO_4, and so on	Slowly in dilute HCl	Dilute HCl, H_2SO_4,	HNO_3, hot concentrated H_2SO_4

Nature of the metal ion[111]:

It is concluded that most stable complexes are obtained when it is made up of oppositely charged ions, and the greater the charge on ions and smaller the ions, the grater is the stability. Thus stability increases with the charge on the metal ions and if the metal ions having same charge the stability of complexes increases as the ionic radius decreases.

In order to understand the role of metal ions in deciding the stability of complexes, the metal ion are classified into three groups viz., Class A, Class B, and borderlines as under:

Class A : H^+, Li^+, Na^+, K^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Mn^{2+}, Al^{3+}, Sc^{3+}, Ga^{3+}, In^{3+}, La^{3+}, Cr^{3+}, Co^{3+}, Fe^{3+}, Ti^{4+}, Sn^{4+}
Class B : Cu^+, Ag^+, Au^+, Ti^+, Hg^+, Hg^{2+}, Pd^{2+}, Pt^{2+}, Pt^{4+}, Ti^{3+}.
Borderlines : Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}.

This classification is based on the relative stability of complexes with ligands having donor atom from groups V-A, VI-A, VII-A. if the stability of the complexes is greatest with the lightest element of each of these groups as the donor atom, the ions are placed in class-A conversely class-B ions form the least stable complexes with the lightest element of each group as donor atom. Further more, class-B ions form stable complexes with CO and olefins while those of class-A do not form such complexes. Some ions frequently form complexes whose stabilities cannot be predicted on the bases of the order generally observed stabilities, and these ions are placed in the borderline class.

Mellor and Maley[112] arranged the metals in order of stability of complexes of bivalent metal ions with salicyladehyde glycene and 8-hydroxy quinoline.

$$Pd > Cu > Ni > Pb > Co > Zn > Cd > Fe > Mn > Mg.$$

They proposed that Pd(II) and Cu(II) are capable of forming strong dsp^2 bonds and hence give the strongest chelates. It was concluded that the strength of the bonding in this chelates depends upon the ability of metal to from homopolar bonds. The stability of complexes of the borderline ions with a given ligand is almost invariably in the order.

$$Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} < Zn^{2+}$$

This order is known as the Irving-Williams series. Irving and Williams[113] correlated the above conclusion by plotting the stability constant against the atomic numbers. The conductometric measurements and exchange studies of Cu, Ni, Zn and Co chelates indicate almost the same stability order.

(A) COBALT:

The trends towards decreased stability of very high oxidation states and the increased stability of the II state relative to the III state, which occur through the series Ti, V, Cr, Mn, and Fe, persist with Co. the highest oxidation state is now IV, and only a few such compounds are known. Cobalt(III) is relatively unstable in simple compounds, but the low spin complexes are exceedingly numerous and stable, especially where the donor atom (usually N) make strong contributions to the ligand field. There are also numerous complexes of Co^I. this oxidation state is better known for cobalt then for any other element of the first transition series except copper. All Co^I complexes have π-acid ligands. Cobalt always occurs in association with Ni and will usually occur also with As. The chief source of Co are "Speisses", which are residue in the smelting of arsenical ores in Ni, Cu, and Pb. Cobalt is relatively unreactive, although it dissolves slowly in dilute mineral acids.

Chemistry of Cobalt(II), d^7

The dissolution of Co, or the hydroxide or carbonate, in dilute acids gives the pink aqua ion, $[Co(H_2O)_6]^{+2}$, which forms many hydrated salts. Addition of OH^- to Co^{+2} gives the hydroxide, which may be blue or pink depending on the conditions. It is weakly amphoteric dissolving in very concentrated OH^- to give a blue solution containing the $[Co(OH)_4]^{2-}$ ion.

The most common Co^{II} complexes may be either octahedral or tetrahedral. There is only a small difference in stability and both types, with the same ligand, may be in equilibrium. Thus for water there is a very small but finite concentration of the tetrahedral ion

$$[Co(H_2O)_6]^{+2} \leftrightarrow [Co(H_2O)_4]^{+2} + 2H_2O$$

Addition of excess Cl^- to pink solution of the aqua ion readily gives the blue tetrahedral species.

$$[Co(H_2O)_6]^{+2} + 4Cl^- \leftrightarrow [CoCl_4]^{-2} + 6H_2O$$

Tetrahedral complexes, are formed by halide, pseudohalide, and OH^- ions. Cobalt(II) forms tetrahedral complexes more readily than any other transition metal ion. The Co^{+2} ion is the only d^7 ion of common occurrence. For a d^7 ion, ligand field stabilization energies disfavor the tetrahedral configuration relative to the octahedral one to a smaller extent than for any other configuration. This argument is valid only in comparing the behavior of one metal ion with another and not for assessing the absolute stabilities of the configurations for any particular ion.

(B) NICKEL:

The trend toward decreased stability of higher oxidation states continues, so that only Ni^{II} normally occurs with a few compounds formally containing Ni^{III} and Ni^{IV}. The relative simplicity of nickel chemistry in terms of oxidation number is balanced by considerable complexity in coordination numbers and geometries. Nickel occurs in combination with arsenic, antimony, and sulfur as in *millerite*(NiS) and garnierite, a magnesium-nickel silicate of variable composition. Nickel is also found alloyed with iron in meteors, the interior of the earth is believed to contain considerable quantities. In general, the ore is roasted in air to give NiO, which is reduced to Ni with C. Nickel is usually purified by electrode position but some high purity nickel is still made by the carbonyl process. Carbon monoxide reacts with impure nickel at 50°C and ordinary pressure or with nickel-copper matte under more strenuous conditions, giving volatile $Ni(CO)_4$, from which metal of 99.90 to 99.99% purity is obtained on thermal decomposition at 200°C.

Nickel is quite resistant to attack by air or water at ordinary temperatures when compact and is, therefore, often electroplated as a protective coating. It dissolves readily in dilute mineral acids. The metal or high Ni alloys are used to handle F_2 and other corrosive fluorides. The finely divided metal is reactive to air and may be pyrophoric. Nickel absorbs considerable amounts of hydrogen when finely divided and special forms of Ni are used for catalytic reduction.

The Chemistry of Nickel(II), d^8

Nickel(II) forms a large number of Complexes with coordination number six, five, and four having all the main structural types: octahedral, trigonal bipyramidal, square pyramidal, tetrahedral and square. It is characteristic that complicated equilibria, which are generally temperature dependent and sometimes concentration dependent, often exist between these structural types.

(C) COPPER:

Copper has a single s electron outside the filled 3d shell. It has little in common with the alkalis except formal stoichiometries in the +1 oxidation state. The filled d shell is much less effective then is a noble gas shell in shielding the s electron from the nuclear charge, so that the first ionization potential of Cu is higher than those of the alkalis. Since the electron of the d shell are also involved in metallic bonding, the heat of sublimation and the melting point of copper are also much higher than those of the alkalis. These factors are responsible for the more noble character of copper. The effect is to make compounds more covalent and to give them higher lattice energies, which are not offset by somewhat smaller radius of Cu^+ (0.93Å) compared with Na^+ (0.95Å) and K^+ (1.33Å). The second and third ionization potentials of Cu are very much lower than those of the alkalis and account in part for the transition metal character.

Copper is not abundant (55 ppm) but is widely distributed as a metal, in sulfides, arsenides, chlorides, and carbonates. The commonest mineral is chalcopyrite, $CuFeS_2$. Copper is extracted by oxidative roasting and smelting, or by microbial-assisted leaching, followed by electrodeposition from sulfate solutions. Copper is used in alloys such as brass and is completely miscible with gold. It is very slowly superficially oxidized in moist air, sometimes giving a green coating of hydroxo carbonate and hydroxo sulfate (from SO_2 in the atmosphere). Copper readily dissolves in nitric acid and in sulfuric acid in presence of oxygen. It is also soluble in KCN or ammonia solutions in the presence of oxygen, as indicated by the potentials.

The Chemistry of Copper (II), d^9

There is well defined aqueous chemistry of Cu^{2+}, and a large number of salts of various anions, many of which are water soluble, that exist in addition to a wealth of complexes. it is pertinent to note the stereochemical consequences of the d^9 configuration of Cu^{II}. This makes Cu^{II} subject to distortions if placed in an environment of cubic (i.e. regular octahedral or tetrahedral) symmetry. The result is that Cu^{II} is nearly always found in environments appreciably distorted from these regular symmetries. The characteristic distortion of the octahedron is such that there are four short Cu-L bonds in the plane and two trans long ones. In the limit, this elongation leads to a situation indistinguishable from square coordination, as found in CuO and many discrete complexes of Cu^{II}. Thus the cases of tetragonally distorted “octahedral” coordination and square coordination can not be sharply differentiated.

METAL CHELATE

Chelates possess a cyclic structure arising from the union of a metal ion with an organic or inorganic molecule, with two or more points of attachment to produce a closed ring[11]. Usually chelate rings contain five or six members, including the metal ion, since these numbers apparently results in a reduced strain and are consequently more stable. Where either a five or six membered ring may be formed, invariably (unless double bonds are involved) the five membered ring is produced, indicating that this is the most stable ring that can be closed. The tendency to form rings of low strain parallels the formation of carbon rings in organic chemistry. The rings may be closed by the formation of covalent linkages, or coordinate bonds, or by a combination of the two. In fact the nature of the linkages has been used as a basis for the classification of the chelate compounds. Covalent bonding is produced by the replacement of a proton in an organic group. Functional groups of this type are sometimes called *acidic* groups because of the fact that hydrogen may be replaced from them. The most common examples of these groups are -COO (carboxyl), $-SO_3$ (sulfonic), -OH (enolic hydroxyl), and =NOH (oxime). Coordinate linkages, without the replacement of hydrogen, are formed by the donation of an electron pair. The most common functional groups which contain donor atoms are $-NH_2$ (primary, secondary and tertiary amines), =NOH (oxime), -OH (alcoholic hydroxyl), =CO (carbonyl), and –S- (thioether). Chelation will therefore be favored when any of the foregoing groups occur in the 1,4 or 1,5 positions of an organic molecule[12].

Classification of Chelates:

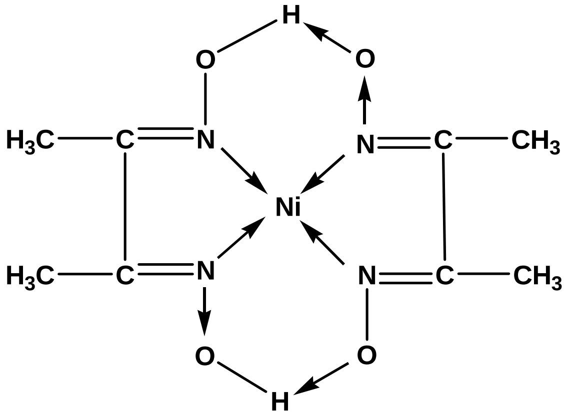
The three types of chelates given in those cyclic compounds in which the metallic ion is attached to the coordinating agent by only two linkages. With the discovery of compounds in which the metal atom is linked to the organic molecule through three or more groups, it became necessary to devise another system of classification[114]. It was G.T.Morgan who first coined the name ***chelate***, from the Greek word for *claw*. Later as other compounds with more than two points of attachment to the central ion were discovered, Morgan originated for these compounds the names tridentate and quadridentate, which literally mean three-toothed and four-toothed. Actually quinquidentate and sexadentate compounds are possible, although very few have been knowingly recorded as such.

Since polydentate molecules may be attached to the central metal atom through two kinds of functional groups, acidic and coordinating, to form covalent and coordinate linkages, the logical classification of chelate compounds should follow the number and kind of attachments involved.

Certain inorganic cations may form coordination compounds with specific organic ions or organic molecules. If the coordination groups are organic ions, the complex produced is usually an anion and is soluble in water. Such an electrolyte is produced when the ferric ion reacts with oxalate ions. A simple equation for the formation of this complex is

$$\mathrm{Fe^{+3} + 3C_2O_4^{-} \rightleftharpoons Fe\,(C_2O_4)_3^{3-}}$$

If the coordination ion or molecule is attached to the central group by two bonds in such a manner as to produce a closed ring, the resulting compound is a chelate. Complexes incorporating ring structures, particularly where there are five or six atoms in the ring, are generally quite stable. One of the most familiar chelate compound, used in analytical chemistry for the determination of nickel ion reacts with dimethylglyoxime. The structure of the complex produced by this reaction may be represented as,



In this compound the nickel atom has a coordination number 4 and is attached to two molecules of dimethylglyoxime by two covalent bonds and two coordinate bonds[115].

The hundred of known chelate compounds have been classified in many ways. These compounds are of sufficient importance for them to be discussed more completely. At present it seems worthwhile to mention a simple method of classification, used by several writers, in which chelates are classified according to the nature of the links that close the ring, or rings, of the cyclic compounds. In respect to the nature of the linkages chelates may be classified into three types.

TYPE-A:

Complexes in which the cation is combined through covalent bonds only. Rings of this type are formed by the replacement of two hydrogen atoms by the metallic cation. Usually the two hydrogen atoms split form hydroxyl or carboxyl groups, where the latter are so positioned as to produce five membered rings.

TYPE-B:

Complexes in which the cation is combined through both covalent and coordinate bonds. Complexes of this type are nonelectrolytes and are insoluble in water. One such complex, nickel dimethylglyoxime, has already been given. Another example is the chelate structure produced by the reaction of the aluminum ion with alizarin red S. in this compound three molecules of the dye combine with one aluminum ion to form a red precipitate.

TYPE-C:

These are complexes in which the cation forms only coordinate bonds in closing a ring. The diamines which have two amine groups, each of which may donate electrons, tie up certain cations with only coordinate linkages. Such a complex is formed by the union of ethylene diamine with platinic chloride.

The stability of the chelates is mainly affected by the size and the number of chelate rings, the basic strength of ligand, the nature of the donor atoms and the steric effect of the substituents in the ligand molecule. It has been established that five and six membered rings are most stable and the stability of the complexes increases with the increase in the number of rings. As a general rule, a complex containing one (or more) five or six membered chelate rings is more stable (has a higher formation constant) than a complex that is as similar as possible but lacks some or all of the chelate rings.

Another way to state the matter is to visualize a chelate ligand with one donor atom attached to a metal ion. The other donor atom cannot than get very far away, and the probability of it, too, becoming attached is greater than if it were in an entirely independent molecule, with access to the entire volume of solution. Thus the chelate effect weakens as ring size increases. The effect is greatest for five and six membered rings, becomes marginal for seven membered rings, and is unimportant thereafter. When the ring to be formed is large, the probability of the second donor atom attaching itself promptly to the same metal atom is no longer large as compared with its encountering a different metal atom, or as compared with the dissociation of the first donor atom before the second one makes contact[3].

In coordination compounds, metals are surrounded by groups that are called ligands. The types of groups that may surround a metal atom or ion are greatly varied, but they may be broadly considered to be of two types: ligand that bond to metal atom or ion through carbon atoms, and ligand that do not. The main justification for classifying many substances as coordination compounds is that their chemistry can conveniently be described in terms of a central cation M^{n+}, about which a great variety of ligands L, L′, L″, and so on, may be placed in an essentially unlimited number of combinations. The overall charge on the resulting complex $[ML_xL'_yL''_z....]$ is determined by the charge on M, and the sum of the charges on the ligands.

The stability of Coordination compounds[3,17,116]:

Equilibrium constant for the formation of complexes in solution:

The formation of complexes in aqueous solution is a matter of great importance not only in inorganic chemistry but also in biochemistry, analytical chemistry, and in a variety of applications. The extent to which a cation combines with ligands to form complex ions is a thermodynamic problem and can be treated in terms of appropriate expression for equilibrium constants. Suppose we put a metal ion M and some monodentate ligand L together in solution. If we assume that no insoluble products or any species containing more than one metal are formed, then equilibrium expressions of the following sort will describe the system:

$$\begin{array}{lll}
M + L = ML & K_1 = & \dfrac{[ML]}{[M]\,[L]} \\
ML + L = ML_2 & K_2 = & \dfrac{[ML_2]}{[ML]\,[L]} \\
ML_2 + L = ML_3 & K_3 = & \dfrac{[ML_3]}{[ML_2]\,[L]} \\
\vdots \qquad \vdots & & \vdots \\
ML_{N-1} + L = ML_N & K_N = & \dfrac{[ML_N]}{[ML_{N-1}]\,[L]}
\end{array}$$

There will be N such equilibria, when N represents the maximum coordination number of the metal ion M for the ligand L. the parameter N may vary from one ligand to another. For instance, Al^{+3} forms $AlCl_4^-$ and AlF_6^{3-}, and Co^{+2} forms $CoCl_4^{2-}$ and $Co(NH_3)_6^{2+}$, as the highest complexes with the ligands indicated.

EDTA analysis:

Many methods of chemical analysis and separation are based on the formation of complexes in solution, and accurate values for formation constants are helpful[117]. For example, different transition metal ions can be selectively determined by complexation with the hexadentate chelate $EDTA^{4-}$, by adjusting the concentration of $EDTA^{4-}$ and the pH, one ion can be complexed while another ion (which is simultaneously in the solution) is not complexed. This is the basis for the determination of Th^{4+} in the presence of divalent cations. The analysis is made possible by the large difference in formation constants for the $EDTA^{4-}$ complexes of the 4+ and 2+ cations. The $EDTA^{4-}$ ligand is less selective among ions of like charge, but the addition of CN^- allows the determination of the alkaline earth cations in the presence of the cations of Zn, Cd, Cu, Co, and Ni, because the latter form more stable complexes with CN^- than with $EDTA^{4-}$.

The Chelate effect:

As a general rule, a complex containing one (or more) five or six membered chelate rings is more stable (has a higher formation constant) than a complex that is as similar as possible but lacks some or all of the chelate rings. Another way to state the matter is to visualize a chelate ligand with one donor atom attached to a metal ion. The other donor atom cannot than get very far away, and the probability of it, too, becoming attached is greater than if it were in an entirely independent molecule, with access to the entire volume of solution. Thus the chelate effect weakens as ring size increases. The effect is greatest for five and six membered rings, becomes marginal for seven membered rings, and is unimportant thereafter. When the ring to be formed is large, the probability of the second donor atom attaching itself promptly to the same metal atom is no longer large as compared with its encountering a different metal atom, or as compared with the dissociation of the first donor atom before the second one makes contact[118].

DETECTION OF COMPLEXES IN SOLUTION:

A number of physical methods are useful for this purpose. Some of the methods which have been widely used are mention below.

(A) Conductance measurements:

This method was extensively used by Werner and others to study metal complexes. In the case of a series of complexes of Co(III) and Pt(IV), Werner assigned the correct formulae on the basis of their molar conductance values measured in freshly prepared dilute solutions[119].

Complex	Molar conducatnce
$[Co(NH_3)_6]\ Cl_3$	431.6
$[Co(NH_3)_5NO_2]\ Cl_2$	246.4
$[Co(NH_3)_4(NO_2)_2]\ Cl$	98.4
$[Co(NH_3)_4(NO_2)_3]$	~ 0

(B) Absorption spectra:

Formation of complex by a transition metal ion is generally accompanied by a sharp color change owing to the characteristic absorption spectrum of the complex being different from that of the simple metal ion. In fact a complex may be identified by its absorption characteristic; i.e., based on the position of the maxima and the minima in the absorption spectrum and their intensities (absorbance or molar extinction coefficient values). The deep blue color which is formed on adding ammonia to a solution of copper (II) salt is a typical example[120].

(C) Potentiometer measurements:

The oxidation potential of the couple $M^{+(m-n)} / M^{+m}$ is shifted significantly on complexation of the cations by the ligands[121].

(D) Polarogrphic measurements:

A shift in the half wave potential of a metal ion in solution in the presence of an added ligand (anion or neutral molecules) is indicative of complex formation[122].

(E) Ion Exchange studies:

Simple metal ions (cations) and cationic complexes are absorbed in a cation exchanger; anionic complexes are absorbed by anion exchangers, while nonionic complexes are not absorbed by cation or anion exchangers. From concentrated hydrochloric acid solution, Iron(III) is completely retained in an anion exchanger but not in a cation exchanger indicating the presence of an anionic complex ($FeCl_4^-$) in the solution[123].

(F) Magnetic properties of complexes:

For studying the electronic structure of transition metal complex, the measurement of magnetic moment is a very useful method. It provide fundamental information about the bonding and stereochemistry of metal complexes. The magnetic properties of coordination compounds are based on the effect of ligand on the spectroscopic terms of metal ion[124].

Gouy's method is the simplest method of measuring magnetic moments. It consist of a suspension of a uniform rod in non-homogeneous magnetic field about 5000 oersteds and measuring the force exerted on it by a conventional weighing techniques. The celebrant usually $Hg[Co(CNS)_4]$ which are easy to prepare, do not decompose and absorb moisture and pack well in the sample tube. All the transition metal ions having from 1 to 9 electrons in the d level of the penultimate valence shell are paramagnetic because of the presence of one or more unpaired electrons. It is a general rule that if a group of n or less electrons occupy a set of n degenerate (equal energy) orbital, they will singly occupy the orbital and give rise to n unpaired spins. This is Hund's rule of maximum multiplicity. This shows that electron pairing is an unfavorable process and requires energy, i.e., the system has to gain energy in the process and is thus destabilized.

PHYSICAL TECHNIQUES USED FOR CHARECETIZATION[125-130]:

(1) Infrared Spectrometry(IR):

Infrared spectroscopy is extremely powerful analytic technique for both qualitative and quantitative analysis. The infrared spectrum of any given substance is interpreted by the use of known group frequencies. It is one of the most widely used tools for the detection of functional group in pure compounds and mixtures, for compound comparison and for identification of the substances.

Infrared spectroscopy evolves twisting, bending, rotational and vibrational motion of the atomic groups in a molecule. Infrared radiation does not possess sufficient energy to cause the excitation of electrons however it causes atoms and groups of atoms to vibrate faster about covalent bond or bond which connect them.

The compounds absorb infrared energy in the particular region of spectrum. A highly complex absorption spectrum is obtained which is characteristic of the functional group comprising the molecule and overall configuration of the atom as well.

The infrared region constitutes three parts:

(i) Near infrared region

In the near infrared region, which meets the visible region at about 12,500 cm^{-1} and extends to about 4000 cm^{-1} are found many absorption bands resulting from harmonic overtones of fundamental bands and combination bands often associated with hydrogen atoms. Among these are the first overtones of the O-H and N-H stretching vibrations near 7140 cm^{-1} and 6667 cm^{-1} respectively. Combination bands resulting from C-H stretching, and deformation vibration of alkyl group at 4548 cm^{-1} and 3850 cm^{-1}.

(ii) Mid infrared region:

Middle infrared region divided into the “Group frequency” region 4000 cm^{-1} to 1300 cm$^{-1,}$ and “finger-print” region, 1300 cm^{-1} to 650 cm^{-1}.

(iii) Far infrared region:

Far infrared region between 667 cm^{-1} to 10 cm^{-1} contain the bending vibrations of carbon, nitrogen, oxygen and fluorine with atoms heavier than mass 19 and additional bending motion in cyclic or unsaturated system.

The Infrared Spectrum can give a perfect picture of the structural formula without a chemical investigation.

(2) UV-Visible Spectrometry:

The spectrum of transition metal complexes depends on the transition of unpaired electrons from the ground state to an excited state. Most of the transition metal complexes are colored; the color is observed due to d-d transition in visible region. Transition between a given set of p or d orbital, where d-d transition are forbidden (e.g. in octahedral complexes), render such complexes colorless.

The electronic structure of coordination compounds is mainly described by the molecular orbital theory. The atomic overlap in metal-ligand bonds allows d-electron to penetrate from the central atom to the ligand. The transitions are affected by the effect of ligands on the energies of d-orbital of the metal ions. Since octahedral, tetrahedral and square planner field cause splitting of d-orbital in different ways, the geometry will have a pronounced effect on the d-d transitions in a metal ion complex. Thus spectral data of these transitions provide useful information about the structure of complexes.

Cu(II) complexes are usually blue or green, exception of this, is generally caused by strong ultraviolet and charge transfer bands tailing off into blue and visible spectrum thus causing the substances to appear red or brown. The blue or green colors are due to the presence of the Cu d-d absorption in 600-900 nm region of the spectrum. The envelops of these bands are generally unsymmetrical to seeming to encompass several overlapping transition, but definite resolution into the proper number of sub-bands with correct location is difficult.

(3) Nuclear Magnetic Resonance (NMR) Spectroscopy:

Nuclear Magnetic Resonance spectroscopy involves transition of a nucleus from one spin state to another with the resultant absorption of electromagnetic radiation by spin active nuclei when they are placed in a magnetic field. The energy associated with NMR experiment is incapable to disrupting even the weakest chemical bonds. NMR spectroscopy pertains to nuclei and only one type of nucleus at a time, e.g. all ^{1}H or ^{13}C or ^{19}F nuclei. When the frequency of the rotating magnetic field and that of the precessing nucleus (larmor frequency) become equal, they are said to be in resonance and absorption or emission of energy by the nucleus can occur. A plot of the peak intensity versus the frequencies of absorption (expressed in δ or τ) constitutes an NMR spectrum.

The ^{1}H nucleus is by far the most commonly studied by NMR spectroscopy because of its high natural abundance (99.98%) and the fact that it is invariably present in the majority of organic compounds. PMR spectrum provides information about the number of different types of proton and also regarding the nature of the immediate environment of each of them. A ^{1}H spectrum consist of a plot of chemical shift against intensity and, since the area under each peak in a ^{1}H NMR spectrum is proportional to the number of ^{1}H nuclei giving rise to the peak, we integrate the spectrum to give the number of protons in each molecular environment.

(4) Mass Spectrometry

Mass spectrometry is a micro analytical technique requiring only a few nanomoles of the sample to obtained characteristic information pertaining to the structure and molecular weight of the analyte. It is unlike the other forms of spectroscopy, in that it is not concerned with non-destructive interactions between molecules and electromagnetic radiation. Instead, it involves the production and separation of ionized molecules and their ionic decomposition products and finally the measurement of the relative abundances of different ions produced. It is, thus, a destructive technique in that the sample is consumed during analysis. In most cases, the nacent molecular ion of the analyte produces fragment ions by cleavage of the bonds and the resulting fragmentation pattern constitutes the mass spectrum. Thus, the mass spectrum of each compound is unique and can be used as a “Chemical fingerprint” to characterize the sample.

Mass spectrometry deals with the examination of the characteristic fragments (ions) arising from the breakdown of organic and inorganic molecules. A mass spectrum is the plot of relative abundance of ions against their mass/charge ratio.

The basic aspect of mass spectrometry consists of bombarding the vapour of a compound with a beam of energetic electron accelerated from a filament to an energy of 70 eV to form positively charged ions (molecular ions). The additional energy of the electron is dissicipated in breaking the bonds in the molecular ion, which undergoes fragmentation to yield several neutral or positively charged species. This fragmentation may result in the formation of an even-electron ion and a radical.

$$M^{+\cdot} \rightarrow A^{+} \text{ (even electron ion)} + B_{\cdot} \text{ (radical)}$$

Or an odd electron ion and a neutral molecule.

$$M^{+\cdot} \rightarrow C^{+\cdot} \text{ (odd electron ion)} + D \text{ (neutral molecule)}$$

Thus, the mass spectral reaction are much more drastic than usual chemical reactions.

(5) ESR (Electron Spin Resonance) Spectrometry

ESR, are also called Electron Paramagnetic Resonance, is form of magnetic resonance spectroscopy, which is possible only for molecules with unpaired electrons[68].

This sensitive technique has proved useful in the study of the electronic structure of many species, including organic free radicals, and more transition metals and rare earth species. Important biological application includes the use of ‘spin labels’ as probe of molecular environment in enzyme active sites and membrane. ESR has also been used to examine interior defects in solid state chemistry and to study reactive chemical species on catalytic surfaces.

ESR gives the chemical information regarding the structure of paramagnetic substances. The number of lines, their spacing and their relative intensities unequivocally indicate a characteristic structure of a molecule. It is observed that when a molecule or ion containing one or more unpaired electrons are placed in a magnetic field. The effect of magnetic field is to lift the spin degeneracy, i.e. to make the energy of the electron differ for its two Ms value, +1/2 and -1/2. The electron lines up its field with the magnetic field and result in an increase of potential energy. A quantum mechanical treatment shows that the energy difference between these two electrons spin alignment is equal to gBH, where g is gyro-magnetic ratio, B is Bohr magneton and H is the strength of magnetic field.

For ESR investigation transition metal ions are simplest example. To understand the spectrum of an ion require a detail consideration both of the individual ion and of its environment. In evaluation of an ESR spectrum, the most important parameter is g value, which is spectroscopic spitting factor.

In case of Cu(II) having $3d^9$ configuration a large Jhan-Teller distortion is observed. A four line spectrum should be observed due to nuclear hyperfine coupling of Cu. Usually three lines spectrum are observed in practice. The g values are around 2.192.

(6) Thermogravimetric Analysis(TGA):

With the development of technology thermal analysis using instruments for measurements of temperature at transition state, weight loss in materials, energies of transitions, dimensional changes etc., have become possible. The most common techniques used in various laboratories are: Thermogravimetry (TG), Differential thermal analysis (DTA), Differential scanning calorimetry (DSC), and Evolved gas analysis (EGA) etc.

In thermogravimetry the change in mass of the sample is recorded as a function of temperature. It provides the analyst with quantitative measurement of change in weight associated with any transition. TG can directly record the loss in weight with time or temperature due to dehydration or decomposition. Thermogravimetry curves are characteristic of a given compound or system because of unique sequence of physico-chemical reaction which occur over definite temperature ranges. In order for a mass change, to be detected, a volatile component must be evolved or absorbed by the sample. The former is the usual mode of measurement, but many examples are also known for latter. Since elevated temperatures are normally required for the evolution of volatile material, mass change measurement are made at increasing rather than decreasing temperature. Routine measurements can be made at temperature range from ambient to 1500°C with inert atmosphere.

BIOLOGICAL IMPORTANCE OF LIGANDS AND METAL CHELATES

Biological importance of Schiff base ligand:

Schiff base appear to be important intermediate in number of enzymatic reaction involving interaction of enzyme with an amino or a carbonyl group of the substrate. One of the most prevalent types of the catalytic mechanism in biochemical processes involves condensation of primary amine in an enzyme, usually that of lysine residue, with a carbonyl group of substrate to form an Imine or Schiff base[131,132].

Stereochemical investigation carried out with the aid of molecular models showed that Schiff base formed between methylglyoxal and the amino group of lysine side chain of protein can bend back in such a way towards the N atoms of peptide groups that a charge transfer can occur between these groups and the oxygen atom of Schiff bases. In this respect pyridoxal Schiff base derived from amino acid have been prepared and studied. Schiff base derived from pyridoxal and amino acids are considered very important ligands from the biological point of view. Transition metal complexes of such ligands are important enzyme models. The rapid development of these ligands resulted in an enhance research activity in the field of coordination chemistry leading to very interesting conclusion[133-137].

Recently certain polymeric Schiff bases have been reported by M. P. Sathisha et al.[138] which possess antitumor activity. The Schiff bases have the highest degree of hydrolysis at pH 5 and the solubility in water is also highest at this pH. The antitumor activity of the bases towards ascetic tumor increases considerably with slight increase in water solubility. Another important role of Schiff base structure is in transmination. Transminases are found in mitochondria and cytosal of eukaryotic cell. All the transminases appear to have the same prosthetic group. i.e. pyridoxal phosphate, which non-covalently linked to enzyme protein[139].

Biological important of Metal Complexes:

There are some metallo-elements without which the normal functioning of the living organism is inconceivable. Among these metallo-elements so called ‘metals of life’, four members form an island. These are Na, Mg, K and Ca. Among the transition elements are V, Cr, Mn, Fe, Co, Ni, Cu and Zn. These elements are present at trace and ultra trace quantity and play vital roles at the molecular level in a living system. These transition elements are known to form Schiff base complexes[27, 139].

In fact metal Schiff base complexes have been known since the mid-nineteenth century and even before the general preparation of Schiff base ligand themselves. Metal complexes of Schiff bases have occupied a central place in the development of coordination chemistry after the work of Jorgenson and Werner[3].

Effect of complexation on biological activity:

The metallo-element which are present in trace and ultra trace quantities, play vital roles at the molecular level in a living system. In a healthy body of an adult, the trace and ultra trace elements weight less than 10 grams in total but life depends upon these elements for more than this figure. The transition metal ions are responsible for the proper functioning of different enzymes. If their concentration exceeds a certain level, then their toxic effect are evident. Drug play a vital role as bioligands in the biological systems. Nitrogen containing bases, such as derivatives of pyridine, pyrimidine, purine, and pyrrole, amine such as histamines, carbohydrates such as pentose, glucose, and different vitamins such as ascorbic acid are well recognized bioligands[131,132].

It has been found that the activity of biometals is attain through the formation of complex with different bioligand and the thermodynamic and kinetic properties of the complexes govern the mode of biological action. Sometimes, the permeability, i.e., lipophilicity of drugs is increased through the formation of chelates *in vivo* and the drug action is significantly increased due to much more effective penetration of the drug into the site of action. The knowledge of drug action *in vivo* is extremely important in designing more potential drugs. Recently J. A. Obaleye et al.[140] have reported less toxic and more potential drug.

It is worth mentioning that many drug substances, such as aspirin, thiosemicarbazides, anticancer drug and antibiotics exhibit the drug action through the complexation with the available bio-metals *in vivo*. In absolutely metal free condition they are inactive. Copper metabolism is somehow related with the rheumatoid arthritis. In case of diabetes, chromium metabolism has an important role to play. A number of diseases and their remedies are dependent on the metabolism of inorganic constituent[26,140].

In the virus replication process, the role of metal ions is extremely important. A virus can penetrate into the host's cell only when it is mediated by some suitable metal ions. For example, zinc present in the cell wall of the bacterium E.coli can coordinate with the sulphur site present in the virus coating. By using any suitable metal complex like $Cd(CN)_3$ which can preferably bind with 'S' site as Virus-(S)-$Cd(CN)_3$. the penetration of the viral DNA into the host cell can be arrested. As a matter of fact, for virus replication, copper and zinc are essentially required, hence by increasing or decreasing their concentration, virus growth may be controlled [141-143].

Interaction of various metal ions with antibiotic may enhance or suppress their antimicrobial activity but usually in many cases the pharmacological activity of antibiotics after complexation with metal is enhanced as compared to that of free ligands[144]. Many of the well known antibiotics, penicillin, streptomycin, bacitracin, tetracycline etc. are chelating agents, their action is improve by the presence of small amount of metal ions. Binding of metal-elements with polydentate ligand to form ring structure, where the metal atom is part of the ring, is called chelation. In chelates metal is firmly held by a number of ligand atoms usually, nitrogen, oxygen or sulphur through co-ordinate covalent bonds. Some of the chelates are model analogues of certain metalloenzymes. Furthermore some of the chelates develop considerable fungicidal and antimicrobial activity. Chelate compounds obtained from Schiff bases are convenient for the study of change in structure and associated biological activity, since varying a substitute in the metal rings permits variation in the three dimensional structure of the molecule. It has been demonstrated through several studies that the biological activity of chelating compounds is enhanced on chelation with a metal atom[145]. El-ajaily et al.[146] have studied many schiff base metal complexes which show good antimicrobial activity.

Some of the inactive ligand develops such properties upon chelation. The antitumor and antibacterial activity of some Schiff bases has been attributed to their ability to chelate with trace transition metals. Several explanations have been suggested for this enhancement in activity of metal complexation. Generally it has been observed that transition metal complexes have grater activity and less toxic effect. Other examples where the antibacterial action of drug is enhanced by metal ions are kojic acid and sodium dimethyl dithiocarbamates. Antibiotics like streptomycin, cycloserin, tetracycline, ampicillin, isoniazide and others are known to have chelating properties. Some antibiotics are delicately balanced so as to be able to complete successfully with the metal binding agent of bacteria while not disturbing the metal processing by the host. The chelating properties of antibiotics may be used in metal transport across membrane or to attach the antibiotics to specific site from which it can interfere with the growth of bacteria[147,148].

Qualitative and quantitative differences in biological activities have been observed among metal chelates, differing in the metal ion or in the ligand. Metal chelates during chemical synthesis can be varied in size, charge distribution, stereochemistry, redox potential and other physical properties.

Metallo-elements under investigation:

Human body contains seven major and twenty two trace elements. Trace elements play important structural, electrochemical and catalytic function in the body. Their excess or deficiency may cause certain diseases. Transition metals exist in biological systems as stable complexes. These complexes are able to undergo ligand exchange with components of the biological systems[139].

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PART - II

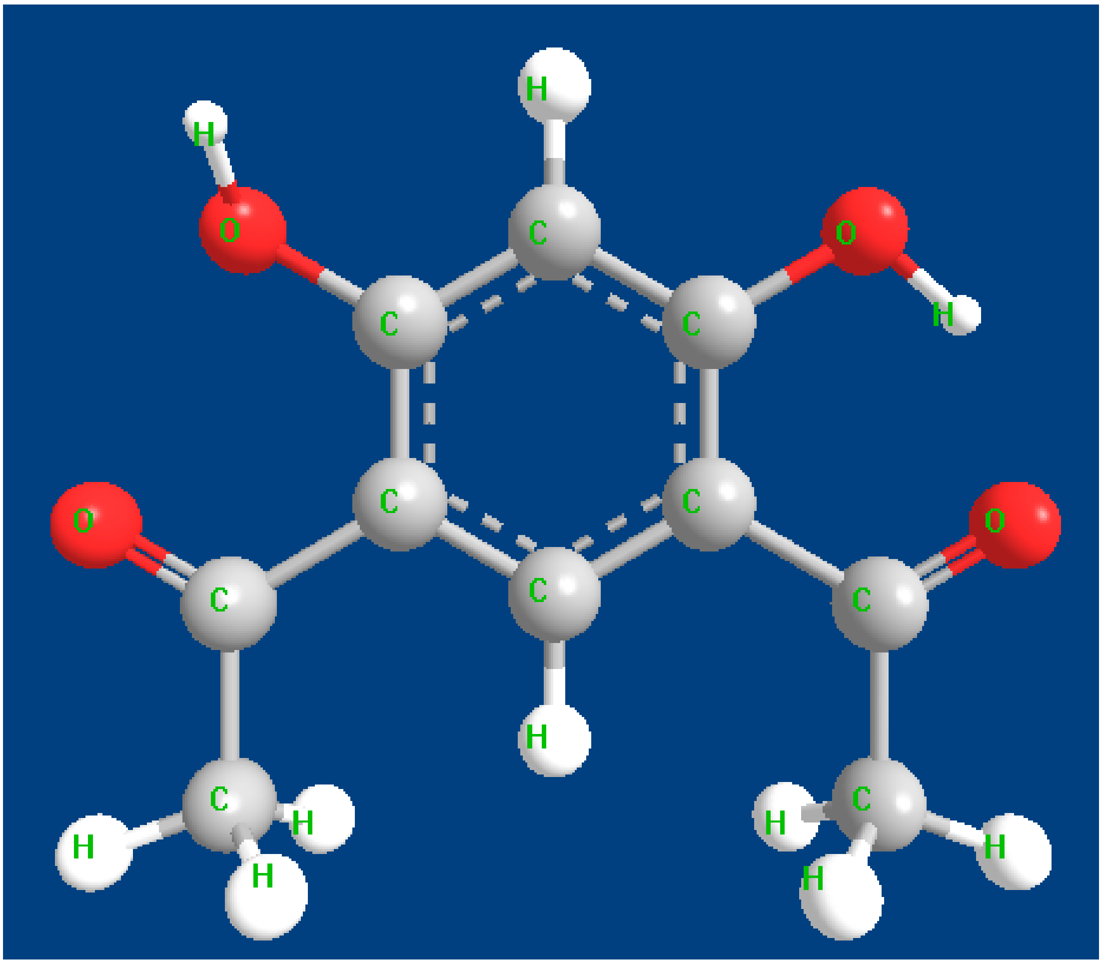
EXPERIMENTAL

CHAPTER – 1
SYNTHESIS AND CHARACTERIZATION OF LIGAND

CHAPTER – 2
SYNTHESIS AND CHARACTERIZATION OF METAL CHELATES

CHAPTER – 3
SYNTHESIS AND CHARACTERIZATION OF MIXED LIGAND METAL COMPLEXES

CHAPTER – 4
BIOLOGICAL EVALUATION OF LIGANDS AND METAL CHELATES



CHAPTER 1

SYNTHESIS AND CHARACTERIZATION OF LIGANDS

1.1 Introduction
1.2 Reaction Scheme
1.3 Experimental
1.4 Physical Data Table
1.5 Spectral Study
1.6 Spectral Characterization of Ligand
1.7 Spectra
1.8 References

1.1 INTRODUCTION

The Chemistry of Resorcinol:

In the present study Schiff base ligand H_2L derived from condensation of 4,6-diacetyl resorcinol with various amines viz. 4-chloro anline, 4-fluoro aniline, 4-iodo aniline, 4-bromo aniline, 4-methyl aniline, 4-methoxy aniline, 2,4-dichloro aniline, 2,4-difluoro aniline, 2,4-methyl aniline, 2-nitro-4-methoxy aniline have been synthesized and studied for their biological activity.

Resorcinol and its derivatives have a wide variety of applications. The largest consumption of resorcinol is in tyre industry, where the preferred hardening resins are based on resorcinol[149,150]. Another value-added application of resorcinol and its derivatives is in cosmetic products.

Gadgil et al. [151] have introduced that some compounds like 2,4-dihydroxy acetophenone have been used in sun protective applications or compositions for providing sun protection. N.G. Bollinger et al. [152] have found derivatives of resorcinol as inflammation inhibitors. S.K. Gupta [153] have reported Resacetophenone as matrix metalloprotease inhibitors and their application in cosmetic and pharmaceutical compositions.

Alkyl resorcinol and aromatic resorcinol are reported to possess valuable therapeutic and antiseptic properties. In particular, 4-alkyl resorcinol is reported to have skin beautifying effect and low toxicity and irritation when applied on to human skin[154,155]. Alkyl resorcinol like 4-n-butyl resorcinol have been used in skin creams and lotions which are claimed to have good bleaching and antimicrobial effect. 2-alkyl resorcinol (where the alkyl group is linear) has been reported to have skin depigmentation properties[151,152].

A process for the preparation of disubstituted derivatives of resorcinol in which the two substituting groups (which may be alkyl or aralkyl) are unlike[89-91]. The process steps include reaction of resorcinol with an acid, acid chloride or acid anhydride of the aliphatic or aromatic series in the presence of a condensing agent like zinc chloride to prepare mono-ketone derivatives[156].

Recently J. H. Pandya and M.K.Shah[80] have synthesized monoketone derivatives from resorcinol.

The mono-ketone derivatives is further reacted with an acid, acid chloride or acid anhydride of the aliphatic or aromatic series, containing a radical different from the substituting radical already present in the resorcinol derivatives in the presence of zinc chloride or other suitable condensing agent to form a diketone derivative.

Anon[157] have introduced novel process and Intermediates of 2-substituted 4,6 diacetyl resorcinols.

C.Lakshmi et al.[158] have synthesized some 5-acyl-2,4-dihydroxybenzoketones derivatives. Asoke Banerji and G.P.Kalena[159] have introduced heterocycles from diacetyl phenols. U. Muralikrishna et al.[160] have prepared resdiactophenone dioxime. A.S.R. Anjaneyulu and B. Meher Isaa[161] have reported thermal and catalytic claisen rearrangement of 4,6-diactyl resorcinol. M.K. Kokila et al.[162] have reported the structure of 4,6-diactyl resorcinol. S.S. Ibrahim et al.[163] have synthesized benzopyrans from 2-bromo-4,6-diacetyl resorcinol. Junji Kawachi et al.[164] have prepared 4,6-diamino resorcinol. A.I. El-Shenawy[165] have introduced new heterocyclic compounds from 4,6-diacetyl resorcinol. Chun-Yan Zhang et al. [166] have introduced new method for synthesis of DAR·2HCl. Kim Ji Hoon et al.[167] have reported conventional microwave-induced, and photochemical Fries rearrangement of resorcinol diacetate.

The Chemistry of Schiff base ligand:

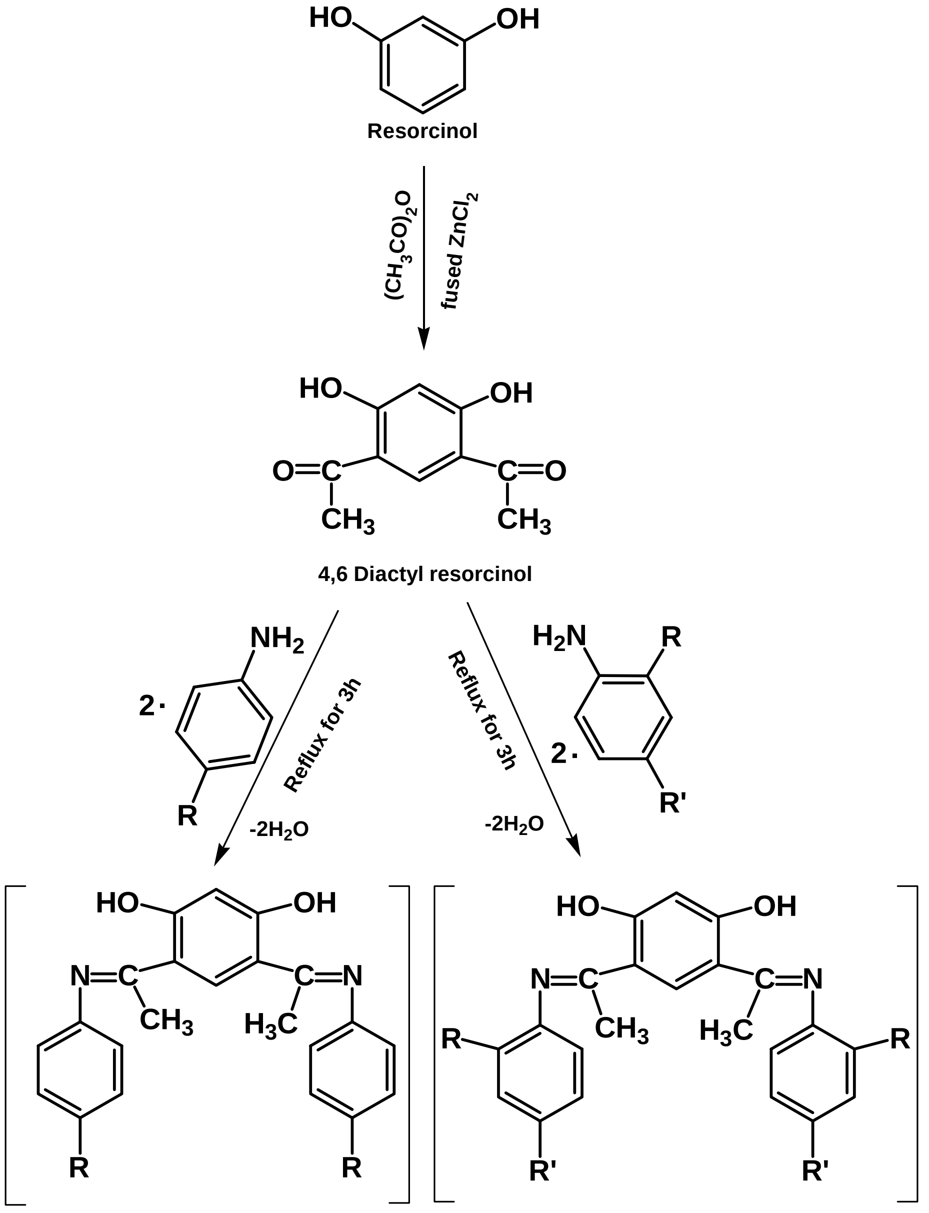
Numerous Schiff bases of 4,6-diacetyl resorcinol and their transition metal complexes have been investigated by various techniques for different purposes. Schiff-base metal complexes have been widely studied because they have industrial, antifungal and biological applications.

Recently J.H.Pandya and K.J.Ganatra[168] have reported biological evaluation of Schiff base metal complexes derived from 4,6-diacetyl resorcinol. B.S. Shyamala and V. Jayatyagaraju[169] have reported divalent nickel and copper complexes derived from 2,4-dihydroxy-5-acetyl acetophenone. J.T. Makode and A.S. Aswar[170] have synthesized transition metal complexes of bis(s-methyldithiocarbazate)resdiacetophenone. Reddy Y. Thirupathi et al.[171] have synthesized 3,5-dialkyl-6-acyl-1H-furo[3,2-f]indazoles as antimicrobial agents.

They serve as models for biologically important species and find applications in biomimetic catalytic reactions. Chelating ligands containing O and N donor atoms show broad biological activity and are of special interest because of the variety of ways in which they are bonded to metal ions. The presence of transition metals in human blood plasma indicates their importance in the mechanism for accumulation, storage and transport of transition metals in living organisms. Transition metals play a key role in biological systems such as cell division, respiration, nitrogen fixation and photosynthesis. Also Schiff bases and their complexes in aqueous solutions have been studied because of their interesting and important properties[172-180].

1.2 REACTION SCHEME

The synthetic route to Schiff base ligands 4,6-bis(1-(4-substituted phenylimino) ethyl)benzene-1,3-diol and 4,6-bis(1-(2,4-disubstitutedphenylimino) ethyl)benzene-1,3-diol is as follows.



Where R = $-Cl, -F, -I, -Br, -CH_3, -OCH_3$

4,6-bis(1-(4-substituted-phenylimino)ethyl)benzene-1,3-diols

Where R = $-Cl, -F, -CH_3, -NO_2$
R = $-Cl, -F, -CH_3, -OCH_3$

4,6-bis(1-(2,4-disubstituted-phenylimino)ethyl)benzene-1,3-diols

REACTION SCHEME

1.3 EXPERIMENTAL

The synthesis of ligands have been divided in two parts. In part I 4,6-diacetyl resorcinol has been coupled with p-substituted anilines with fluoro, chloro, iodo, bromo methyl and methoxy as the substituents, and in part II 4,6-diacetyl resorcinol has been coupled with 2,4-disubstituted anilines with fluoro, chloro, methyl and nitro-methxy as the substituents.

PART-I: 4,6 Diacetyl resorcinol + p-substituted anilines

The following mentioned ligands have been synthesized.

(I) DAR : 4,6 diacetyl resorcinol OR 2,4-Dihydroxy-5-acetylacetophenone
(II) H_2L^1 : 4,6-bis(1-(4-chlorophenylimino)ethyl)benzene-1,3-diol
(III) H_2L^2 : 4,6-bis(1-(4-fluorophenylimino)ethyl)benzene-1,3-diol
(IV) H_2L^3 : 4,6-bis(1-(4-iodophenylimino)ethyl)benzene-1,3-diol
(V) H_2L^4 : 4,6-bis(1-(4-bromophenylimino)ethyl)benzene-1,3-diol
(VI) H_2L^5 : 4,6-bis(1-(p-tolylimino)ethyl)benzene-1,3-diol
(VII) H_2L^6 : 4,6-bis(1-(4-methoxyphenylimino)ethyl)benzene-1,3-diol

(I) DAR: Synthesis of 4,6 Diactyl resorcinol OR 2,4-Dihydroxy-5-acetylacetophenone

A mixture of acetic anhydride (9.28 g, 91.0 mmol) and freshly fused zinc chloride (10.0 g) was stirred under reflux until all zinc chloride dissolved in it. To this was added resorcinol (5.00 g, 45.5 mmol) portion-wise over a period of 10 minutes. The reaction mixture continuously stirred under the reflux at 140°C in paraffin bath for 20 minutes. At the end of this period, the reaction mass was cooled and quenched carefully with 1:1 HCl solution over a period of 30 minutes. The precipitated solid was found to be produced in 82% yield[181].
The Melting Point is 178°C, The Molecular Weight is 194.18

(II) H_2L^1: Synthesis of 4,6-bis(1-(4-chlorophenylimino)ethyl)benzene-1,3-diols

The Schiff base, H_2L^1 Ligand was synthesized by adding DAR(4.85 g, 25.0 mmol) dissolved in hot absolute EtOH (20 cm^3) to 4-chloroaniline(6.37 g, 50.0 mmol) in absolute EtOH (20 cm^3). The reaction mixture was refluxed for 3 h. The product obtained was filtered off and washed several times with a few amount of EtOH then ether and air dried. The product was kept in desiccators until used. Recrystallization was carried out in EtOH. The progress of reaction was monitered by TLC.

Yield obtained-75%, Melting point- 170°C (Decompose)

(III) H_2L^2: Synthesis of 4,6-bis(1-(4-fluorophenylimino)ethyl)benzene-1,3-diols

The Schiff base, H_2L^2 Ligand was synthesized by adding DAR(4.85 g, 25.0 mmol) dissolved in hot absolute EtOH (20 cm^3) to 4-flouroaniline(5.55 g, 50.0 mmol) in absolute EtOH (20 cm^3). The reaction mixture was refluxed for 3 h. The product obtained was filtered off and washed several times with a few amount of EtOH then ether and air dried. The product was kept in desiccators until used. Recrystallization was carried out in EtOH. The progress of reaction was monitered by TLC. Yield obtained- 82%, Melting point- 210°C

(IV) H_2L^3: Synthesis of 4,6-bis(1-(4-iodophenylimino)ethyl)benzene-1,3-diols

The Schiff base, H_2L^3 Ligand was synthesized by adding DAR (4.85 g, 25.0 mmol) dissolved in hot absolute EtOH (20 cm^3) to 4-Iodoaniline (10.9 g, 50.0 mmol) in absolute EtOH (20 cm^3). The reaction mixture was refluxed for 3 h. The product obtained was filtered off and washed several times with a few amount of EtOH then ether and air dried. The product was kept in desiccators until used. Recrystallization was carried out in EtOH. The progress of reaction was monitered by TLC. Yield obtained- 76%, Melting point- 180°C

(V) H_2L^4: Synthesis of 4,6-bis(1-(4-bromophenylimino)ethyl)benzene-1,3-diols

The Schiff base, H_2L^4 Ligand was synthesized by adding DAR (4.85 g, 25.0 mmol) dissolved in hot absolute EtOH (20 cm^3) to 4-bromoaniline (8.6 g, 50.0 mmol), in absolute EtOH (20 cm^3). The reaction mixture was refluxed for 3 h. The product obtained was filtered off and washed several times with a few amount of EtOH then ether and air dried. The product was kept in desiccators until used. Recrystallization was carried out in EtOH. The progress of reaction was monitered by TLC. Yield obtained- 80%, Melting point- 195°C

(VI) H_2L^5: Synthesis of 4,6-bis(1-(p-tolylimino)ethyl)benzene-1,3-diols

The Schiff base, H_2L^5 Ligand was synthesized by adding DAR(4.85 g, 25.0 mmol) dissolved in hot absolute EtOH(20 cm^3) to 4-methylaniline(5.35 g, 50.0 mmol) in absolute EtOH (20 cm^3). The reaction mixture was refluxed for 3 h. The product obtained was filtered off and washed several times with a few amount of EtOH then ether and air dried. The product was kept in desiccators until used. Recrystallization was carried out in EtOH. The progress of reaction was monitered by TLC.

Yield obtained- 78%, Melting point- 190°C

(VII) H_2L^6: Synthesis of 4,6-bis(1-(4-methoxyphenylimino)ethyl)benzene-1,3-diol

The Schiff base, H_2L^6 Ligand was synthesized by adding DAR(4.85g, 25.0 mmol) dissolved in hot absolute EtOH (20 cm^3) to 4-methoxyaniline(6.15 g, 50.0 mmol) in absolute EtOH (20 cm^3). The reaction mixture was refluxed for 3 h. The product obtained was filtered off and washed several times with a few amount of EtOH then ether and air dried. The product was kept in desiccators until used. Recrystallization was carried out in EtOH. The progress of reaction was monitered by TLC. Yield obtained- 81%, Melting point- 203°C

PART-II: 4,6 Diacetyl resorcinol + 2,4 di-substituted anilines

The following mentioned ligands have been synthesized.

(VIII) H_2L^7 : 4,6-bis(1-(2,4-dichlorophenylimino)ethyl)benzene-1,3-diol
(IX) H_2L^8 : 4,6-bis(1-(2,4-difluorophenylimino)ethyl)benzene-1,3-diol
(X) H_2L^9 : 4,6-bis(1-(2,4-dimethylphenylimino)ethyl)benzene-1,3-diol
(XI) H_2L^{10} : 4,6-bis(1-(4-methoxy-2-nitrophenylimino)ethyl)benzene-1,3-diol

(VIII) H_2L^7: Synthesis of 4,6-bis(1-(2,4-dichlorophenylimino)ethyl)benzene-1,3-diol

The Schiff base, H_2L^7 Ligand was synthesized by adding DAR(4.85g, 25.0 mmol) dissolved in hot absolute EtOH (20 cm^3) to 2,4-dichloroaniline(8.10 g, 50.0 mmol) in absolute EtOH (20 cm^3). The reaction mixture was refluxed for 3 h. The product obtained was filtered off and washed several times with a few amount of EtOH then ether and air dried. The product was kept in desiccators until used. Recrystallization was carried out in EtOH. The progress of reaction was monitered by TLC. Yield obtained- 73%, Melting point- 175°C (Decompose)

(IX) H_2L^8: Synthesis of 4,6-bis(1-(2,4-difluorophenylimino)ethyl)benzene-1,3-diol

The Schiff base, H_2L^8 Ligand was synthesized by adding DAR(4.85g, 25.0 mmol) dissolved in hot absolute EtOH (20 cm^3) to 2,4-difluoroaniline(6.45 g, 50.0 mmol) in absolute EtOH (20 cm^3). The reaction mixture was refluxed for 3 h. The product obtained was filtered off and washed several times with a few amount of EtOH then ether and air dried. The product was kept in desiccators until used. Recrystallization was carried out in EtOH. The progress of reaction was monitered by TLC. Yield obtained- 80%, Melting point- 213°C

(X) H_2L^9: Synthesis of 4,6-bis(1-(2,4-dimethylphenylimino)ethyl)benzene-1,3-diol

The Schiff base, H_2L^9 Ligand was synthesized by adding DAR(4.85g, 25.0 mmol) dissolved in hot absolute EtOH (20 cm^3) to 2,4-dimethylaniline(6.5 g, 50.0 mmol) in absolute EtOH (20 cm^3). The reaction mixture was refluxed for 3 h. The product obtained was filtered off and washed several times with a few amount of EtOH then ether and air dried. The product was kept in desiccators until used. Recrystallization was carried out in EtOH. The progress of reaction was monitered by TLC. Yield obtained- 78%, Melting point- 195°C

(XI) H_2L^{10}: Synthesis of 4,6-bis(1-(4-methoxy-2-nitrophenylimino)ethyl) benzene -1,3-diol

The Schiff base, H_2L^{10} Ligand was synthesized by adding DAR(4.85g, 25.0 mmol) dissolved in hot absolute EtOH(20cm^3) to 2-nitro-4-methoxyaniline(8.40g, 50.0 mmol) in absolute EtOH (20cm^3). The reaction mixture was refluxed for 3 h. The product obtained was filtered off and washed several times with a few amount of EtOH then ether and air dried. The product was kept in desiccators until used. Recrystallization was carried out in EtOH. The progress of reaction was monitered by TLC. Yield obtained- 72%, Melting point- 201°C

1.4 PHYSICAL DATA TABLE

TABLE-1.4.1: THE ANALYTICAL AND PHYSICAL DATA OF THE LIGANDS

Ligand		Molecular Formula	Molecular Weight	Color	Yield (%)	Melting point (°C)
1.	DAR	$C_{10}H_{10}O_4$	194.18	Brown	82%	178
2.	H_2L^1	$C_{22}H_{18}Cl_2N_2O_2$	413.3	Reddish brown	75%	170
3.	H_2L^2	$C_{22}H_{18}F_2N_2O_2$	380.39	Reddish brown	82%	210
4.	H_2L^3	$C_{22}H_{18}I_2N_2O_2$	596.2	Purple	76%	180
5.	H_2L^4	$C_{22}H_{18}Br_2N_2O_2$	502.2	Reddish brown	80%	195
6.	H_2L^5	$C_{24}H_{24}N_2O_2$	372.46	Reddish brown	78%	190
7.	H_2L^6	$C_{24}H_{24}N_2O_4$	404.46	Brown	81%	200
8.	H_2L^7	$C_{22}H_{16}Cl_4N_2O_2$	482.19	Brown	73%	175
9.	H_2L^8	$C_{22}H_{16}F_4N_2O_2$	416.37	Reddish Brown	80%	213
10.	H_2L^9	$C_{26}H_{28}N_2O_2$	400.51	Brown	78%	195
11.	H_2L^{10}	$C_{24}H_{22}N_4O_8$	494.45	Orange	72%	201

1.5 SPECTRAL STUDY

IR spectra (4000-400 cm^{-1}) of the ligands were obtained using KBr discs, on a 8400 FTIR SHIMADZU spectrometer. ^1H NMR spectra of the ligand and its complexes, in DMSO-*d6*, were recorded on a BRUKER AVANCE II 400 Spectrometer at room temperature using TMS as internal standard. Mass spectra were recorded at QP 2010 SHIMADZU GCMS spectrometer.

1.5.1 Infra Red Spectra

Infra Red spectra of ligands were taken on SHIMADZU 8400 FT-IR-435 Spectrometer using KBr Pellet method. The IR spectra of the ligands, DAR, H_2L^1, H_2L^2, H_2L^3, H_2L^4, H_2L^5, H_2L^6, H_2L^7, H_2L^8, H_2L^9, H_2L^{10} and its precursors are shown in figure-1.1, 1.2 & 1.3.

The IR spectra are consistent with the formation of H_2L ligands. The vibrational assignments were aided by comparison with the vibrational frequencies of the related compounds, such as, the Schiff bases of salicylaldehyde and resacetophenone[182,183]. The fundamental stretching mode of the azomethine moiety, ν(–C=N–), is readily assigned by comparison with the infrared spectra of 4,6-diacetylresorcinol (DAR), and substituted amines. The intense band at 1620-1612 cm^{-1} for the ligands are assigned to the –C=N– stretching frequency and is characterized for the azomethine moiety of most Schiff base compounds. In the infrared spectrum of the H_2L ligand, the absorption band of the C=O group in the 4,6-diacetylresorcinol disappeared, which indicates that the condensation has occurred. The IR spectrum of the ligand shows a broad band at 3500-3200 cm^{-1} due to the stretching vibration of phenolic hydroxyl group, the broadness is due to intermolecular hydrogen bonding between the phenolic groups and the azomethine groups[184,185].

1.5.2 NMR Spectra:

^1H NMR spectra of ligands were recorded on Bruker Avance II 400 MHz FT-NMR Spectrometer using TMS (Tetramethyl Silane) as an internal standard and DMSO-*d6* as a solvent.

The ^1H NMR spectrum of DAR and H_2L in DMSO-*d6* showed signals at δ (ppm) 2.1 (6H, CH_3), 12.92 (2H, OH-phenolic), 6.36 - 7.64 (m ArH) and 2.35 (3H, CH_3). The difference observed in these values may be due to expected H-bonding between the hydrogen atoms of the –OH groups and the azomethine nitrogen atoms [186,187]. The values of proton are given in figure 1.4, 1.5 & 1.6.

1.5.3 Mass spectra:

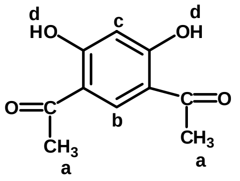
The mass spectrum of compounds was recorded by GCMS-QP2010 spectrometer (EI method). The mass spectrum of compounds was obtained by positive chemical ionization mass spectrometry. The molecular ion peak and the base peak in all compounds were clearly obtained in mass spectrum study. The molecular ion peak (M+) values are in good agreement with molecular formula of all the compounds synthesized[188,189].(Figure-1.7-1.11)

1.6 SPECTRAL CHARACTERIZATION OF LIGAND

(I) DAR: 4,6 Diactyl resorcinol

IR (KBr) cm^{-1}: 3510 (-OH aromatic), 1658 (-C=O of $COCH_3$), 3078 (Ar C-H), 2920 (C-H of CH_3), 1600, 1550, 1489, 1450 (Ar -C=C- ring skeletal), 1180 (C-O of -OH), 1050 (C-C), 840 (O=C-C)

(^{1}H NMR 400 MHz DMSO-*d6*, δ ppm):

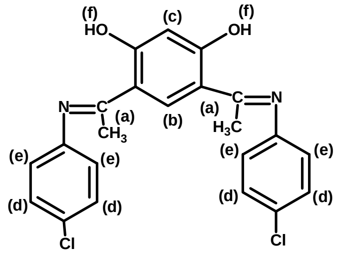
DAR	Signal	Chemical shift in δ ppm	Multiplicity	Functional group
	H_a	2.63 (6H)	S	$-COCH_3$ (x 2)
	H_{b-c}	6.41-8.20 (2H)	S	Ar-H
	H_d	12.92 (2H)	S	-OH (x 2)

Mass [m/e (%)], M. Wt.: 194, 179, 161, 147, 133, 123, 105, 95, 77, 69, 43.

(II) H_2L^1: 4,6-bis(1-(4-chlorophenylimino)ethyl)benzene-1,3-diols

IR (KBr) cm^{-1}: 3300 (-OH aromatic), 1600 (-C=N-), 3050 (Ar C-H), 2950 (C-H of CH_3), 1500, 1450, 1400 (Ar -C=C- ring skeletal), 1250 (C-O of -OH), 850 (C-H bending for p-sub.)

(^{1}H NMR 400 MHz DMSO-*d6*, δ ppm):

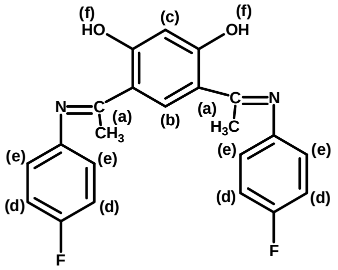
H_2L^1	Signal	Chemical shift in δ ppm	Multiplicity	Functional group
	H_a	2.16 (6H)	S	$-CH_3$ (x 2)
	H_{b-e}	6.59-7.94 (10H)	S & dd	Ar-H
	H_f	12.66 (2H)	S	-OH (x 2)

Mass [m/e (%)], M. Wt.: 414, 377, 301,287, 275, 260, 228, 194, 179, 161, 147, 133, 123, 105, 95, 77, 69, 43.

(III) H_2L^2: 4,6-bis(1-(4-fluorophenylimino)ethyl)benzene-1,3-diols

IR (KBr) cm^{-1}: 3360 (-OH aromatic), 1610 (-C=N-), 3030 (Ar C-H), 2950 (C-H of CH_3), 1480, 1430, 1390 (Ar -C=C- ring skeletal), 1250 (C-O of -OH), 830 (C-H bending for p-sub. benzene)

(^{1}H NMR 400 MHz DMSO-*d6*, δ ppm):

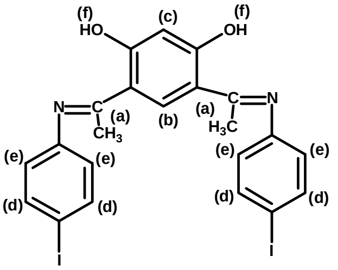
H_2L^2	Signal	Chemical shift in δ ppm	Multiplicity	Functional group
	H_a	2.10 (6H)	S	$-CH_3$ (x 2)
	H_{b-e}	6.89-7.36 (10H)	S & dd	Ar-H
	H_f	12.38 (2H)	S	-OH (x 2)

Mass [m/e (%)], M. Wt.: 380, 365, 287, 271, 254, 244, 226, 194, 176, 161, 148, 136, 122, 111, 95, 75, 69, 44.

(IV) H_2L^3: 4,6-bis(1-(4-iodophenylimino)ethyl)benzene-1,3-diols

IR (KBr) cm^{-1}: 3320(-OH aromatic), 1608 (-C=N-), 3060 (Ar C-H), 2950 (C-H of CH_3), 1510, 1440, 1380 (Ar -C=C- ring skeletal), 1250 (C-O of -OH), 810 (C-H bending for p-sub. benzene)

(^{1}H NMR 400 MHz DMSO-*d6*, δ ppm):

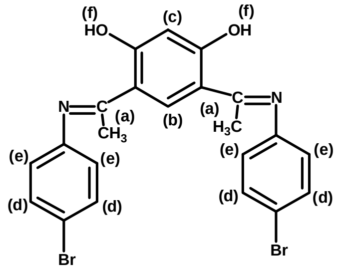
H_2L^3	Signal	Chemical shift in δ ppm	Multiplicity	Functional group
	H_a	2.15 (6H)	S	$-CH_3$ (x 2)
	H_{b-e}	6.60-7.40 (10H)	S & dd	Ar-H
	H_f	12.20 (2H)	S	-OH (x 2)

Mass [m/e (%)], M. Wt.: 596, 395, 380, 219, 194, 179, 161, 149, 125, 109, 92, 71, 57, 44.

(V) H_2L^4: 4,6-bis(1-(4-bromophenylimino)ethyl)benzene-1,3-diols

IR (KBr) cm^{-1}: 3400 (-OH aromatic), 1614 (-C=N-), 3080 (Ar C-H), 2980 (C-H of CH_3), 1530, 1470, 1420 (Ar -C=C- ring skeletal), 1250 (C-O of -OH), 870 (C-H bending for p-sub. benzene).

(^{1}H NMR 400 MHz DMSO-*d6*, δ ppm):

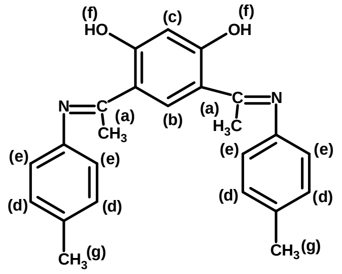
H_2L^4	Signal	Chemical shift in δ ppm	Multiplicity	Functional group
	H_a	2.17 (6H)	S	$-CH_3$ (x 2)
	H_{b-e}	6.30-7.70 (10H)	S & dd	Ar-H
	H_f	12.30 (2H)	S	-OH (x 2)

Mass [m/e (%)], M. Wt.: 501, 421, 345, 331, 319, 286, 208, 194, 176, 161, 148, 136, 122, 111, 95, 75, 69, 44.

(VI) H_2L^5: 4,6-bis(1-(p-tolylimino)ethyl)benzene-1,3-diol

IR (KBr) cm^{-1}: 3310 (-OH aromatic), 1600 (-C=N-), 3030 (Ar C-H), 2920 (C-H of CH_3), 1500, 1430, 1370 (Ar -C=C- ring skeletal), 1250 (C-O of -OH), 820 (C-H bending for p-sub. benzene).

(^{1}H NMR 400 MHz DMSO-*d6*, δ ppm):

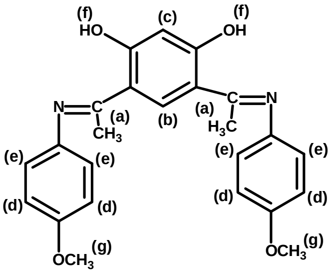
H_2L^5	Signal	Chemical shift in δ ppm	Multiplicity	Functional group
	H_a	2.13 (6H)	S	$-CH_3$ (x 2)
	H_{b-e}	6.98-7.73 (10H)	S & dd	Ar-H
	H_f	12.30 (2H)	S	-OH (x 2)
	H_g	2.58 (6H)	S	$-CH_3$ (x 2)

Mass [m/e (%)], M. Wt.: 372, 365, 287, 272, 254, 245, 226, 194, 176, 161, 148, 137, 111, 95, 81, 69, 41.

(VI) H_2L^6: 4,6-bis(1-(4-methoxyphenylimino)ethyl)benzene-1,3-diol

IR (KBr) cm^{-1}: 3300 (-OH aromatic), 1607 (-C=N-), 3030 (Ar C-H), 2920 (C-H of CH_3), 1500, 1430, 1370 (Ar -C=C- ring skeletal), 1250 (C-O of -OH), 820 (C-H bending for p-sub. benzene).

(^{1}H NMR 400 MHz DMSO-*d6*, δ ppm):

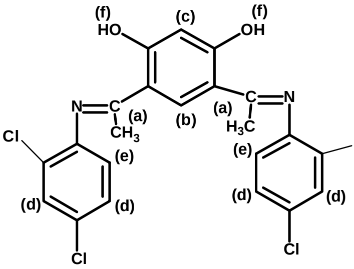
H_2L^6	Signal	Chemical shift in δ ppm	Multiplicity	Functional group
	H_a	2.13 (6H)	S	-CH_3 (x 2)
	H_{b-e}	6.70-7.60 (10H)	S & dd	Ar-H
	H_f	12.30 (2H)	S	-OH (x 2)
	H_g	2.30 (6H)	S	-CH_3 (x 2)

Mass [m/e (%)], M. Wt.: 404, 389, 373, 299, 283, 266, 251, 238, 223, 194, 182, 160, 148, 132, 123, 108, 92, 77, 57, 44.

(VIII) H_2L^7: 4,6-bis(1-(2,4-dichlorophenylimino)ethyl)benzene-1,3-diol

IR (KBr) cm^{-1}: 3340 (-OH aromatic), 1610 (-C=N-), 3050 (Ar C-H), 2930 (C-H of CH_3), 1500, 1450, 1400 (Ar -C=C- ring skeletal), 1250 (C-O of -OH).

(^{1}H NMR 400 MHz DMSO-*d6*, δ ppm):

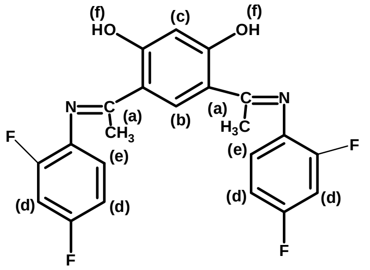
H_2L^7	Signal	Chemical shift in δ ppm	Multiplicity	Functional group
	H_a	2.12 (6H)	S	-CH_3 (x 2)
	H_{b-e}	6.28-7.72 (8H)	S	Ar-H
	H_f	12.84 (2H)	S	-OH (x 2)

Mass [m/e (%)], M. Wt.: 480.8, 463.4, 420.4, 413.4, 389.4, 381.4, 353.3, 331.3, 314.1, 301.2, 281.2, 241.2, 214.2, 202.2, 174.2.

(IX) H_2L^8: 4,6-bis(1-(2,4-difluorophenylimino)ethyl)benzene-1,3-diol

IR (KBr) cm^{-1}: 3330 (-OH aromatic), 1612 (-C=N-), 3050 (Ar C-H), 2930 (C-H of CH_3), 1510, 1460, 1430 (Ar -C=C- ring skeletal), 1265 (C-O of -OH).

(^{1}H NMR 400 MHz DMSO-*d6*, δ ppm):

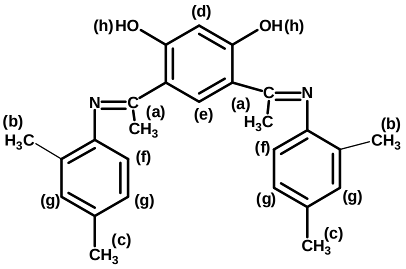
H_2L^8	Signal	Chemical shift in δ ppm	Multiplicity	Functional group
	H_a	2.20 (6H)	S	$-CH_3$ (x 2)
	H_{b-e}	6.34-7.80 (8H)	S	Ar-H
	H_f	12.92 (2H)	S	-OH (x 2)

Mass [m/e (%)], M. Wt.: 416.11, 397.11, 379.12, 303.09, 289.09, 277.27, 262.06, 248.05, 231.05, 215.05, 197.06, 179.07, 161.06, 147.04, 133, 123, 105, 95, 77, 69, 43.

(X) H_2L^9: 4,6-bis(1-(2,4-dimethylphenylimino)ethyl)benzene-1,3-diol

IR (KBr) cm^{-1}: 3310 (-OH aromatic), 1600 (-C=N-), 3030 (Ar C-H), 2920 (C-H of CH_3), 1500, 1430, 1370 (Ar -C=C- ring skeletal), 1250 (C-O of -OH)

(^{1}H NMR 400 MHz DMSO-*d6*, δ ppm):

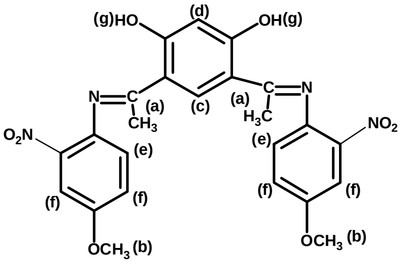
H_2L^9	Signal	Chemical shift in δ ppm	Multiplicity	Functional group
	H_a	2.12 (6H)	S	$-CH_3$ (x 2)
	H_b	2.32 (6H)	S	$-CH_3$ (x 2)
	H_c	2.32 (6H)	S	$-CH_3$ (x 2)
	H_{d-g}	6.28-7.86 (8H)	S	Ar-H
	H_h	12.62 (2H)	S	-OH (x 2)

Mass [m/e (%)], M. Wt.: 400, 385, 371, 298, 281, 263, 250, 234, 221, 194, 182, 160, 148, 132, 123, 108, 92, 77, 57, 44.

(XI) H_2L^{10}: 4,6-bis(1-(4-methoxy-2-nitrophenylimino)ethyl)benzene-1,3-diol

IR (KBr) cm^{-1}: 3400 (-OH aromatic), 1606 (-C=N-), 3010 (Ar C-H), 2930 (C-H of CH_3), 1510, 1440, 1385 (Ar -C=C- ring skeletal), 1260 (C-O of -OH).

(^{1}H NMR 400 MHz DMSO-*d6*, δ ppm):

H_2L^{10}	**Signal**	**Chemical shift in δ ppm**	**Multiplicity**	**Functional group**
	H_a	2.13 (6H)	S	$-CH_3$ (x 2)
	H_b	2.38 (6H)	S	$-OCH_3$ (x 2)
	H_{c-f}	6.24-7.99 (8H)	S	Ar-H
	H_g	12.63 (2H)	S	-OH (x 2)

Mass [m/e (%)], M. Wt.: 494.14, 463.12, 433.11, 388.13, 343.14, 267.11, 253.11, 238.08, 226.08, 150.05, 138.09, 124.12, 110.11, 95, 75, 69, 44.

1.7 SPECTRA

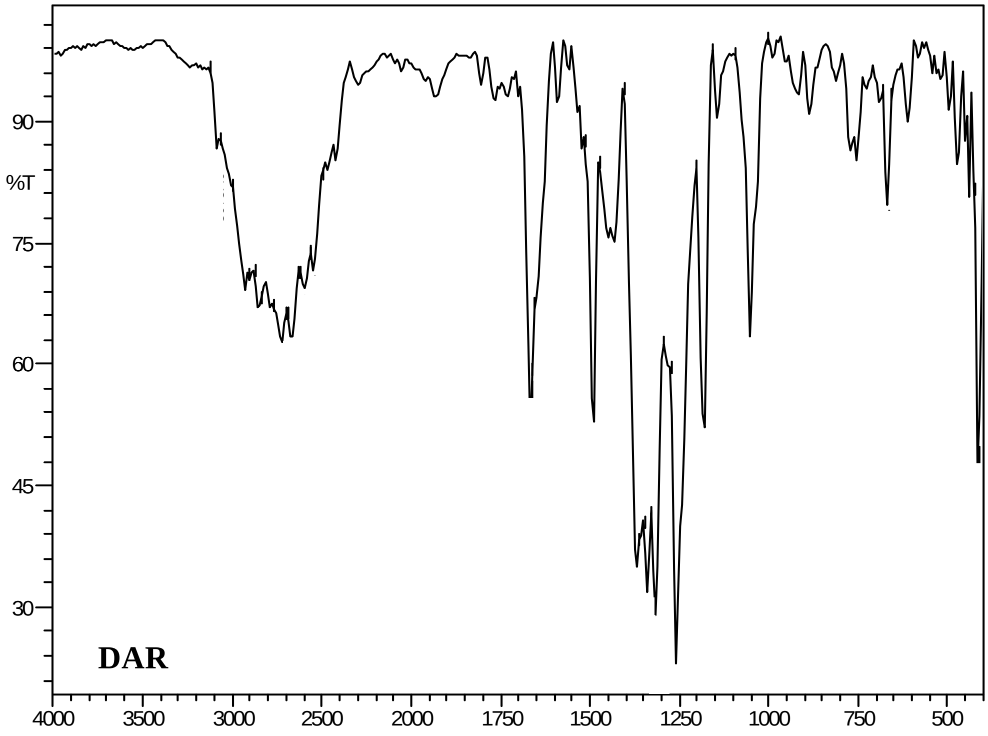


Figure-1.1

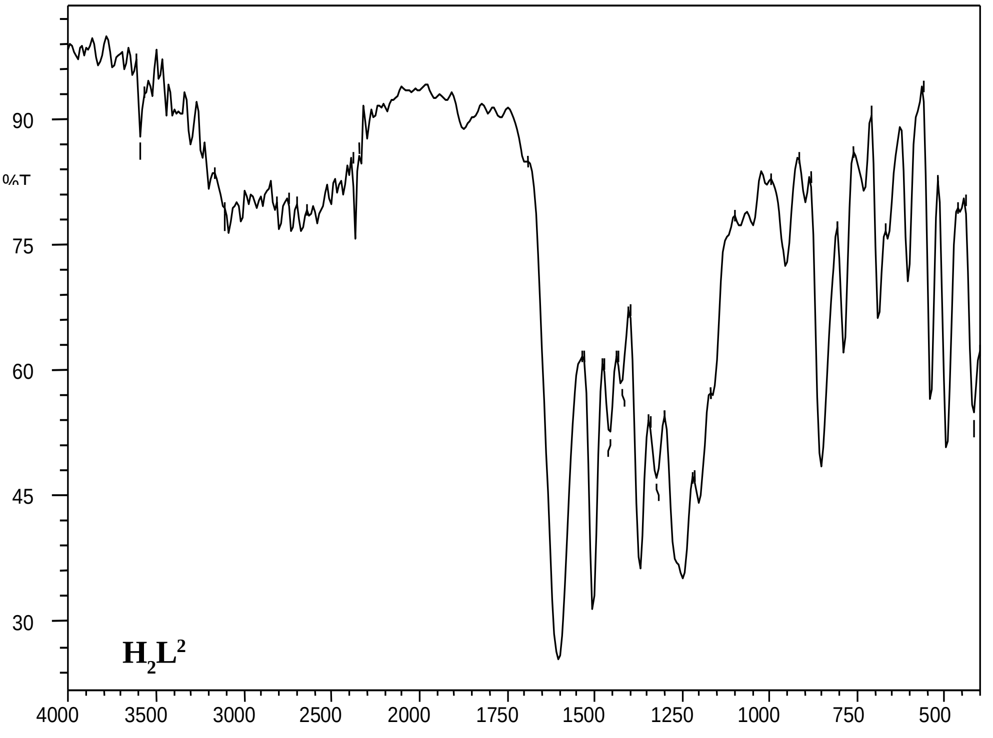


Figure-1.2

H_2L^{10}

Figure-1.3

DAR

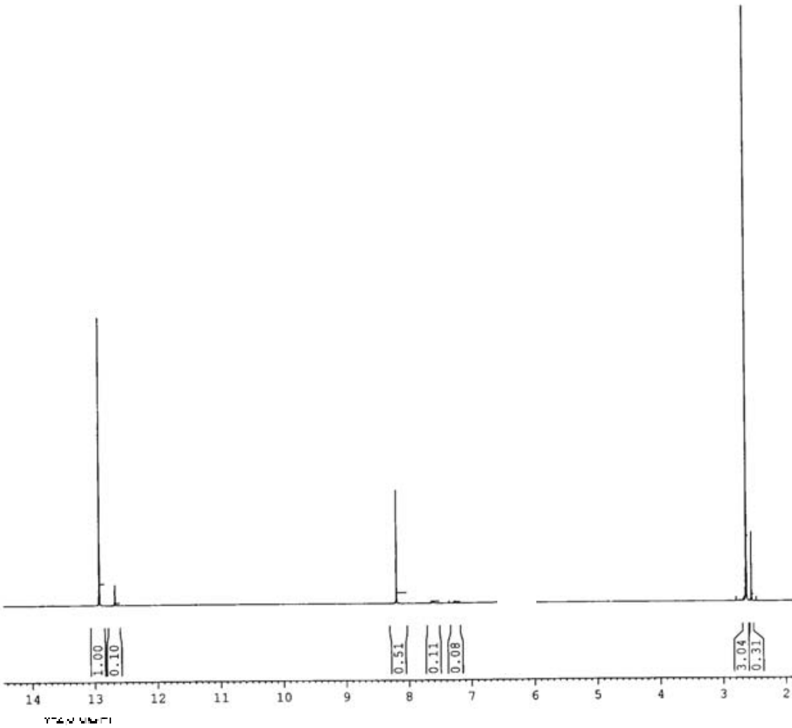


Figure-1.4

H_2L^1

Figure-1.5

H_2L^7

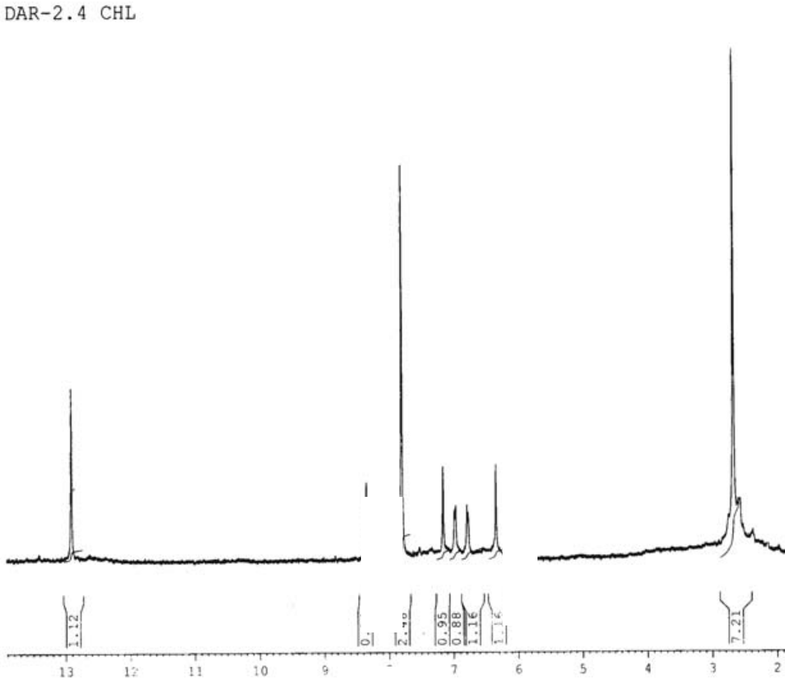


Figure-1.6

DAR

Figure-1.7

H_2L^2

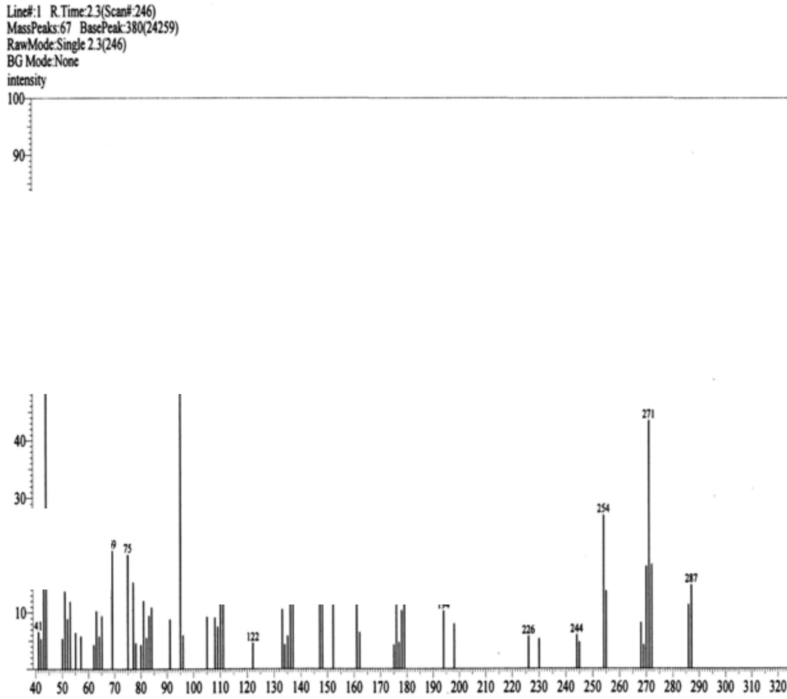


Figure-1.8

H_2L^3

Figure-1.9

H_2L^6

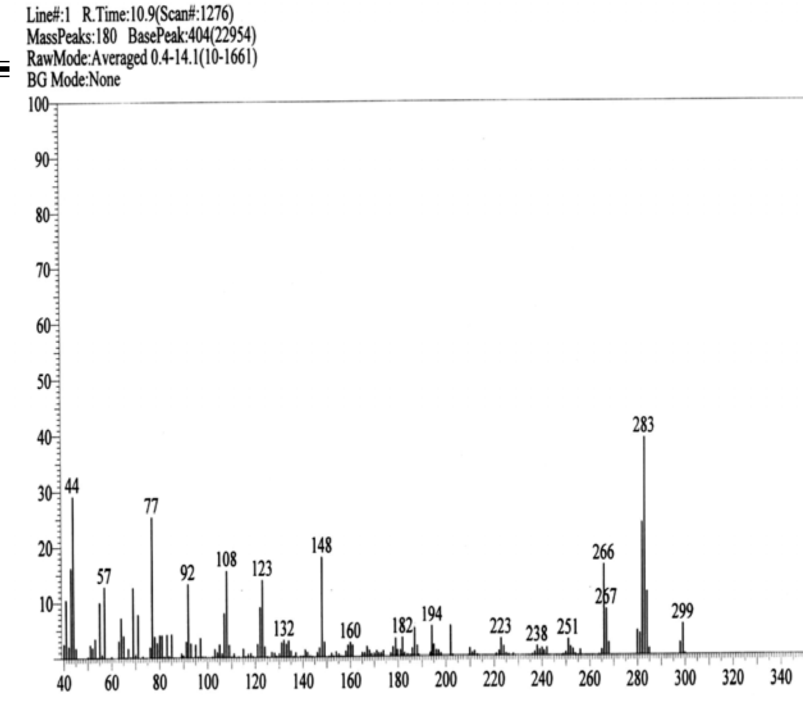
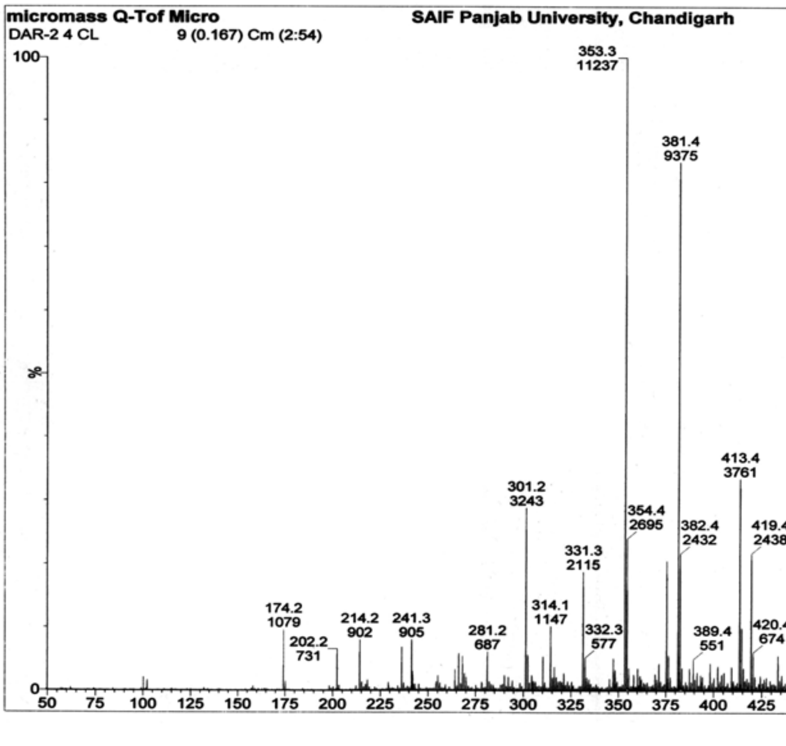


Figure-1.10

H_2L^7

Figure-1.11



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CHAPTER-2

SYNTHESIS AND CHARACTERIZATION OF METAL CHELATES

2.1 Introduction
2.2 Reaction Scheme
2.3 Experimental
2.4 Physical Data Table
2.5 Spectral Study
2.6 Spectral Characterization of Metal Chelate
2.7 Spectra
2.8 References

2.1 INTRODUCTION

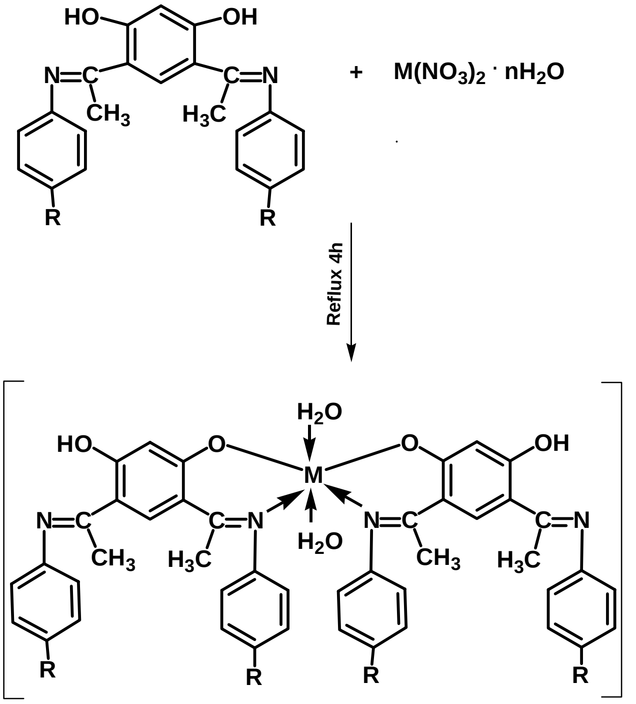
The interest of the coordination complexes of Schiff bases stems from their versatile catalytic reactions for organic synthesis and its use in degradation of organic substances and in radiopharmaceuticals and their ability to reversibly bind oxygen and photochromic properties, and the complexing ability towards transition metals[190-197].

Metal chelation is involved in many important biological processes where the coordination can occur between a variety of the metal ions and a wide range of ligands[198-202]. Generally, the chelating ligand is a polyfunctional molecule which can encase the metal in an organic sphere. Many types of the Schiff base ligands are known and the properties of their derived metal chelates have been investigated[203]. Acyclic ligands having nitrogen, oxygen and sulphur donor atoms in their structures can act as good chelating agents for transition and non-transition metal ions[204-208]. The thermal decomposition of various nickel, palladium and platinum complexes is used for the production of metal and metal oxides which are extensively applied as catalysts in a variety of important chemical processes. Transition metal complexes of multidentate Schiff base ligand especially tetradentate Schiff bases have great applicabilities in catalysis and material chemistry. Tetradentate Schiff bases with N_2O_2 donor set atoms provide suitable coordination environments for a wide variety of metal ions [209-214].

Moreover metal complexes of Schiff bases can increase its dimensionality and can form supramolecular architectures through O–H---N and N–H--- O type of hydrogen bonds. Szlyk along with their respective groups worked on Nickel(II) complexes of tetradentate Schiff base ligands as such complexes of nickel can exhibit several oxidation states [215]. Recently, Mitra and coworkers have explored the chemistry of Nickel(II) complex using a symmetric N_4 donor tetradentate Schiff base ligand. Apart from this, transition metal complexes with symmetric and asymmetric Schiff bases have also been explored by Mitra et al. [216]. Cobalt complexes of tetradentate Schiff base ligands have gained importance as they biomimic the metal-containing sites in cobalamine (B_{12}) coenzymes, metalloproteins and metalloenzymes [217-220]. They also act as oxygen activators and as a model system for dioxygen carriers [221,222]. Copper Schiff base complexes are also used as potent antiviral, antibacterial and antitumor agents [223].

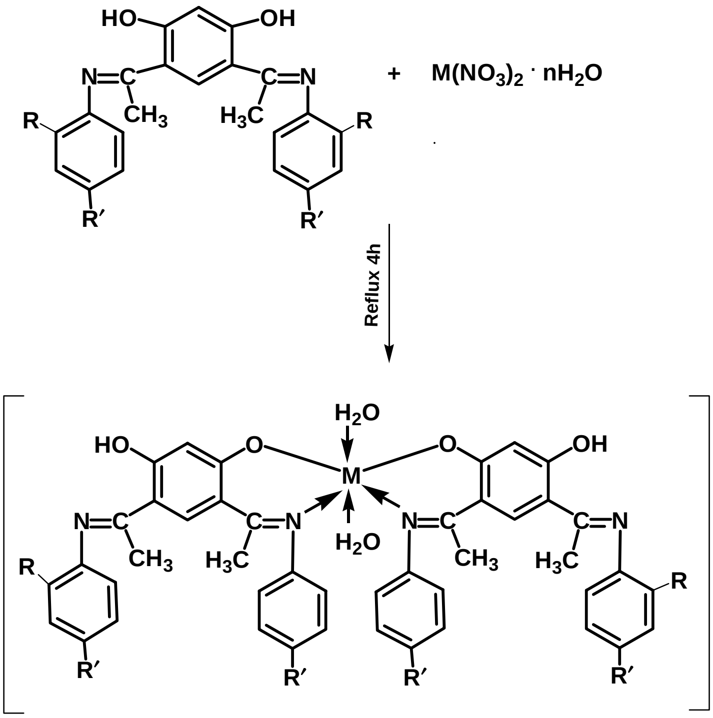
2.2 REACTION SCHEMES

The synthetic route to Schiff base metal chelates of Co(II), Ni(II) and Cu(II) is as follows



Where R = -Cl, -F, -I, -Br, $-CH_3$, $-OCH_3$
M = Co(II), Ni(II), Cu(II)

SCHEME-1



Where R = -Cl, -F, $-CH_3$, $-No_2$
R′ = -Cl, -F, $-CH_3$, $-OCH_3$
M = Co(II), Ni(II), Cu(II)

SCHEME-2

2.3 EXPERIMENTAL

The newly synthesized ligands have been reacted with salts of Cobalt, Nickel and Copper to give their corresponding metal chelates.

2.3.1 Synthesis of H_2L^1 complexes

(I) Synthesis of Cobalt complex

The metal chelate was prepared by refluxing the Cobalt(II) nitrate(hexahydrate) (2.91 gm, 1mmol) in 10 ml of methanol with the ligand, H_2L^1 (8.26 gm, 2 mmol) in 20ml of methanol on a water bath for about 4hrs. The pH of the solution was adjusted to 7 by drop wise addition of 10% methanolic ammonia solution. The metal chelates got separated after cooling the solution overnight. The metal chelates thus separated were washed with methanol followed by pet ether (60-80^{0}C) and dried in vacuum. The complexes are insoluble in water and alcohol but soluble in DMSO. The progress of reaction was monitered by TLC. Yield obtained- 72%. (Scheme-1)

(II) Synthesis of Nickel complex

The metal chelate was prepared by refluxing the Nickel(II) nitrate(hexahydrate) (2.90 gm, 1mmol) in 10 ml of methanol with the ligand, H_2L^1 (8.26 gm, 2 mmol) in 20ml of methanol on a water bath for about 4hrs. The pH of the solution was adjusted to 7 by drop wise addition of 10% methanolic ammonia solution. The metal chelates got separated after cooling the solution overnight. The metal chelates thus separated were washed with methanol followed by pet ether (60-80^{0}C) and dried in vacuum. The complexes are insoluble in water and alcohol but soluble in DMSO. The progress of reaction was monitered by TLC. Yield obtained-78%. (Scheme-1)

(III) Synthesis of Copper complex

The metal chelate was prepared by refluxing the Copper(II) nitrate(trihydrate) (2.41 gm, 1mmol) in 10 ml of methanol with the ligand, H_2L^1 (8.26 gm, 2 mmol) in 20ml of methanol on a water bath for about 4hrs. The pH of the solution was adjusted to 7 by drop wise addition of 10% methanolic ammonia solution. The metal chelates got separated after cooling the solution overnight. The metal chelates thus separated were washed with methanol followed by pet ether (60-80^{0}C) and dried in vacuum. The complexes are insoluble in water and alcohol but soluble in DMSO. The progress of reaction was monitered by TLC. Yield obtained- 79%. (Scheme-1)

2.3.2 Synthesis of H_2L^2 complexes

(I) Synthesis of Cobalt complex

Cobalt(II) nitrate(hexahydrate) (2.91 gm, 1mmol) in MeOH (10 cm^3) was added gradually with constant stirring to a solution of the deprotonated ligand, H_2L^2, (7.60 gm, 2mmol) in MeOH (20 cm^3). The stoichiometry of the metal ion to ligand was 1:2. The solution was refluxed for 3 h. A reddish brown precipitate was formed and washed several times with small amounts of MeOH, then ether. The progress of reaction was monitered by TLC. Yield obtained- 72%. (Scheme-1)

(II) Synthesis of Nickel complex

Nickel(II) nitrate (hexahydrate) (2.90 gm, 1mmol) in MeOH (10 cm^3) was added gradually with constant stirring to a solution of the deprotonated ligand, H_2L^2, (7.60 gm, 2mmol) in MeOH (20 cm^3). The stoichiometry of the metal ion to ligand was 1:2. The solution was refluxed for 3 h. A green precipitate was formed and washed several times with small amounts of MeOH, then ether. The progress of reaction was monitered by TLC. Yield obtained- 76%. (Scheme-1)

(II) Synthesis of Copper complex

Copper(II) nitrate (trihydrate) (2.41 gm, 1mmol) in MeOH (10 cm^3) was added gradually with constant stirring to a solution of the deprotonated ligand, H_2L^2, (7.60 gm, 2mmol) in MeOH (20 cm^3). The stoichiometry of the metal ion to ligand was 1:2. The solution was refluxed for 3 h. A bluish green precipitate was formed and washed several times with small amounts of MeOH, then ether. The progress of reaction was monitered by TLC. Yield obtained- 78%. (Scheme-1)

2.3.3 Synthesis of H_2L^3 complexes

(I) Synthesis of Cobalt complex

The Schiff base ligand (11.92 gm, 2mmol) dissolved in methanol (20 ml) were mixed with respective Cobalt(II) nitrate (hexahydrate) (2.91 gm, 1mmol) in methanol (10 ml). The reaction mixture was refluxed for 2-3 h. The resulting solutions were concentrated and cooled. On cooling brown colored precipitates formed, which were filtered, washed with methanol, and dried. The progress of reaction was monitered by TLC. Yield obtained- 69%. (Scheme-1)

(II) Synthesis of Nickel complex

The Schiff base ligand (11.92 gm, 2mmol) dissolved in methanol (20 ml) were mixed with respective Nickel(II) nitrate (hexahydrate) (2.90 gm, 1mmol) in methanol (10 ml). The reaction mixture was refluxed for 2-3 h. The resulting solutions were concentrated and cooled. On cooling green colored precipitates formed, which were filtered, washed with methanol, and dried. The progress of reaction was monitered by TLC. Yield obtained- 75%. (Scheme-1)

(III) Synthesis of Copper complex

The Schiff base ligand (11.92 gm, 2mmol) dissolved in methanol (20 ml) were mixed with respective Copper(II) nitrate (trihydrate) (2.41 gm, 1mmol) in methanol (10 ml). The reaction mixture was refluxed for 2-3 h. The resulting solutions were concentrated and cooled. On cooling blue colored precipitates formed, which were filtered, washed with methanol, and dried. The progress of reaction was monitered by TLC. Yield obtained- 79%. (Scheme-1)

2.3.4 Synthesis of H_2L^4 complexes

(I) Synthesis of Cobalt complex

A methanolic solution (10 ml) of the Cobalt(II) nitrate (hexahydrate) (2.91 gm, 1mmol) was added to a magnetically stirred methanol solution (20 ml) of the Schiff base (10.04 gm, 2mmol). The mixture was refluxed for 2 h, then cooled to room temperature, filtered and reduced to nearly half of its volume. The concentrated solution was left standing overnight at room temperature, which resulted in the formation of a solid product. The product thus obtained was filtered, washed with methanol, then the ether, and dried. Crystallization in aqueous ethanol (50%) gave the desired metal complexes. The progress of reaction was monitered by TLC. Yield obtained- 80%. (Scheme-1)

(II) Synthesis of Nickel complex

A methanolic solution (10 ml) of the Nickel(II) nitrate (hexahydrate) (2.90 gm, 1mmol) was added to a magnetically stirred methanol solution (20 ml) of the Schiff base (10.04 gm, 2mmol). The mixture was refluxed for 2 h, then cooled to room temperature, filtered and reduced to nearly half of its volume. The concentrated solution was left standing overnight at room temperature, which resulted in the formation of a solid product. The product thus obtained was filtered, washed with methanol, then the ether, and dried. Crystallization in aqueous ethanol (50%) gave the desired metal complexes. The progress of reaction was monitered by TLC. Yield obtained- 85%. (Scheme-1)

(III) Synthesis of Copper complex

A methanolic solution (10 ml) of the Copper(II) chloride (trihydrate) (2.41 gm, 1mmol) was added to a magnetically stirred methanol solution (20 ml) of the Schiff base (10.04 gm, 2mmol). The mixture was refluxed for 2 h, then cooled to room temperature, filtered and reduced to nearly half of its volume. The concentrated solution was left standing overnight at room temperature, which resulted in the formation of a solid product. The product thus obtained was filtered, washed with methanol, then the ether, and dried. Crystallization in aqueous ethanol (50%) gave the desired metal complexes. The progress of reaction was monitered by TLC. Yield obtained- 82%. (Scheme-1)

2.3.5 Synthesis of H_2L^5 complexes

(I) Synthesis of Cobalt complex

The Cobalt complex was synthesized by addition of the Cobalt (II) Nitrate (hexahydrate) (2.91 gm, 1mmol, in 10 cm^3 MeOH) to a hot solution of the ligands (7.44 gm, 2mmol, in 20 cm^3 MeOH). The pH was adjusted to 8.0 using alcoholic ammonia (0.01 M). The resulting solution was refluxed on a water bath at 90 ^{0}C for 4 h. The volume of the obtained solution was reduced to one half by evaporation. The crystal products were collected by filtration, washed with MeOH, and finally dried under vacuum. The progress of reaction was monitered by TLC. Yield obtained- 85%. (Scheme-1)

(II) Synthesis of Nickel complex

The Nickel complex was synthesized by addition of the Nickel (II) Nitrate (hexahydrate) (2.90 gm, 1mmol, in 10 cm^3 MeOH) to a hot solution of the ligands (7.44 gm, 2mmol, in 20 cm^3 MeOH). The pH was adjusted to 8.0 using alcoholic ammonia (0.01 M). The resulting solution was refluxed on a water bath at 90 ^{0}C for 4 h. The volume of the obtained solution was reduced to one half by evaporation. The crystal products were collected by filtration, washed with MeOH, and finally dried under vacuum. The progress of reaction was monitered by TLC. Yield obtained 85%. (Scheme-1)

(III) Synthesis of Copper complex

The Copper complex was synthesized by addition of the Copper (II) Nitrate (trihydrate) (2.41 gm, 1mmol, in 10 cm^3 MeOH) to a hot solution of the ligands (7.44 gm, 2mmol, in 20 cm^3 MeOH). The pH was adjusted to 8.0 using alcoholic ammonia (0.01 M). The resulting solutions was refluxed on a water bath at 90 ^{0}C for 4 h. The volume of the obtained solution was reduced to one half by evaporation. The crystal products were collected by filtration, washed with MeOH, and finally dried under vacuum. The progress of reaction was monitered by TLC. Yield obtained- 85%. (Scheme-1)

2.3.6 Synthesis of H_2L^6 complexes

(I) Synthesis of Cobalt complex

The metal chelat was prepared by refluxing the Cobalt(II) nitrate(hexahydrate) (2.91 gm, 1mmol) in 10 ml of methanol with the ligand, H_2L^6 (8.08 gm, 2 mmol) in 20ml of methanol on a water bath for about 4hrs. The pH of the solution was adjusted to 7 by drop wise addition of 10% methanolic ammonia solution. The metal chelates got separated after cooling the solution overnight. The metal chelate thus separated were washed with methanol followed by pet ether (60-80^{0}C) and dried in vacuum. The complex is insoluble in water and alcohol but soluble in DMSO. The progress of reaction was monitered by TLC. Yield obtained- 79%.(Scheme-1)

(II) Synthesis of Nickel complex

The metal chelate was prepared by refluxing the Nickel(II) nitrate(hexahydrate) (2.90 gm, 1mmol) in 10 ml of methanol with the ligand, H_2L^6 (8.08 gm, 2 mmol) in 20ml of methanol on a water bath for about 4hrs. The pH of the solution was adjusted to 7 by drop wise addition of 10% methanolic ammonia solution. The metal chelate got separated after cooling the solution overnight. The metal chelate thus separated were washed with methanol followed by pet ether (60-80^{0}C) and dried in vacuum. The complex is insoluble in water and alcohol but soluble in DMSO. The progress of reaction was monitered by TLC. Yield obtained 80%.(Scheme-1)

(III) Synthesis of Copper complex

The metal chelate was prepared by refluxing the Copper(II) nitrate(trihydrate) (2.41 gm, 1mmol) in 10 ml of methanol with the ligand, H_2L^6 (8.08 gm, 2 mmol) in 20ml of methanol on a water bath for about 4hrs. The pH of the solution was adjusted to 7 by drop wise addition of 10% methanolic ammonia solution. The metal chelate got separated after cooling the solution overnight. The metal chelate thus separated were washed with methanol followed by pet ether (60-80^{0}C) and dried in vacuum. The complex are insoluble in water and alcohol but soluble in DMSO. The progress of reaction was monitered by TLC. The yield is 84%. (Scheme-1)

2.3.7 Synthesis of H_2L^7 complexes

(I) Synthesis of Cobalt complex

Cobalt(II) nitrate(hexahydrate) (2.91 gm, 1mmol) in MeOH (10 cm^3) was added gradually with constant stirring to a solution of the deprotonated ligand, H_2L^7, (9.64 gm, 2mmol) in MeOH (20 cm^3). The stoichiometry of the metal ion to ligand was 1:2. The solution was refluxed for about 3 h. A reddish brown precipitate was formed and washed several times with small amounts of MeOH and then ether. The progress of reaction was monitered by TLC. Yield obtained- 74%. (Scheme-2)

(II) Synthesis of Nickel complex

Nickel(II) nitrate (hexahydrate) (2.90 gm, 1mmol) in MeOH (10 cm^3) was added gradually with constant stirring to a solution of the deprotonated ligand, H_2L^7, (9.64 gm, 2mmol) in MeOH (20 cm^3). The stoichiometry of the metal ion to ligand was 1:2. The solution was refluxed for about 3 h. A green precipitate was formed and washed several times with small amounts of MeOH and then ether. The progress of reaction was monitered by TLC. Yield obtaned- 76%. (Scheme-2)

(II) Synthesis of Copper complex

Copper(II) nitrate (trihydrate) (2.41 gm, 1mmol) in MeOH (10 cm^3) was added gradually with constant stirring to a solution of the deprotonated ligand, H_2L^7, (9.64 gm, 2mmol) in MeOH (20 cm^3). The stoichiometry of the metal ion to ligand was 1:2. The solution was refluxed for about 3 h. A bluish green precipitate was formed and washed several times with small amounts of MeOH, then ether. The progress of reaction was monitered by TLC. The yield was 83%. (Scheme-2)

2.3.8 Synthesis of H_2L^8 complexes

(I) Synthesis of Cobalt complex

The Schiff base ligand, H_2L^8 (8.32 gm, 2mmol) dissolved in methanol (20 ml) were mixed with respective Cobalt(II) nitrate (hexahydrate) (2.91 gm, 1mmol) in methanol (10 ml). The reaction mixture was refluxed for 2-3 h. The resulting solutions were concentrated and cooled. On cooling brown colored precipitates formed, which were filtered, washed with methanol, and dried. The progress of reaction was monitered by TLC. Yield obtained- 78%. (Scheme-2)

(II) Synthesis of Nickel complex

The Schiff base ligand, H_2L^8 (8.32 gm, 2mmol) dissolved in methanol (20 ml) were mixed with respective Nickel(II) nitrate (hexahydrate) (2.90 gm, 1mmol) in methanol (10 ml). The reaction mixture was refluxed for 2-3 h. The resulting solutions were concentrated and cooled. On cooling green colored precipitates formed, which were filtered, washed with methanol, and dried. The progress of reaction was monitered by TLC. Yield obtained- 79%. (Scheme-2)

(III) Synthesis of Copper complex

The Schiff base ligand, H_2L^8 (8.32 gm, 2mmol) dissolved in methanol (20 ml) were mixed with respective Copper(II) nitrate (trihydrate) (2.41 gm, 1mmol) in methanol (10 ml). The reaction mixture was refluxed for 2-3 h. The resulting solutions were concentrated and cooled. On cooling blue colored precipitates formed, which were filtered, washed with methanol, and dried. The progress of reaction was monitered by TLC. Yield obtained- 84%. (Scheme-2)

2.3.9 Synthesis of H_2L^9 complexes

(I) Synthesis of Cobalt complex

A methanolic solution (10 ml) of the Cobalt(II) nitrate (hexahydrate) (2.91 gm, 1mmol) was added to a magnetically stirred methanol solution (20 ml) of the Schiff base ligand, H_2L^9 (8.00 gm, 2mmol). The mixture was refluxed for 2 h, then cooled to room temperature, filtered and reduced to nearly half of its volume. The concentrated solution was left standing overnight at room temperature, which resulted in the formation of a solid product. The product thus obtained was filtered, washed with methanol, then the ether, and dried. Crystallization in aqueous ethanol (50%) gave the desired metal complexes. The progress of reaction was monitered by TLC. Yield obtained- 80%. (Scheme-2)

(II) Synthesis of Nickel complex

A methanolic solution (10 ml) of the Nickel(II) nitrate (hexahydrate) (2.90 gm, 1mmol) was added to a magnetically stirred methanol solution (20 ml) of the Schiff base ligand, H_2L^9 (8.00 gm, 2mmol). The mixture was refluxed for 2 h, then cooled to room temperature, filtered and reduced to nearly half of its volume. The concentrated solution was left standing overnight at room temperature, which resulted in the formation of a solid product. The product thus obtained was filtered, washed with methanol, then the ether, and dried. Crystallization in aqueous ethanol (50%) gave the desired metal complexes. The progress of reaction was monitered by TLC. Yield obtained- 85%. (Scheme-2)

(III) Synthesis of Copper complex

A methanolic solution (10 ml) of the Copper(II) chloride (trihydrate) (2.41 gm, 1mmol) was added to a magnetically stirred methanol solution (20 ml) of the Schiff base ligand, H_2L^9 (8.00 gm, 2mmol). The mixture was refluxed for 2 h, then cooled to room temperature, filtered and reduced to nearly half of its volume. The concentrated solution was left standing overnight at room temperature, which resulted in the formation of a solid product. The product thus obtained was filtered, washed with methanol, then the ether, and dried. Crystallization in aqueous ethanol (50%) gave the desired metal complexes. The progress of reaction was monitered by TLC. Yield obtained- 82%.(Scheme-2)

2.3.10 Synthesis of H_2L^{10} complexes

(I) Synthesis of Cobalt complex

The Cobalt complex was synthesized by addition of the Cobalt (II) Nitrate (hexahydrate) (2.91 gm, 1mmol, in 10 cm^3 MeOH) to a hot solution of the ligand, H_2L^{10} (9.88 gm, 2mmol, in 20 cm^3 MeOH). The pH was adjusted to 8.0 using alcoholic ammonia (0.01 M). The resulting solution was refluxed on a water bath at 90 ^{0}C for 4 h. The volume of the obtained solution was reduced to one half by evaporation. The crystal products were collected by filtration, washed with MeOH, and finally dried under vacuum. The progress of reaction was monitered by TLC. Yield obtained- 75%. (Scheme-2)

(II) Synthesis of Nickel complex

The Nickel complex was synthesized by addition of the Nickel (II) Nitrate (hexahydrate) (2.90 gm, 1mmol, in 10 cm^3 MeOH) to a hot solution of the ligand, H_2L^{10} (9.88 gm, 2mmol, in 20 cm^3 MeOH). The pH was adjusted to 8.0 using alcoholic ammonia (0.01 M). The resulting solution was refluxed on a water bath at 90 ^{0}C for 4 h. The volume of the obtained solution was reduced to one half by evaporation. The crystal products were collected by filtration, washed with MeOH, and finally dried under vacuum. The progress of reaction was monitered by TLC. Yield obtained- 85%. (Scheme-2)

(III) Synthesis of Copper complex

The Copper complex was synthesized by addition of the Copper (II) Nitrate (trihydrate) (2.41 gm, 1mmol, in 10 cm^3 MeOH) to a hot solution of the ligand, H_2L^{10} (9.88 gm, 2mmol, in 20 cm^3 MeOH). The pH was adjusted to 8.0 using alcoholic ammonia (0.01 M). The resulting solution was refluxed on a water bath at 90 ^{0}C for 4 h. The volume of the obtained solution was reduced to one half by evaporation. The crystal products were collected by filtration, washed with MeOH, and finally dried under vacuum. The progress of reaction was monitered by TLC. Yield obtained- 85%. (Scheme-2)

2.4 PHYSICAL DATA TABLE

TABLE-2.4.1: THE ANALYTICAL AND PHYSICAL DATA OF METAL CHELATES

	Complex	Molecular Formula	Molecular Weight*	Color	Yield (%)	Melting point (°C)
1	$[Co(L^1)_2(H_2O)_2]$	$C_{44}H_{34}Cl_4\mathbf{Co}N_4O_4$	955.54	Reddish brown	72%	>300
2	$[Ni(L^1)_2(H_2O)_2]$	$C_{44}H_{34}Cl_4N_4\mathbf{Ni}O_4$	919.27	Green	78%	>300
3	$[Cu(L^1)_2(H_2O)_2]$	$C_{44}H_{34}Cl_4\mathbf{Cu}N_4O_4$	924.12	Deep blue	79%	>300
4	$[Co(L^2)_2(H_2O)_2]$	$C_{44}H_{34}\mathbf{Co}F_4N_4O_4$	853.69	Reddish brown	72%	>300
5	$[Ni(L^2)_2(H_2O)_2]$	$C_{44}H_{34}F_4N_4\mathbf{Ni}O_4$	853.45	Green	76%	>300
6	$[Cu(L^2)_2(H_2O)_2]$	$C_{44}H_{34}\mathbf{Cu}F_4N_4O_4$	858.3	Deep blue	78%	>300
7	$[Co(L^3)_2(H_2O)_2]$	$C_{44}H_{34}I_4\mathbf{Co}N_4O_4$	1285.32	Reddish brown	69%	>300
8	$[Ni(L^3)_2(H_2O)_2]$	$C_{44}H_{34}I_4N_4\mathbf{Ni}O_4$	1285.08	Green	75%	>300
9	$[Cu(L^3)_2(H_2O)_2]$	$C_{44}H_{34}I_4\mathbf{Cu}N_4O_4$	1289.93	Deep blue	79%	>300
10	$[Co(L^4)_2(H_2O)_2]$	$C_{44}H_{34}Br_4\mathbf{Co}N_4O_4$	1097.31	Reddish brown	80%	>300
11	$[Ni(L^4)_2(H_2O)_2]$	$C_{44}H_{34}Br_4N_4\mathbf{Ni}O_4$	1097.07	Green	85%	>300
12	$[Cu(L^4)_2(H_2O)_2]$	$C_{44}H_{34}Br_4\mathbf{Cu}N_4O_4$	1101.93	Deep blue	82%	>300
13	$[Co(L^5)_2(H_2O)_2]$	$C_{48}H_{46}\mathbf{Co}N_4O_4$	837.84	Reddish brown	69%	>300
14	$[Ni(L^5)_2(H_2O)_2]$	$C_{48}H_{46}N_4\mathbf{Ni}O_4$	837.06	Green	75%	>300
15	$[Cu(L^5)_2(H_2O)_2]$	$C_{48}H_{46}\mathbf{Cu}N_4O_4$	842.45	Deep blue	79%	>300
16	$[Co(L^6)_2(H_2O)_2]$	$C_{48}H_{46}\mathbf{Co}N_4O_8$	901.83	Reddish brown	79%	>300
17	$[Ni(L^6)_2(H_2O)_2]$	$C_{48}H_{46}\mathbf{Ni}N_4O_8$	901.59	Green	80%	>300
18	$[Cu(L^6)_2(H_2O)_2]$	$C_{48}H_{46}\mathbf{Cu}N_4O_8$	906.45	Deep blue	84%	>300

	Complex	**Molecular Formula**	**Molecular Weight***	**Color**	**Yield (%)**	**Melting point (°C)**
19	$[Co(L^7)_2(H_2O)_2]$	$C_{44}H_{30}Cl_8\mathbf{Co}N_4O_4$	1057.29	Reddish brown	74%	>300
20	$[Ni(L^7)_2(H_2O)_2]$	$C_{44}H_{30}Cl_8\mathbf{Ni}N_4O_4$	1057.05	Green	76%	>300
21	$[Cu(L^7)_2(H_2O)_2]$	$C_{44}H_{30}Cl_8\mathbf{Cu}N_4O_4$	1061.90	Deep blue	83%	>300
22	$[Co(L^8)_2(H_2O)_2]$	$C_{44}H_{30}F_8\mathbf{Co}N_4O_4$	925.65	Reddish brown	78%	>300
23	$[Ni(L^8)_2(H_2O)_2]$	$C_{44}H_{30}F_8\mathbf{Ni}N_4O_4$	925.41	Green	79%	>300
24	$[Cu(L^8)_2(H_2O)_2]$	$C_{44}H_{30}F_8\mathbf{Cu}N_4O_4$	930.27	Deep blue	84%	>300
25	$[Co(L^9)_2(H_2O)_2]$	$C_{52}H_{54}\mathbf{Co}N_4O_4$	893.94	Reddish brown	80%	>300
26	$[Ni(L^9)_2(H_2O)_2]$	$C_{52}H_{54}\mathbf{Ni}N_4O_4$	893.70	Green	85%	>300
27	$[Cu(L^9)_2(H_2O)_2]$	$C_{52}H_{54}\mathbf{Cu}N_4O_4$	898.56	Deep blue	82%	>300
28	$[Co(L^{10})_2(H_2O)_2]$	$C_{48}H_{42}\mathbf{Co}N_8O_{16}$	1081.82	Reddish brown	75%	>300
29	$[Ni(L^{10})_2(H_2O)_2]$	$C_{48}H_{42}\mathbf{Ni}N_8O_{16}$	1081.58	Green	85%	>300
30	$[Cu(L^{10})_2(H_2O)_2]$	$C_{48}H_{42}\mathbf{Cu}N_8O_{16}$	1086.44	Deep blue	85%	>300

*** Molecular Weight of the complexes given with Coordinate water molecule**

2.5 SPECTRAL STUDY

IR spectra (4000-400 cm^{-1}) of the metal chelates were obtained using KBr discs, on a 8400 FTIR SHIMADZU Spectrometer. ESI Mass spectra of complexes were recorded VG-70-S Spectrometer. Electronic spectra of the metal complexes in DMF were recorded on a perkin elmer lambda 19 spectrophotometer, and ESR was recorded on E-112 ESR Spectrometer, at X-band microwave frequency (9.5 GHz) with sensitivity of 5×10^{10} ΔH spins. Thermal Gravimetric Analyses (TGA) have been carried out by using Perkin Elmer (Pyris 1 TGA) from room temperature to 800°C under heating rate of 10°C/min. Elemental analysis (C, H and N) were carried out on Elemental Analyzer PERKIN ELMER 2400. Magnetic moment of the compound measured by GOUY balance using Hg[Co(CNS)] as standard.

2.5.1 Infra Red Spectra

The bonding of the ligand to metallo-elements was investigated by comparing the FT-IR spectra of the complexes with those of the free ligands. The FT-IR spectra of the complexes contain all the absorption bands form the ligands and some new absorption bands indicative of coordination of the ligands with metal ions through N and O. The spectra of these complexes exhibited a broad band around 3380-3500 cm^{-1} which is assigned to water molecules, ν(OH), associated with the complexes. Coordinated water exhibited, in addition to this modes, the $\rho_r(H_2O)$ rocking near 892, 840 cm^{-1}, $\rho_w(H_2O)$, wagging near 530-550 cm^{-1}. FT-IR spectra of all the ligands contained a band at 1610-1632 cm^{-1}, ν(C=N), which shifted slightly to a lower value in all the complexes suggesting that the ligands are coordinated to the metal ion through C=N. New absorption bands ν (M-N) and ν (M-O), appeared at 580-612 cm^{-1} and 438-558 cm^{-1} respectively, in the spectra of the complexes indicating coordination of the ligands through N and O. These assignments were made by comparison with related Schiff base complexes[224-226]. (Figure-2.1,2.2)

2.5.2 Electronic Absorption Spectra (UV-Vis.)

The electronic absorption spectra show that when DAR and substituted amine mixed together, the imines formation occurred which was indicated by yellowing of the solution and development of an absorption band in the visible range[227].

The electronic spectral data for a DMF solution of the ligands showed four absorption bands in the range 210–226 nm, 232–268 nm, 363–373nm and 390–410 nm. The former two bands are assigned to the absorption of ($^1L_a\rightarrow{}^1A_1$) and ($^1L_b\rightarrow{}^1A_1$) of the phenyl ring, while the third band is assigned to ($\pi\rightarrow\pi^*$)transition of the azomethine group, which is shifted to lower wavelength on coordination, as a result of the participation of the two azomethine nitrogens in coordination. The latter broad band is assigned to the intermolecular CT and (n→π*) transition from the ligand to the metal ions.

The electronic spectra of the complexes showed several absorption bands, including absorption bands of the ligands and d–d transitions of the metal ions. Spectra of the complexes, which reveal maxima at the wavelength of the first band of the ligands(210-226 nm), are independent of complexation. The second band for the complexes lies in the range 270-287nm, markedly different for the second band of the free ligands, and there is a great increase of absorption. The third band is ascribed to π→π* transitions involving the azomethine found at 345-365nm. The band at 390-430nm is assigned to charge transfer transition. Lower energy bands in the range 515-760 nm are assigned to d–d transitions of the metal cations.

The spectra of the brown Co(II), complexes show two d–d transition bands in the 515–650 nm region for complexes. The two bands are assigned to the $^4T_{1g}\rightarrow{}^4T_{1g}(P)$ and $^4T_{1g}\rightarrow{}^4T_{1g}(F)$ transitions of octahedral geometry. The color agrees well with the proposed geometry. The visible spectra of the green Ni(II) complexes show three bands. The most intense band at ~470nm is assigned to the $^3A_{2g}\rightarrow{}^3T_{1g}(P)$ transition in complexes at the same region. The latter transition is a less intense peak at 670–760 nm, assigned to the $^3A_{2g}\rightarrow{}^3T_{2g}$ transition due to the existence of octahedral environment. The Cu(II) complexes exhibit five absorption maxima. The first three maxima in the range 210–365 nm were ascribed previously to the ligands, while the fourth maximum lies in the range 410–415nm and is probably due to the ligand–metal charge transfer transition. The absorption maxima at 520-594 for complexes are due to the d–d transition to ($^2Eg\rightarrow{}^2T_{2g}$) for the octahedral or distorted octahedral geometry[228,229]. (Figure- 2.3, 2.4)

2.5.3 Thermal Gravimetric Analysis (TGA)

Thermal Gravimetric (TG) analysis was used as a probe to proof the associated water or solvent molecules to be in the coordination sphere or in the crystalline form. Thermo gravimetric analysis of metal chelates is very important tool for assessing their thermal stability. TGA is generally carried out in nitrogen atmosphere at different heating rates. The loss in weight of the complex material with increase in temperature forms a TG curve. Normally sample starts loosing weight at a slow rate up to a particular temperature. Thereafter, the rate of loss in weight becomes higher over a narrow range of temperature. After this stage the loss in weight levels off. The shape of TG curve depends upon the nature of the degradation reaction. The percentage weight loss at different temperature and the percentage weight left at 800°C for all the synthesized chelates were studied. In case of all the metal chelates the curved showed first weight loss corresponding to coordinate water molecules in the temperature range of 50-200^{o}C. The presence of water molecules in the metal chelates have also been supported by IR studies[230,231].

All the synthesized metal chelates are decomposed in three stages.

The first stage with loss of the total weight is due to the removal of water molecules. The second stage corresponds to the decomposition of ligand. The third stage the loss of the total weight is due to the decomposition of the complex and formation of metal oxides. (Figure- 2.9, 2.10)

2.5.4 Elemental Analysis

Elemental analysis (C, H, N and M) of the compounds was carried out on Elemental analyzer Perkin Elmer 2400 at SAIF, Punjab University, Chandigarh, and the results are in agreement with the structures assigned.

2.5.5 Magnetic Moments

The magnetic moments of the synthesized metal chelates are given in spectral characterization. The general structural formula of the complexes is shown in figures. It was determined that all complexes were paramagnetic. The magnetic moments of the Copper complexes are in the 1.86–1.91 B.M. range at room temperature. These values can be assigned to one unpaired electron and offer evidence for the distorted octahedral geometry of copper complexes. The magnetic moments of the Nickel complexes lie in the 2.92–3.05 B.M. range at room temperature, corresponding to two unpaired electrons. These values are attributed to octahedral nickel complexes. The magnetic moments of the cobalt complexes were found to be in the 4.22–4.48 B.M. range at room temperature. These results agree with the reported values for octahedral cobalt(II) complexes. Infrared spectra and thermogravimetric studies showed the presence of two coordinated water molecule. Molecular models indicate that there is presence of steric strains as a result of the octahedral and distorted octahedral geometry for the metal chelates[232,233].

2.5.6 ESI Mass Spectra

Electrospray Ionization (ESI) was first employed more than 20 years ago, but it is fairly recently that it became a routine technique for the soft ionization of a wide range of polar analytes, including biomolecules. For this technique, the analyte is usually dissolved in a mixture of an organic solvent and water with a pH modifier. The presence of the pH modifier ensures that ionization takes place in the solution state. This is the only common case where ionization occurs before ion vaporization. Because ionization has taken place in the solution state by protonation or deprotonation of the analyte the molecular species detected is almost exclusively [M+H$^+$] in positive ion mode and [M-H]$^-$ in negative ion mode, and both these species undergo very little fragmentation. The advantage of ESI mass is that it often gives multiply charged ions for large molecules with many ionizable functional groups. This has the advantage of lowering the m/z ratio and there by allowing the determination of the masses of large molecule without the need for a detector that has a large mass range[234]. It is very sensitive to contaminants in the solvents, particularly alkali metals, and we often see ions which corresponds to [M+Na]$^+$ or [M+NH$_4$]$^+$. (Figure- 2.5-2.8)

2.5.7 Electron Spin Resonance (ESR)

The EPR parameters of copper complexes: there was a general correspondence between the powder and solution spectra, however, the $g\perp$ region was well resolved in solution. The spectra were indicative of rhombic distortion from axial symmetry. Owing to coordination of two different kinds of atoms (O and N) with the metal ion. The spectra were characteristic of magnetically dilute system with Cu(II) ions in the $d_{x^2-y^2}$ ground state. Hyperfine as a result of nitrogen were visible on the main absorption line, $g\perp$, confirming the coordination through N. based on the experimental evidence thus obtained the complexes were characterized as six coordinates with the fifth and sixth position occupied by two water molecules[235].

The ESR spectra of all copper complex show intense broad bands with g = 2.00277, the value of g and the shape of the ESR signals suggest octahedral coordination around the Cu(II) ions. (Figure- 2.11)

2.6 SPECTRAL CHARACTERIZATION OF METAL CHELATES

(1) Complex-1: $[Co(L^1)_2(H_2O)_2]$

IR (KBr) cm^{-1}: 3480 (-OH of H_2O), 1610 (-C=N-), 590 (M–N), 490 (M–O), 3012 (Ar C-H), 2920 (C-H of CH_3), 1440-1615 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 365, 412, 550, 650.

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700
Weight loss %	4.50	9.60	24.98	50.80	68.70	82.10	90.90

Elemental analysis, Calculated: C, 57.47; H, 4.17; N, 6.09; Co, 6.41, **Found:** C, 57.30; H, 4.10; N, 5.96; Co, 6.50.

Magnetic moment (μ): 4.25 B.M.

ESI mass[m/e (%)]: 956.54

(2) Complex-2: $[Ni(L^1)_2(H_2O)_2]$

IR (KBr) cm^{-1}: 3510 (-OH of H_2O), 1608 (-C=N-), 580 (M–N), 488 (M–O), 3015 (Ar C-H), 2938 (C-H of CH_3), 1440-1610 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 360, 410, 473, 675.

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700
Weight loss %	4.90	9.20	23.83	51.60	69.60	82.00	89.70

Elemental analysis, Calculated: C, 59.83; H, 3.88; N, 6.34; Ni, 6.65, **Found:** C, 59.93; H, 3.73; N, 6.21; Ni, 6.55.

Magnetic moment (μ): 2.90 B.M.

ESI mass[m/e (%)]: 920.27

(3) Complex-3: $[Cu(L^1)_2(H_2O)_2]$

IR (KBr) cm^{-1}: 3500 (-OH of H_2O), 1612 (-C=N-), 592 (M–N), 490 (M–O), 3000 (Ar C-H), 2935 (C-H of CH_3), 1430-1590 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 364, 410, 520.

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700
Weight loss %	4.70	9.70	25.30	50.60	66.60	84.10	92.80

Elemental analysis, Calculated: C, 59.50; H, 3.86; N, 6.31; Cu, 7.16, **Found:** C, 59.30; H, 3.73; N, 6.15; Cu, 7.22,

Magnetic moment (µ): 1.90 B.M.

ESI mass[m/e (%)]: 925.15

(4) Complex-4: $[Co(L^2)_2(H_2O)_2]$

IR (KBr) cm^{-1}: 3515 (-OH of H_2O), 1608 (-C=N-), 595 (M–N), 495 (M–O), 3013 (Ar C-H), 2931 (C-H of CH_3), 1440-1610 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 360, 410, 515, 550.

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700
Weight loss %	4.40	9.55	25.10	50.80	69.70	82.00	92.70

Elemental analysis, Calculated: C, 64.63; H, 4.19; N, 6.85; Co, 7.21, **Found:** C, 64.50; H, 4.13; N, 6.90; Co, 7.30.

Magnetic moment (µ): 4.28 B.M.

ESI mass[m/e (%)]: 854.70

(5) Complex-5: $[Ni(L^2)_2(H_2O)_2]$

IR (KBr) cm^{-1}: 3495 (-OH of H_2O), 1610 (-C=N-), 592 (M–N), 490 (M–O), 3007 (Ar C-H), 2929 (C-H of CH_3), 1435-1605 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 365, 410, 470, 760

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700
Weight loss %	4.50	9.80	25.00	50.80	69.60	83.10	91.90

Elemental analysis, Calculated: C, 64.65; H, 4.19; N, 6.85; Ni, 7.18, **Found:** C, 64.50; H, 4.10; N, 6.80; Ni, 7.17.

Magnetic moment (μ): 2.98 B.M.

ESI mass: 854.50

(6) Complex-6: [Cu(L^2)$_2$(H_2O)$_2$]

IR (KBr) cm^{-1}: 3510 (-OH of H_2O), 1605 (-C=N-), 591 (M–N), 488 (M–O), 3014 (Ar C-H), 2931 (C-H of CH_3), 1440-1600 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 365, 410, 594.

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700
Weight loss %	4.41	9.62	25.03	50.89	69.81	83.16	92.91

Elemental analysis, Calculated: C, 64.27; H, 4.17; N, 6.81; Cu, 7.73, **Found:** C, 64.11; H, 4.10; N, 6.74; Cu, 7.55,

Magnetic moment (μ): 1.91 B.M.

ESI mass[m/e (%)]: 859.50

(7) Complex-7: [Co(L^3)$_2$(H_2O)$_2$]

IR (KBr) cm^{-1}: 3492 (-OH of H_2O), 1607 (-C=N-), 588 (M–N), 491 (M–O), 3014 (Ar C-H), 2920 (C-H of CH_3), 1430-1608 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 355, 430, 570, 610.

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700
Weight loss %	4.44	9.30	25.00	50.90	68.80	81.95	90.60

Elemental analysis, Calculated: C, 42.30; H, 2.74; N, 4.48; Co, 4.72, **Found:** C, 42.22; H, 2.61; N, 4.37; Co, 4.60.

Magnetic moment (μ): 4.23 B.M.

ESI mass[m/e (%)]: 1286.39

(8) Complex-8: [Ni(L^3)$_2$(H_2O)$_2$]

IR (KBr) cm^{-1}: 3510 (-OH of H_2O), 1611 (-C=N-), 595 (M–N), 490 (M–O), 3010 (Ar C-H), 2935 (C-H of CH_3), 1450-1615 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 365, 410, 475, 670.

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700
Weight loss %	4.30	9.40	24.98	50.55	69.72	83.10	91.90

Elemental analysis, Calculated: C, 42.31; H, 2.74; N, 4.49; Ni, 4.70, **Found:** C, 42.17; H, 2.79; N, 4.38; Ni, 4.86.

Magnetic moment (μ): 2.92 B.M.

ESI mass[m/e (%)]: 1286.10

(9) Complex-9: $[Cu(L^3)_2(H_2O)_2]$

IR (KBr) cm^{-1}: 3508 (-OH of H_2O), 1600 (-C=N-), 592 (M–N), 490 (M–O), 3015 (Ar C-H), 2940 (C-H of CH_3), 1445-1609 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 350, 415, 586.

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700
Weight loss %	4.71	9.45	25.10	51.00	69.70	83.00	92.00

Elemental analysis, Calculated: C, 42.15; H, 2.73; N, 4.47; Cu, 5.07, **Found:** C, 42.04; H, 2.66; N, 4.50; Cu, 4.98.

Magnetic moment (μ): 1.89 B.M.

ESI mass[m/e (%)]: 1290.90

(10) Complex-10: $[Co(L^4)_2(H_2O)_2]$

IR (KBr) cm^{-1}: 3510 (-OH of H_2O), 1606 (-C=N-), 595 (M–N), 490 (M–O), 3006 (Ar C-H), 2920 (C-H of CH_3), 1450-1600 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 365, 412, 550, 650.

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700
Weight loss %	4.60	9.21	24.87	50.89	69.20	82.95	92.30

Elemental analysis, Calculated: C, 49.79; H, 3.23; N, 5.28; Co, 5.55, **Found:** C, 49.90; H, 3.12; N, 5.14; Co, 5.66.

Magnetic moment (μ): 4.40 B.M.

ESI mass: 1098.31

(11) Complex-11: $[Ni(L^4)_2(H_2O)_2]$

IR (KBr) cm^{-1}: 3480 (-OH of H_2O), 1610 (-C=N-), 590 (M–N), 490 (M–O), 3012 (Ar C-H), 2920 (C-H of CH_3), 1440-1615 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 360, 410, 473, 675.

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700
Weight loss %	4.71	9.41	25.12	50.90	69.70	83.00	92.70

Elemental analysis, Calculated: C, 49.81; H, 3.23; N, 5.28; Ni, 5.53, **Found:** C, 49.92; H, 3.31; N, 5.13; Ni, 5.40.

Magnetic moment (μ): 3.00 B.M.

ESI mass[m/e (%)]: 1098.10

(12) Complex-12: $[Cu(L^4)_2(H_2O)_2]$

IR (KBr) cm^{-1}: 3510 (-OH of H_2O), 1608 (-C=N-), 580 (M–N), 488 (M–O), 3015 (Ar C-H), 2938 (C-H of CH_3), 1440-1610 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 364, 410, 520.

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700
Weight loss %	4.77	9.80	25.33	50.90	69.88	82.98	91.88

Elemental analysis, Calculated: C, 49.58; H, 3.22; N, 5.26; Cu, 5.96, **Found:** C, 49.67; H, 3.12; N, 5.33; Cu, 6.03.

Magnetic moment (μ): 1.86 B.M.

ESI mass[m/e (%)]: 1110.95

(13) Complex-13: $[Co(L^5)_2(H_2O)_2]$

IR (KBr) cm^{-1}: 3500 (-OH of H_2O), 1612 (-C=N-), 592 (M–N), 490 (M–O), 3000 (Ar C-H), 2935 (C-H of CH_3), 1430-1590 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 360, 410, 515, 550.

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700
Weight loss %	4.91	9.62	24.88	52.30	70.10	83.90	93.00

Elemental analysis, Calculated: C, 71.90; H, 5.78; N, 6.99; Co, 7.35, **Found:** C, 71.73; H, 5.65; N, 6.76; Co, 7.48.

Magnetic moment (μ): 4.46 B.M.

ESI mass[m/e (%)]: 838.85

(14) Complex-14: [Ni(L^5)$_2$(H_2O)$_2$]

IR (KBr) cm^{-1}: 3515 (-OH of H_2O), 1608 (-C=N-), 595 (M–N), 495 (M–O), 3013 (Ar C-H), 2931 (C-H of CH_3), 1440-1610 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 365, 410, 470, 760

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700
Weight loss %	4.30	9.90	24.30	51.00	69.89	81.99	92.90

Elemental analysis, Calculated: C, 71.92; H, 5.78; N, 6.99; Ni, 7.32, **Found:** C, 71.90; H, 5.63; N, 7.09; Ni, 7.46.

Magnetic moment (μ): 3.05 B.M.

ESI mass[m/e (%)]: 838.10

(15) Complex-15: [Cu(L^5)$_2$(H_2O)$_2$]

IR (KBr) cm^{-1}: 3495 (-OH of H_2O), 1610 (-C=N-), 592 (M–N), 490 (M–O), 3007 (Ar C-H), 2929 (C-H of CH_3), 1435-1605 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 365, 410, 594.

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700
Weight loss %	4.41	9.61	25.02	50.89	69.80	83.15	92.91

Elemental analysis, Calculated: C, 71.49; H, 5.75; N, 6.95; Cu, 7.88, **Found:** C, 71.35; H, 5.68; N, 6.86; Cu, 8.00.

Magnetic moment (μ): 1.88 B.M.

ESI mass[m/e (%)]: 843.45

(16) Complex-16: $[Co(L^6)_2(H_2O)_2]$

IR (KBr) cm^{-1}: 3510 (-OH of H_2O), 1605 (-C=N-), 591 (M–N), 488 (M–O), 3014 (Ar C-H), 2931 (C-H of CH_3), 1440-1600 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 355, 430, 570, 610.

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700
Weight loss %	4.50	9.60	24.98	50.80	68.70	82.10	90.90

Elemental analysis, Calculated: C, 66.58; H, 5.35; N, 6.47; Co, 6.81, **Found:** C, 66.66; H, 5.30; N, 6.35; Co, 6.60.

Magnetic moment (μ): 4.25 B.M.

ESI mass[m/e (%)]: 902.90

(17) Complex-17: $[Ni(L^6)_2(H_2O)_2]$

IR (KBr) cm^{-1}: 3492 (-OH of H_2O), 1607 (-C=N-), 588 (M–N), 491 (M–O), 3014 (Ar C-H), 2920 (C-H of CH_3), 1430-1608 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 365, 410, 475, 670.

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700
Weight loss %	4.90	9.20	23.83	51.60	69.60	82.00	89.70

Elemental analysis, Calculated: C, 66.60; H, 5.36; N, 6.47; Ni, 6.78, **Found:** C, 66.54; H, 5.30; N, 6.33; Ni, 6.89.

Magnetic moment (μ): 2.90 B.M.

ESI mass[m/e (%)]: 902.60

(18) Complex-18: $[Cu(L^6)_2(H_2O)_2]$

IR (KBr) cm^{-1}: 3510 (-OH of H_2O), 1611 (-C=N-), 595 (M–N), 490 (M–O), 3010 (Ar C-H), 2935 (C-H of CH_3), 1450-1615 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 350, 415, 586.

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700
Weight loss %	4.70	9.70	25.30	50.60	66.60	84.10	92.80

Elemental analysis, Calculated: C, 66.23; H, 5.33; N, 6.44; Cu, 7.30, **Found:** C, 66.18; H, 5.20; N, 6.52; Cu, 7.44.

Magnetic moment (μ): 1.90 B.M.

ESI mass[m/e (%)]: 907.45

(19) Complex-19: $[Co(L^7)_2(H_2O)_2]$

IR (KBr) cm^{-1}: 3508 (-OH of H_2O), 1600 (-C=N-), 592 (M–N), 490 (M–O), 3015 (Ar C-H), 2940 (C-H of CH_3), 1445-1609 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 365, 412, 550, 650.

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700
Weight loss %	4.40	9.55	25.10	50.80	69.70	82.00	92.70

Elemental analysis, Calculated: C, 51.75; H, 2.96; N, 5.49; Co, 5.77, **Found:** C, 51.61; H, 2.86; N, 5.42; Co, 5.88.

Magnetic moment (μ): 4.28 B.M.

ESI mass[m/e (%)]: 1058.30

(20) Complex-20: $[Ni(L^7)_2(H_2O)_2]$

IR (KBr) cm^{-1}: 3510 (-OH of H_2O), 1606 (-C=N-), 595 (M–N), 490 (M–O), 3006 (Ar C-H), 2920 (C-H of CH_3), 1450-1600 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 360, 410, 473, 675.

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700
Weight loss %	4.50	9.80	25.00	50.80	69.60	83.10	91.90

Elemental analysis, Calculated: C, 51.76; H, 2.96; N, 5.49; Ni, 5.75, **Found:** C, 51.70; H, 2.90; N, 5.57; Ni, 5.67.

Magnetic moment (μ): 2.98 B.M.

ESI mass[m/e (%)]: 1058.10

(21) Complex-21: $[Cu(L^7)_2(H_2O)_2]$

IR (KBr) cm^{-1}: 3480 (-OH of H_2O), 1610 (-C=N-), 590 (M–N), 490 (M–O), 3012 (Ar C-H), 2920 (C-H of CH_3), 1440-1615 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 364, 410, 520.

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700
Weight loss %	4.41	9.62	25.03	50.89	69.81	83.16	92.91

Elemental analysis, Calculated: C, 51.51; H, 2.95; N, 5.46; Cu, 6.19, **Found:** C, 51.39; H, 3.03; N, 5.33; Cu, 6.30.

Magnetic moment (μ): 1.91 B.M.

ESI mass[m/e (%)]: 1062.90

(22) Complex-22: $[Co(L^8)_2(H_2O)_2]$

IR (KBr) cm^{-1}: 3510 (-OH of H_2O), 1608 (-C=N-), 580 (M–N), 488 (M–O), 3015 (Ar C-H), 2938 (C-H of CH_3), 1440-1610 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 360, 410, 515, 550.

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700
Weight loss %	4.44	9.30	25.00	50.90	68.80	81.95	90.60

Elemental analysis, Calculated: C, 59.40; H, 3.40; N, 6.30; Co 6.62, **Found:** C, 59.32; H, 3.29; N, 6.20; Co, 6.74.

Magnetic moment (μ): 4.23 B.M.

ESI mass[m/e (%)]: 926.66

(23) Complex-23: $[Ni(L^8)_2(H_2O)_2]$

IR (KBr) cm^{-1}: 3500 (-OH of H_2O), 1612 (-C=N-), 592 (M–N), 490 (M–O), 3000 (Ar C-H), 2935 (C-H of CH_3), 1430-1590 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 365, 410, 470, 760

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700
Weight loss %	4.30	9.40	24.98	50.55	69.72	83.10	91.90

Elemental analysis, Calculated: C, 59.42; H, 3.40; N, 6.30; Ni, 6.60, **Found:** C, 59.30; H, 3.30; N, 6.41; Ni, 6.71.

Magnetic moment (μ): 2.92 B.M.

ESI mass[m/e (%)]: 926.41

(24) Complex-24: $[Cu(L^8)_2(H_2O)_2]$

IR (KBr) cm^{-1}: 3515 (-OH of H_2O), 1608 (-C=N-), 595 (M–N), 495 (M–O), 3013 (Ar C-H), 2931 (C-H of CH_3), 1440-1610 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 365, 410, 594.

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700
Weight loss %	4.71	9.45	25.10	51.00	69.70	83.00	92.00

Elemental analysis, Calculated: C, 59.10; H, 3.38; N, 6.27; Cu, 7.11, **Found:** C, 59.00; H, 3.23; N, 6.16; Cu, 7.28.

Magnetic moment (μ): 1.89 B.M.

ESI mass[m/e (%)]: 931.31

(25) Complex-25: $[Co(L^9)_2(H_2O)_2]$

IR (KBr) cm^{-1}: 3495 (-OH of H_2O), 1610 (-C=N-), 592 (M–N), 490 (M–O), 3007 (Ar C-H), 2929 (C-H of CH_3), 1435-1605 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 355, 430, 570, 610.

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700
Weight loss %	4.60	9.21	24.87	50.89	69.20	82.95	92.30

Elemental analysis, Calculated: C, 72.80; H, 6.34; N, 6.53; Co, 6.87, **Found:** C, 72.72; H, 6.41; N, 6.60; Co, 6.60.

Magnetic moment (μ): 4.40 B.M.

ESI mass[m/e (%)]: 894.94

(26) Complex-26: $[Ni(L^9)_2(H_2O)_2]$

IR (KBr) cm^{-1}: 3510 (-OH of H_2O), 1605 (-C=N-), 591 (M–N), 488 (M–O), 3014 (Ar C-H), 2931 (C-H of CH_3), 1440-1600 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 365, 410, 475, 670.

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700
Weight loss %	4.71	9.41	25.12	50.90	69.70	83.00	92.70

Elemental analysis, Calculated: C, 72.82; H, 6.35; N, 6.53; Ni, 6.84, **Found:** C, 72.72; H, 6.28; N, 6.50; Ni, 7.00.

Magnetic moment (μ): 3.01 B.M.

ESI mass[m/e (%)]: 894.74

(27) Complex-27: $[Cu(L^9)_2(H_2O)_2]$

IR (KBr) cm^{-1}: 3492 (-OH of H_2O), 1607 (-C=N-), 588 (M–N), 491 (M–O), 3014 (Ar C-H), 2920 (C-H of CH_3), 1430-1608 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 350, 415, 586.

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700
Weight loss %	4.77	9.80	25.33	50.90	69.88	82.98	91.88

Elemental analysis, Calculated: C, 72.41; H, 6.31; N, 6.50; Cu, 7.37, **Found:** C, 72.50; H, 6.43; N, 6.37; Cu, 7.50.

Magnetic moment (μ): 1.86 B.M.

ESI mass[m/e (%)]: 899.60

(28) Complex-28: $[Co(L^{10})_2(H_2O)_2]$

IR (KBr) cm^{-1}: 3510 (-OH of H_2O), 1611 (-C=N-), 595 (M–N), 490 (M–O), 3010 (Ar C-H), 2935 (C-H of CH_3), 1450-1615 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 365, 412, 550, 650.

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700
Weight loss %	4.30	9.90	24.30	51.00	69.89	81.99	92.90

Elemental analysis, Calculated: C, 55.13; H, 4.05; N, 10.71; Co, 5.64, **Found:** C, 55.07; H, 3.97; N, 10.55; Co, 5.80.

Magnetic moment (µ): 4.46 B.M.

ESI mass[m/e (%)]: 1082.82

(29) Complex-29: $[Ni(L^{10})_2(H_2O)_2]$

IR (KBr) cm^{-1}: 3508 (-OH of H_2O), 1600 (-C=N-), 592 (M–N), 490 (M–O), 3015 (Ar C-H), 2940 (C-H of CH_3), 1445-1609 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 360, 410, 473, 675.

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700
Weight loss %	4.77	9.80	25.33	50.90	69.88	82.98	91.88

Elemental analysis, Calculated: C, 55.14; H, 4.05; N, 10.72; Ni, 5.61, **Found:** C, 55.05; H, 4.10; N, 10.84; Ni, 5.75.

Magnetic moment (µ): 3.05 B.M.

ESI mass[m/e (%)]: 1082.58

(30) Complex-30: $[Cu(L^{10})_2(H_2O)_2]$

IR (KBr) cm^{-1}: 3510 (-OH of H_2O), 1606 (-C=N-), 595 (M–N), 490 (M–O), 3006 (Ar C-H), 2920 (C-H of CH_3), 1450-1600 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 364, 410, 520.

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700
Weight loss %	4.41	9.61	25.02	50.89	69.80	83.15	92.91

Elemental analysis, Calculated: C, 54.88; H, 4.03; N, 10.67; Cu, 6.05, **Found:** C, 54.66; H, 3.89; N, 10.55; Cu, 6.17.

Magnetic moment (µ): 1.88 B.M.

ESI mass[m/e (%)]: 1087.44

2.7 SPECTRA

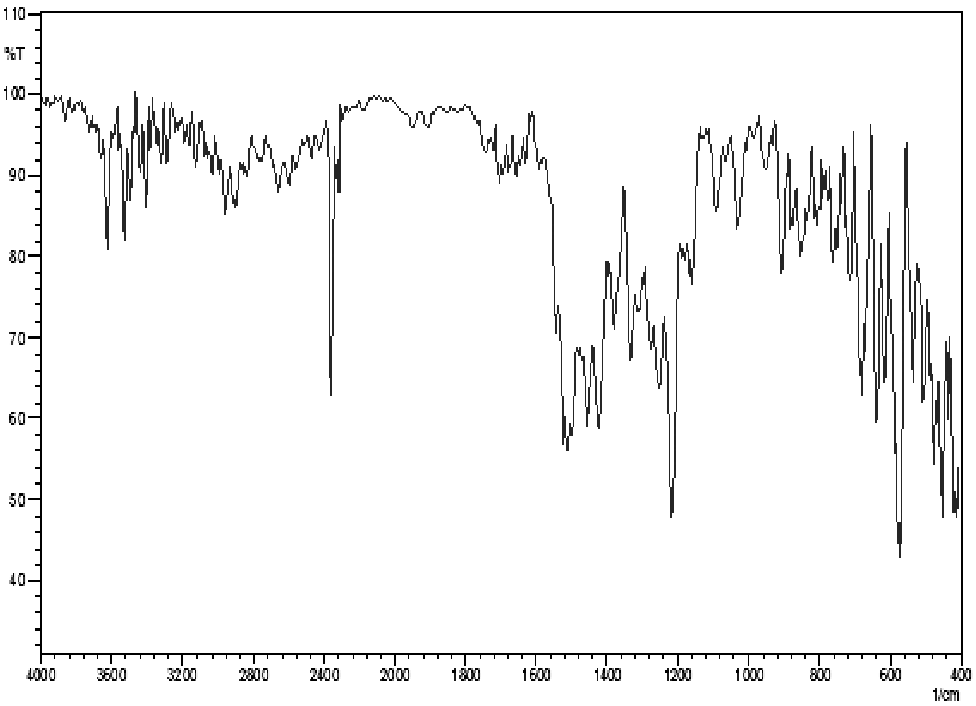


Figure-2.1

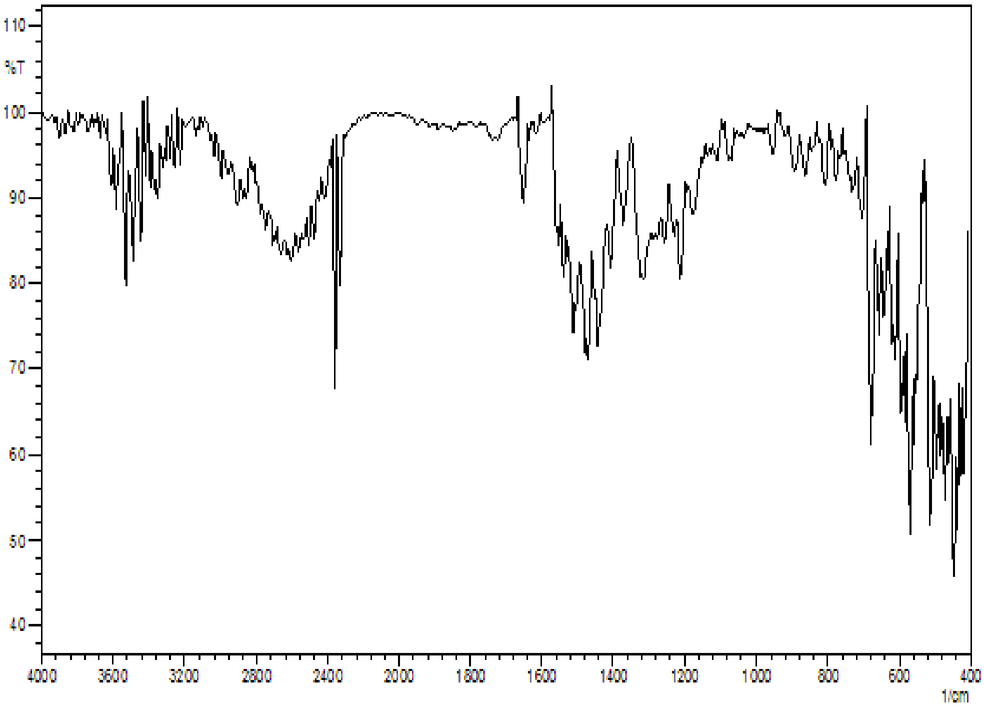


Figure-2.2

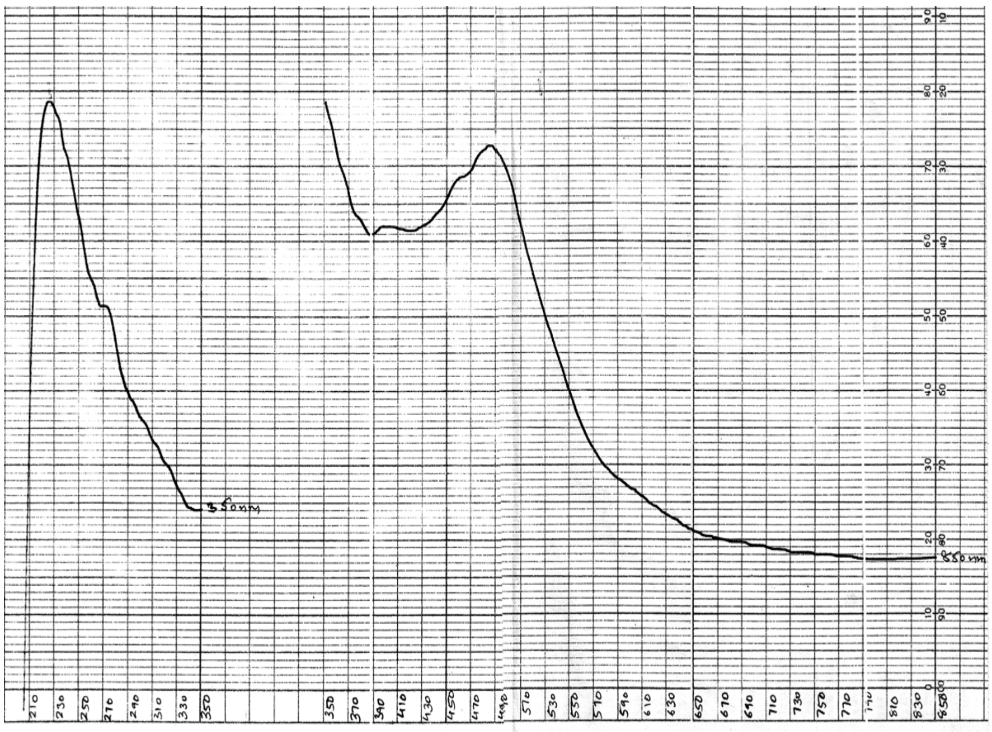
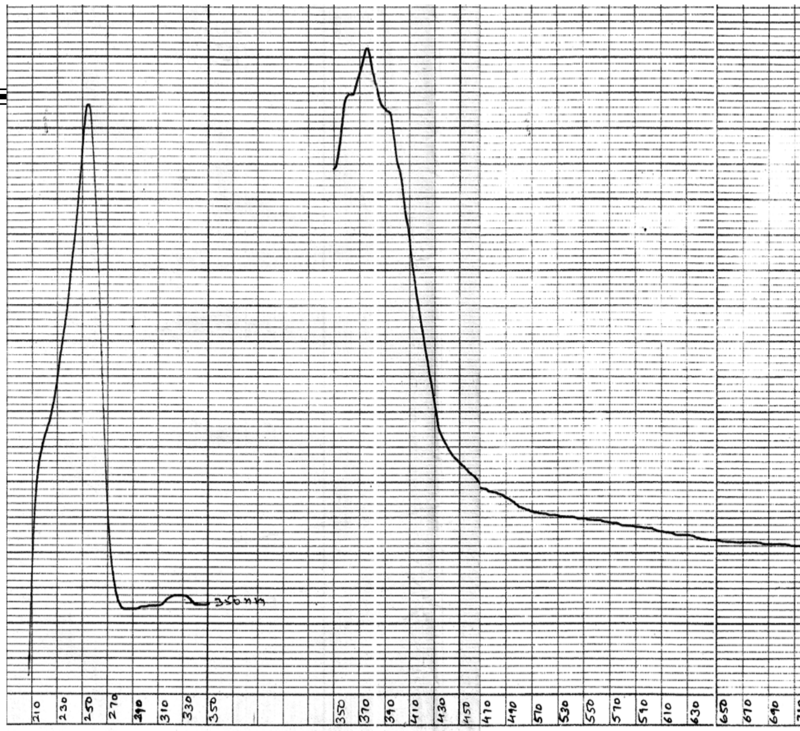


Figure-2.3



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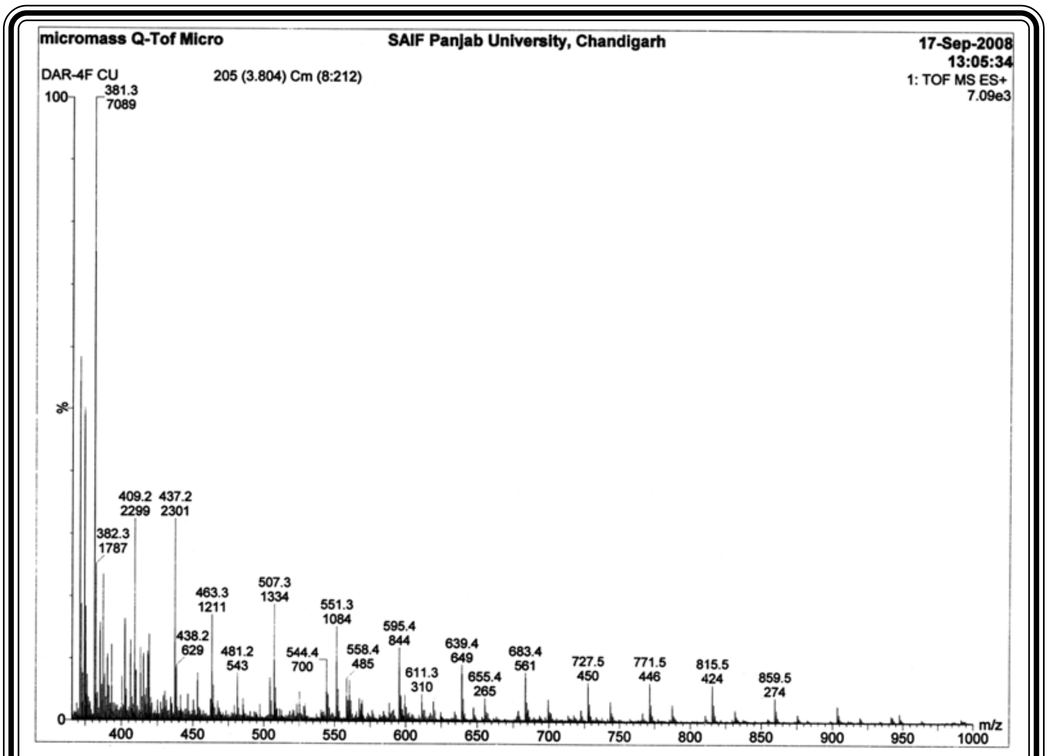


Figure-2.5

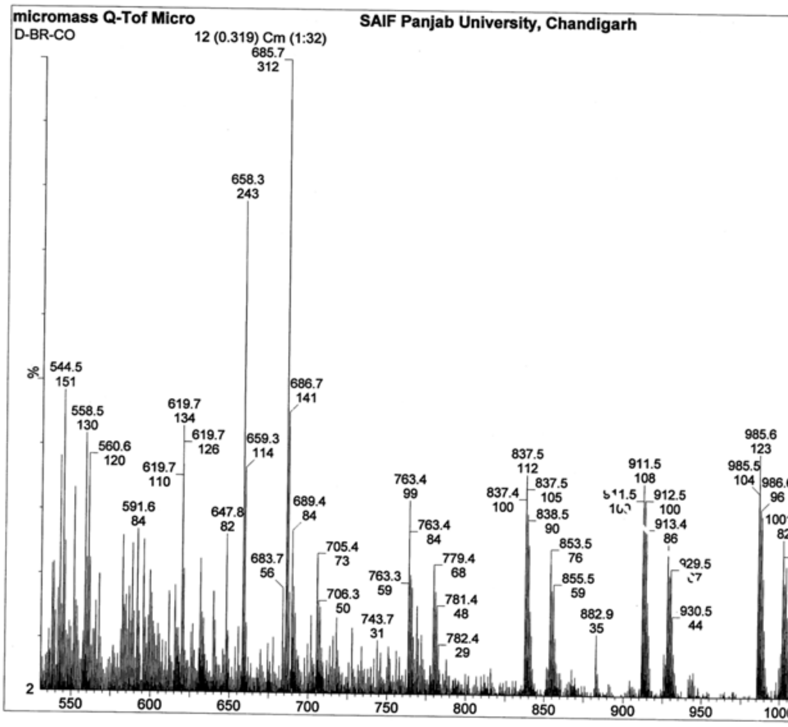
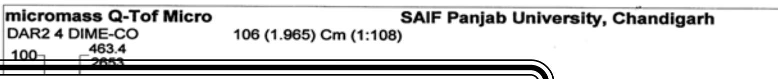
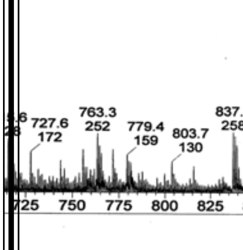


Figure-2.6

Figure-2.7





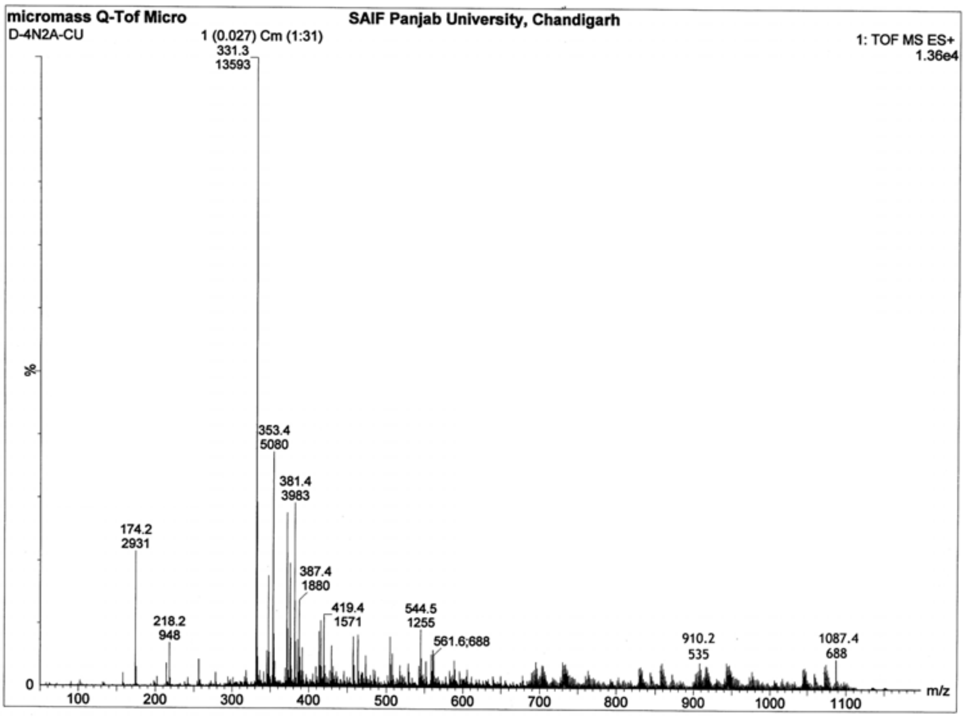


Figure-2.8

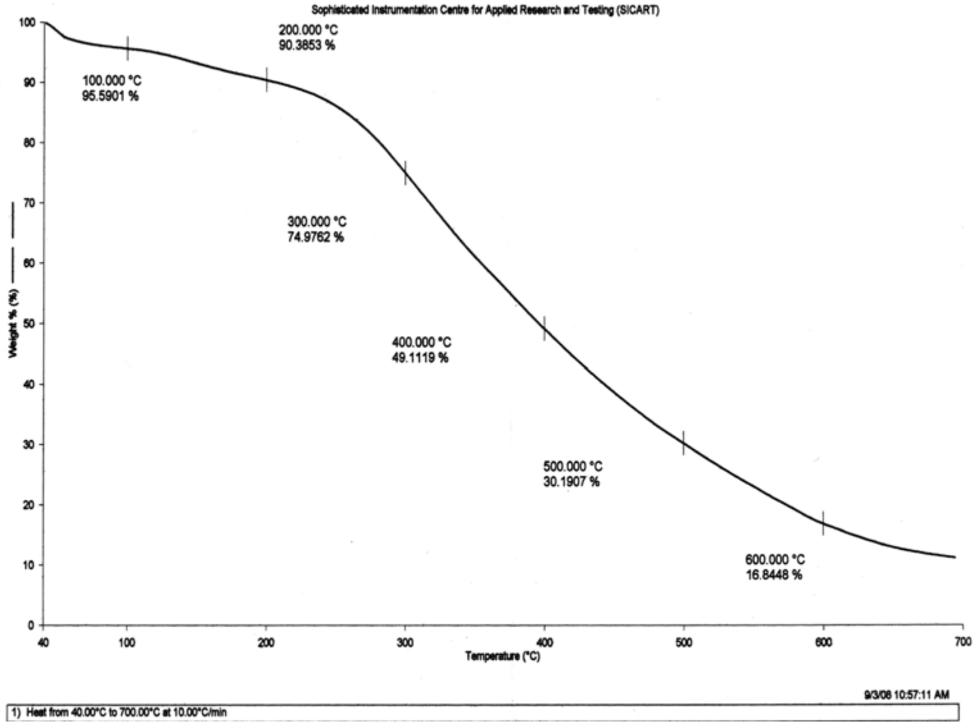


Figure-2.9

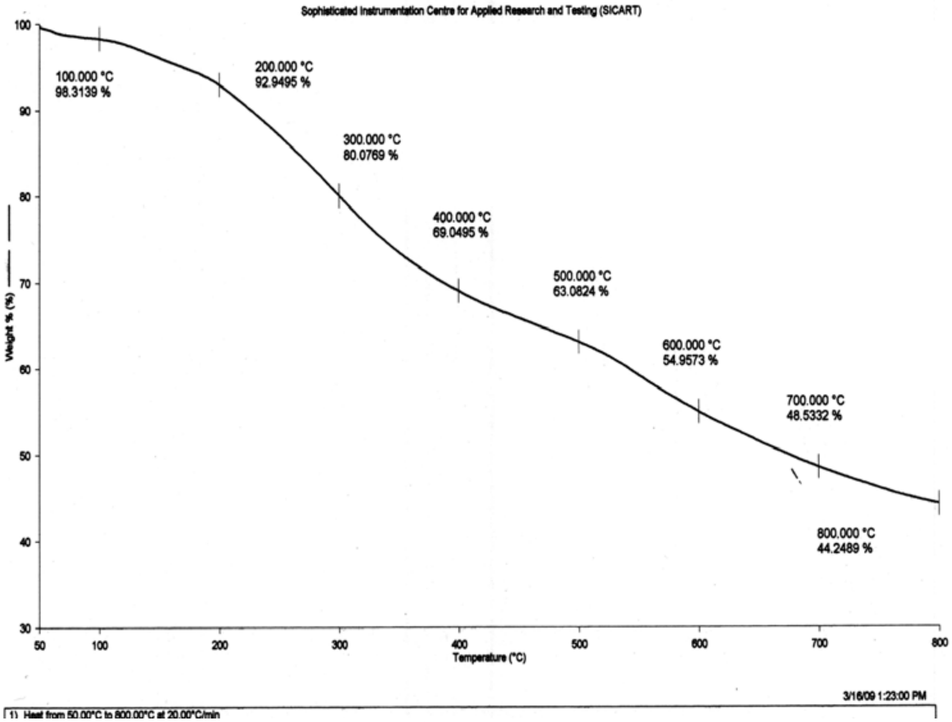
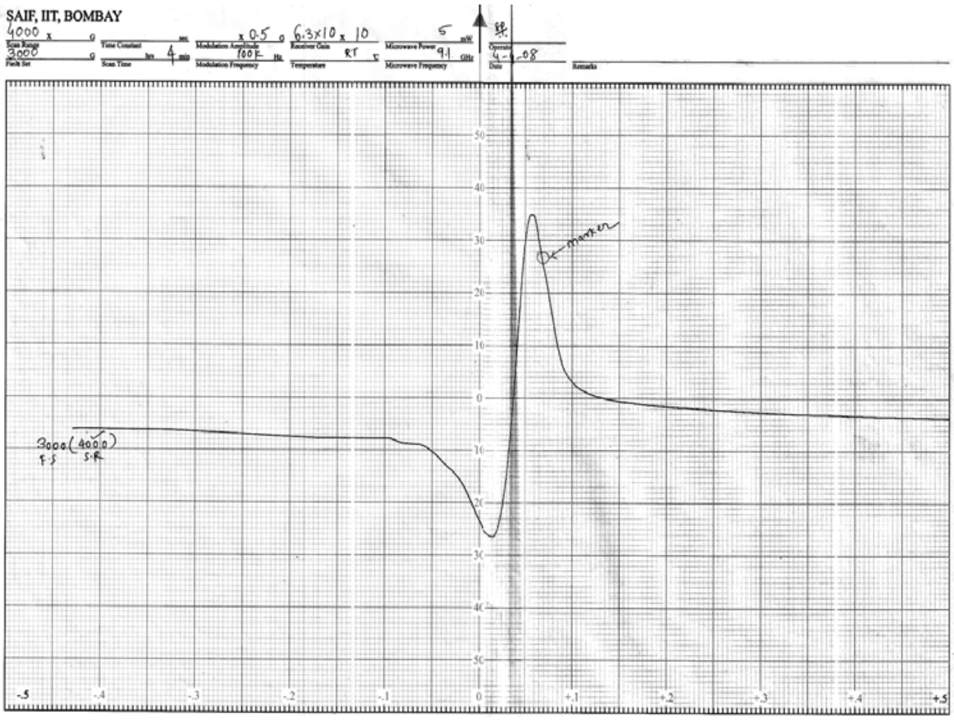


Figure-2.10



SAIF, IIT, BOMBAY

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Receiver Gain: 6.3×10 x 10
Temperature: RT °
Microwave Power: 5 mW
Microwave Frequency: 9.1 GHz
Operator:
Date: 4-[illegible]-08
Remarks

Figure-2.11

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CHAPTER 3

SYNTHESIS AND CHARACTERIZATION OF MIXED LIGAND METAL COMPLEXES

3.1 Introduction
3.2 Reaction Scheme
3.3 Experimental
3.4 Physical Data Table
3.5 Spectral Study
3.6 Spectral Characterization of Metal Complexes
3.7 Spectra
3.8 References

3.1 INTRODUCTION

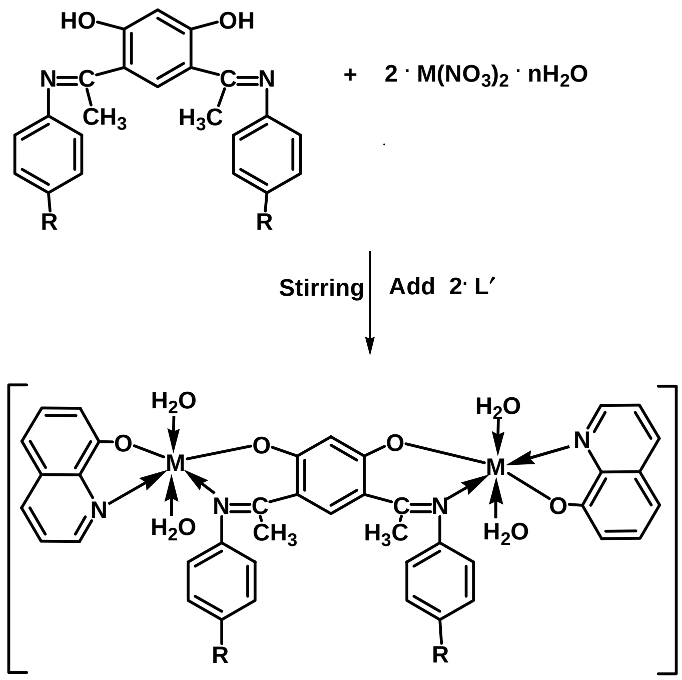
Transition metal Schiff-base complexes are important stereo-chemical models in coordination chemistry due to their preparative accessibility and structural diversity [236–238]. A comprehensive review on cyclic and acyclic Schiff-bases and related derivatives appeared recently, particularly dealing with the development of synthetic procedures for the preparation of mono-, di- and polynuclear Schiff-base complexes and their reduced analogues. Some Schiff-base complexes show catalytic properties, or act as oxygen carriers and antifungal agents increased by the presence of hydroxyl groups in the ligands [239–246].

Investigations concerning the structural configuration and chemical properties of polynuclear transition metal compounds have aroused considerable interest mainly because of their implications for topics such as the nature of orbital interactions, electron transfer in redox processes, and biological electron transport chains[247-249]. Considerable attention has focussed on the chemistry of polynuclear Cu(II) complexes due to the presence of multicopper active sites in blue copper oxidases(e.g., laccase, ascorbate oxidase, and ceruloplasmin) and in the development of new inorganic materials showing molecular ferromagnetism [250-252].

8-Hydroxyquinoline and 1,10-Phenanthroline have been extensively used as a ligand in both analytical and preparative coordination chemistry. As an important building block, both the ligands units play an important role in the development of the supramolecular chemistry[253-255]. The metal chelating properties of 1,10-phenanthroline have been widely utilized in all aspects of coordination chemistry as well as in its recent applications to develop biomimetic models of metalloenzymes and to prepare supromolecules, self-assembling systems or metal complexes with interesting anticancer properties[256,257].

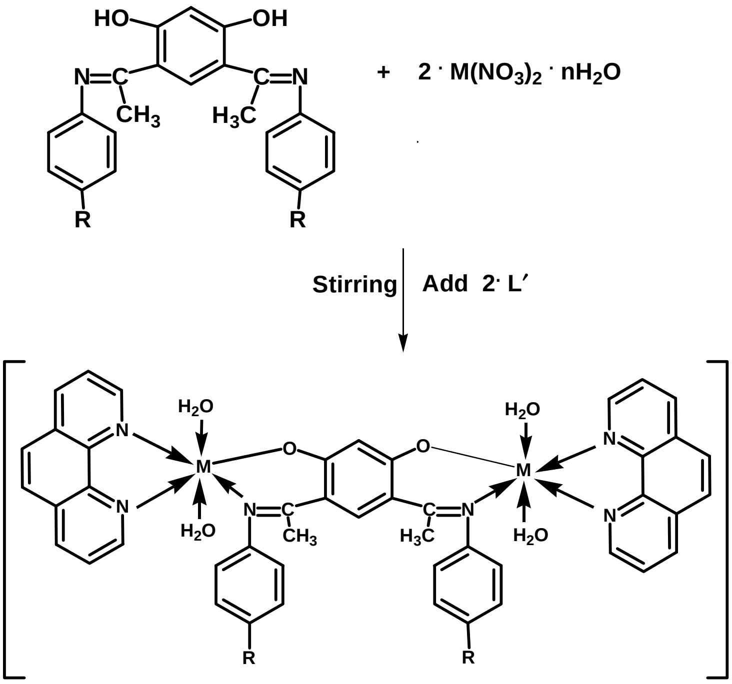
3.2 REACTION SCHEME

The syntheric route of schiff base mixed ligand complex of Co(II), Ni(II) and Cu(II) is as follows.



Where R = -F, -Br, $-CH_3$, $-OCH_3$
M = Co(II), Ni(II), Cu(II)
L′ = 8-Hydroxy Quinoline

SCHEME-1



Where R = -F, -Br, $-CH_3$, $-OCH_3$
M = Co(II), Ni(II), Cu(II)
L′ = 1,10-Phenanthroline

SCHEME-2

3.3 EXPERIMENTAL

The newly synthesized ligands from 4,6 diacetyl resorcinol and other ligands namely 8-hydroxy qunoline and 1,10-phenanthroline have been reacted with salts of Cobalt, Nickel and Copper to give mixed ligand metal complexes.

PART– I: SYNTHESIS OF METAL COMPLEX CONTAINING L′ = 8-HYDROXY QUINOLINE (Scheme-1)

3.3.1 Synthesis of H_2L^2 complexes

(I) Synthesis of Cobalt complex

An ethanolic solution of the cobalt(II) nitrate (hexahydrate) (5.82 gm, 2 mmol) (20 ml) was gradually added to an ethanolic (30 ml) solution of the ligand H_2L^2 (3.80 gm, 1 mmol) in 2:1 molar ratio and the solution was stirred for 1 h. An ethanolic solution of the other ligands L (L′ = 8-HQ) (2.90 gm, 2 mmol) was then added to the previous solution in the molar ratio 2:1. The solution was continuously stirred for 4h, during which the metal complex precipitated. The resulting precipitates were filtered off, washed with ethanol then diethyl ether and finally air-dried. The complex is air stable in the solid state and soluble in DMF and/or DMSO. The progress of reaction was monitored by TLC.

(II) Synthesis of Nickel complex

An ethanolic solution of the Nickel(II) nitrate (hexahydrate) (5.80 gm, 2 mmol) (20 ml) was gradually added to an ethanolic (30 ml) solution of the ligand H_2L^2 (3.80 gm, 1 mmol) in 2:1 molar ratio and the solution was stirred for 1 h. An ethanolic solution of the other ligands L′ (L′ = 8-HQ) (2.90 gm, 2 mmol) was then added to the previous solution in the molar ratio 2:1. The solution was continuously stirred for 4h, during which the metal complex precipitated. The resulting precipitates were filtered off, washed with ethanol then diethyl ether and finally air-dried. The complex is air stable in the solid state and soluble in DMF and/or DMSO. The progress of reaction was monitored by TLC.

(III) Synthesis of Copper complex

An ethanolic solution of the Copper(II) nitrate (trihydrate) (4.82 gm, 2 mmol) (20 ml) was gradually added to an ethanolic (30 ml) solution of the ligand H_2L^2 (3.80 gm, 1 mmol) in 2:1 molar ratio and the solution was stirred for 1 h. An ethanolic solution of the other ligands L′ (L′ = 8-HQ) (2.90 gm, 2 mmol) was then added to the previous solution in the molar ratio 2:1. The solution was continuously stirred for 4h, during which the metal complex precipitated. The resulting precipitates were filtered off, washed with ethanol then diethyl ether and finally air-dried. The complex is air stable in the solid state and soluble in DMF and/or DMSO. The progress of reaction was monitored by TLC.

3.3.2 Synthesis of H_2L^4 complexes

(I) Synthesis of Cobalt complex

An ethanolic solution of the cobalt(II) nitrate (hexahydrate) (5.82 gm, 2 mmol) (20 ml) was gradually added to an ethanolic (30 ml) solution of the ligand H_2L^4 (5.02 gm, 1 mmol) in 2:1 molar ratio and the solution was stirred for 1 h. An ethanolic solution of the other ligands L′ (L′ = 8-HQ) (2.90 gm, 2 mmol) was then added to the previous solution in the molar ratio 2:1. The solution was continuously stirred for 4h, during which the metal complex precipitated. The resulting precipitates were filtered off, washed with ethanol then diethyl ether and finally air-dried. The complex is air stable in the solid state and soluble in DMF and/or DMSO. The progress of reaction was monitored by TLC.

(II) Synthesis of Nickel complex

An ethanolic solution of the Nickel(II) nitrate (hexahydrate) (5.80 gm, 2 mmol) (20 ml) was gradually added to an ethanolic (30 ml) solution of the ligand H_2L^4 (5.02 gm, 1 mmol) in 2:1 molar ratio and the solution was stirred for 1 h. An ethanolic solution of the other ligands L′ (L′ = 8-HQ) (2.90 gm, 2 mmol) was then added to the previous solution in the molar ratio 2:1. The solution was continuously stirred for 4h, during which the metal complex precipitated. The resulting precipitates were filtered off, washed with ethanol then diethyl ether and finally air-dried. The complex is air stable in the solid state and soluble in DMF and/or DMSO. The progress of reaction was monitored by TLC.

(III) Synthesis of Copper complex

An ethanolic solution of the Copper(II) nitrate (trihydrate) (4.82 gm, 2 mmol) (20 ml) was gradually added to an ethanolic (30 ml) solution of the ligand H_2L^4 (5.02 gm, 1 mmol) in 2:1 molar ratio and the solution was stirred for 1 h. An ethanolic solution of the other ligands L′ (L′ = 8-HQ) (2.90 gm, 2 mmol) was then added to the previous solution in the molar ratio 2:1. The solution was continuously stirred for 4h, during which the metal complex precipitated. The resulting precipitates were filtered off, washed with ethanol then diethyl ether and finally air-dried. The complex is air stable in the solid state and soluble in DMF and/or DMSO. The progress of reaction was monitored by TLC.

3.3.3 Synthesis of H_2L^5 complexes

(I) Synthesis of Cobalt complex

An ethanolic solution of the cobalt(II) nitrate (hexahydrate) (5.82 gm, 2 mmol) (20 ml) was gradually added to an ethanolic (30 ml) solution of the ligand H_2L^5 (3.72 gm, 1 mmol) in 2:1 molar ratio and the solution was stirred for 1 h. An ethanolic solution of the other ligands L′ (L′ = 8-HQ) (2.90 gm, 2 mmol) was then added to the previous solution in the molar ratio 2:1. The solution was continuously stirred for 4h, during which the metal complex precipitated. The resulting precipitates were filtered off, washed with ethanol then diethyl ether and finally air-dried. The complex is air stable in the solid state and soluble in DMF and/or DMSO.

(II) Synthesis of Nickel complex

An ethanolic solution of the Nickel(II) nitrate (hexahydrate) (5.80 gm, 2 mmol) (20 ml) was gradually added to an ethanolic (30 ml) solution of the ligand H_2L^5 (3.72 gm, 1 mmol) in 2:1 molar ratio and the solution was stirred for 1 h. An ethanolic solution of the other ligands L′ (L′ = 8-HQ) (2.90 gm, 2 mmol) was then added to the previous solution in the molar ratio 2:1. The solution was continuously stirred for 4h, during which the metal complex precipitated. The resulting precipitates were filtered off, washed with ethanol then diethyl ether and finally air-dried. The complex is air stable in the solid state and soluble in DMF and/or DMSO. The progress of reaction was monitored by TLC.

(III) Synthesis of Copper complex

An ethanolic solution of the Copper(II) nitrate (trihydrate) (4.82 gm, 2 mmol) (20 ml) was gradually added to an ethanolic (30 ml) solution of the ligand H_2L^5 (3.72 gm, 1 mmol) in 2:1 molar ratio and the solution was stirred for 1 h. An ethanolic solution of the other ligands L′ (L′ = 8-HQ) (2.90 gm, 2 mmol) was then added to the previous solution in the molar ratio 2:1. The solution was continuously stirred for 4h, during which the metal complex precipitated. The resulting precipitates were filtered off, washed with ethanol then diethyl ether and finally air-dried. The complex is air stable in the solid state and soluble in DMF and/or DMSO. The progress of reaction was monitored by TLC.

3.3.4 Synthesis of H_2L^6 complexes

(I) Synthesis of Cobalt complex

An ethanolic solution of the cobalt(II) nitrate (hexahydrate) (5.82 gm, 2 mmol) (20 ml) was gradually added to an ethanolic (30 ml) solution of the ligand H_2L^6

(4.04 gm, 1 mmol) in 2:1 molar ratio and the solution was stirred for 1 h. An ethanolic solution of the other ligands L′ (L′ = 8-HQ) (2.90 gm, 2 mmol) was then added to the previous solution in the molar ratio 2:1. The solution was continuously stirred for 4h, during which the metal complex precipitated. The resulting precipitates were filtered off, washed with ethanol then diethyl ether and finally air-dried. The complex is air stable in the solid state and soluble in DMF and/or DMSO. The progress of reaction was monitored by TLC.

(II) Synthesis of Nickel complex

An ethanolic solution of the Nickel(II) nitrate (hexahydrate) (5.80 gm, 2 mmol) (20 ml) was gradually added to an ethanolic (30 ml) solution of the ligand H_2L^6 (4.04 gm, 1 mmol) in 2:1 molar ratio and the solution was stirred for 1 h. An ethanolic solution of the other ligands L′ (L′ = 8-HQ) (2.90 gm, 2 mmol) was then added to the previous solution in the molar ratio 2:1. The solution was continuously stirred for 4h, during which the metal complex precipitated. The resulting precipitates were filtered off, washed with ethanol then diethyl ether and finally air-dried. The complex is air stable in the solid state and soluble in DMF and/or DMSO. The progress of reaction was monitored by TLC.

(III) Synthesis of Copper complex

An ethanolic solution of the Copper(II) nitrate (trihydrate) (4.82 gm, 2 mmol) (20 ml) was gradually added to an ethanolic (30 ml) solution of the ligand H_2L^6 (4.04 gm, 1 mmol) in 2:1 molar ratio and the solution was stirred for 1 h. An ethanolic solution of the other ligands L′ (L′ = 8-HQ) (2.90 gm, 2 mmol) was then added to the previous solution in the molar ratio 2:1. The solution was continuously stirred for 4h, during which the metal complex precipitated. The resulting precipitates were filtered off, washed with ethanol then diethyl ether and finally air-dried. The complex is air stable in the solid state and soluble in DMF and/or DMSO. The progress of reaction was monitored by TLC.

PART– II: SYNTHESIS OF METAL COMPLEX CONTAINING L′ = 1,10-PHENANTHROLINE (Scheme-2)

3.3.5 Synthesis of H_2L^2 complexes

(I) Synthesis of Cobalt complex

An ethanolic solution of the cobalt(II) nitrate (hexahydrate) (5.82 gm, 2 mmol) (20 ml) was gradually added to an ethanolic (30 ml) solution of the ligand H_2L^2 (3.80 gm, 1 mmol) in 2:1 molar ratio and the solution was stirred for 1 h. An ethanolic solution of the other ligands L′ (L′ = 1,10-Phen) (3.60 gm, 2 mmol) was then added to the previous solution in the molar ratio 2:1. The solution was continuously stirred for 4h, during which the metal complex precipitated. The resulting precipitates were filtered off, washed with ethanol then diethyl ether and finally air-dried. The complex is air stable in the solid state and soluble in DMF and/or DMSO. The progress of reaction was monitored by TLC.

(II) Synthesis of Nickel complex

An ethanolic solution of the Nickel(II) nitrate (hexahydrate) (5.80 gm, 2 mmol) (20 ml) was gradually added to an ethanolic (30 ml) solution of the ligand H_2L^2 (3.80 gm, 1 mmol) in 2:1 molar ratio and the solution was stirred for 1 h. An ethanolic solution of the other ligands L′ (L′ = 1,10-Phen) (3.60 gm, 2 mmol) was then added to the previous solution in the molar ratio 2:1. The solution was continuously stirred for 4h, during which the metal complex precipitated. The resulting precipitates were filtered off, washed with ethanol then diethyl ether and finally air-dried. The complex is air stable in the solid state and soluble in DMF and/or DMSO. The progress of reaction was monitored by TLC.

(III) Synthesis of Copper complex

An ethanolic solution of the Copper(II) nitrate (trihydrate) (4.82 gm, 2 mmol) (20 ml) was gradually added to an ethanolic (30 ml) solution of the ligand H_2L^2 (3.80 gm, 1 mmol) in 2:1 molar ratio and the solution was stirred for 1 h. An ethanolic solution of the other ligands L′ (L′ = 1,10-Phen) (3.60 gm, 2 mmol) was then added to the previous solution in the molar ratio 2:1. The solution was continuously stirred for 4h, during which the metal complex precipitated. The resulting precipitates were filtered off, washed with ethanol then diethyl ether and finally air-dried. The complex is air stable in the solid state and soluble in DMF and/or DMSO. The progress of reaction was monitored by TLC.

3.3.6 Synthesis of H_2L^4 complexes

(I) Synthesis of Cobalt complex

An ethanolic solution of the cobalt(II) nitrate (hexahydrate) (5.82 gm, 2 mmol) (20 ml) was gradually added to an ethanolic (30 ml) solution of the ligand H_2L^4 (5.02 gm, 1 mmol) in 2:1 molar ratio and the solution was stirred for 1 h. An ethanolic solution of the other ligands L′ (L′ = 1,10-Phen) (3.60 gm, 2 mmol) was then added to the previous solution in the molar ratio 2:1. The solution was continuously stirred for 4h, during which the metal complex precipitated. The resulting precipitates were filtered off, washed with ethanol then diethyl ether and finally air-dried. The complex is air stable in the solid state and soluble in DMF and/or DMSO. The progress of reaction was monitored by TLC.

(II) Synthesis of Nickel complex

An ethanolic solution of the Nickel(II) nitrate (hexahydrate) (5.80 gm, 2 mmol) (20 ml) was gradually added to an ethanolic (30 ml) solution of the ligand H_2L^4 (5.02 gm, 1 mmol) in 2:1 molar ratio and the solution was stirred for 1 h. An ethanolic solution of the other ligands L′ (L′ = 1,10-Phen) (3.60 gm, 2 mmol) was then added to the previous solution in the molar ratio 2:1. The solution was continuously stirred for 4h, during which the metal complex precipitated. The resulting precipitates were filtered off, washed with ethanol then diethyl ether and finally air-dried. The complex is air stable in the solid state and soluble in DMF and/or DMSO. The progress of reaction was monitored by TLC.

(III) Synthesis of Copper complex

An ethanolic solution of the Copper(II) nitrate (trihydrate) (4.82 gm, 2 mmol) (20 ml) was gradually added to an ethanolic (30 ml) solution of the ligand H_2L^4 (5.02 gm, 1 mmol) in 2:1 molar ratio and the solution was stirred for 1 h. An ethanolic solution of the other ligands L′ (L′ = 1,10-Phen) (3.60 gm, 2 mmol) was then added to the previous solution in the molar ratio 2:1. The solution was continuously stirred for 4h, during which the metal complex precipitated. The resulting precipitates were filtered off, washed with ethanol then diethyl ether and finally air-dried. The complex is air stable in the solid state and soluble in DMF and/or DMSO. The progress of reaction was monitored by TLC.

3.3.7 Synthesis of H_2L^5 complexes

(I) Synthesis of Cobalt complex

An ethanolic solution of the cobalt(II) nitrate (hexahydrate) (5.82 gm, 2 mmol) (20 ml) was gradually added to an ethanolic (30 ml) solution of the ligand H_2L^5 (3.72 gm, 1 mmol) in 2:1 molar ratio and the solution was stirred for 1 h. An ethanolic solution of the other ligands L′ (L′ = 1,10-Phen) (3.60 gm, 2 mmol) was then added to the previous solution in the molar ratio 2:1. The solution was continuously stirred for 4h, during which the metal complex precipitated. The resulting precipitates were filtered off, washed with ethanol then diethyl ether and finally air-dried. The complex is air stable in the solid state and soluble in DMF and/or DMSO. The progress of reaction was monitored by TLC.

(II) Synthesis of Nickel complex

An ethanolic solution of the Nickel(II) nitrate (hexahydrate) (5.80 gm, 2 mmol) (20 ml) was gradually added to an ethanolic (30 ml) solution of the ligand H_2L^5 (3.72 gm, 1 mmol) in 2:1 molar ratio and the solution was stirred for 1 h. An ethanolic solution of the other ligands L′ (L′ = 1,10-Phen) (3.60 gm, 2 mmol) was then added to the previous solution in the molar ratio 2:1. The solution was continuously stirred for 4h, during which the metal complex precipitated. The resulting precipitates were filtered off, washed with ethanol then diethyl ether and finally air-dried. The complex is air stable in the solid state and soluble in DMF and/or DMSO. The progress of reaction was monitored by TLC.

(II) Synthesis of Copper complex

An ethanolic solution of the Copper(II) nitrate (trihydrate) (4.82 gm, 2 mmol) (20 ml) was gradually added to an ethanolic (30 ml) solution of the ligand H_2L^5 (3.72 gm, 1 mmol) in 2:1 molar ratio and the solution was stirred for 1 h. An ethanolic solution of the other ligands L′ (L′ = 1,10-Phen) (3.60 gm, 2 mmol) was then added to the previous solution in the molar ratio 2:1. The solution was continuously stirred for 4h, during which the metal complex precipitated. The resulting precipitates were filtered off, washed with ethanol then diethyl ether and finally air-dried. The complex is air stable in the solid state and soluble in DMF and/or DMSO. The progress of reaction was monitored by TLC.

3.3.8 Synthesis of H_2L^6 complexes

(I) Synthesis of Cobalt complex

An ethanolic solution of the cobalt(II) nitrate (hexahydrate) (5.82 gm, 2 mmol) (20 ml) was gradually added to an ethanolic (30 ml) solution of the ligand H_2L^6 (4.04 gm, 1 mmol) in 2:1 molar ratio and the solution was stirred for 1 h. An ethanolic solution of the other ligands L′ (L′ = 1,10-Phen) (3.60 gm, 2 mmol) was then added to the previous solution in the molar ratio 2:1. The solution was continuously stirred for 4h, during which the metal complex precipitated. The resulting precipitates were filtered off, washed with ethanol then diethyl ether and finally air-dried. The complex is air stable in the solid state and soluble in DMF and/or DMSO. The progress of reaction was monitored by TLC.

(II) Synthesis of Nickel complex

An ethanolic solution of the Nickel(II) nitrate (hexahydrate) (5.80 gm, 2 mmol) (20 ml) was gradually added to an ethanolic (30 ml) solution of the ligand H_2L^6 (4.04 gm, 1 mmol) in 2:1 molar ratio and the solution was stirred for 1 h. An ethanolic solution of the other ligands L′ (L′ = 1,10-Phen) (3.60 gm, 2 mmol) was then added to the previous solution in the molar ratio 2:1. The solution was continuously stirred for 4h, during which the metal complex precipitated. The resulting precipitates were filtered off, washed with ethanol then diethyl ether and finally air-dried. The complex is air stable in the solid state and soluble in DMF and/or DMSO. The progress of reaction was monitored by TLC.

(III) Synthesis of Copper complex

An ethanolic solution of the Copper(II) nitrate (trihydrate) (4.82 gm, 2 mmol) (20 ml) was gradually added to an ethanolic (30 ml) solution of the ligand H_2L^6 (4.04 gm, 1 mmol) in 2:1 molar ratio and the solution was stirred for 1 h. An ethanolic solution of the other ligands L′ (L′ = 1,10-Phen) (3.60 gm, 2 mmol) was then added to the previous solution in the molar ratio 2:1. The solution was continuously stirred for 4h, during which the metal complex precipitated. The resulting precipitates were filtered off, washed with ethanol then diethyl ether and finally air-dried. The complex is air stable in the solid state and soluble in DMF and/or DMSO. The progress of reaction was monitored by TLC.

3.4 PHYSICAL DATA TABLE

TABLE-3.4.1: THE ANALYTICAL AND PHYSICAL DATA OF THE METAL COMPLEXES

	Complex	Molecular Formula	Molecular Weight*	Color	Yield (%)	Melting point (°C)
1	$[Co_2(L^2)(8\text{-}HQ)_2(H_2O)_4]$	$C_{40}H_{28}Co_2F_2N_4O_4$	856.54	Reddish brown	79%	>300
2	$[Ni_2(L^2)(8\text{-}HQ)_2(H_2O)_4]$	$C_{40}H_{28}F_2N_4Ni_2O_4$	856.06	Green	84%	>300
3	$[Cu_2(L^2)(8\text{-}HQ)_2(H_2O)_4]$	$C_{40}H_{28}Cu_2F_2N_4O_4$	865.76	Deep blue	82%	>300
4	$[Co_2(L^4)(8\text{-}HQ)_2(H_2O)_4]$	$C_{40}H_{28}Br_2Co_2N_4O_4$	978.35	Reddish brown	85%	>300
5	$[Ni_2(L^4)(8\text{-}HQ)_2(H_2O)_4]$	$C_{40}H_{28}Br_2N_4Ni_2O_4$	977.87	Green	81%	>300
6	$[Cu_2(L^4)(8\text{-}HQ)_2(H_2O)_4]$	$C_{40}H_{28}Br_2Cu_2N_4O_4$	987.57	Deep blue	86%	>300
7	$[Co_2(L^5)(8\text{-}HQ)_2(H_2O)_4]$	$C_{42}H_{34}Co_2N_4O_4$	848.61	Reddish brown	72%	>300
8	$[Ni_2(L^5)(8\text{-}HQ)_2(H_2O)_4]$	$C_{42}H_{34}N_4Ni_2O_4$	848.13	Green	76%	>300
9	$[Cu_2(L^5)(8\text{-}HQ)_2(H_2O)_4]$	$C_{42}H_{34}Cu_2N_4O_4$	857.84	Deep blue	78%	>300
10	$[Co_2(L^6)(8\text{-}HQ)_2(H_2O)_4]$	$C_{42}H_{34}Co_2N_4O_6$	880.61	Reddish brown	81%	>300
11	$[Ni_2(L^6)(8\text{-}HQ)_2(H_2O)_4]$	$C_{42}H_{34}N_4Ni_2O_6$	880.13	Green	79%	>300
12	$[Cu_2(L^6)(8\text{-}HQ)_2(H_2O)_4]$	$C_{42}H_{34}Cu_2N_4O_6$	889.83	Deep blue	83%	>300
13	$[Co_2(L^2)(1,10\text{-}Phen)_2(H_2O)_4]$	$C_{46}H_{32}Co_2F_2N_6O_2$	928.65	Reddish brown	85%	>300
14	$[Ni_2(L^2)(1,10\text{-}Phen)_2(H_2O)_4]$	$C_{46}H_{32}F_2N_6Ni_2O_2$	928.17	Green	84%	>300
15	$[Cu_2(L^2)(1,10\text{-}Phen)_2(H_2O)_4]$	$C_{46}H_{32}Cu_2F_2N_6O_2$	937.87	Deep blue	86%	>300
16	$[Co_2(L^4)(1,10\text{-}Phen)_2(H_2O)_4]$	$C_{46}H_{32}Br_2Co_2N_6O_2$	1050.46	Reddish brown	78%	>300
17	$[Ni_2(L^4)(1,10\text{-}Phen)_2(H_2O)_4]$	$C_{46}H_{32}Br_2N_6Ni_2O_2$	1049.98	Green	76%	>300

	Complex	**Molecular Formula**	**Molecular Weight***	**Color**	**Yield (%)**	**Melting point (°C)**
18	$[Cu_2(L^4)(1,10\text{-Phen})_2(H_2O)_4]$	$C_{46}H_{32}Br_2Cu_2N_6O_2$	1059.69	Deep blue	84%	>300
19	$[Co_2(L^5)(1,10\text{-Phen})_2(H_2O)_4]$	$C_{48}H_{38}Co_2N_6O_2$	920.72	Reddish brown	70%	>300
20	$[Ni_2(L^5)(1,10\text{-Phen})_2(H_2O)_4]$	$C_{48}H_{38}N_6Ni_2O_2$	920.24	Green	72%	>300
21	$[Cu_2(L^5)(1,10\text{-Phen})_2(H_2O)_4]$	$C_{48}H_{38}Cu_2N_6O_2$	929.95	Deep blue	68%	>300
22	$[Co_2(L^6)(1,10\text{-Phen})_2(H_2O)_4]$	$C_{48}H_{38}Co_2N_6O_4$	952.72	Reddish brown	67%	>300
23	$[Ni_2(L^6)(1,10\text{-Phen})_2(H_2O)_4]$	$C_{48}H_{38}N_6Ni_2O_4$	952.24	Green	62%	>300
24	$[Cu_2(L^6)(1,10\text{-Phen})_2(H_2O)_4]$	$C_{48}H_{38}Cu_2N_6O_4$	961.95	Deep blue	72%	>300

*** Molecular Weight of the complexes given with Coordinate water molecule**

3.5 SPECTRAL STUDY

IR spectra (4000-400 cm^{-1}) of the metal complexes were obtained using KBr discs, on a 8400 FTIR SHIMADZU spectrometer. ESI Mass spectra of complexes were recorded VG-70-S Spectrometer. Electronic spectra of the metal complexes in DMF were recorded on a perkin elmer lambda 19 Spectrophotometer, and ESR was recorded on E-112 ESR Spectrometer, at X-band microwave frequency (9.5 GHz) with sensitivity of 5×10^{10} ΔH spins. Thermal Gravimetric Analyses (TGA) have been carried out by using Perkin Elmer (Pyris 1 TGA) from room temperature to 800°C under heating rate of 10°C/min. Elemental analysis (C, H and N) were carried out on Elemental Analyzer PERKIN ELMER 2400. Magnetic moment of the compound measured by GOUY balance using Hg[Co(CNS)] as standard.

3.5.1 Infra Red Spectra

IR spectra of the complexes were recorded to confirm their structures. The vibrational frequencies and their tentative assignments for transition metal complexes are given. The assignments were aided by comparison with the vibrational frequencies of the free ligand and their related compounds. There are three conceptual features in the infrared spectra of the complexes. The former one is the shift of the stretching frequencies of the azomethine (–C=N–) group of the transition metal complexes to lower frequencies and lie in the range of 1610-1630 cm^{-1}, compared with the free ligand bands at 1642 and 1631 cm^{-1}, which may be due to the coordination of the two azomethine groups to metal ions. This lowering shift is not significant in most cases as expected and it is believed that, this is due to the interference with the deformation of the water molecules associated with the complexes. The second feature is the bands in the range of 3352–3572 cm^{-1} which can be assigned to the stretching frequencies of the ν(OH) of water molecules associated to the complexes which are also confirmed by the TG analysis. The third feature is the weak to medium bands in the two ranges 440–560 and 576–610 cm^{-1}, which could be assigned to the stretching frequencies of the ν(M–O) and (M–N) bands, respectively, supporting that the bonding of the ligands to the metal ions is achieved by the phenolic oxygen, and azomethine nitrogen atoms of the ligands[258-260].

The infrared spectra of the free ligands L'; L' = 8-HQ, and 1,10-Phen, have been compared with those after coordination. The spectrum of the free 8-hydroxyquinoline shows a strong band at 1586 cm^{-1} due to the stretching vibrations of the (C=N) group. This band is shifted to a higher wave number on coordination for complexes (1-12) suggesting that the lone pair on nitrogen is involved in the formation of a bond with metal. Moreover, the broad stretching vibration at 3242 cm^{-1} due to O–H group of the free 8-HQ ligand was found to be absent in the latter complexes, suggesting the formation of an M–O bond with 8-hydroxyquinolate. Thus, 8-hydroxyquinolinate in all the complexes is a bidentate chelating ligand. Changes are observed in the infrared spectrum of 1,10-Phen when it is coordinated with the metal centers. The characteristic band of the C=N group in complexes (13-24) are shifted to higher wave number compared with the free ligand at 1570 cm^{-1}. This suggests that both nitrogens of 1,10-Phen are coordinated to the metal ion[261-264]. (Figure-3.1,3.2)

3.5.2 Electronic Absorption Spectra (UV-Vis.)

The electronic spectra of the complexes showed several absorption bands, including absorption bands of the ligands and d-d transitions of the metal ions. Spectra of the complexes, which reveal maxima at the wavelength of the first band of the ligands (210-226 nm), are independent of complexation. The second band is ascribed to π-π^* transitions involving the azomethine found at 325-370nm. The band at 390-430nm is assigned to charge transfer transition. Lower energy bands in the range 500-672 nm are assigned to d–d transitions of the metal cations [265-267].

The spectra of the brown Co(II), complexes show two d–d transition bands in the 500–650 nm region for complexes. The two bands are assigned to the

${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$ and ${}^4T_{1g} \rightarrow {}^4T_{1g}(F)$ transitions of octahedral geometry[268,269].

The spectra of the green Ni(II) complexes show three bands. The most intense band at ~430nm is assigned to the ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transition in complexes at the same region. The latter transition is a less intense peak at 510-650 nm, assigned to the ${}^3A_{2g} \rightarrow {}^3T_{2g}$ transition due to the octahedral geometry[270,271].

The Cu(II) complexes exhibit five absorption maxima. The first three maxima in the range 240–320 nm were ascribed previously to the ligands, while the fourth maximum lies in the range 360–370nm and is probably due to the ligand–metal charge transfer transition. The absorption maxima at 450-530 for complexes are due to the d–d transition to (${}^2Eg \rightarrow {}^2T_{2g}$) for the octahedral or distorted octahedral geometry[272]. (Figure- 3.3,3.4)

3.5.3 Thermal Gravimetric Analysis (TGA)

Thermal Gravimetric (TG) analysis was used as a probe to proof the associated water or solvent molecules to be in the coordination sphere or in the crystalline form. Thermo gravimetric analysis of metal complexes is very important tool for assessing their thermal stability. TGA is generally carried out in nitrogen atmosphere at different heating rates. The loss in weight of the complex material with increase in temperature forms a TG curve. Normally sample starts loosing weight at a slow rate up to a particular temperature. Thereafter, the rate of loss in weight becomes higher over a narrow range of temperature. After this stage the loss in weight levels off. The shape of TG curve depends upon the nature of the degradation reaction. The percentage weight loss at different temperature and the percentage weight left at 800°C for all the synthesized chelates were studied. The analyses of the thermal curves of the complexes clearly show that the water molecules present in all complexes is lost at 100°C, indicating that the molecule is coordinated to the metal ion. The TG curves indicate that above 110°C the compounds start to lose mass with partial evaporation of L′ ligand up to 200°C. In the temperature range 200–500°C the molecules of the Schiff base ligands are lost. In all cases the final products are the metal oxides. These results are in good accordance with the composition of the complexes[273,274]. (Figure- 3.9,3.10)

2.5.4 Elemental Analysis

Elemental analysis (C, H, N, and M) of the compounds was carried out on Elemental Analyzer Perkin Elmer 2400. The results are in agreement with the structures assigned.

3.5.5 Magnetic Moments

The magnetic moment data are presented in spectral characterization. The magnetic moment value of the Cu(II) complex (1.70 B.M.) is very close to the spin-only value (1.73 B.M.) expected for one unpaired electron which offers the possibility of an octahedral geometry. The larger variation in the magnetic moment values (2.9-3.4 B.M.) for a high-spin Ni(II) complex (2.83 B.M.) depends on the magnitude of the orbital contribution. The magnetic moment value (2.88 B.M.) in the present work is within the range expected for similar octahedral Ni(II) ions. The magnetic moment values for the Co(II) complexes have been used as criterion to determine the type of coordination around the metal ion. Due to the intrinsic orbital angular momentum in the ground state, there is consistently a considerable orbital contribution and the effective magnetic moment lies between 4.7 and 5.2 B.M. at room temperature. In the present complexes the magnetic moment value (4.74 B.M.) suggest an octahedral geometry for the Co(II) complex in the high-spin state[232,233].

3.5.6 ESI Mass Spectra

Electrospray ionization (ESI) was first employed more than 20 years ago, but it is fairly recently that it became a routine technique for the soft ionization of a wide range of polar analytes, including biomolecules. For this technique, the analyte is usually dissolved in a mixture of an organic solvent and water with a pH modifier. The presence of the pH modifier ensures that ionization takes place in the solution state. This is the only common case where ionization occurs before ion vaporization. Because ionization has taken place in the solution state by protonation or deprotonation of the analyte the molecular species detected is almost exclusively $[M+H^+]$ in positive ion mode and $[M-H]^-$ in negative ion mode, and both these species undergo very little fragmentation. The advantage of ESI mass is that it often gives multiply charged ions for large molecules with many ionizable functional groups. This has the advantage of lowering the m/z ratio and there by allowing the determination of the masses of large molecule without the need for a detector that has a large mass range[234]. It is very sensitive to contaminants in the solvents, particularly alkali metals, and we often see ions which corresponds to $[M+Na]^+$ or $[M+NH_4]^+$. (Figure- 3.5-3.8)

3.5.7 Electron Spin Resonance (ESR)

The EPR parameters of copper complexes: there was a general correspondence between the powder and solution spectra; however, the $g\perp$ region was well resolved in solution. The spectra were indicative of rhombic distortion from axial symmetry. Owing to coordination of two different kinds of atoms (O and N) with the metal ion. The spectra were characteristic of magnetically dilute system with Cu(II) ions in the $d_{x^2-y^2}$ ground state. Hyperfine as a result of nitrogen were visible on the main absorption line, g⊥, confirming the coordination through N. based on the experimental evidence thus obtained the complexes were characterized as six coordinates with the fifth and sixth position occupied by two water molecules. The ESR spectra of all copper complex show intense broad bands with g = 2.00255, the value of g and the shape of the ESR signals suggest octahedral coordination around the Cu(II) ions[275]. (Figure- 3.11)

3.6 SPECTRAL CHARACTERIZATION OF METAL COMPLEXES

(1) Complex-1: $[Co_2(L^2)(8\text{-}HQ)_2(H_2O)_4]$

IR (KBr) cm^{-1}: 3530 (-OH of H_2O), 1620 (-C=N-), 600 (M–N), 500 (M–O), 3012 (Ar C-H), 2920 (C-H of CH_3), 1440-1615 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 350, 410, 510, 650.

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700	800
Weight loss %	1.55	17.59	54.01	59.54	61.79	64.21	66.44	68.06

Elemental analysis, Calculated: C, 61.24; H, 3.60; N, 7.14; Co, 15.02, **Found:** C, 61.12; H, 3.51; N, 7.07; Co, 15.18.

Magnetic moment (μ): 4.70 B.M.

ESI mass[m/e (%)]: 859

(2) Complex-2: $[Ni_2(L^2)(8\text{-}HQ)_2(H_2O)_4]$

IR (KBr) cm^{-1}: 3500 (-OH of H_2O), 1610 (-C=N-), 594 (M–N), 483 (M–O), 3010 (Ar C-H), 2935 (C-H of CH_3), 1440-1610 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 350, 430, 510, 640.

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700	800
Weight loss %	1.60	17.40	54.11	58.49	61.61	64.20	68.00	69.10

Elemental analysis, Calculated: C, 61.27; H, 3.60; N, 7.15; Ni, 14.97, **Found:** C, 61.15; H, 3.51; N, 7.22; Ni, 15.12.

Magnetic moment (μ): 2.88 B.M.

ESI mass[m/e (%)]: 858

(3) Complex-3: $[Cu_2(L^2)(8\text{-}HQ)_2(H_2O)_4]$

IR (KBr) cm^{-1}: 3486 (-OH of H_2O), 1612 (-C=N-), 600 (M–N), 520 (M–O), 3011 (Ar C-H), 2935 (C-H of CH_3), 1440-1600 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 320, 360, 530.

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700	800
Weight loss %	1.65	16.41	54.10	59.50	62.00	64.00	67.80	70.10

Elemental analysis, Calculated: C, 60.53; H, 3.56; N, 7.06; Cu, 16.01, **Found:** C, 60.40; H, 3.60; N, 6.96; Cu, 16.15.

Magnetic moment (μ): 1.70 B.M.

ESI mass[m/e (%)]: 868

(4) Complex-4: $[Co_2(L^4)(8\text{-}HQ)_2(H_2O)_4]$

IR (KBr) cm^{-1}: 3500 (-OH of H_2O), 1608 (-C=N-), 610 (M–N), 540 (M–O), 3008 (Ar C-H), 2900 (C-H of CH_3), 1435-1620 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 340, 420, 500, 670.

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700	800
Weight loss %	1.70	18.00	54.30	60.00	62.30	64.70	66.81	67.80

Elemental analysis, Calculated: C, 53.01; H, 3.11; N, 6.18; Co, 13.00, **Found:** C, 53.10; H, 3.04; N, 6.06; Co, 13.20.

Magnetic moment (μ): 4.70 B.M.

ESI mass[m/e (%)]: 980

(5) Complex-5: $[Ni_2(L^4)(8\text{-}HQ)_2(H_2O)_4]$

IR (KBr) cm^{-1}: 3510 (-OH of H_2O), 1625 (-C=N-), 590 (M–N), 480 (M–O), 3030 (Ar C-H), 2930 (C-H of CH_3), 1450-1610 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 355, 420, 520, 650.

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700	800
Weight loss %	1.80	17.30	52.88	59.60	61.30	65.00	67.67	69.69

Elemental analysis, Calculated: C, 53.04; H, 3.12; N, 6.18; Ni, 12.96, **Found:** C, 53.10; H, 3.07; N, 7.12; Ni, 12.90.

Magnetic moment (µ): 2.89 B.M.

ESI mass[m/e (%)]: 979

(6) Complex-6: $[Cu_2(L^4)(8\text{-}HQ)_2(H_2O)_4]$

IR (KBr) cm^{-1}: 3440 (-OH of H_2O), 1618 (-C=N-), 588 (M–N), 510 (M–O), 3030 (Ar C-H), 2930 (C-H of CH_3), 1445-1610 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 310, 365, 525.

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700	800
Weight loss %	2.00	18.00	54.60	60.01	62.10	64.30	66.20	71.08

Elemental analysis, Calculated: C, 52.47; H, 3.08; N, 6.12; Cu, 13.88, **Found:** C, 52.52; H, 3.00; N, 6.02; Cu, 13.70.

Magnetic moment (µ): 1.72 B.M.

ESI mass[m/e (%)]: 989

(7) Complex-7: $[Co_2(L^5)(8\text{-}HQ)_2(H_2O)_4]$

IR (KBr) cm^{-1}: 3530 (-OH of H_2O), 1620 (-C=N-), 600 (M–N), 500 (M–O), 3012 (Ar C-H), 2920 (C-H of CH_3), 1440-1615 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 350, 410, 510, 650.

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700	800
Weight loss %	1.70	17.59	55.15	59.54	61.79	65.10	66.44	68.06

Elemental analysis, Calculated: C, 64.96; H, 4.41; N, 7.21; Co, 15.18, **Found:** C, 64.80; H, 4.35; N, 7.18; Co, 15.30.

Magnetic moment (µ): 4.72 B.M.

ESI mass[m/e (%)]: 852

(8) Complex-8: $[Ni_2(L^5)(8\text{-}HQ)_2(H_2O)_4]$

IR (KBr) cm^{-1}: 3500 (-OH of H_2O), 1610 (-C=N-), 594 (M–N), 483 (M–O), 3010 (Ar C-H), 2935 (C-H of CH_3), 1440-1610 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 350, 430, 510, 640.

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700	800
Weight loss %	1.91	18.08	54.11	59.59	63.66	64.20	66.33	70.07

Elemental analysis, Calculated: C, 65.00; H, 4.42; N, 7.22; Ni, 15.12, **Found:** C, 65.10; H, 4.33; N, 7.30; Ni, 15.25.

Magnetic moment (μ): 2.89 B.M.

ESI mass[m/e (%)]: 850

(9) Complex-9: $[Cu_2(L^5)(8\text{-}HQ)_2(H_2O)_4]$

IR (KBr) cm^{-1}: 3486 (-OH of H_2O), 1612 (-C=N-), 600 (M–N), 520 (M–O), 3011 (Ar C-H), 2935 (C-H of CH_3), 1440-1600 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 320, 360, 530.

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700	800
Weight loss %	1.54	17.35	53.20	59.50	60.60	64.00	65.81	70.99

Elemental analysis, Calculated: C, 64.19; H, 4.36; N, 7.13; Cu, 16.17, **Found:** C, 64.06; H, 4.28; N, 7.05; Cu, 16.31.

Magnetic moment (μ): 1.72 B.M.

ESI mass[m/e (%)]: 860

(10) Complex-10: $[Co_2(L^6)(8\text{-}HQ)_2(H_2O)_4]$

IR (KBr) cm^{-1}: 3500 (-OH of H_2O), 1608 (-C=N-), 610 (M–N), 540 (M–O), 3008 (Ar C-H), 2900 (C-H of CH_3), 1435-1620 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 340, 420, 500, 670.

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700	800
Weight loss %	1.70	18.00	54.30	60.00	62.30	64.70	67.00	68.30

Elemental analysis, Calculated: C, 62.38; H, 4.24; N, 6.93; Co, 14.58, **Found:** C, 62.27; H, 4.17; N, 7.00; Co, 14.70.

Magnetic moment (μ): 4.70 B.M.

ESI mass[m/e (%)]: 883

(11) Complex-11: [$Ni_2(L^6)(8\text{-}HQ)_2(H_2O)_4$]

IR (KBr) cm^{-1}: 3510 (-OH of H_2O), 1625 (-C=N-), 590 (M–N), 480 (M–O), 3030 (Ar C-H), 2930 (C-H of CH_3), 1450-1610 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 355, 420, 520, 650.

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700	800
Weight loss %	1.58	17.30	55.18	59.60	62.11	65.00	66.70	69.88

Elemental analysis, Calculated: C, 62.42; H, 4.24; N, 6.93; Ni, 14.53, **Found:** C, 62.30; H, 4.18; N, 6.88; Ni, 14.40.

Magnetic moment (μ): 2.90 B.M.

ESI mass[m/e (%)]: 882

(12) Complex-12: [$Cu_2(L^6)(8\text{-}HQ)_2(H_2O)_4$]

IR (KBr) cm^{-1}: 3440 (-OH of H_2O), 1618 (-C=N-), 588 (M–N), 510 (M–O), 3030 (Ar C-H), 2930 (C-H of CH_3), 1445-1610 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 315, 360, 520.

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700	800
Weight loss %	2.01	18.18	56.00	61.00	62.81	64.30	67.00	72.00

Elemental analysis, Calculated: C, 61.68; H, 4.19; N, 6.85; Cu, 15.54, **Found:** C, 61.79; H, 4.27; N, 6.70; Cu, 15.50.

Magnetic moment (μ): 1.71 B.M.

ESI mass[m/e (%)]: 892

(13) Complex-13: $[Co_2(L^2)(1,10\text{-}Phen)_2(H_2O)_4]$

IR (KBr) cm^{-1}: 3530 (-OH of H_2O), 1620 (-C=N-), 600 (M–N), 500 (M–O), 3012 (Ar C-H), 2920 (C-H of CH_3), 1440-1615 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 350, 410, 510, 650.

TGA: Weight loss data

Temp. ^0C	100	200	300	400	500	600	700	800
% Weight loss	1.77	25.57	37.99	52.53	70.08	84.04	92.91	95.09

Elemental analysis, Calculated: C, 61.24; H, 3.60; N, 7.14; Co, 15.02, **Found:** C, 61.12; H, 3.55; N, 7.07; Co, 15.11.

Magnetic moment (µ): 4.70 B.M.

ESI mass[m/e (%)]: 931

(14) Complex-14: $[Ni_2(L^2)(1,10\text{-}Phen)_2(H_2O)_4]$

IR (KBr) cm^{-1}: 3500 (-OH of H_2O), 1610 (-C=N-), 594 (M–N), 483 (M–O), 3010 (Ar C-H), 2935 (C-H of CH_3), 1440-1610 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 350, 430, 510, 640.

TGA: Weight loss data

Temp. ^0C	100	200	300	400	500	600	700	800
Weight loss %	1.77	25.57	37.99	52.53	70.08	84.04	92.91	95.09

Elemental analysis, Calculated: C, 61.27; H, 3.60; N, 7.15; Ni, 14.97, **Found:** C, 61.30; H, 3.51; N, 7.20; Ni, 14.90.

Magnetic moment (µ): 2.88 B.M.

ESI mass[m/e (%)]: 930

(15) Complex-15: $[Cu_2(L^2)(1,10\text{-}Phen)_2(H_2O)_4]$

IR (KBr) cm^{-1}: 3486 (-OH of H_2O), 1612 (-C=N-), 600 (M–N), 520 (M–O), 3011 (Ar C-H), 2935 (C-H of CH_3), 1440-1600 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 320, 360, 530.

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700	800
Weight loss %	1.77	25.57	37.99	52.53	70.08	84.04	92.91	95.09

Elemental analysis, Calculated: C, 60.53; H, 3.56; N, 7.06; Cu, 16.01, **Found:** C, 60.40; H, 3.49; N, 7.00; Cu, 16.15.

Magnetic moment (µ): 1.70 B.M.

ESI mass[m/e (%)]: 940

(16) Complex-16: [$Co_2(L^4)(1,10\text{-Phen})_2(H_2O)_4$]

IR (KBr) cm^{-1}: 3500 (-OH of H_2O), 1608 (-C=N-), 610 (M–N), 540 (M–O), 3008 (Ar C-H), 2900 (C-H of CH_3), 1435-1620 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 340, 420, 500, 670.

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700	800
Weight loss %	1.77	25.57	37.99	52.53	70.08	84.04	92.91	95.09

Elemental analysis, Calculated: C, 53.01; H, 3.11; N, 6.18; Co, 13.00, **Found:** C, 52.88; H, 3.04; N, 6.06; Co, 13.20.

Magnetic moment (µ): 4.70 B.M.

ESI mass[m/e (%)]: 1052

(17) Complex-17: [$Ni_2(L^4)(1,10\text{-Phen})_2(H_2O)_4$]

IR (KBr) cm^{-1}: 3510 (-OH of H_2O), 1625 (-C=N-), 590 (M–N), 480 (M–O), 3030 (Ar C-H), 2930 (C-H of CH_3), 1450-1610 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 355, 420, 520, 650.

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700	800
Weight loss %	1.77	25.57	37.99	52.53	70.08	84.04	92.91	95.09

Elemental analysis, Calculated: C, 53.04; H, 3.12; N, 6.18; Ni, 12.96, **Found:** C, 53.10; H, 3.07; N, 7.12; Ni, 13.13.

Magnetic moment (µ): 2.89 B.M.

ESI mass[m/e (%)]: 1053

(18) Complex-18: $[Cu_2(L^4)(1,10\text{-Phen})_2(H_2O)_4]$

IR (KBr) cm^{-1}: 3440 (-OH of H_2O), 1618 (-C=N-), 588 (M–N), 510 (M–O), 3030 (Ar C-H), 2930 (C-H of CH_3), 1445-1610 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 310, 365, 525.

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700	800
Weight loss %	1.77	25.57	37.99	52.53	70.08	84.04	92.91	95.09

Elemental analysis, Calculated: C, 52.47; H, 3.08; N, 6.12; Cu, 13.88, **Found:** C, 52.40; H, 3.00; N, 6.02; Cu, 13.70.

Magnetic moment (μ): 1.72 B.M.

ESI mass[m/e (%)]: 1062

(19) Complex-19: $[Co_2(L^5)(1,10\text{-Phen})_2(H_2O)_4]$

IR (KBr) cm^{-1}: 3530 (-OH of H_2O), 1620 (-C=N-), 600 (M–N), 500 (M–O), 3012 (Ar C-H), 2920 (C-H of CH_3), 1440-1615 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 350, 410, 510, 650.

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700	800
Weight loss %	1.77	25.57	37.99	52.53	70.08	84.04	92.91	95.09

Elemental analysis, Calculated: C, 64.96; H, 4.41; N, 7.21; Co, 15.18, **Found:** C, 64.80; H, 4.35; N, 7.18; Co, 15.00.

Magnetic moment (μ): 4.72 B.M.

ESI mass[m/e (%)]: 923

(20) Complex-20: $[Ni_2(L^5)(1,10\text{-Phen})_2(H_2O)_4]$

IR (KBr) cm^{-1}: 3500 (-OH of H_2O), 1610 (-C=N-), 594 (M–N), 483 (M–O), 3010 (Ar C-H), 2935 (C-H of CH_3), 1440-1610 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 350, 430, 510, 640.

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700	800
Weight loss %	1.77	25.57	37.99	52.53	70.08	84.04	92.91	95.09

Elemental analysis, Calculated: C, 65.00; H, 4.42; N, 7.22; Ni, 15.12, **Found:** C, 65.10; H, 4.36; N, 7.13; Ni, 15.00.

Magnetic moment (µ): 2.89 B.M.

ESI mass[m/e (%)]: 922

(21) Complex-21: $[Cu_2(L^5)(1,10\text{-Phen})_2(H_2O)_4]$

IR (KBr) cm^{-1}: 3486 (-OH of H_2O), 1612 (-C=N-), 600 (M–N), 520 (M–O), 3011 (Ar C-H), 2935 (C-H of CH_3), 1440-1600 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 320, 360, 530.

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700	800
Weight loss %	1.77	25.57	37.99	52.53	70.08	84.04	92.91	95.09

Elemental analysis, Calculated: C, 64.19; H, 4.36; N, 7.13; Cu, 16.17, **Found:** C, 64.25; H, 4.24; N, 7.07; Cu, 16.30.

Magnetic moment (µ): 1.72 B.M.

ESI mass[m/e (%)]: 933

(22) Complex-22: $[Co_2(L^6)(1,10\text{-Phen})_2(H_2O)_4]$

IR (KBr) cm^{-1}: 3500 (-OH of H_2O), 1608 (-C=N-), 610 (M–N), 540 (M–O), 3008 (Ar C-H), 2900 (C-H of CH_3), 1435-1620 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 340, 420, 500, 670.

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700	800
Weight loss %	1.77	25.57	37.99	52.53	70.08	84.04	92.91	95.09

Elemental analysis, Calculated: C, 62.38; H, 4.24; N, 6.93; Co, 14.58, **Found:** C, 62.30; H, 4.17; N, 6.88; Co, 14.73.

Magnetic moment (µ): 4.70 B.M.

ESI mass[m/e (%)]: 955

(23) Complex-23: [$Ni_2(L^6)(1,10\text{-}Phen)_2(H_2O)_4$]

IR (KBr) cm^{-1}: 3510 (-OH of H_2O), 1625 (-C=N-), 590 (M–N), 480 (M–O), 3030 (Ar C-H), 2930 (C-H of CH_3), 1450-1610 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 355, 420, 520, 650.

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700	800
Weight loss %	1.77	25.57	37.99	52.53	70.08	84.04	92.91	95.09

Elemental analysis, Calculated: C, 62.42; H, 4.24; N, 6.93; Ni, 14.53, **Found:** C, 62.30; H, 4.18; N, 6.84; Ni, 14.62.

Magnetic moment (µ): 2.90 B.M.

ESI mass[m/e (%)]: 954

(24) Complex-24: [$Cu_2(L^2)(1,10\text{-}Phen)_2(H_2O)_4$]

IR (KBr) cm^{-1}: 3440 (-OH of H_2O), 1618 (-C=N-), 588 (M–N), 510 (M–O), 3030 (Ar C-H), 2930 (C-H of CH_3), 1445-1610 (Ar -C=C- ring skeletal).

Electronic spectra (nm): 315, 360, 520.

TGA: Weight loss data

Temp. ^{0}C	100	200	300	400	500	600	700	800
Weight loss %	1.77	25.57	37.99	52.53	70.08	84.04	92.91	95.09

Elemental analysis, Calculated: C, 61.68; H, 4.19; N, 6.85; Cu, 15.54, **Found:** C, 61.77; H, 4.25; N, 6.70; Cu, 15.45.

Magnetic moment (µ): 1.71 B.M.

ESI mass[m/e (%)]: 964

3.7 SPECTRA

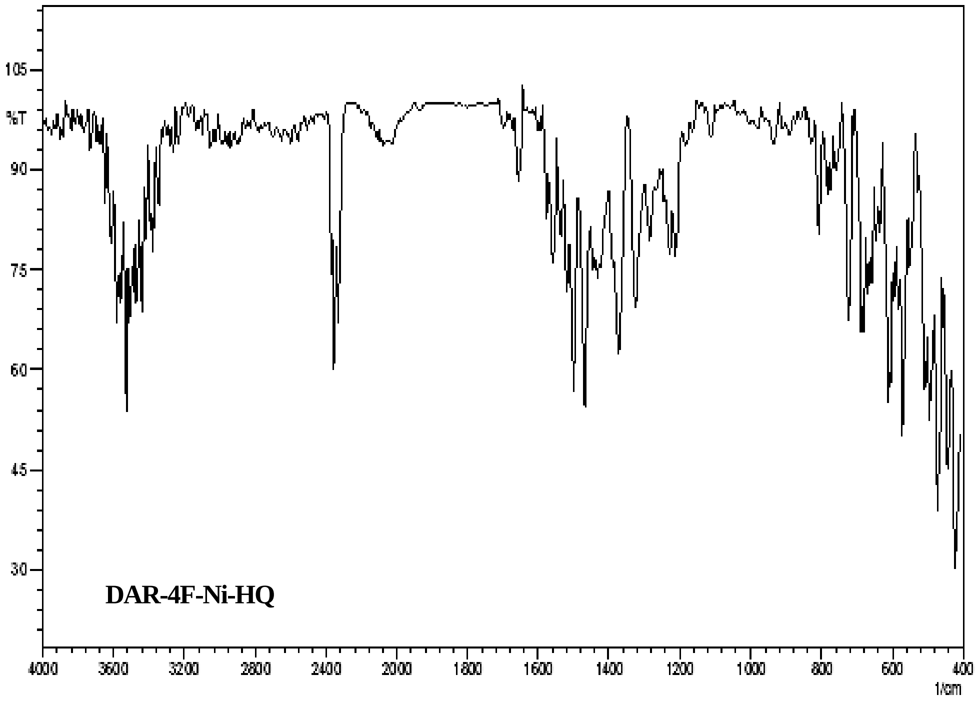
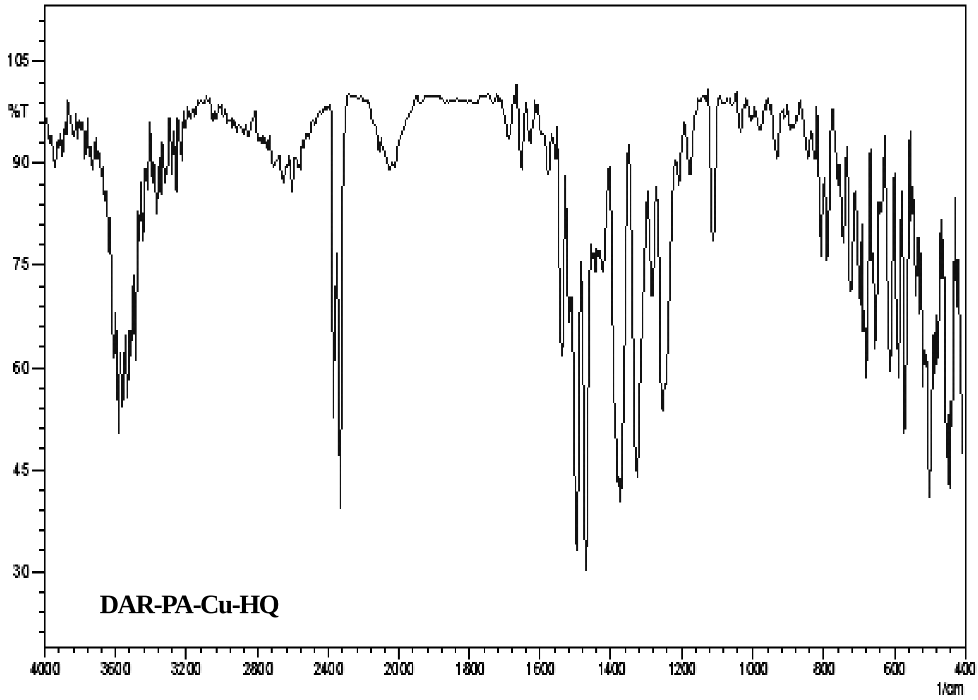


Figure-3.1



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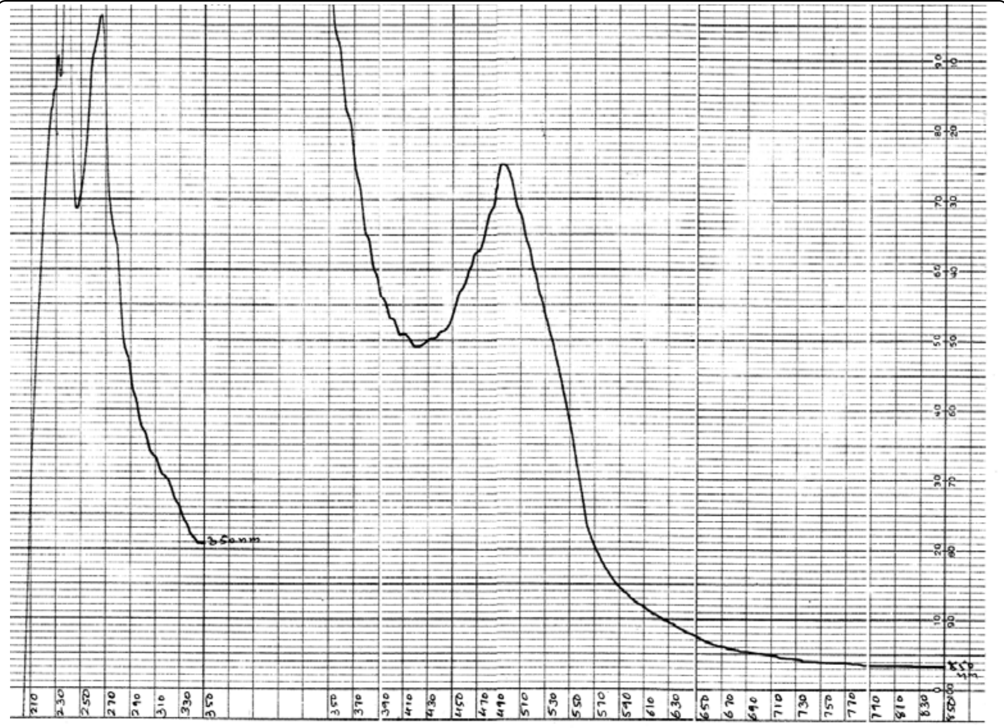
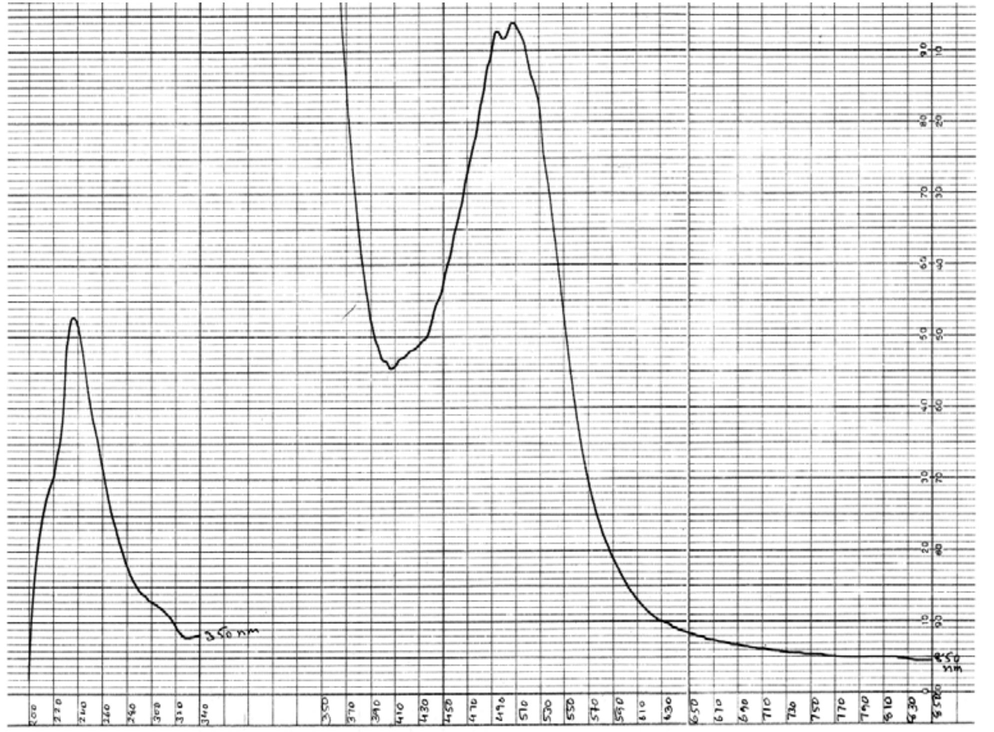
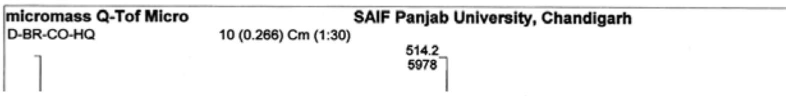


DAR-4F-Cu-HQ Figure-3.3



DAR-4Br-Ni-PHEN Figure-3.4

Figure-3.5



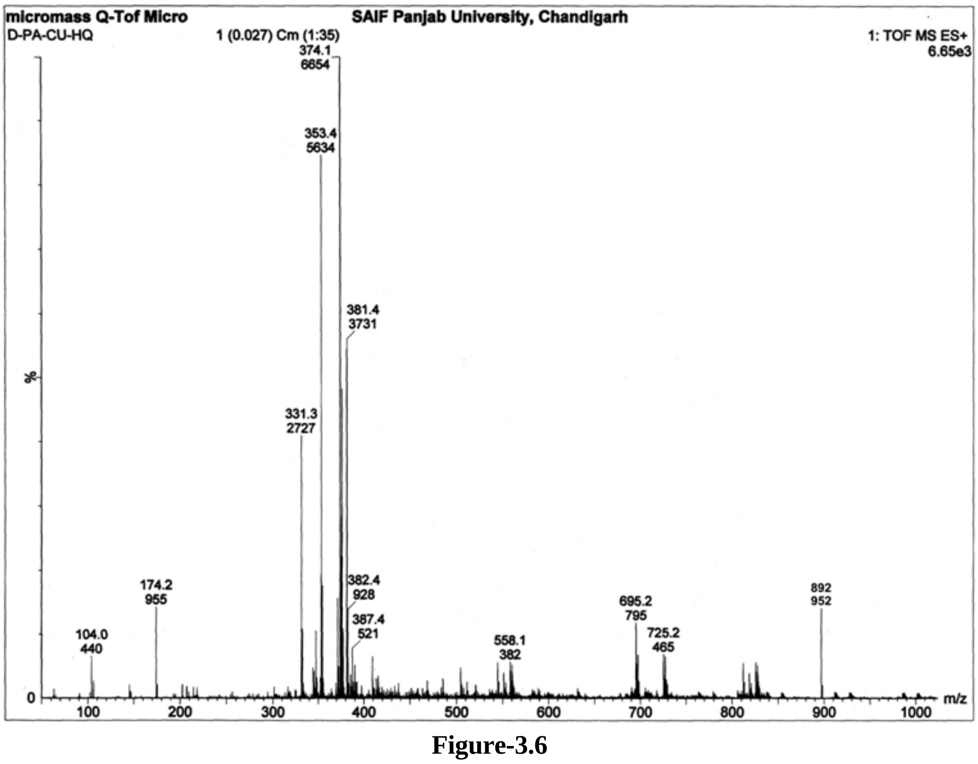
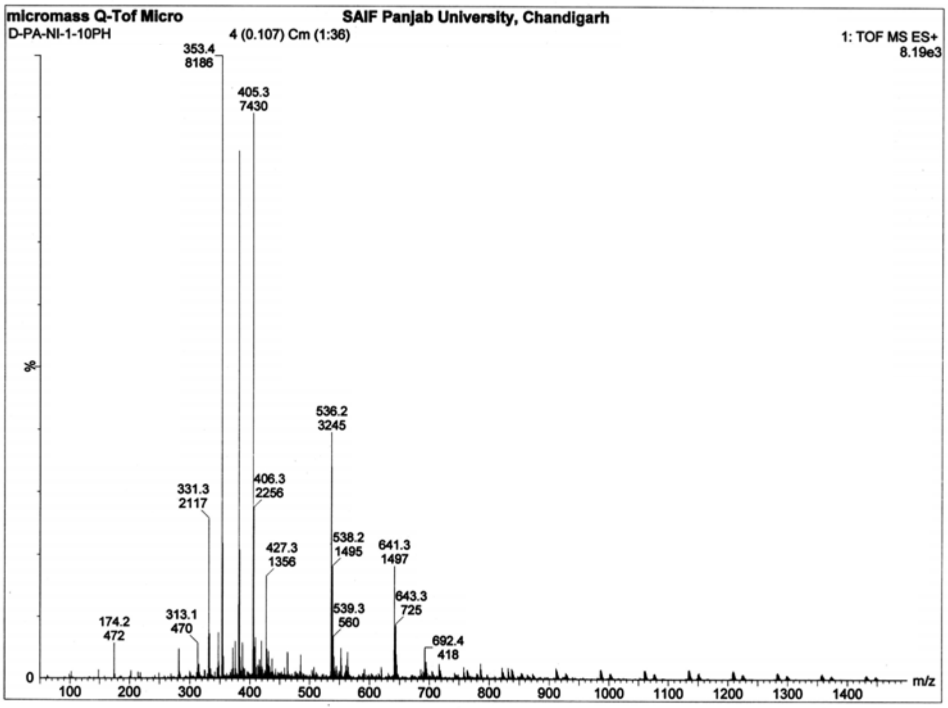


Figure-3.6



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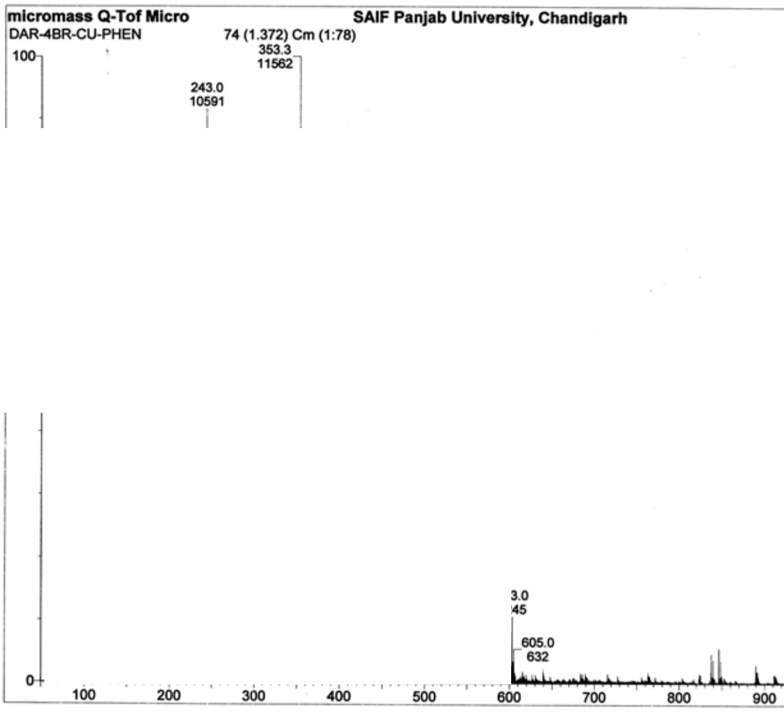
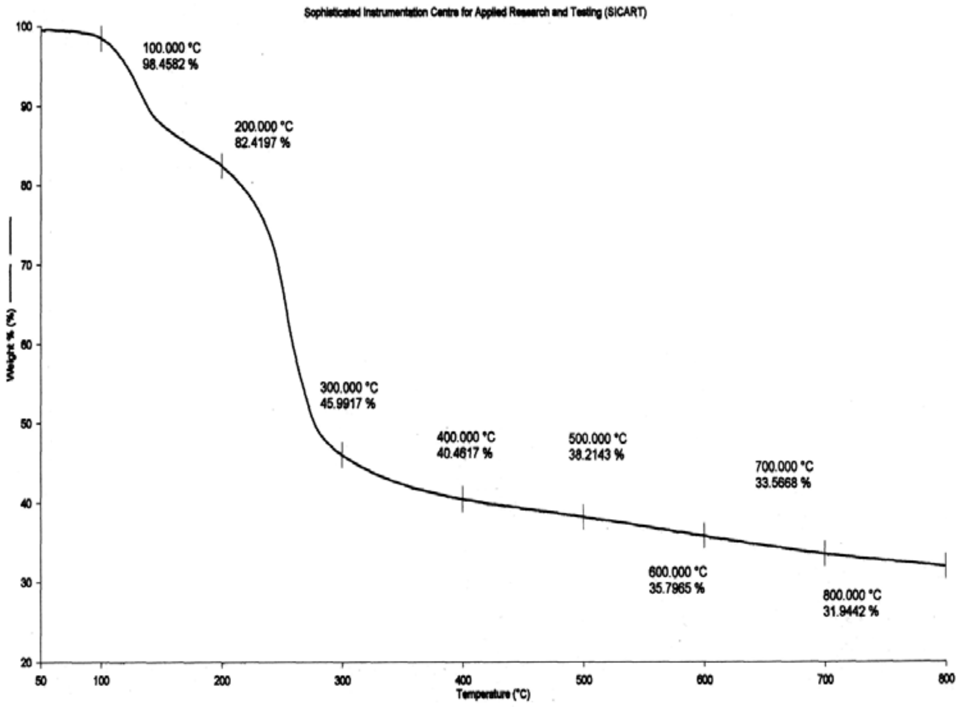


Figure-3.8



DAR-4F-Cu-HQ

Figure-3.9

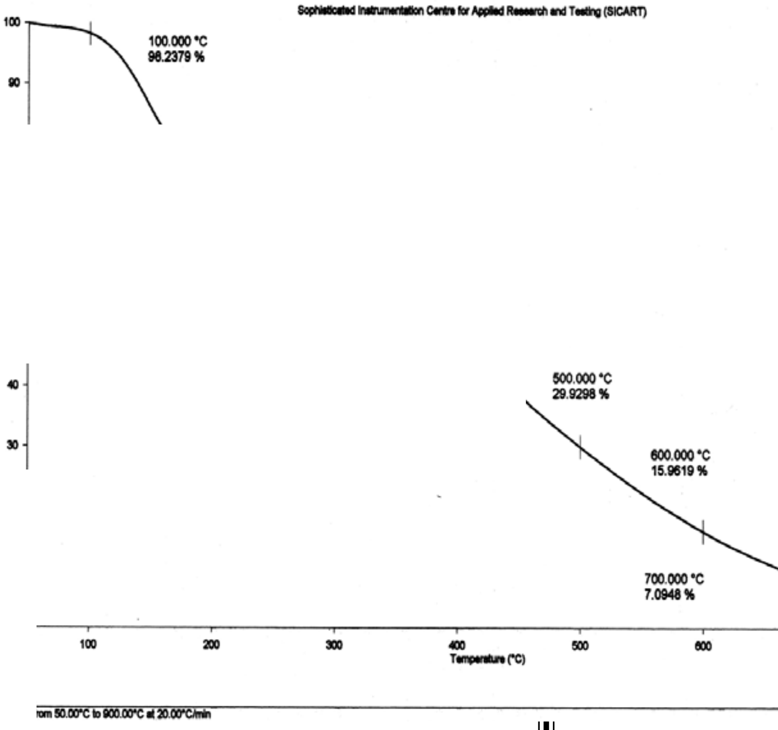
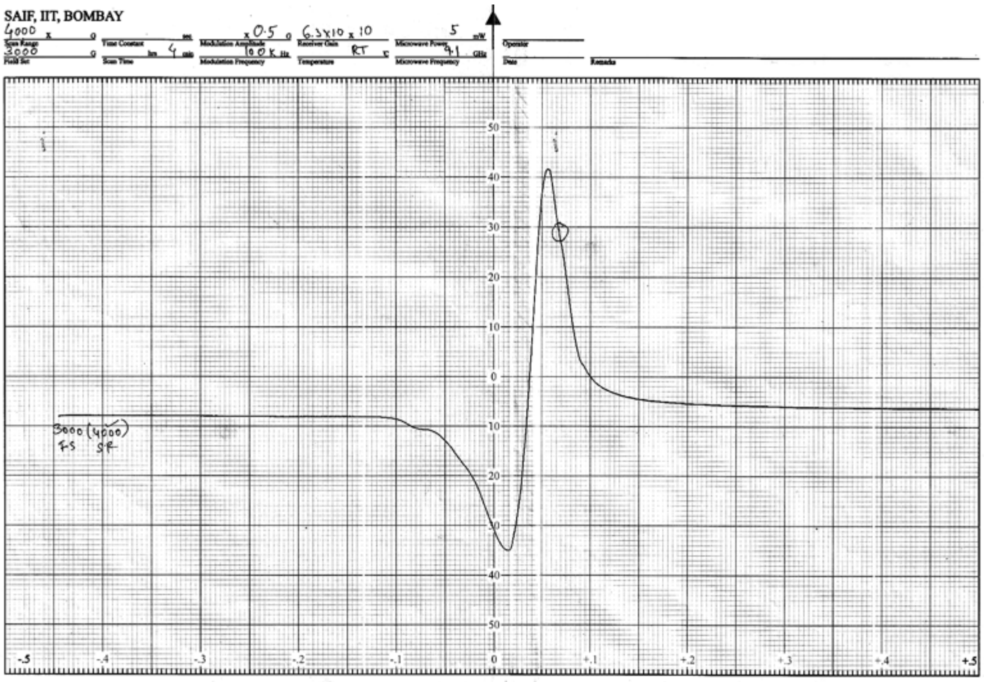


Figure-3.10

DAR-PA-Ni-PHEN



SAIF, IIT, BOMBAY

Scan Range 4000 x G
Field Set 3000 G
Time Constant sec
Scan Time hrs 4 min
Modulation Amplitude x 0.5 G
Modulation Frequency 100 K Hz
Receiver Gain 6.3x10 x 10
Temperature RT °C
Microwave Power 5 mW
Microwave Frequency 9.1 GHz
Operator
Date
Remarks

3000 (4000)
FS SR

DAR-4F-Cu-HQ

Figure-3.11

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CHAPTER 4

BIOLOGICAL EVALUATION OF LIGANDS AND METAL CHELATES

4.1 Introduction
4.2 Experimental
4.3 Activity Table
4.4 Activity Chart
4.5 References

4.1 INTRODUCTION

Many drugs possess modified pharmacological and toxicological properties when administered in the form of metallic complexes. Probably the most widely studied cations in this respect is Cu^{2+} and Co^{2+} since a host of low-molecular-weight copper and cobalt complexes have been proven beneficial against several diseases such as tuberculosis, rheumatoid, gastric ulcers, and cancers [276-279]. Transition metal complexes with biologically active ligands frequently exhibit higher biological activity and lower toxicity than the initial ligands [280].

Researchers in this area have synthesized new nitrogen-sulphur donor ligand through Schiff base condensation with various aldehyde and ketones. The properties of these ligands can be greatly modified by introduction of organic substituents. The number of these type of compounds synthesized continues to increase because of the intriguing observation that different ligand show different biological properties, although they may differ only slightly in their molecular structures, transition metal complexes of this ligands are also wildly studied because of their potential for therapeutic use[281-288]. They also find applications in health and skin care products and in paint manufacturing[289]. Antioxidant properties are of interest to biochemists and health professional because they may help the body protect itself against damage caused by reactive oxygen-based species and degenerative diseases[290].

Although ligands having oxygen and nitrogen as donor atoms are by far the most extensively studied, interest in sulfur donor chelating agents has grown over the years and the number of chemical studies in this area has increased considerably [291]. Interest in complexes of these ligand systems now covers several areas, ranging from general considerations of the effect of sulfur and electron delocalization in transition metal complexes to potential biological activity and practical application [292-294].

The antimicrobial properties of metals have been recognized for centuries and have represented some of the most fundamental breakthroughs in medicinal history [295]. Many studies stressed the role of metal ions in important biological processes, whereas the inorganic pharmacology started to be an important field with more than 25 inorganic compounds, being used in therapy as antibacterial, antiviral, and anticancer drugs [296,297]. Kirschner et al. [298] have suggested that the transfer of the metal ion from the ligand to the cancer-associated viruses was an important mechanism for designing new anticancer therapies. The inverse process, that is, coordinating a metal ion from an important biomolecule, such as, for instance, a zinc finger protein, has recently been used to design novel antiviral therapies, targeted against human immunodeficiency (HIV) and human papilloma virus (HPV) infections [299]. We have already drawn attention to the strong relationship between metals or their complexes [300-302], and antibacterial [303], antitumour [304], and anticancer [305] activities. A number of in vivo studies have indicated that biologically active compounds become more bacteriostatic and carcinostatic upon chelation[306].

BACTERIA

In 1928, A German Scientist C.E. Chenberg First used the term "Bacterium" to denote small microscopic organism with a relatively simple and primitive form of the cellular organization known as "Prokaryotic".

Danish physician, Gram in peculiarity, bacteria are generally unicellular E.G. Cocci, Bacilli, Etc. Filamentous, Eg, Actinomycetes, some being sheathed having certain cells specialized for reproduction. The microorganism are capable of producing diseases in host are known as "Pathogenic". Most of the microorganisms present on the skin and mucous membrane are non-pathogenic and are often referred to as "commensals" or if they live on food residues as in intestine, they may be called "Saprophytes". Generally, The pathogenic Cocci and Bacilli are gram positive and the pathogenic Coco Bacilli are gram negative.

From evaluation of antibacterial activity in our case, we have used Staphylococcus Aureus and Staphylococcus Pyogenes from gram positive group of bacteria and Escherichia Coli and Pseudomonas Aeruginosa from gram negative group of baceria.

1. STAPHYLOCOCCUS AUREUS

(I) Genus: Staphylococcus[Microccaceae]

Staphylococci are differentiated from micrococcus, a genus of the same family by its ability to utilize to be found on the skin or mucous membranes of the animal body, especially of the nose and mouth where they occur in large numbers even under normal conditions.

(II) Species: Staphylococcus Aureus

The individual cells of S. Aureus are 0.8 to 0.9 micro in diameter. They are ovoid or spherical, non motile, non capsulated, non sporing stain with ordinary aniline dyes and gram positive, typically arranged in groups of irregular clusters like branches of groups found in pus, singly or in pairs. The optimum temperature for the growth us 37° C, optimum pH is 7.4 to 7.6. They produce golden yellow pigment, which develops best at room temperature. They cause pyoregenic of pus forming [suppurative] conditions, mastitis of women and cows, boils, carbuncles infantile impetigo, internal abscess and food poisoning.

2. ESCHERICHIA COLI

(I) Genus: Escherichia [Enterobacteriacea]

This genus comprises Escherichia and several variants and are of particular interest to the sanitarian since they occur commonly in the formal intestinal tract of man and animals. Their presence in foods or in drinking water may indicate faecal pollution. E.Coli is the most distinctively recognized Feacal species.

(II) Species: Escherichia coli

E.Coli is the most important type in this species, which contains number of other types Escherichia in 1885 discovered in from the faces of the newborn and showed the organisms in the intesting within three days after birth. It is a commensals of the human intesting and found in the intestinal of men and animals and is also found in the sewage water, land, soil contaminated by Faecal matters. The gram negative rods are 2 to 4 micro by 0.4 micro in size, commonly seen in coccobacillary form and rarely in filamentous form. They are facultative anaerobes and grow in all laboratory media. Colonies are circular, raised smooth and emit a faecal odor, E.Coli are generally non pathogenic and are incriminated as pathogens because in certain instances some strains have been found to produce septicemia, inflammations of liver and gall bladder, appendix, meningitis, pneumonia and other infections and this species is a recognized pathogen in the veterinary field.

3. STREPTOCOCCUS PYOGENES

(I) Genus: Streptococcus

The term Streptococcus was fist introduced by Bilroth[1874] and the term Streptococcus Pyogenes was used by Rosenbach[1884]. These are spherical or ovoid cells; divide in one axis and form chains; nonsporing. The growth is absence of native proteins in the medium; they produce characteristic haemolytic changes in media containing blood; produce acid only by fermentation of carbohydrates; often fail to liquefy gelatin; some strains produce exotoxin and extracellular products; a few of them are Anaerobic.

(II) Species: Streptococcus Pyogenes

Streptococcus Pyogenes is pathogenic to human and found in sore throat, follicular tonsillitis, septicemia, acute or malignant ulcerative endocarditis etc. these are spherical Cocci 0.5 to 0.75 micro in diameter, arranged in moderately long chains of round Cocci and easily differentiated from Enterococci that from short chains of 2 to 4 spares. Streptococcus Pygenes is recently isolated from throat or other lesion; they show either mucoid or matt colonies. On keeping in the laboratory, they undergo varation to a glossy type. Streptococci are susceptible to destructive agents, and to penicillin and sulphomamides.

4. PSEUDOMONAS AERUGINOSA

(I) Genus: Pseudomonas

Genus Pseudomonas is characterized by gram negative motile rods, nonsporing aerobes, oxidase positive, bluish green or yellowish pigment diffusing into the medium. Out of 140 species, only one is pathogenic to human.

(II) Species: Pseudomonas aeruginosa

Psaeruginosa a commensal in the intestine of human and animal's but, when the defensive mechanism of the body is poor. It acts as a minor pathogen producing suppurative wound, otitis media, peritonitis, cystitis, bronchopneumonia and empyema. In children it causes diarrhea and septicemia. The pus produced by Psaeruginosa is greenish blue. These are gram negative, actively motile, non sporing organisms' 1.5-3 micro by 0.5 micro with rounded ends and bipolar flagella. They occur singly or in pair, of short chains. They grow well in ordinary media under aerobic conditions, producing diffusible pigment.

FUNGUS

It has been estimated that the life expectancy of humans has increased by at least 10 years since the discovery of antimicrobial agents for the treatment of microbial infections. A consequence of our success with antimicrobial agents and improved medical care is the number of fungal infections.

The incidence of fungal infections has increased dramatically in the past 20 years partly because of the increase in the number of people whose immune system are compromised by wither AIDS, aging, organ transplantation or cancer therapy. Accordingly, the increase in rates of morbidity and mortality because of fungal infections has been now recognized as a major problem in response to the increased incidence of fungal infections, the pharmaceutical industry has developed a number of newer less toxic antifungal for clinical use. The increased use of antifungal, often for prolonged periods, has lead to recognition of the phenomenon of acquired antifungal resistance to one or more of the available antifungal.

Fungi are nonphotosyntheitc eukaryotes growing either as colonies of single cells(yeasts) or as filamentous multicellular aggregate [molds]. Most fungi live as saprophytes in soil or on dead plant material and are important in the mineralization of organic matter. A smaller number produce disease in human and animals. The *in vitro* methods used for detections of antifungal potency are similar to those used in antibacterial screening. As with bacteria, it is easy to discover several synthetic and natural compounds that, in small quantity, can retard or prevent growth of fungi in culture media.

1. CANDIDA ALBICANS

(I) Genus: Candida

Candida species reproduce by yeast like budding cells but they also show formation pseudomycellum. These pseudomycellum are chains of elongated cells formed from buds and the buds elongated without breaking of the mother cell. They are very fragile and separate easily. Mycelia also form by the elongation of the germ tube produced by a mother celll.

Species: Candida albicans

Candida albicans may remain as commensal of the mucous membrane with of without causing any pathologic changes to the deeper tissues of the same fungus may cause pathological lesion of the skin. Such a fungus under favorable conditions can cause superficial, intermediate of deep mycoses depending on the condition of the host.

2. ASPERGILLUS NIGER AND ASPERGILLUS CLAVATUS

(I) Genus: Aspergillus

The Aspergillus are widespread in nature, being found on fruits, vegetables and other substates, which may provide nutriment. Some species are involved in food spoilage. They are important economically because they are used in a number of industrial fermentations, including the production of citric acid gluconic acid. Aspergillus grow in high concentrations of sugar and salt, indicating that they can extract water required for their growth from relatively dry substances.

4.2 EXPERIMENTAL

4.2.1 Evaluation Techniques

The following conditions must be met for the screening of antimicrobial activity:

(A) There should be intimate contact between the test organisms and substance to be evaluated.

(B) Required conditions should be provided for the growth of micro organisms.

(C) Conditions should be same through the study.

(D) Aseptic / sterile environment should be maintained.

Various methods have been used from time to time by several workers to evaluate the antimicrobial activity. The evaluation can be done by the following methods:

(a) Turbidometric method

(b) Agar streak dilution method

(c) Serial dilution method

(d) Agar diffusion method

Following Techniques are used as agar diffusion method:

(a) Agar Cup method

(b) Agar Ditch method

(c) Paper Disc method

We have used the **“Broth Dilution Method”** to evaluate the antibacterial activity.

It is one of the non automated in vitro bacterial susceptibility tests. This classic method yields a quantitative result for the among of antimicrobial agents that is needed to inhibit growth of specific micro organisms. It is carried out in tubes.

(a) Macro-dilution Method in Tubes.

(b) Micro-dilution format using plastic trays.

4.2.2 Materials and Method

Determination of minimal bactericidal concentrations by agar cup method

All the synthesized drugs were used for antibacterial and antifungal test producers

All necessary controls like:

- Drug control
- Vehicle control
- Agar control
- Organism control
- Known antibacterial drugs control

All MTCC cultures were tested against above mentioned known and unknown drugs. Inoculums size for test strain was adjust to 108 Cfu [Colony Forming Unit] per milliliter by comparing the turbidity

Minimal Bactericidal Concentration [MBC] and Minimal Fungicidal Concentration [MFC]

The main advantage of the 'Broth Dilution Method' for MBC determination lies in the fact that it can readily be converted to determine the MBC as well.

1. Serial dilutions were prepared in primary and secondary screening.
2. The control tube containing no antibiotic is immediately sub cultured [before inoculation] by spreading a loopful evenly over quarter of plate on medium suitable for the growth of the test organism and put for incubation at 37^o C OVERNIGHT. The tubes are then incubated overnight.
3. The MBC of the control organism is read to check the accuracy of the drug concentrations.
4. The lowest concentration inhibiting growth of the organism is recorded as the MBC.
5. All the tubes not showing visible growth in the same manner as control tube described above] are sub cultured and incubated overnight at 37^o C.
6. The amount of growth from the control tuybe before incubation [which represents the original inoculum] is compared.
7. Subcultures may show: Similar number of colonies indicating bacteriostatic, a reduced number of colonies-indicating a partial or slow bactericidal activity & no growth – if the whole inoculum has been killed. The test must include a second set of the same dilutions inoculated with an organism of known sensitivity.

Method used for primary and secondary screening

Each synthesized drug was diluted obtaining 200 microgram / ml concentration, as a stock solution.

Primary screen: In primary screening 500 micro/ml, 250 micro/ml and 125 micro/ml concentrations of the synthesized drugs were taken. The active synthesized drugs found in this primary screening were further tested in a second set of dilution against all micro organisms.

Secondary screen: The drugs found active in primary screening were similarly diluted to obtain 100 micro/ml, 50 micro/ml, 25 micro/ml, 12.5 micro/ml, 6.250 micro/ml, 3.125 micro/ml and 1.5625 micro/ml concentrations.

Reading Result: The highest dilution showing at least 99% inhibition zone is taken as MIC. The result of this is much affected by the size of the inoculum. The test mixture should contain 10^8 organism/ml.

Following common standard strains were used for screening of antibacterial and antifungal activities:

(I) Escherichia coli	[Gram negative]	MTCC-442
(II) Pseudomonas aeruginosa	[Gram negative]	MTCC-441
(III) Staphylococcus aureus	[Gram positive]	MTCC-96
(IV) Streptococcus Pyogenes	[Gram [positive]	MTCC-443
(V) Candida albicans	[Fungus]	MTCC-227
(VI) Aspergillus Niger	[Fungus]	MTCC-282
(VII) Aspergillus clavatus	[Fungus]	MTCC-1323

DMSO was used as diluents / vehicle to get desired concentration of drugs to test upon standard bacterial strains.

The Standard Drugs:

Minimal Bactericidal Concentration

Drug	E. Coli	P. Aeruginosa	S. Aureus	S. Pyogenus
	MTCC-443	**MTCC-441**	**MTCC-96**	**MTCC-442**
		μg/ml		
Ampicillin	100	100	250	100
Chloramphenicol	50	50	50	50
Ciprofloxacin	25	25	50	50
Norfloxacin	10	10	10	10

Minimal Fungicidal Concentration

Drug	C. Albicans	A. Niger	A. Clavatus
	MTCC-227	**MTCC-282**	**MTCC-1323**
		μg/ml	
Nystatin	100	100	100
Greseofulvin	500	100	100

4.3 ACTIVITY TABLE

4.3.1 ANTIBACTERIAL ACTIVITY OF LIGANDS

		MINIMAL BACTERICIDAL CONCENTRATION (μg/ml)			
Sr. No.	**Ligand**	**E. Coli**	**P. Aeruginosa**	**S. Aureus**	**S. Pyogenus**
1.	DAR	250	500	500	500
2.	H_2L^1	125	500	250	250
3.	H_2L^2	250	250	250	250
4.	H_2L^3	500	500	1000	1000
5.	H_2L^4	250	250	250	250
6.	H_2L^5	500	500	1000	500
7.	H_2L^6	250	100	250	250
8.	H_2L^7	100	100	500	500
9.	H_2L^8	250	250	500	250
10.	H_2L^9	500	500	500	500
11.	H_2L^{10}	100	500	500	500

4.3.2 ANTIFUNGAL ACTIVITY OF LIGANDS

		MINIMAL FUNGICIDAL CONCENTRATION (μg/ml)		
Sr. No.	**Ligand**	**C. ALBICANS**	**A. NIGER**	**A. CLAVATUS**
1.	DAR	500	1000	1000
2.	H_2L^1	500	250	250
3.	H_2L^2	500	500	500
4.	H_2L^3	1000	500	500
5.	H_2L^4	1000	500	500
6.	H_2L^5	1000	1000	1000
7.	H_2L^6	250	250	250
8.	H_2L^7	250	500	500
9.	H_2L^8	500	500	1000
10.	H_2L^9	500	250	250
11.	H_2L^{10}	500	1000	1000

4.3.3 ANTIBACTERIAL ACTIVITY OF METAL CHELATES

MINIMAL BACTERICIDAL CONCENTRATION (μg/ml)					
Sr. No.	**METAL COMPLEX**	**E. Coli**	**P. Aeruginosa**	**S. Aureus**	**S. Pyogenus**
1.	$[Co(L^1)_2(H_2O)_2]$	500	250	250	125
2.	$[Ni(L^1)_2(H_2O)_2]$	1000	1000	500	1000
3.	$[Cu(L^1)_2(H_2O)_2]$	125	250	100	62.5
4.	$[Co(L^2)_2(H_2O)_2]$	250	250	250	250
5.	$[Ni(L^2)_2(H_2O)_2]$	250	500	500	1000
6.	$[Cu(L^2)_2(H_2O)_2]$	125	500	500	250
7.	$[Co(L^3)_2(H_2O)_2]$	250	500	250	250
8.	$[Ni(L^3)_2(H_2O)_2]$	500	250	1000	500
9.	$[Cu(L^3)_2(H_2O)_2]$	500	1000	500	500
10.	$[Co(L^4)_2(H_2O)_2]$	500	250	100	125
11.	$[Ni(L^4)_2(H_2O)_2]$	1000	500	250	250
12.	$[Cu(L^4)_2(H_2O)_2]$	500	250	100	1000
13.	$[Co(L^5)_2(H_2O)_2]$	250	250	500	1000
14.	$[Ni(L^5)_2(H_2O)_2]$	500	100	1000	1000
15.	$[Cu(L^5)_2(H_2O)_2]$	62.5	100	1000	500
16.	$[Co(L^6)_2(H_2O)_2]$	500	1000	250	250
17.	$[Ni(L^6)_2(H_2O)_2]$	1000	1000	1000	500
18.	$[Cu(L^6)_2(H_2O)_2]$	500	250	125	100
19.	$[Co(L^7)_2(H_2O)_2]$	250	250	500	500
20.	$[Ni(L^7)_2(H_2O)_2]$	1000	1000	500	1000
21.	$[Cu(L^7)_2(H_2O)_2]$	500	250	100	125
22.	$[Co(L^8)_2(H_2O)_2]$	500	500	250	500
23.	$[Ni(L^8)_2(H_2O)_2]$	250	250	125	100
24.	$[Cu(L^8)_2(H_2O)_2]$	1000	1000	250	250
25.	$[Co(L^9)_2(H_2O)_2]$	1000	100	100	250
26.	$[Ni(L^9)_2(H_2O)_2]$	100	125	250	500

Sr. No.	METAL COMPLEX	E. Coli	P. Aeruginosa	S. Aureus	S. Pyogenus
27.	$[Cu(L^9)_2(H_2O)_2]$	500	500	500	1000
28.	$[Co(L^{10})_2(H_2O)_2]$	1000	250	100	250
29.	$[Ni(L^{10})_2(H_2O)_2]$	500	250	500	250
30.	$[Cu(L^{10})_2(H_2O)_2]$	250	1000	250	1000

4.3.4 ANTIFUNGAL ACTIVITY OF METAL CHELATES

MINIMAL FUNGICIDAL CONCENTRATION (μg/ml)				
Sr. No.	**METAL COMPLEX**	**C. ALBICANS**	**A. NIGER**	**A. CLAVATUS**
1.	$[Co(L^1)_2(H_2O)_2]$	500	1000	1000
2.	$[Ni(L^1)_2(H_2O)_2]$	1000	1000	1000
3.	$[Cu(L^1)_2(H_2O)_2]$	500	1000	1000
4.	$[Co(L^2)_2(H_2O)_2]$	500	500	1000
5.	$[Ni(L^2)_2(H_2O)_2]$	500	1000	1000
6.	$[Cu(L^2)_2(H_2O)_2]$	250	250	500
7.	$[Co(L^3)_2(H_2O)_2]$	250	1000	500
8.	$[Ni(L^3)_2(H_2O)_2]$	500	500	1000
9.	$[Cu(L^3)_2(H_2O)_2]$	250	1000	1000
10.	$[Co(L^4)_2(H_2O)_2]$	1000	1000	1000
11.	$[Ni(L^4)_2(H_2O)_2]$	500	500	1000
12.	$[Cu(L^4)_2(H_2O)_2]$	250	500	500
13.	$[Co(L^5)_2(H_2O)_2]$	500	250	250
14.	$[Ni(L^5)_2(H_2O)_2]$	1000	500	500
15.	$[Cu(L^5)_2(H_2O)_2]$	250	500	500
16.	$[Co(L^6)_2(H_2O)_2]$	1000	1000	1000
17.	$[Ni(L^6)_2(H_2O)_2]$	1000	500	500
18.	$[Cu(L^6)_2(H_2O)_2]$	500	500	250
19.	$[Co(L^7)_2(H_2O)_2]$	1000	1000	1000
20.	$[Ni(L^7)_2(H_2O)_2]$	500	1000	500
21.	$[Cu(L^7)_2(H_2O)_2]$	1000	1000	1000

Sr. No.	METAL COMPLEX	C. ALBICANS	A. NIGER	A. CLAVATUS
22.	$[Co(L^8)_2(H_2O)_2]$	500	500	500
23.	$[Ni(L^8)_2(H_2O)_2]$	250	250	1000
24.	$[Cu(L^8)_2(H_2O)_2]$	1000	500	500
25.	$[Co(L^9)_2(H_2O)_2]$	250	250	125
26.	$[Ni(L^9)_2(H_2O)_2]$	500	1000	1000
27.	$[Cu(L^9)_2(H_2O)_2]$	250	250	250
28.	$[Co(L^{10})_2(H_2O)_2]$	250	250	500
29.	$[Ni(L^{10})_2(H_2O)_2]$	500	1000	1000
30.	$[Cu(L^{10})_2(H_2O)_2]$	500	500	500

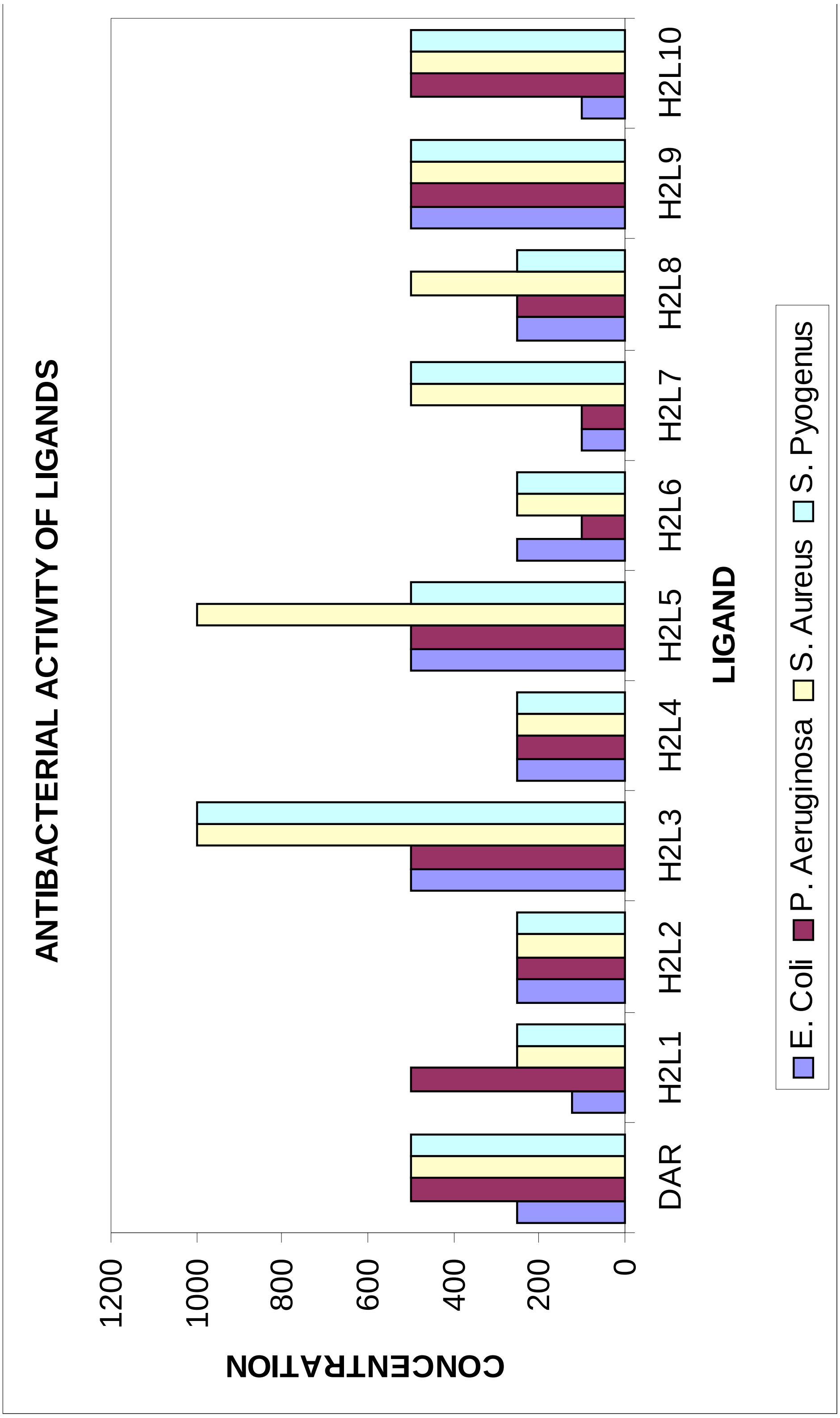
4.3.5 ANTIBACTERIAL ACTIVITY OF MIXED LIGAND METAL COMPLEXES

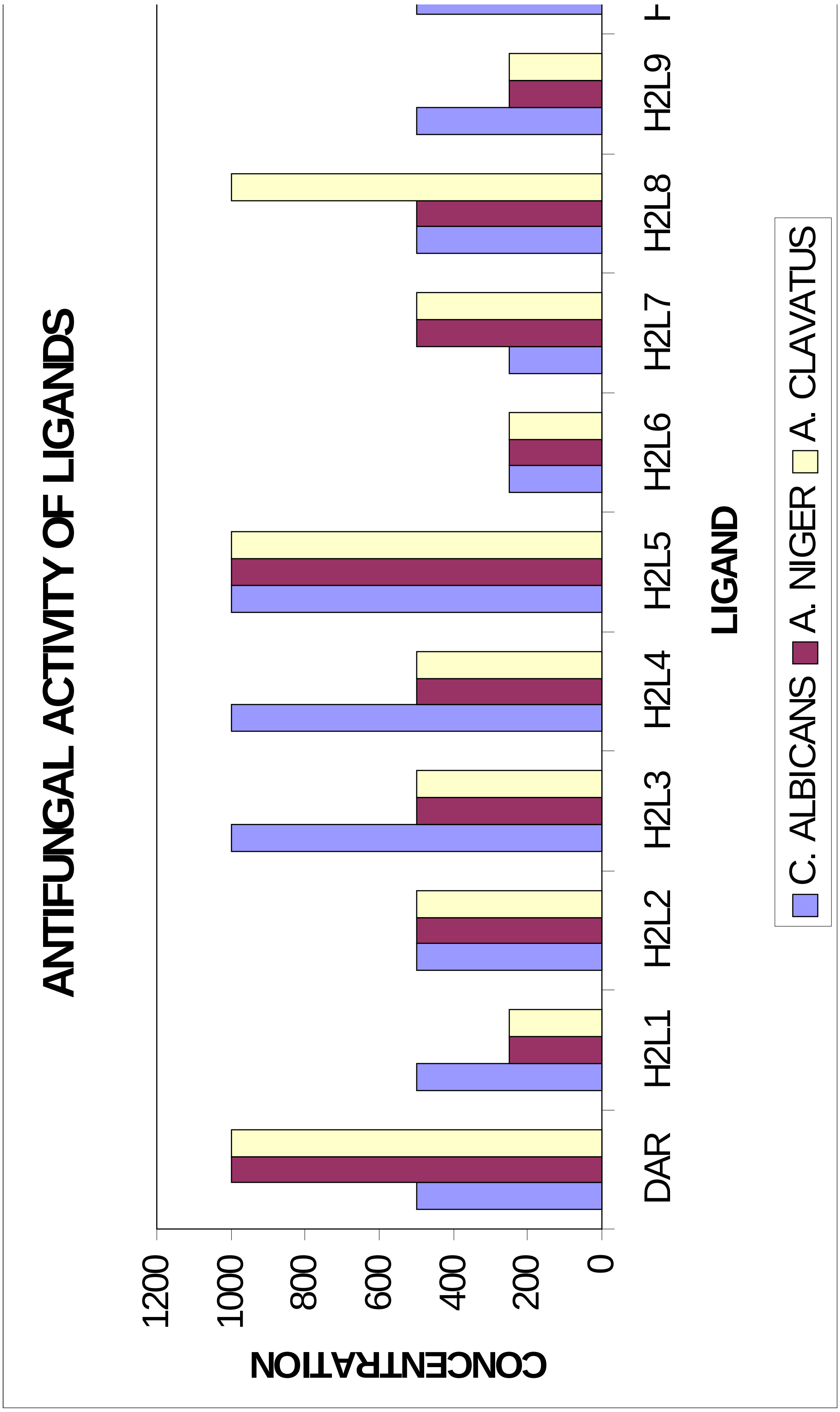
MINIMAL BACTERICIAL CONCENTRATION (μg/ml)					
Sr. No.	**METAL COMPLEX**	**E. Coli**	**P. Aeruginosa**	**S. Aureus**	**S. Pyogenus**
1.	$[Co_2(L^2)(8\text{-}HQ)_2(H_2O)_4]$	250	100	500	500
2.	$[Ni_2(L^2)(8\text{-}HQ)_2(H_2O)_4]$	1000	250	250	250
3.	$[Cu_2(L^2)(8\text{-}HQ)_2(H_2O)_4]$	100	100	100	100
4.	$[Co_2(L^4)(8\text{-}HQ)_2(H_2O)_4]$	250	250	500	500
5.	$[Ni_2(L^4)(8\text{-}HQ)_2(H_2O)_4]$	500	500	1000	1000
6.	$[Cu_2(L^4)(8\text{-}HQ)_2(H_2O)_4]$	125	250	500	1000
7.	$[Co_2(L^5)(8\text{-}HQ)_2(H_2O)_4]$	250	250	250	200
8.	$[Ni_2(L^5)(8\text{-}HQ)_2(H_2O)_4]$	250	250	500	250
9.	$[Cu_2(L^5)(8\text{-}HQ)_2(H_2O)_4]$	500	500	1000	250
10.	$[Co_2(L^6)(8\text{-}HQ)_2(H_2O)_4]$	250	100	250	500
11.	$[Ni_2(L^6)(8\text{-}HQ)_2(H_2O)_4]$	100	500	500	100
12.	$[Cu_2(L^6)(8\text{-}HQ)_2(H_2O)_4]$	500	250	500	250
13.	$[Co_2(L^2)(1,10\text{-}Phen)_2(H_2O)_4]$	500	500	100	100
14.	$[Ni_2(L^2)(1,10\text{-}Phen)_2(H_2O)_4]$	250	250	250	100
15.	$[Cu_2(L^2)(1,10\text{-}Phen)_2(H_2O)_4]$	100	250	500	500
16.	$[Co_2(L^4)(1,10\text{-}Phen)_2(H_2O)_4]$	62.5	125	200	250
17.	$[Ni_2(L^4)(1,10\text{-}Phen)_2(H_2O)_4]$	100	125	500	500
18.	$[Cu_2(L^4)(1,10\text{-}Phen)_2(H_2O)_4]$	500	500	250	500
19.	$[Co_2(L^5)(1,10\text{-}Phen)_2(H_2O)_4]$	500	500	500	100
20.	$[Ni_2(L^5)(1,10\text{-}Phen)_2(H_2O)_4]$	250	250	500	500
21.	$[Cu_2(L^5)(1,10\text{-}Phen)_2(H_2O)_4]$	100	500	1000	1000
22.	$[Co_2(L^6)(1,10\text{-}Phen)_2(H_2O)_4]$	250	250	100	500
23.	$[Ni_2(L^6)(1,10\text{-}Phen)_2(H_2O)_4]$	250	500	500	500
24.	$[Cu_2(L^6)(1,10\text{-}Phen)_2(H_2O)_4]$	500	1000	500	250

4.3.6 ANTIFUNGAL ACTIVITY OF MIXED LIGAND METAL COMPLEXES

MINIMAL FUNGICIDAL CONCENTRATION (μg/ml)				
Sr. No.	**METAL COMPLEX**	**C. ALBICANS**	**A. NIGER**	**A. CLAVATUS**
1	$[Co_2(L^2)(8\text{-}HQ)_2(H_2O)_4]$	100	500	1000
2	$[Ni_2(L^2)(8\text{-}HQ)_2(H_2O)_4]$	250	1000	1000
3	$[Cu_2(L^2)(8\text{-}HQ)_2(H_2O)_4]$	125	500	1000
4	$[Co_2(L^4)(8\text{-}HQ)_2(H_2O)_4]$	500	400	1000
5	$[Ni_2(L^4)(8\text{-}HQ)_2(H_2O)_4]$	500	500	250
6	$[Cu_2(L^4)(8\text{-}HQ)_2(H_2O)_4]$	500	1000	500
7	$[Co_2(L^5)(8\text{-}HQ)_2(H_2O)_4]$	100	100	100
8	$[Ni_2(L^5)(8\text{-}HQ)_2(H_2O)_4]$	250	500	1000
9	$[Cu_2(L^5)(8\text{-}HQ)_2(H_2O)_4]$	500	500	500
10	$[Co_2(L^6)(8\text{-}HQ)_2(H_2O)_4]$	1000	1000	500
11	$[Ni_2(L^6)(8\text{-}HQ)_2(H_2O)_4]$	1000	500	250
12	$[Cu_2(L^6)(8\text{-}HQ)_2(H_2O)_4]$	500	100	500
13	$[Co_2(L^2)(1,10\text{-}Phen)_2(H_2O)_4]$	125	125	1000
14	$[Ni_2(L^2)(1,10\text{-}Phen)_2(H_2O)_4]$	1000	250	250
15	$[Cu_2(L^2)(1,10\text{-}Phen)_2(H_2O)_4]$	1000	1000	125
16	$[Co_2(L^4)(1,10\text{-}Phen)_2(H_2O)_4]$	250	250	100
17	$[Ni_2(L^4)(1,10\text{-}Phen)_2(H_2O)_4]$	250	250	1000
18	$[Cu_2(L^4)(1,10\text{-}Phen)_2(H_2O)_4]$	500	1000	1000
19	$[Co_2(L^5)(1,10\text{-}Phen)_2(H_2O)_4]$	500	100	100
20	$[Ni_2(L^5)(1,10\text{-}Phen)_2(H_2O)_4]$	500	1000	1000
21	$[Cu_2(L^5)(1,10\text{-}Phen)_2(H_2O)_4]$	250	500	1000
22	$[Co_2(L^6)(1,10\text{-}Phen)_2(H_2O)_4]$	500	500	1000
23	$[Ni_2(L^6)(1,10\text{-}Phen)_2(H_2O)_4]$	1000	1000	1000
24	$[Cu_2(L^6)(1,10\text{-}Phen)_2(H_2O)_4]$	1000	1000	1000

4.4 ACTIVITY CHART




ANTIFUNGAL ACTIVITY OF LIGANDS
CONCENTRATION
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800
600
400
200
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DAR
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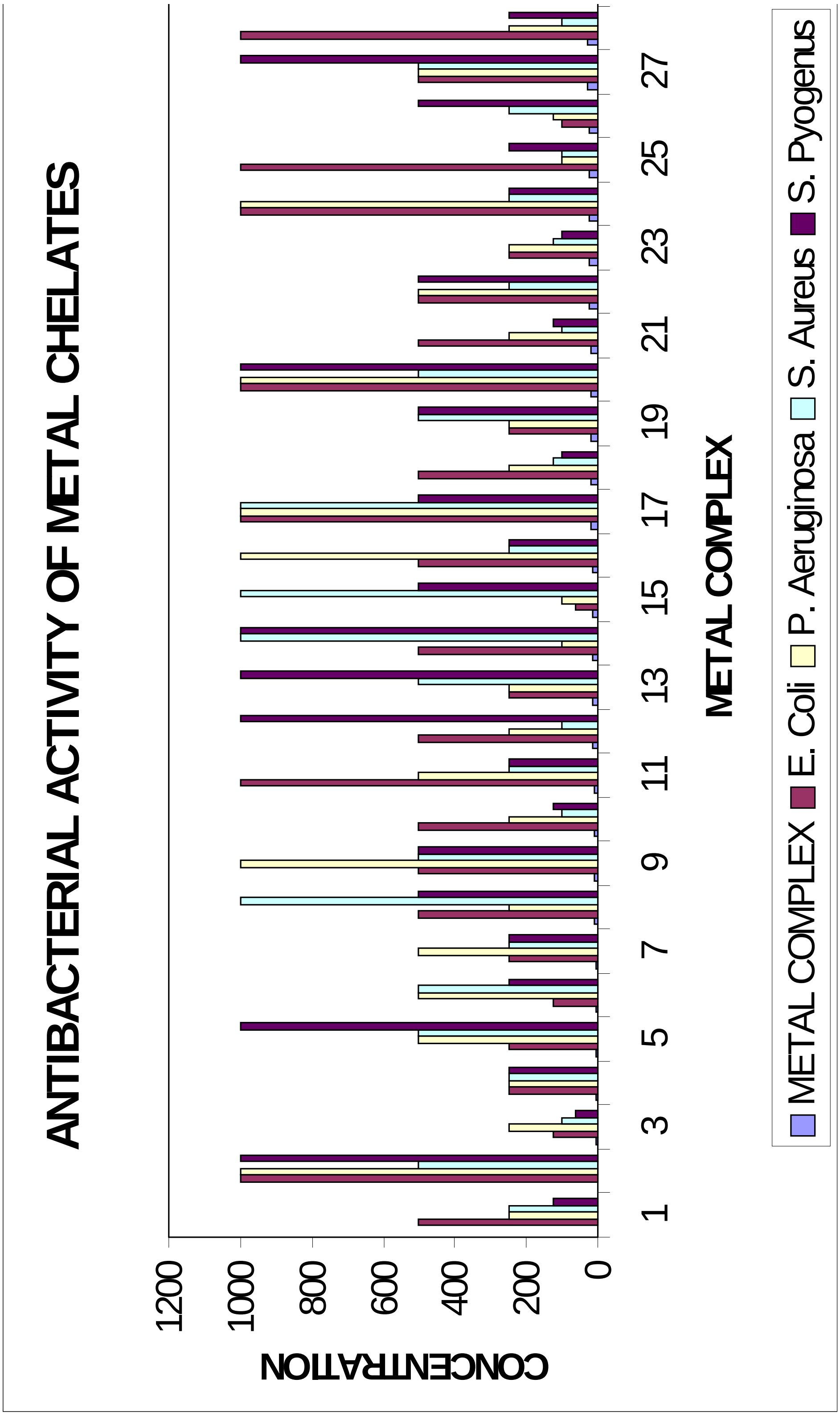
H2L2
H2L3
H2L4
H2L5
H2L6
H2L7
H2L8
H2L9
LIGAND
C. ALBICANS
A. NIGER
A. CLAVATUS


ANTIBACTERIAL ACTIVITY OF METAL CHELATES
CONCENTRATION
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600
400
200
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METAL COMPLEX
1
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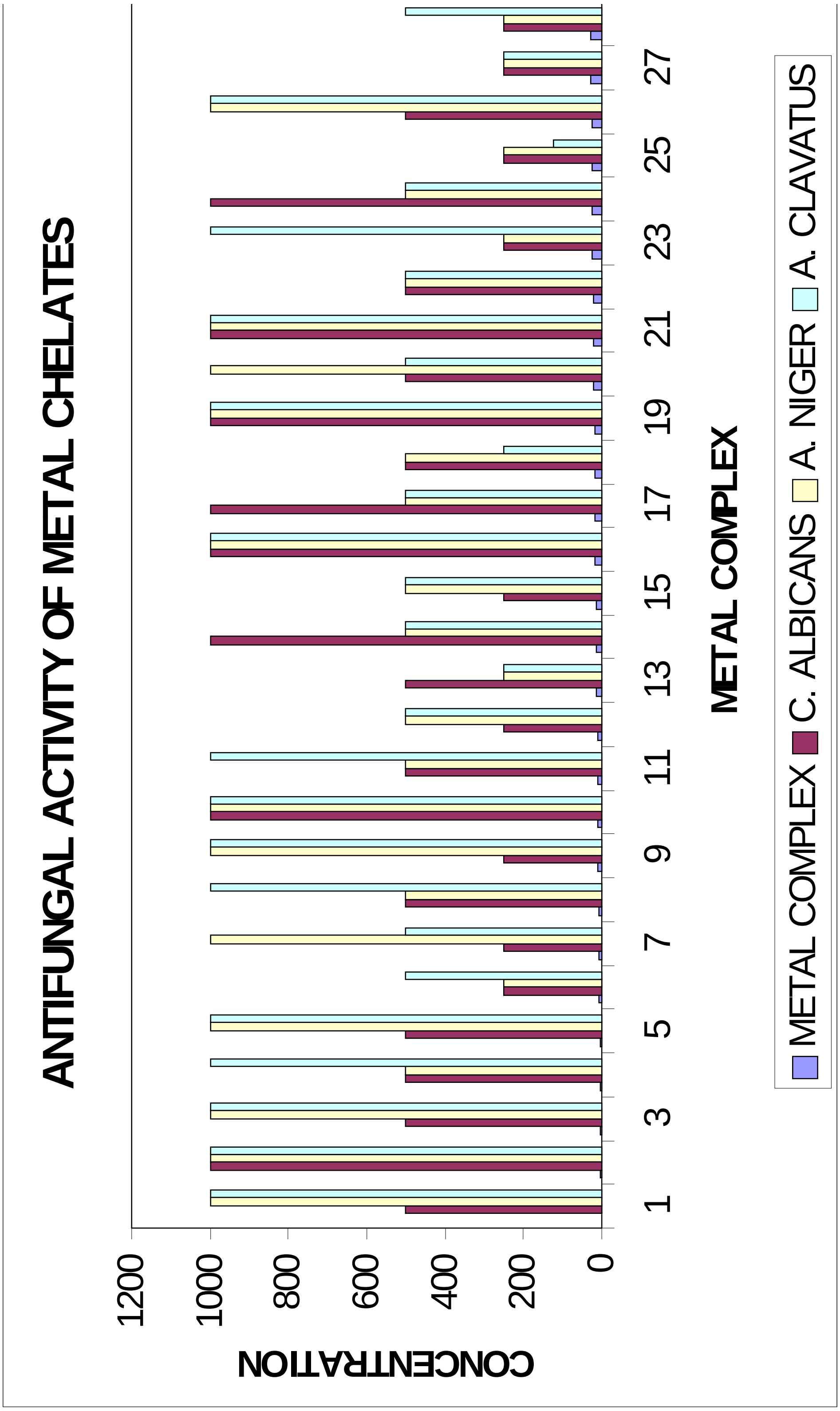
27
METAL COMPLEX
E. Coli
P. Aeruginosa
S. Aureus
S. Pyogenus


ANTIFUNGAL ACTIVITY OF METAL CHELATES
CONCENTRATION
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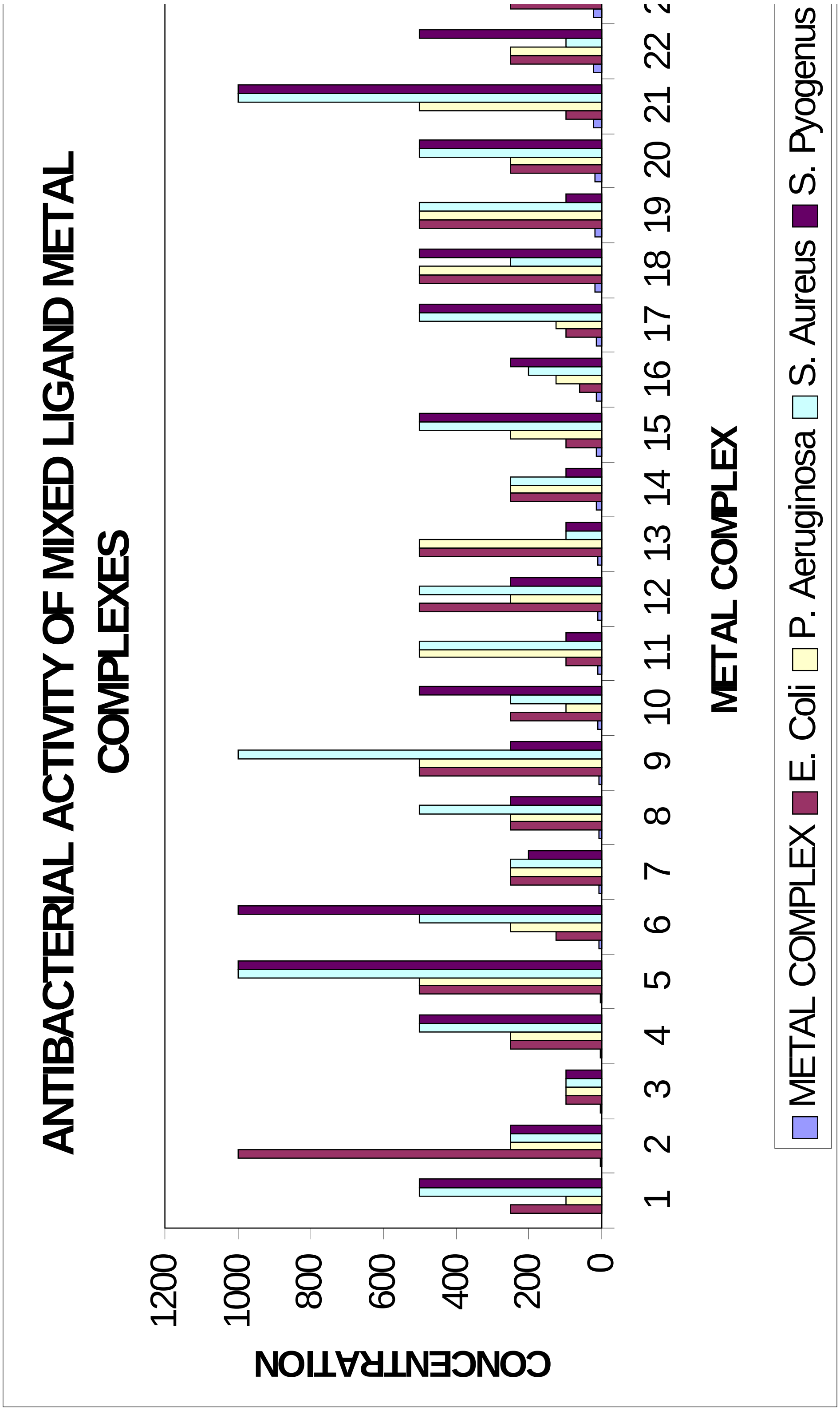
METAL COMPLEX
METAL COMPLEX
C. ALBICANS
A. NIGER
A. CLAVATUS


ANTIBACTERIAL ACTIVITY OF MIXED LIGAND METAL COMPLEXES
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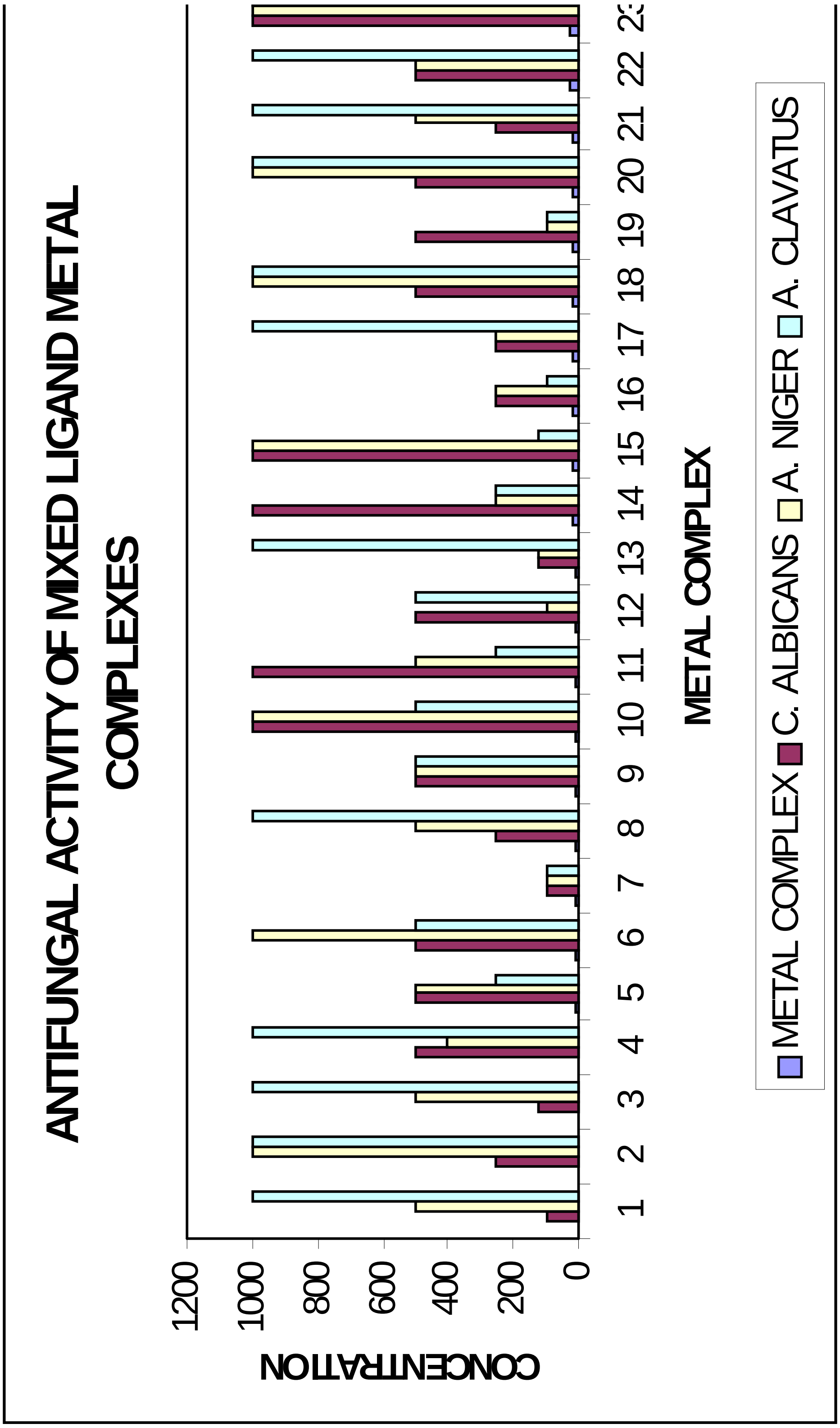
METAL COMPLEX
METAL COMPLEX
E. Coli
P. Aeruginosa
S. Aureus
S. Pyogenus


ANTIFUNGAL ACTIVITY OF MIXED LIGAND METAL COMPLEXES
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METAL COMPLEX
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23
METAL COMPLEX
C. ALBICANS
A. NIGER
A. CLAVATUS

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PART - III

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

In the present study 65 new compounds were synthesized from Diacetyl resorcinol. These compounds are Schiff bases and their metal chelates.

The analytical data and spectral study confirm the structure of the newly synthesized compounds. The diacetyl resorcinol reacts with different substituted amines and to give Schiff bases, which are mainly, confirmed by IR, ^{1}H NMR and Mass spectroscopy. Theses Schiff base ligands further react with bivalent metal salts and gives metal chelates. In case of mixed ligand complexes it reacts further with another organic ligand. The formation of metal chelates and mixed ligand complexes is confirmed by IR, Electronic spectra, ESI Mass spectroscopy, ESR spectroscopy, elemental analysis, magnetic properties and TGA. The IR spectra of metal chelates indicates mainly two types of frequencies, i.e. stretching frequency of H_2O (Coordinate water molecule) and lowering value of C=N group. The percentage of metal in metal chelates obtained by elemental analysis. The molecular weight of metal chelates is confirm by ESI mass spectra. The electronic spectral study is used to determine the geometry or symmetry of metal chelates. The electronic spectral study reveals the symmetry of all Co(II) and Ni(II) complexes to be octahedral, while the symmetry of all Cu(II) complexes is distorted octahedral. The ligand metal ratio in metal chelates is 2:1 and the ligand metal ligand ratio in mixed ligand complexes is 1:2:2. All metal complexes are paramagnetic in nature.

All the Schiff base ligands and their metal chelates were tested for their biological activity. The antibacterial and antifungal activity of the newly synthesized ligands and their metal complexes was tested on gram positive bacteria, Staphylococcus Aureus and Streptococcus Pyogenes and gram negative bacteria Escherichia coli and Pseudomonas aeruginosa and fungi, Candida Albicans, Aspergillus Niger and Aspergillus Clavatus.

The Minimal Bactericidal Concentration (MBC) values of the ligands H_2L^1(125), H_2L^7(100) and H_2L^{10}(100) against E. Coli are comparable to the standard drug ampicillin. The ligands H_2L^6(100) and H_2L^7(100) show identical MBC values against P. Aeruginosa with reference to ampicillin. The ligands H_2L^1(250), H_2L^2(250) and H_2L^4(250) exhibit similar MBC values against S. Aureus in comparison to ampicillin. All the ligands reveal remarkably high MBC values against S. Pyogenus in comparison to standard drug taken. The Minimal Fungicidal Concentration (MFC) values of the ligands H_2L^6(250) and H_2L^7(250) are half, while those of the ligands DAR, H_2L^1(500), H_2L^2(500), H_2L^8(500), H_2L^9(500) and H_2L^{10}(500) are identical to the MFC value of standard drug Greseofulvin against the fungi C. Albicans. All the ligands reveal high MFC values against A. Niger and A. Clavatus in comparison to standard drugs. The identical MBC values of ligands H_2L^7 and H_2L^{10} indicates equivalent antibacterial activity in comparison to standard drug ampicillin. The low MFC values of Schiff base ligands H_2L^6 and H_2L^7 containing methoxy(-OCH3) and chloro(-Cl) groups as substituents respectively indicates good antifungal activity as compared to standard drug greseofulvin against C.Albicans.

The MBC values of metal chelates 3(125) and 6(125) are slightly more and the MBC values of chelate 26(100) is equivalent to the MBC value of ampicillin against E.Coli. The MBC value of metal chelate 15(62.5) is slightly more than the standard Chloramphenicol against E. Coli. The MBC values of the metal chelates 14(100), 15(100) and 25(100) are equivalent to that of standard ampicillin against P. Aeruginosa. The MBC values of the chelates 1(250), 4(250), 7(250), 11(250), 16(250), 24(250), 26(250) and 30(250) against S. Aureus are similar to that of the standard ampicillin, while chelates 3(100), 10(100), 12(100), 18(125), 21(100), 23(125), 25(100) and 28(100) show relatively low MBC values. The metal chelate 3(62.5) is quite low with reference to ampicillin, while chelates 18(100) and 23(100) reveals identical MBC values against S. Pyogenus. The MFC values of metal chelates 1(500), 3(500), 4(500), 5(500), 8(500), 11(500), 13(500), 18(500), 20(500), 22(500), 26(500), 29(500) and 30(500) against C. Albicans are similar to that of the standard drug Greseofulvin, while the chelates 6(250), 7(250), 9(250), 12(250), 15(250), 23(250), 25(250), 27(250) and 28(250) show relatively half MFC values. All metal chelates reveal remarkably high values of MFC against A. Niger and A. Clavatus in comparison with standard drugs. The low MBC value of metal chelate $[Cu(L^5)_2(H_2O)_2]$ containing copper metal ion and Schiff base ligand of 4-methyl anilin in comparison to standard drug ampicillin against E.Coli reveals good activity. The metal chelates of Co,Ni and Cu and halogenated Schiff bases ($[Cu(L^2)_2(H_2O)_2]$.$[Co(L^3)_2(H_2O)_2]$,$[Cu(L^3)_2(H_2O)_2]$,$[Cu(L^4)_2(H_2O)_2]$,$[Cu(L^5)_2(H_2O)_2]$,$[Ni(L^8)_2(H_2O)_2]$,$[Co(L^9)_2(H_2O)_2]$,$[Cu(L^9)_2(H_2O)_2]$,$[Co(L^{10})_2(H_2O)_2]$ exhibits half the values of MFC against C-Albicans as compaired to greseofulvin is an indication of very good activity against the same.

The MBC values of Mixed ligand metal complexes 3(100), 6(100), 11(100), 15(100), 17(100), 21(100), against E. Coli are similar to that of the standard drug ampicillin, while the complex 16(62.5) show relatively low MBC value. The MBC values of the complexes 1(100), 3(100), 10(100), 16(100) and 17(100) are equivalent to that of standard ampicillin against P. Aeruginosa. The metal complexes 3(100), 13(100), 22(100) are quite low with reference to ampicillin, while the complexes 2(250), 7(250), 10(250), 14(250), 16(250) and 18(250) reveals identical

MBC values against S. Aureus. The MBC values of the complexes 3(100), 11(100), 13(100), 14(100) and 19(100) against S. Pyogenus are comparable to the standard drug ampicillin. The MFC values of the mixed ligand metal complexes 4(500), 5(500), 6(500), 9(500), 12(500), 18(500), 19(500), 20(500) and 22(500) against C. Albicans are similar to that of the standard drug Greseofulvin, while the complexes 2(250), 8(250), 16(250), 17(250) and 21(250) show relatively half MFC values. The metal complexes 1(100), 3(125), 7(100) and 13(125) reveals identical MFC values against C. Albicans with reference to the Nystatin. The MFC values of the complexes 7(100), 12(100), 13(100) and 19(100) against A. Niger and the complexes 7(100), 15(100), 16(100) and 19(100) against A. Clavatus are comparable to the standard drugs Nystatin and Greseofulvin.

The low MBC value of the metal complex $[Co_2(L^4)(1,10\text{-Phen})_2(H_2O)_4]$ against E.Coli as compaired to ampicillin is related to bromo substituted Schiff base and organic ligand 1,10-phenthrolin with Nickel metal ion. The MFC value of complexes $[Co_2(L^5)(8\text{-HQ})_2(H_2O)_4]$ and $[Co_2(L^5)\ (1,10\text{-Phen})_2(H_2O)_4]$ indicates good antifungal activity against both fungi A.Niger and A.Clavatus as compaired to the standard drug Nystatin and greseofulvin is related to the methyl and methoxy substituted Schiff base ligands with cobalt and nickel as central metal ions.

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Synthesis, characterization and biological evaluation of *bis*-bidentate Schiff base metal complexes

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ABSTRACT

A novel series of 4,6-bis(1-(4-substitutedphenylimino)ethyl)benzene-1,3-diols *bis*-bident Schiff base transition metal complexes, H_2L^1, H_2L^2 and H_2L^3 were synthesized. The Schiff base H_2L^1, H_2L^2 and H_2L^3, ligands were synthesized by the condensation of 4,6-diacetylresorcinol with 4-chloroaniline, 4-flouroaniline and 4-methylaniline respectively. The ligands behave as dibasic bis-bidentates yielding polymeric complexes. The ligands and their metal complexes have been characterized by ^{1}H NMR, IR, mass, ESR and elemental analysis. The bonding sites are the azomethine and phenolic oxygen atoms. The metal complexes exhibit different geometrical arrangements such as square planar, tetrahedral, octahedral and distorted octahedral arrangement. The Schiff base and its new complexes were tested for antibacterial activity against gram positive bacteria; *Staphylococcus aureus* and gram negative bacteria; *Escherichia coli* including the resistance bacteria *Pseudomonas aeruginosa*.

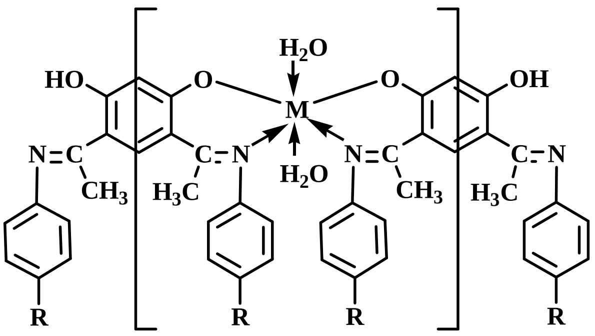
KEYWORDS

Bis-schiff-base complexes;
Diacetyl resorcinol;
Anti-bacterial activity.

INTRODUCTION

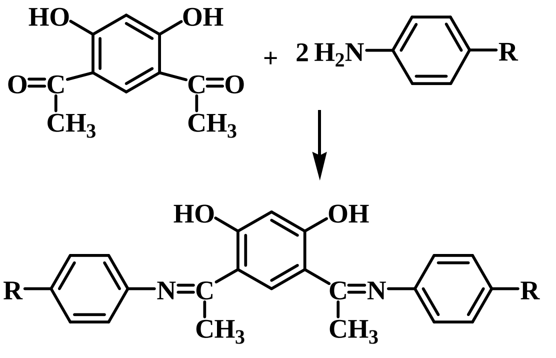
The interest of the coordination complexes of Schiff bases stems from their versatile catalytic reactions for organic synthesis[1-4] and its use in degradation of organic substances[5] and in radiopharmaceuticals[6] and their ability to reversibly bind oxygen[7] and photochromic properties[8], and the complexing ability towards transition metals. Due to such a wide range of applications, new three series of binuclear complexes of copper(II), nickel(II), and cobalt(II) ions with three Schiff base, H_2L^1, H_2L^2 and H_2L^3 ligands are of particular interest. The purpose is to alter the metal ion coordination environment, which is primarily responsible for the properties exhibited by the complex.

Due to such a wide range of applications[9,10], new three series of binuclear complexes of 4,6-bis(1-(4-substitutedphenylimino)ethyl)benzene-1,3-diols have been prepared by the condensation of 4,6-diacetylresorcinol with 4-chloroaniline, 4-flouroaniline and 4-methylaniline, to afford the corresponding Schiff base ligands, which serves as tetradentate Schiff base ligands, abbreviated as H_2L^1, H_2L^2 and H_2L^3, respectively. The ligands are either di- or tetra-basic with two symmetrical sets of either OON or NNO tridentate chelating sites. Reaction of the Schiff base, H_2L^1, H_2L^2 and H_2L^3, ligands with copper(II), nickel(II), cobalt(II), in molar 2:1 ratio afforded the corresponding transition metal complexes (SCHEME 1). The structures of the ligands and the newly prepared complexes were iden-



Where R= Cl, F, CH_3 and M= Cu(II), Co(II) and Ni(II)

SCHEME 1: Structure of metal complex



where R=Cl,F,CH_3

SCHEME 2: General reaction for Schiff base ligands

tified by elemental analyses, infrared, electronic, mass, ^{1}H-N.M.R. and ESR spectra as well as thermal gravimetric analysis (TGA). The bonding sites are the azomethine and phenolic and alcoholic oxygen atoms, the metal complexes exhibit different geometrical arrangements such as tetrahedral, octahedral and distorted octahedral arrangement. The biological evaluation of the ligands and metal complexes against some pathogenic bacteria are also reported[23].

EXPERIMENTAL

Materials

4,6-Diacetylresocinol was synthesized according to the literature method[11,12]. Copper(II), nickel(II) and cobalt(II) were used as nitrate salts and were Merck or BDH. Organic solvents EtOH, absolute EtOH, MeOH, acetone, dimethylformamide (DMF) and dimethylsulfoxide (DMSO) were reagent grade and were used without further purification.

Synthesis of the Schiff base ligand

The Schiff base, H_2L^1, H_2L^2 and H_2L^3, Ligands were synthesized by adding 4,6-diacetylresorcinol (4.85g, 25.0mmol) dissolved in hot absolute EtOH ($20cm^3$) to 4-chloroaniline (6.37g, 50.0mmol), 4-flouroaniline (5.55g, 50.0 mmol) and 4-methylaniline (5.35g, 50.0mmol) respectively, in absolute EtOH ($20cm^3$). The reaction mixtures were heated to reflux for 3h. The products obtained were filtered off and washed several times with a few amount of EtOH then ether and air dried. The products were kept in a desiccator until used. Recrystallization was carried out in EtOH. The yields were 8.4 g (75%), for H_2L^1 and 7.8g (75%) for H_2L^2 and H_2L^3. m.p. of these three ligands are >170°C. A general chemical reaction for ligand is formulated as in (SCHEME 2).

Synthesis of metal complexes

The metal chelates were prepared by refluxing the respective metal(II) nitrate(hexahydrate) (1mmol) in 20 ml of methanol with the ligand, H_2L (2 mmol) in 20ml of methanol on a water bath for about 4hrs. The pH of the solution was adjusted to 7 by drop wise addition of 10% methanol ammonia solution. The metal chelates got separated after cooling the solution overnight. The metal chelates thus separated were washed with methanol followed by pet ether (60-80°) and dried in vacuum. The yield is 72-79%. The complexes (SCHEME 1) are insoluble in water and alcohol but soluble in DMSO[13].

Bacterial culture

The strains of bacteria used were *Escherichia coli, B.Spinzinii, Pseudomonas aeruginosa,* and *Staphylococcus aureus.* All strains were used standard. The identity of all the strains was confirmed[24]. A bacterial pension was prepared and added to the sterilized medium before solidification. The media with bacteria was poured into sterilized Petri dishes under aseptic condition. Different weights of Schiff base, Co(II), Cu(II), Ni(II) Schiff bases complexes; (1mg, 5mg and 10mg) were placed on the surface of the culture and incubated at 37^0C for 24 h. After incubation the inhibition (mm) and the average of inhibition zones recorded.

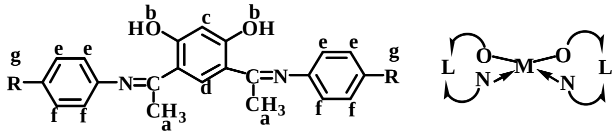
RESULTS AND DISCUSSION

UV-vis spectra of the metal complexes in DMF

TABLE 1: The analytical and physical data of the ligand and metal complexes

Ligand or complex		Formula	M.W.	Color	Yield (%)	m.p. (°C)	Elemental analysis, % found/(Calcd)			
							C	H	N	M
1	H_2L^1	$C_{22}H_{18}Cl_2N_2O_2$	413.3	Reddish brown	75%	170	63.90 (63.93)	4.37 (4.39)	6.75 (6.78)	-
2	H_2L^2	$C_{22}H_{18}F_2N_2O_2$	380.39	Reddish brown	75%	210	69.44 (69.46)	4.73 (4.77)	7.34 (7.36)	-
3	H_2L^3	$C_{24}H_{24}N_2O_2$	372.46	Reddish brown	75%	190	77.36 (77.39)	6.47 (6.49)	7.49 (7.52)	-
4	$[NiL^1(H_2O)]_n$	$C_{44}H_{34}Cl_4N_4NiO_4$	883.27	Green	78%	>300	59.78 (59.83)	3.85 (3.88)	6.33 (6.34)	6.61 (6.65)
5	$[NiL^2(H_2O)]_n$	$C_{44}H_{34}F_4N_4NiO_4$	817.45	Green	76%	>300	64.61 (64.65)	4.17 (4.19)	6.83 (6.85)	7.13 (7.18)
6	$[NiL^3(H_2O)]_n$	$C_{48}H_{46}N_4NiO_4$	801.6	Green	75%	>300	71.90 (71.92)	5.75 (5.78)	6.96 (6.99)	7.28 (7.32)
7	$[CuL^1(H_2O)]_n$	$C_{44}H_{34}Cl_4CuN_4O_4$	888.12	Deep brown	79%	>300	59.47 (59.50)	3.82 (3.86)	6.28 (6.31)	7.12 (7.16)
8	$[CuL^2(H_2O)]_n$	$C_{44}H_{34}CuF_4N_4O_4$	822.3	Deep brown	78%	>300	64.24 (64.27)	4.16 (4.17)	6.79 (6.81)	7.67 (7.73)
9	$[CuL^3(H_2O)]_n$	$C_{48}H_{46}CuN_4O_4$	806.45	Deep brown	79%	>300	71.48 (71.49)	5.74 (5.75)	6.93 (6.95)	7.83 (7.88)
10	$[CoL^1(H_2O)]_n$	$C_{44}H_{34}Cl_4CoN_4O_4$	883.51	Reddish brown	72%	>300	59.76 (59.81)	3.84 (3.88)	6.33 (6.34)	6.60 (6.67)
11	$[CoL^2(H_2O)]_n$	$C_{44}H_{34}CoF_4N_4O_4$	817.69	Reddish brown	72%	>300	64.60 (64.63)	4.17 (4.19)	6.81 (6.85)	7.17 (7.21)
12	$[CoL^3(H_2O)]_n$	$C_{48}H_{46}CoN_4O_4$	801.84	Reddish brown	69%	>300	71.89 (71.90)	5.75 (5.78)	6.97 (6.99)	7.28 (7.35)

TABLE 2: ¹HNMR spectral data of ligand and metal complexes



Assignment	H_2L^1	H_2L^2	H_2L^3	Complexes
H^a	2.1(6H)	2.1(6H)	2.1(6H)	2.1(6H)
H^b	12.92(1H)	12.92(1H)	12.92(1H)	-
H^c	6.36(1H)	6.36(1H)	6.36(1H)	6.36(1H)
H^d	7.64(1H)	7.64(1H)	7.64(1H)	7.64(1H)
H^e	6.61(2H)	6.61(2H)	6.61(2H)	6.61(2H)
H^f	7.0(2H)	7.0(2H)	7.0(2H)	7.0(2H)
H^g	-	-	2.35(6H)	2.35(6H) (H_2L^3 complex)

were recorded on a Jasco 550 Spectrophotometer. IR spectra of the ligands and their metal complexes, as KBr discs, were recorded on an 8400 FTIR Simadzu Spectrometer. ¹HNMR spectra of the ligand and its complexes, in DMSO-d6, were recorded on a Bruker Avance II 400 Spectrometer at room temperature using TMS as internal standard. Mass spectra were recorded at QP 2010 Shimadzu GCMS Spectrometer. and ESR was recorded on E-112 ESR Spectrometer, at X-band microwave frequency (9.5 GHz) with sensitivity of 5×10^{10} ΔH spins. TG and DT analyses[14] were recorded on NETZSCH TGA-DTA/DSC instrument.

The reactions of the Schiff-base, H_2L, with different metal ions produce a new series of binuclear metal complexes, $M^{1/2}$, Ni(II), Cu(II), and Co(II). The analytical and physical data of the Ligand and Metal complexes are listed in (TABLE 1).

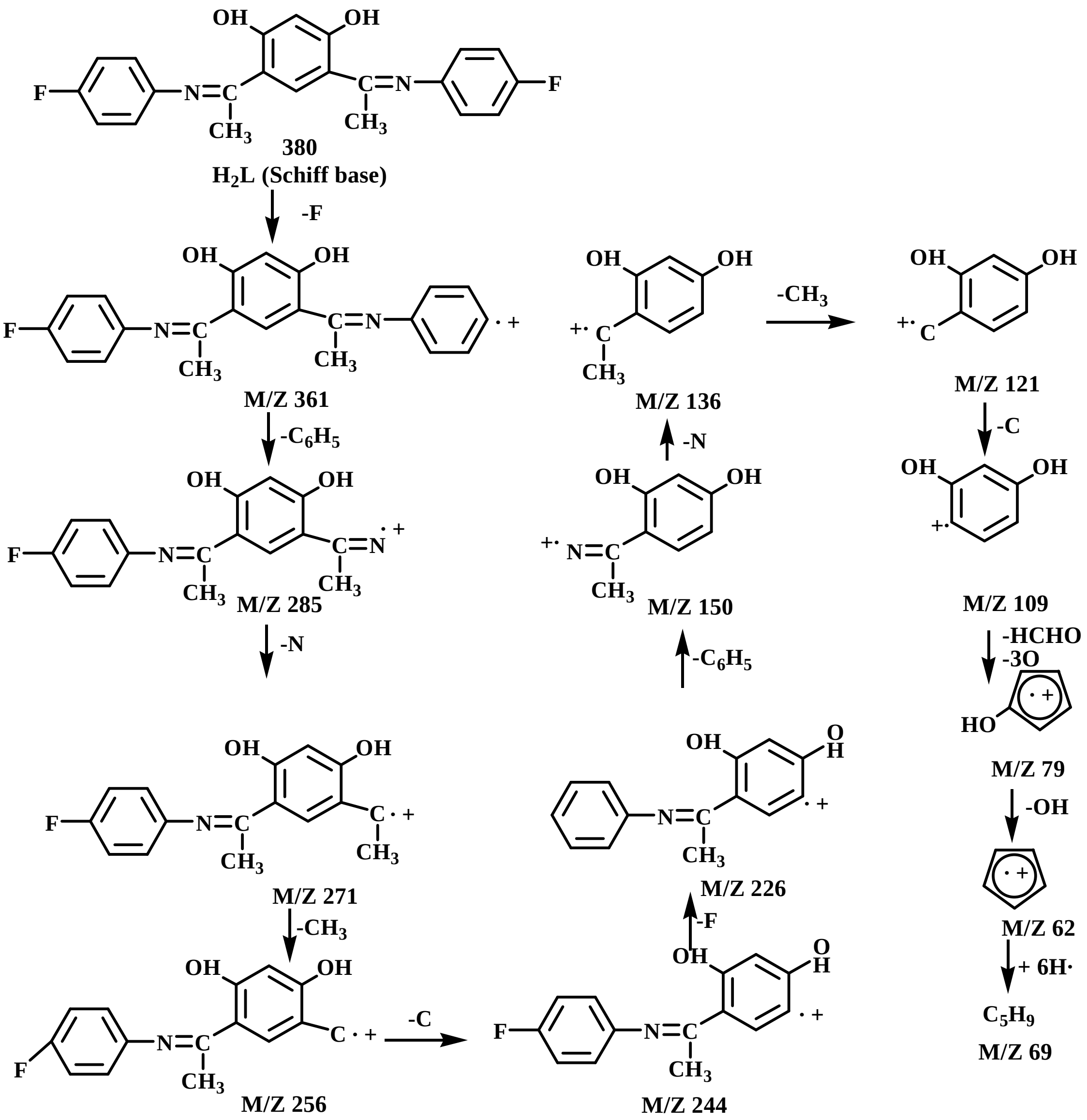
Characterization of the ligands and metal complexes

Mass spectroscopy was performed on the H_2L ligand to determine its molecular weight and fragmentation pattern. The molecular ion peak was observed at m/e 412, m/e 380, m/e 372, confirming its formula weight (FW) 413, 380, 372 for H_2L^1, H_2L^2 and H_2L^3 respectively. Which are same as the calculated m^+ values. The general schematic fragmentation of the ligand is depicted in (SCHEME 3).

The ¹H NMR spectrum of H_2L and complexes in DMSO-d6 (TABLE 2) showed signals at δ (ppm) 2.1 (3H, CH_3^a), 12.92 (1H, OH-phenolic^b), 6.36 (1H, Ar-H^c), 7.64 (1H, Ar-H^d), 6.61 (2H, Ar-H^e), 7.0(2H, Ar–H^f), and 2.35 (3H, CH_3^g). It is observed that the signal due to the proton (12.92, phenolic-OH^b) completely disappeared on adding D_2O, while the other signals still exist at their expected positions. The integral ratio of the protons is in agreement with the expected structure of the ligand and metal complex[15].

The IR spectrum of the ligand shows a broad band at 3430 cm^{-1} due to the stretching vibrations of phenolic hydroxyl groups. The broadness is due to intermolecular hydrogen bonding between the phenolic groups and the azomethine groups. The band at 1246 cm^{-1} is ascribed to the ν(C–O) stretching vibrations, where the strong band observed at 1610 cm^{-1} is assigned to the stretching vibrations of the azomethine group. The band for p-substitution at 686 & 770[16].

The characteristic bands of the infrared spectra the metal complexes are listed in (TABLE 3). The IR spectra of complexes (4–12) exhibit a broad band around 3200-3463 cm^{-1} assigned to ν(OH) of water molecules associated with the complex, which are also confirmed by elemental and thermal analyses. The IR spectra of the complexes show a shift of the ν (C=N) band towards lower wavenumbers of 1635-1665 cm^{-1} compared with the free ligand band at 1680 cm^{-1}. This shift indicates coordination of the two azomethine groups to the metal ions. Coordination through the phenolic oxygen after deprotonation is revealed by the appearance of a band due to ν(C-O) at much lower frequencies (1205-1225 cm^{-1}) in all the complexes compared to



SCHEME 3: The schematic fragmentations of H_2L ligand

that of H_2L (1236 cm^{-1}), suggesting that the hydroxyl groups of the Schiff-base coordinate[17] with the metal ions.

Thermo gravimetric analysis shows that the weight loss is observed in all the divalent complexes[18]. The weight loss is found to be two mole of coordinated water per mole of the complex. Differential thermal analysis shows that one endothermic peak is observed in each complex. This indicates that the weight loss occurs in a single step. The loss of coordinated water occurs at 130^0C for Cu(II), 140^0C for Ni(II), 150^0C for Co(II), complexes respectively.

The electronic spectrum of the ligand H_2L(10^{-3}M in DMF), shows mainly three bands at 210, 242 and 370nm due to ($^1L_a \rightarrow {}^1A_1$) and ($^1L_b \rightarrow {}^1A_1$) transitions of the phenyl ring and π-π* transition within the C=N group. In addition, a broad band at 410nm is due to the n-π* transition which is overlapping with the intermolecular CT from the phenyl ring to the azomethine group.

TABLE 3: The characterization bands of the infrared spectrum of H_2L, and their metal complexes

	Ligand or complex	-OH (Phenolic or crystalline)	ν(C=N)	ν(M–O)	ν(M–N)
1	H_2L^1	3430br	1680s	-	-
2	H_2L^2	3409br	1680s	-	-
3	H_2L^3	3356br	1680s	-	-
4	$[NiL^1(H_2O)]_n$	3240br	1654s	558m	390w
5	$[NiL^2(H_2O)]_n$	3370br	1660s	467m	372w
6	$[NiL^3(H_2O)]_n$	3380br	1640s	495m	-
7	$[CuL^1(H_2O)]_n$	3463br	1635s	467m	365w
8	$[CuL^2(H_2O)]_n$	3430br	1653s	455m	370w
9	$[CuL^3(H_2O)]_n$	3433br	1645s	465m	372w
10	$[CoL^1(H_2O)]_n$	3200br	1645s	504m	346w
11	$[CoL^2(H_2O)]_n$	3233m	1652s	416m	-
12	$[CoL^3(H_2O)]_n$	3238br	1655s	480m	370w

S=Strong, w=weak, m=medium and br=broad.

The electronic spectrum of Co (II) complex has multiple bands observed at 20000-19230, 16393-5625 and 7143 cm^{-1}. These bands are ascribed to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(\nu1)$; $^4T_{1g}(F) \rightarrow {}^4A_{2g}$ (ν2)and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν3) transitions respectively. The ν2/ν1 ratio is in the range. 295-2.187, which is consistent with the octahedral geometry[19]. The Ni(II) complex has three spin allowed transitions at 10000, 18518, 20833-23256 and 29412 cm^{-1}.These bands are correlated to $^3A_{2g} \rightarrow {}^3T_{2g}$; $^3A_{2g} \rightarrow {}^3T_{1g}$(F) and $^3A_{2g} \rightarrow {}^3T_{1g}$ (P) transitions respectively in an octahedral stereochemistry[20]. The electronic spectrum of Cu(II) complex shows a multiple structured broad band in the range 13250-17390 cm^{-1} which may be assigned as a combination of three transitions $^2B_{1g} \rightarrow {}^2A_{2g}$; $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2E_g$ in a distorted octahedral geometry[21]. Based on the magnetic data and electronic spectral data octahedral geometries have been proposed for all the complexes.

ESR spectrum of Cu (II) complex was recorded at room temperature using DPPH as the standard. The spectrum consists of a single intense signal. The g value has been found to be 2.0027, which is greater than the free electron value[22]. This indicates that the unpaired electron is largely localized on the metal ion.

Antibacterial activity

TABLE 4 exhibits the zone of bacterial growth inhibition of the Schiff base which synthesized from

TABLE 4: Antibacterial activities of ligand and metal complexes

	Compound/Organism	*E-Coli*	*E-aeroges*	*B.spinzinii*	*Pseudomonas aeruginosa*	*Staphylococcus aureus*
		Zone of inhibition in mm				
1	H_2L^1	5	-	6	-	7
2	H_2L^2	-	-	5	-	6
3	H_2L^3	-	-	8	5	7
4	$[NiL^1(H_2O)]_n$	5	-	6	-	5
5	$[NiL^2(H_2O)]_n$	5	-	5	-	4
6	$[NiL^3(H_2O)]_n$	6	-	7	3	6
7	$[CuL^1(H_2O)]_n$	9	8	8	7	7
8	$[CuL^2(H_2O)]_n$	6	5	5	-	5
9	$[CuL^3(H_2O)]_n$	8	5	9	7	9
10	$[CoL^1(H_2O)]_n$	7	5	8	5	8
11	$[CoL^2(H_2O)]_n$	4	4	7	4	7
12	$[CoL^3(H_2O)]_n$	9	6	8	5	9

E.Coli = Escherichia coli

Diacetyl resorcinol and its complexes of Co(II), Cu(II) and Ni(II) against the tested bacteria. The Schiff base (H_2L) and metal complexes displays effect against all bacteria tested. The test results presented in TABLE 4 show that moderate effect against both gram positive and gram negative bacteria in comparison with standard drugs ampicillin, amoxicillin, and sefalexin in this study. The study indicates that the Cu(II), Co(II) solid complex has antibacterial activity against all bacteria used[23,24].

CONCLUSION

The ligand H_2L behaves as a dibasic tetradentate ligand with O:N:N:O donor sequence coordinating through the nitrogen of the azomethine free and both oxygen of phenol groups. All the complexes have a polymeric octahedral geometry with a metal to ligand ratio of 1:2 Coordinated water molecule is found in all the divalent complexes. On the basis of analytical, magnetic and electronic spectral data polymeric octahedral geometries have been proposed for all the complexes (SCHEME 1). The complex screen for antibacterial activity and result show moderate in comparison with standard drugs.

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