SYNTHESIS AND CHARACTERISATION OF SOME TRANSITION METAL COMPLEXES OF MULTIDENTATE LIGANDS

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December 30, 2002

CERTIFICATE

This is to certify that the thesis entitled **"Synthesis And Characterisation Of Some Transition Metal Complexes Of Multidentate Ligands"**, submitted by **Ms. Chandini R. Nayar**, in partial fulfillment of the requirements of the degree of Doctor of Philosophy, to the Cochin University of Science and Technology, Kochi-22 is an authentic record of the original research work carried out by her under my guidance and supervision. The results embodied in this thesis, in full or in part, have not been submitted for the award of any other degree.

M. R. Prathapachandra Kurup
(Supervisor)

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INTRODUCTION

Coordination chemistry, precisely, is the chemistry of metal atoms "coordinated" by atoms or molecules. Coordination chemistry has always been a challenge to the inorganic chemist. In the early days of chemistry they seemed unusual (hence the name complexes) and seemed to defy the usual rules of valence. Today they comprise a large body of current inorganic research. A survey of articles in recent issues of journal *Inorganic chemistry* indicates that perhaps 70% could be considered to deal with coordination compounds. Although the usual bonding theories can be extended to accommodate these compounds, they still provide stimulating problems to be resolved. In synthetic work, they continue to provide a challenge in the laboratory. Interdisciplinary research is a hallmark of modern inorganic chemistry, and many chemists today are applying the methods and concepts of modern coordination chemistry to problems in areas such as biochemistry, catalysis, energy conversion, and materials chemistry. The rapidly developing field of bioinorganic chemistry is centered on the presence of coordination compounds in living systems.

The concept of fixed valencies, which developed since the time of Kekule, was beneficial for the evolution of organic chemistry, but not for inorganic chemistry. Compounds that formed from inorganic salts and neutral molecules, cobalt chlorides and ammonia, for instance were at first wrongly interpreted on the basis of fixed valencies. They were called complexes, from which the complex chemistry was developed. This rather unjust name was soon replaced by coordination chemistry, to indicate the metal atom within an environment of other atoms. However, the word still suggests the bonds between the metal and it's surrounding atoms to be different, for instance a carbon atom and four hydrogen atoms in CH_4. The great variety in properties of the bonds around metals is the beauty of coordination chemistry. This is the reason for the nature to use metals on special places in enzymes for highly specialized jobs and for most industrial syntheses of chemicals to employ metal compound catalysis.[1-5]

1.1. LIGANDS OR COORDINATING GROUPS

Coordination complexes are formed by the union of a cation with one or more neutral or charged species The neutral molecules or ions (usually anions) which are attached with the central ion in complex compounds are called ligands or coordinating groups. The term *ligand*, which originated from the Latin word *liogare* was first introduced by Alfred stock in 1896, in relation to silicon chemistry. According to Lewis, in most of the complex compounds, the ligands act as Lewis bases (electron pair donors) and central metal ion acts as a Lewis acid (electron acceptor), i.e., in most of the complexes, the ligands donate one or more electron pairs to the central metal ion.

$$M^{n+} \quad + \quad xL \quad \longrightarrow \quad [ML_x]^{n+}$$

The ligands are attached to the central metal ion through their donor atoms. The metallic atom with which the ligands are attached through coordinating bonds is called the central metallic atom. The metallic atom may be in zero, positive or negative oxidation state. Ligands are classified according to the number of donor atoms contained and are known as uni, di, tri, or quadridentate ligands, where the concept of teeth was introduced. When a singly coordinating group or ligand occupies two or more coordination positions on the same central metal ion, a complex possessing a closed ring is formed. The phenomenon of ring formation is called chelation and ring formed is called chelate ring. The term chelate was first introduced in 1920 by Morgan and Drew.[6]

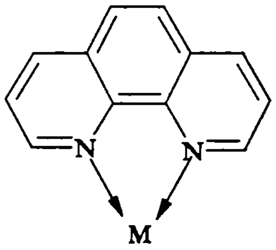


Figure 1. 1,10-phenanthroline (phen)

In some cases, multiple bonding will be there, i.e. ligands act simultaneously as donor and acceptor, for eg, in metallic carbonyls, CO molecule can both accept and donate electron pair.

1.2. COORDINATION NUMBER OF CENTRAL METAL ATOM / ION

Coordination number of the central metal atom in a given complex compound is equal to the total number of donor atoms, which are actually attached with the central metallic atom. In other words, we can say that the coordination number of the central metallic atom is equal to the number of sites at which the ligands are attached to central metallic ion. In the case of complex compounds that contain only monodentate ligands, the coordination number of the central metallic atom is equal to the number of monodentate ligands coordinated to the metallic atom. This rule does not hold good for the complexes containing polydentate ligands.

Coordination number of metallic atom predicts the geometry of the complex compound. Thus for coordination number equal to 2,3,4,5 and 6, the geometry of the complex compound formed is linear, trigonal, planar, tetrahedral or square planar , trigonal bipyramidal and octahedral respectively. Coordination number gives us an idea about the way in which the ligands are arranged around the central metallic atom.

1.3. COORDINATION SPHERE AND IONISATION SPHERE

While writing the structural formula of a given compound, the central metal atom and ligands attached with it are always written in a square bracket, called coordination or inner sphere. The portion outside the coordination sphere is called ionization or outer sphere. Thus in $[Co(NH_3)Cl]Cl_2$, the square bracket which contains the central metal ion Co^{3+} and the ligands of five ammonia molecules and one chloride ion, is *coordination sphere* and the portion that contains two chloride ions is *ionization sphere.*

1.4. SCHIFF BASES

Over the past twenty five years, extensive chemistry has surrounded the use of Schiff base ligands in inorganic chemistry. Schiff base can be represented by the general formula $RCH{=}NR^{l}$ where R and R^{l} are various substituents. These compounds are formed by the condensation of a primary amine with compounds containing active carbonyl group. It was named after the scientist Hugo Schiff. Since the seminal work by Schiff and co-workers, metal chelate Schiff base complexes have continued to play the role of one of the most important stereochemical models in main group and transition metal coordination chemistry due to their preparative accessibility, diversity and structural variability.[7-8]

Schiff bases are the key intermediates in a large number of synthetic and biological reactions. Metal derivatives of Schiff bases have been known since 1840, but the synthetic study of complexes was commenced by Pfeiffer and coworkers in 1931.

The coordination chemistry of Schiff bases is of considerable interest due to their various magnetic, catalytic and biological applications. Ligands containing sp^2 hybridized nitrogen atoms, particularly those in which the N-atom is a part of the aromatic system, show very extensive coordination chemistry, especially when they are bi or tridentate ligands. In 1931, Dubsky and Sokol isolated N-N'-bis(salicylidine ethylene diamino) copper(II) and nickel(II) complexes, which ended in the formation of a new group of ligands called *salen*. These ligands are often of choice for several reasons. These are multidentate with several binding sites. So there are several vacant sites for potential catalytic and enzymatic activity. Furthermore, substitution at the aromatic ring can modify the electronic and steric properties of the resulting complexes, which can enable fine tuning of properties.

1.4.1. 3-Formylsalicylic acid

3-Formylsalicylic acid is a type of aldehyde, which forms a wide variety of Schiff bases. They have an additional coordinating group and hence give wide variety of polynuclear, i. e., both hetero- and homo- nuclear compounds.

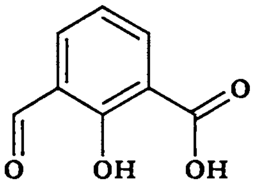


Figure 2. 3-Formylsalicylic acid

In 1974, Hisashi Okawa and coworkers reported that 3-formylsalicylic acid and its Schiff bases with alkyl amines form binuclear copper(II) and nickel(II) complexes.[9-10] In these complexes, the phenolic oxygen operates as a bridging group, while the carboxylate oxygen and/or imino nitrogen coordinate to metal ion. The Schiff bases derived from diamines and 3-formylsalicylic acid also form binucleating complexes bridged by phenolic oxygen. In the first case, two organic moieties are constructed *trans* to each other whereas in the latter case, they are *cis* with respect to the imino nitrogen and carboxylate oxygen.

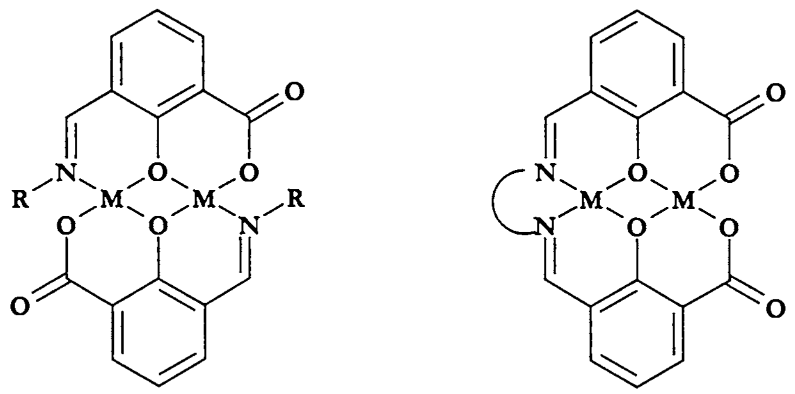
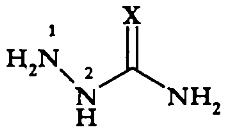


Figure 3. Binucleating complexes

In the latter case, the inside coordination site has N_2O_2 coordinating atoms, while the outside has O_4 coordinating atoms. Since there is considerable difference in the ligand field strength between the inside and outside coordination spheres, the binuclear nickel(II) complex reported composed of one paramagnetic and one diamagnetic metal ions. Synthesis of binuclear complexes containing two different metal ions were also reported and these Schiff bases have coordinating selectivity. First hetero-nuclear metal complex synthesis was reported in 1974 by Okawa and coworkers itself.[11] They synthesized hetero-metal complexes of Cu(II)-Ni(II), Cu(II)-Co(II), Cu(II)-Fe(II) etc., which can be represented by the general formula MM'(L).[12] They are of interest in connection with the spin exchange and charge transfer between metal ions and in the field of metallo enzymes and homogeneous catalysis. The exchange coupled polymetallic systems constitute a common ground for areas of current interest - molecular magnetism, metal sites in biology etc., and these ligands are called compartmental ligands. More recently, studies of polynuclear homo and hetero metallic complexes derived from 3- formylsalicylic acid are reported.[13-17]

1.4.2. Semicarbazones and thiosemicarbazones

Semicarbazones and thisemicarbazones are a group of highly reactive compounds that form chelate complexes with transition metal ions. They have the general formula:



X = O, Semicarbazone
X = S, Thiosemicarbazone

Figure 4. Structure of semi- and thio-carbazone.

When their ^4N nitrogen is substituted, they can be represented by the following formula:

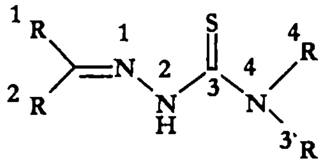


Figure 6. ^{4}N, ^{4}N- Substituted thio semicarbazone

Where, ^{1}R is generally an alkyl or aryl group and ^{2}R is hydrogen, methyl, higher aliphatic or aromatic groups. ^{4}R and ^{3}R can be the same aliphatic or aromatic group or both can be a part of cyclic system.

Semicarbazones and thiosemicarbazones generally exist in the enonic or thionic form in the solid state respectively, but in solution they probably exist as an equilibrium mixture of enone and enol or thione and thiol. They usually act as the chelating agents with metal ions by bonding through X and hydrazine nitrogen atoms.[18]

Depending on the nature of coordination, they can act as neutral bidentate or sometimes as anionic bidentate by bonding through deprotonation of thiol or alcohol. These molecules are planar and –NH_2 are trans with respect to the C-N bond. Additional bonding sites are made available by condensing the aldehydes having functional groups like -OH, -NH_2 etc. and this will bring more options when it comes to complexation.[19]

The semicarbazones and thiosemicarbazones are molecules of great interest due to their chemistry and pharmacological properties. They attracted attention as potential drugs in the early years of twentieth century and were found to be effective against a variety of diseases. There are scores of reports regarding the biological activity of this class of compounds as potential antitumour, antiviral,[20] antimalarial,[21] antibacterial[22] and antifungal[23] agents.

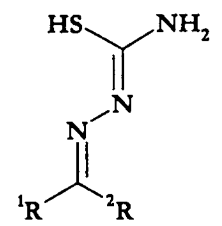
1.4.2.1. Structure, bonding and stereochemistry

The TSCs generally exist in the thione form in the solid state but in solution it would tend to exist as an equilibrium mixture of thiol and thione forms as shown below.

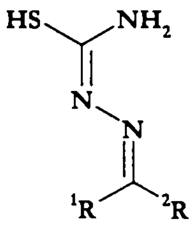
Thione

Thiol

The previously mentioned strategies to vary the structural features of the TSCs could in fact bring about changes in the bonding and stereochemistry of the compound, which in turn may decide the mechanism of action of the compound in biological systems. It is expected that the TSC may generally exist in the ***E*** form (*trans*) but in such situation the compound may act as a unidentate ligand, by bonding through sulfur only.[24] In case the sulfur center is substituted, the bonding may occur through the hydrazine nitrogen and the amide nitrogen.[25]

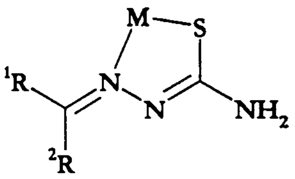


Z (cis)



E (trans)

But the studies have shown that the stereochemistry of the ligand is much decided by steric effects of the various substituents in the TSC moiety.[26] It is found that in most cases the compound is in the *Z*-form while coordinating to the metal ions. This phenomenon is assumed to be due to the "chelate effect" - increased stability due to better electron delocalisation in a chelated ring system- resulting from the coordination with the metal center.



Chelate Effect

Generally, the coordination occurs through the thiol/thione sulfur and the hydrazine nitrogen. When additional binding sites are available adjacent to the SN donor system the ligand was found to act as tridentate species. In most of the reported cases the third coordinating species will be in the aldehydic or ketonic moiety.[27] The availability of the third coordinating site brings so many other options when it comes to complexation. Some of them could lead to the formation of polymeric complexes[28] or it could change the oxidation state of the metal or could bring changes in the coordination environment of the metal ion. These changes could in turn affect the biological properties of the compound. The alkylation of the thiocarbonyl sulfur induces a complexation through terminal amido group and hence accounts for the mono acidic character of the ligand.[29] Sometimes such ligands condense with a second aldehyde or ketone to yield quadridentate ligands.

The stereochemistry adopted by the TSC ligands with the transition metal ion depends essentially on the presence of additional coordination sites in the ligand moiety and the charge on the ligand, which in turn is influenced by the thiol-thione equilibrium in the reaction medium. The thiol-thione equilibrium and the nature of complexation depend on the pH of the medium/solvent(s) used for reaction. Generally, the TSCs act as neutral bidentate ligands, leading to octahedral and square planar geometries as found common among their metal complexes. But some 5-coordinate complexes are also formed by 2-acetylpyridine TSC derivatives that show increased biological activity as antitumour, antimalarial agents.[30]

1.5. STRUCTURAL CHARACTERIZATION TECHNIQUES

Various techniques are used to elucidate the bonding structure and stereochemistry of the ligands and the complexes prepared. While the ligands are characterized by usual methods such as elemental analysis, IR, UV-Visible and NMR spectral techniques, it differs for complexes depending on the nature of the ligands and the metal ions involved. Ligands on complexation with some metal ions having paired or unpaired electrons give diamagnetic or paramagnetic complexes respectively. Some of the common physicochemical methods adopted by inorganic chemists are discussed below.

1.5.1. Magnetic measurements

In a magnetic field, the paramagnetic compounds will be attracted while the diamagnetic compounds get repelled. In paramagnetic complexes, often the magnetic moment gives the spin only value corresponding to the number of unpaired electron. The variation from the spin only value is attributed to the orbital contribution and it varies with the nature of coordination and consequent delocalisation. In some cases two magnetic centers may be coupled together and may result in extraordinary increase or decrease in the magnetic moment of the complex. For example, a mononuclear complex of copper where Cu is in the +2 oxidation state, is expected to have a magnetic moment of 1.73 BM - corresponding to d^9 configuration, but, in the case of $[Cu(OAc)_2]_2$, the value is lower than 1.73 BM. This is explained on the basis of the assumption that the individual magnetic moments are aligned in opposite directions so that they cancel each other to some extent or can be ascribed as due to anti-ferromagnetic coupling. Thus the value of magnetic moment of a complex would give valuable insights into its constitution and structure. In some cases the variation in the magnetic moment can be explained on the assumption that the compound may be an equilibrium mixture of tetrahedral and square planar geometries -the number of unpaired electrons differ in either geometries and hence the magnetic moment. The magnetic susceptibility measurements thus help to predict the oxidation state of the metal ion to a limited extent and to establish the possible geometry of the compound.

The most widely adopted method for determining the magnetic moment of a complex is by Gouy's method in which the weight difference experienced by a given amount of a substance in the presence and absence is measured. This is compared with that of a standard substance and magnetic moment is determined with the help of suitable equations.[31]

1.5.2. Electronic spectroscopy

Electronic spectroscopy is an important and valuable tool for most chemists to draw important information about the structural aspects of the complexes. The ligands, which are mainly organic compounds, have absorption in the ultraviolet region -hence do have bands in the region of the 200 to 350 nm of the electromagnetic spectrum- and in some cases these bands extend over to higher wavelength region due to conjugation. But upon complexation with transition metal ions, due to interaction with the metal ion there will be an interesting change in the electronic properties of the system. New features or bands in the visible region due to d-d absorption and charge transfer spectra from metal to ligand (M→L) or ligand to metal (L→M) can be observed and this data can be processed to obtain information regarding the structure and geometry of the compounds[32]. This technique along with other spectral techniques viz., EPR serves to find out the structural features and to calculate the bonding parameters such (α^2, β^2, γ^2, $K_{\|}$, $K_{\perp}$ etc.) [33-35] and Racah Parameters (B and C).[36]

The electronic spectroscopy is also widely used to explore the change in the structural features with change in the pH of the medium. The electronic and structural features of the complexes are widely utilized to investigate the kinetics and mechanisms of the reactions involving transition metal complexes. [37-38] The kinetics of 4-nitrophenylacetate cleavages by oxime in the presence of Zn^{2+}ions was investigated.[39-40]

1.5.3. Infrared spectroscopy

The IR spectroscopy is widely used as a characterization technique for metal complexes. The basic theory involved is that the stretching modes of the ligands changes upon complexation due to weakening/strengthening of the bonds involved in the bond formation resulting in subsequent change in the position of the bands appearing in the IR spectrum. The changes in the structural features of the ligands are observed as changes in bands observed, mainly in the fingerprint region i.e., in the 1500 - 750 cm^{-1}. Nakamoto discusses at length the characterization of metal complexes with the help of IR spectroscopy.[41] The bands due to the metal ligand bonds are mainly observed in the far IR region i.e., 50 - 500 cm^{-1}.

1.5.4. EPR spectroscopy

For complexes those are paramagnetic, in addition to the elemental analysis, IR, and electronic spectroscopic techniques, Electron Paramagnetic Resonance (EPR) spectroscopy acts as an effective and valuable tool to explore the structural features and bonding characteristics of metal complexes. The advances in the ESR spectroscopy have benefited the inorganic chemists with the help of high field and high-resolution spectrometers that helps to resolve the $g_{\|}$ and $g_{\perp}$ features of the paramagnetic species. The information obtainable from a low temperature spectrum of diamagnetically diluted paramagnetic species provides important clues to structural traits and bonding properties of the complexes.[42] The single crystal EPR spectrum measurements are also widely employed to derive more information about the geometry of the paramagnetic species formed.[43] Hathaway had extensively surveyed the studies on complexes by using EPR spectroscopy. [44-45] Various simulation packages are extensively used to simulate the experimental spectrum and hence help to establish the absolute geometry and accurate bonding and structural characteristics of the complexes. [45-46]

1.5.5. NMR spectroscopy

For diamagnetic complexes, NMR spectroscopy still remains as a valuable tool for establishing the structural characterizations.

Assignment of protonated carbons were made by two dimensional heteronuclear-correlated experiment using delay values which corresponds to

${}^{1}J$(C,H). The HMQC experiment provides correlation between protons and their attached heteronuclei through the heteronuclear scalar coupling. This sequence is very sensitive (compare to the older HETCOR) as it is based on proton detection (instead of the detection of the least sensitive low gamma heteronuclei

1.5.6. X-Ray crystallography

The diffraction/scattering of X-ray radiations by array of atoms in a single crystal of a compound is exploited to establish the structure and geometry of the complexes. At present this versatile techniques is valued as the final word by many chemists for establishing the accurate structure of the complex compounds.

1.5.7 Physical methods

The carbon, nitrogen and hydrogen analyses were carried out using a Heraeus Elemental Analyser, at CDRI, Lucknow. Magnetic measurements were done in the polycrystalline state with a simple Gouy balance using cobaltmercuricthiocynate, $Hg[Co(SCN)_4]$, as reference and with a VSM at IIT, Roorkee.[55] FT IR spectra were recorded on Perkin Elmer FTIR spectrophotometer at CDRI Lucknow and at SCTIMST, Trivandrum, using KBr pellets. The EPR spectra were recorded using a Varian E-112 Spectrometer with TCNE as the standard at RSIC, IIT, Bombay and the NMR spectra were recorded with Bruker DRX 500 spectrometer using appropriate deuteriated solvents and TMS as reference at SIF, IISC, Bangalore. Single crystal XRD study was performed on a SMART CCD diffractometer at University Sains Malaysia. Electronic spectra were recorded on an Ocean Optics, DRS spectrophotometer, and Schimadzu 160A UV-Vis spectrophotometer.

1.6. OBJECTIVES AND SCOPE OF THE PRESENT WORK

The use of molecules or molecular assemblies for information processing is one of the most appealing aims of modern molecular chemistry. Hence molecule – based magnets are the focus of considerable current research effort, from both the fundamental and device related perspectives. One of the most exciting developments in recent years is the design of magnets from a consideration of the sign and magnitude of superexchange between adjacent paramagnetic metal centers. The study of molecules with usually large number of unpaired electrons has taken on added impetus as this area has been identified as the source of a new phenomenon of magnetic materials. To synthesise polynuclear arrays, macrocyclic ligands or compartmental ligands are useful.[46-47]

Yet another equally important facet among the applications of coordination complexes is their ability to act as potential bioactive agents. Studies on semicarbazones and thiosemicarbazones ascertain themselves as promising antitumour, antiviral, antimalarial and antifungal agents. Thiosemicarbazones usually react as chelating ligands with transition metal ions by bonding through S and hydrazinic N atom. The group =N-C=S is responsible for the pharmacological activity. In the light of these revelations, we have decided to prepare metal complexes using compartmental ligands, semicarbazones and thiosemicarbazones. We have prepared some nearly twenty complexes and they are characterized by various physico-chemical methods.[48]

SYNTHESIS AND SPECTRAL CHARACTERIZATION OF Mn(II), Cu(II) AND Ni(II) COMPLEXES OF SCHIFF BASE DERIVED FROM 3-FORMYLSALICYLIC ACID AND HISTAMINE BASE

2.1 INTRODUCTION

In the past two decades or so, a large number of multimetallic compounds have been investigated. The studies of these compounds have often been performed either in relation to the modeling of some metallic enzymes containing several kinds of metal ions or with the perspective to design novel molecular magnets. The search for rational routes leading to polynuclear complexes with low nuclearities has been stimulated by the potential relevance of these compounds in bioinorganic chemistry.[49-51]

Furthermore, extensive magneto-structural investigation of discrete homo- and hetero-polynuclear complexes have contributed to the understanding of the factors governing the sign and the magnitude of the exchange interactions between paramagnetic centres, both identical and different.[52-53]

A synthetic strategy for discrete polynuclear complexes must fulfill the following conditions;

i) Control the nuclearity, that is, the number of metallic ions within the molecular entity.
ii) Control the topology of the metallic centers, which are usually paramagnetic ions.

Several synthetic approaches have been proposed to design discrete polynuclear complexes. One of them consists in the ingenious use of compartmental ligands, which are organic molecules able to hold together two or more metal ions. The Schiff bases derived from 2,6-diformyl-4-methylphenol (Robson-type ligands) and from 3-formylsalicylic acid are among the most popular ligands belonging to this family. These ligands are especially appropriate to generate either homobinuclear complexes, symmetrical or dissymmetrical, or heteropolynuclear complexes.

Here, we focus on the spectral studies and X-ray crystallographic studies of a new type of unsymmetrical tetradentate Schiff bases derived from 3-formylsalicylic acid, which is very suitable for the design of polynuclear complexes. Some complexes have been prepared with the Schiff base as ligand. This chapter encloses a discussion on some spectral data of three complexes, a mononuclear manganese complex, a binuclear nickel complex and a trinuclear copper complex.

2.1 EXPERIMENTAL

2.2.1 Materials and methods

Histamine base (Sigma–Aldrich) and hexammine (Merck) are used as received. Salicylic acid (Qualigen's Fine Chemicals) and metal salts (BDH) were purified by standard methods. All solvents were purified by standard methods.

2.2.2 Synthesis

2.2.2.1 Synthesis of 3-formylsalicylic acid

Salicylic acid (40 g), hexamethylenetetramine (27 g), and water (300 ml) were boiled under reflux for 16 hrs, cooled the solution and acidified with 4N HCl (300 ml), The yellow precipitate dried and extracted with lots of benzene (100 ml) at 70°C. The insoluble portion crystallizes from boiling water yielded 7.5 g of 5- Formylsalicylic acid. The benzene solution was evaporated, the residue dissolved in 3N ammonia (200 ml), and 10% of $BaCl_2$ (100 ml) and 2N NaOH (50 ml) added at 50°C. After 2 hrs, the precipitate of barium 3-formylsalicylate was collected and decomposed with dilute HCl, and 3.3 g of 3-formylsalicylic acid obtained by crystallization of the resulting precipitate from the boiling water. Salicylic acid (20 g) was recovered from the alkaline precipitate. [54]

2.2.2.2. Synthesis of ligands

A mixture of 3-formylsalicylic acid (2 mmol) and histamine base (2 mmol) in absolute alcohol was refluxed for 1 hr, in an inert atmosphere. An yellow solution obtained which produced yellow crystals after three days. It was filtered and recrystallised from water. Single crystal suitable for X-ray diffraction studies were grown by slow evaporation from water in a period of few weeks.

2.2.2.3. Synthesis of manganese(II) complexes

A mixture of 3-formylsalicylic acid (2 mmol) and histamine base (2 mmol) in absolute ethanol were mixed. It was refluxed in an inert atmosphere. After 15 minutes, 2 mmol of manganese acetate was added and then the refluxing was continued for half an hour. A light yellow coloured precipitate that formed was collected, washed with water, alcohol, and ether and dried *in vacuo*. The yield was estimated to be 57% (249 mg).

2.2.2.4. Synthesis of nickel(II) complex

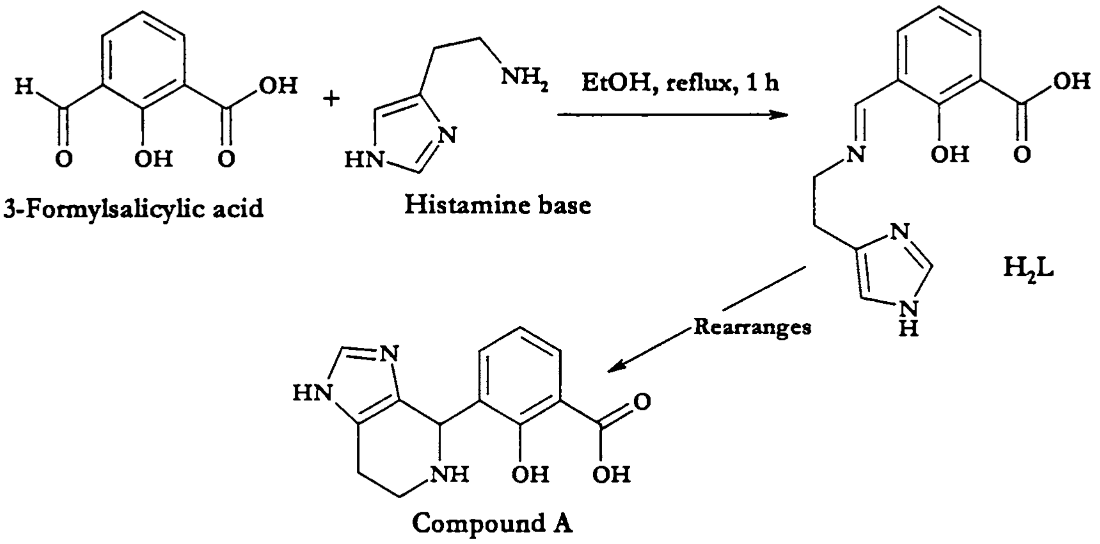
A mixture of 3-formylsalicylic acid (2 mmol) and 2 mmol of histamine base (2 mmol) in 30 ml absolute alcohol was refluxed in inert atmosphere. After 15 minutes, 2 mmol of nickel acetate was added and again refluxed for an hour. A light green coloured precipitate formed was collected, washed with water, alcohol and ether and dried *in vacuo*.. The yield was found to be 61% (385 mg).

2.2.2.5. Synthesis of copper(II) complex

3-Formylsalicylic acid (2 mmol), sodium carbonate (0.212 g) and histamine base (2 mmol) were dissolved in 30 ml of absolute alcohol and stirred in inert atmosphere for 15 minutes. To this an aqueous solution of 1.8 mmol of copper chloride was added and the refluxing was continued for one more hour. A green coloured precipitate formed was collected, washed with water, alcohol and ether and finally dried *in vacuo*. The yield was found to be 61% (385 mg).

2.3. RESULTS AND DISCUSSIONS

3-Formylsalicylic acid was prepared according to the method of Duff and Bills.[54] We have attempted to prepare a Schiff base (H_2L) by condensing 3-formylsalicylic acid and histamine base and elemental analysis corresponds to the composition, $H_2L{\cdot}H_2O$ (Scheme 1). However, the compound isolated from the reaction medium is not a simple condensation product. It is found that some cyclisation of H_2L has occurred during condensation reaction. The structure for this compound, hereafter compound **A** was completely solved by single crystal XRD. NMR and IR spectral studies were undertaken for this compound and the data obtained are in good agreement with this structure.



Scheme 1

All the complexes were prepared by template method, where the ligand is not isolated from the reaction mixture as it is the most suitable method and gives better yield. The colors, elemental analyses and magnetic moment results are given in the Table 2.1.

Elemental analysis of the copper(II) complex (3) reveals the presence of three copper atoms, two dianionic ligands and two chloride anions and corresponds to the composition $[Cu_3L_2]Cl_2$. The complex is soluble in polar solvents and insoluble in nonpolar solvents. The compound is soluble in DMF in which the conductance was measured. The manganese(II) complex (1) is pale yellow in colour and the elemental analysis suggests a stoichiometry of MnHLOAc containing one manganese atom, a monoanionic ligand (HL) and an acetate ion. It is soluble only in DMF and DMSO. Mn(II) and Ni(II) complexes were non conductors in DMF solution, whereas, the Cu(II) complex behave as a 1:2 electrolyte with a conductance value of 108 $\Omega^{-1}cm^2mol^{-1}$ The nickel(II) complex (2) is pale green in color and found to be the dinuclear complex with empirical formula $Ni_2L_2 \cdot 0.5\ H_2O$. It is soluble in polar solvents and is a non-electrolyte.

Table 2.1. Colors, Partial elemental analysis and magnetic moments of the complexes

Compound	Colour	Elemental analysis Found (Calcd) % C	H	N	Magnetic moments (B.M)
A	Pale yellow	57.59 (57.72)	5.89 (5.88)	14.79 (14.42)	
MnHLOAc (1)	Pale yellow	48.75 (48.53)	4.29 (3.80)	11.75 (11.75)	5.05
Ni_2L_2 (2)	Pale green	49.04 (49.02)	4.51(4.56)	13.51(13.55)	2.94
$[Cu_3L_2]Cl_2$ (3)	Green	42.35 (42.19)	3.77 (5.45)	10.54 (15.5)	2.08

2.3.1. X-Ray crystal structure of compound A

The crystal structure determination of the compound was undertaken with a view to obtain a clear understanding of the coordination geometry of this potential ligand.

Colorless, single crystals of the compound A were obtained by slow evaporation of a methanol solution of the compound. A crystal, of size $0.46\times0.20\times0.12$ mm^3, was mounted on glass fiber with epoxy cement for the X-ray crystallographic study. A summary of the crystallographic data for the title complex at 293 K is gathered in Table 2.2. The data was collected with a 1-K SMART CCD diffractometer using graphite-monochromated MoK_α radiation with a detector distance of 4 cm and swing angle of –35°. Out of the 77773 reflections collected 3013 unique reflections were used for empirical absorption correction. A hemisphere of the reciprocal space was covered by combination of three sets of exposures; each set had a different of angle (0, 88, 180°) and each exposure of 30 sec covered 0.3° in ω. The structures were solved by direct methods and refined by least-square on F_o^2 using the SHELXTL [14] software package. All H- atoms were refined. The selected bond lengths and bond angles of the compound A are listed in Table 2. 3. and Table 2. 4 lists the H- bonding and intermolecular interaction parameters.

Compound A is a monohydrate and exists as a zwitterion, in which the positive and negative charges are localized on tetrahydropyridinium atom N3 and benzoate atom O1, respectively. This is also confirmed by the geometric parameters and the unambiguous location and refinement of all H atoms in the structure. All bond lengths and angles have normal values.[56]

The compound is composed of three rings (Figure 2.1), viz. the tetrahydropyridinium ring (C7/C8/C10-C12/N3), the imidazoline ring (C8-C10/N1/N2) and the benzoate aromatic ring (C1-C6). The tetrahydropyridinium ring adopts an envelop conformation, with atom C12 displaced by 0.279 (3) Å from the C7/C8/C10/C11/N3 plane. This plane is nearly coplanar with the plane of the imidazoline ring with dihedral angle 5.5 (1)°. The relative configuration of the attached bezoate aromatic ring, with respect to the tetrahydropyridinium ring is conditioned by the sp^3 hybridised C7 atom (the average angle subtended at C7 atom is 110.3°). The dihedral angle between the mean plane of the tetrahydropyridinium and benzoate aromatic rings is 56.4 (1)°. The plane of the carboxylate group (O1/O2/C13/C1) is slightly twisted about the C–C bond with respect to its aromatic ring, by 14.0 (1)°. This relatively small twist angle is due to atom O1 being hydrogen bonded to the hydroxy group (O3– H103....O1), forming a six-membered O1–C13–C1–C6– O3–H103 ring. Within the asymmetric unit, the water molecule is linked to the zwitterion and acts as a hydrogen-bond acceptor via an N2–H2....O1W hydrogen bond. In the crystal packing, the water molecule acts as a hydrogen-bond donor to the zwitterion via an O1W–H1W1.....$O2^{iii}$ hydrogen bond [symmetry code: (iii) x, y, 1 + z]. Therefore, the water molecule acts as a bridge between the zwitterions; in this manner, a $C^2_2(12)$ chain.[57] is generated running along the c direction. Both N^+–H bonds also play important roles in the crystal packing; N3-H3B forms an N3-H3B...O2^{ii} hydrogen bond to carboxylate atom O2 at (x, ½ - y, ½ + z), interconnecting two adjacent molecular chains into ribbons. The ribbons, as shown in Figure 2.2, are comprised of R^2_2 (16) and R^6_6 (24) ring patterns of hydrogen bonds which are centered at (n, 1/2, 1/2 + n) and (n, 1 /2, n), respectively (n = zero or integer). The ribbons are stacked one above the other along the b direction (Figure3) and are interconnected by two hydrogen bonds, viz. N3–H3A....O1^{i}, formed from another N^+–H bond of the zwitterion to carboxylate atom O1 at (2 - x, 1- y, 1 - z), and O1W–H2W1....N1^{iv}, formed from the water molecule to imidazoline atom N1 of the zwitterion at (x, 3 /2 - y, 1/ 2 + z). In the packing (Fig. 2), across the center of symmetry, the C...π distance for the C11–H11B....$\pi_{benzoate}$ contact is 3.776 (2) A , while the distance between the centroids of the imidazoline and benzoate aromatic rings is 3.882 (4) Å . These rather long distances indicate that the C–H π and aromatic π..π interactions are weak. Compound A crystallizes in a centrosymmetic space group. All H atoms were located in difference Fourier maps and were refined isotropically. The C–H, N–H and O–H bond-length ranges are 0.90 (3)-1.01 (3), 0.89 (3)- 1.01 (3) and 0.76 (4)-0.90 (3) Å , respectively.

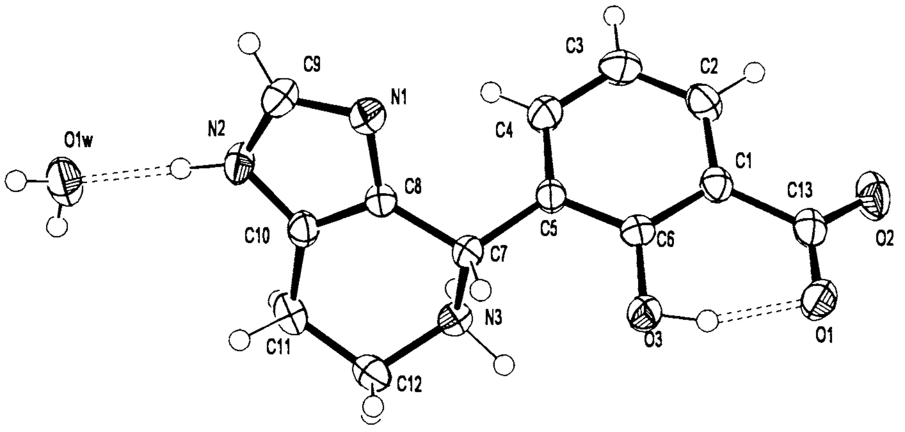


Figure 2.1. ORTEP drawing of compound A, at 50% probability. All hydrogen atoms are placed as spheres of arbitrary radii. Dotted lines indicate intra molecular H- bonding interactions.

Table 2.2 Crystal data and structure refinement for compound A

Empirical formula	$C_{13}H_{13}N_3O_3.H_2O$
Formula weight (M)	*277.28*
Temperature (T) K	293
Wave length (Mo Kα), Å	0.71073
Crystal system	Monoclinic,
Space group	*P21/c*
Unit cell dimensions	
a, Å	12.4975(13)
B, Å	7.784(8)
c, Å	13.132(1)
α, deg	90
β, deg	100.402
γ, deg	90
Volume (V), $Å^3$	1256.4 (2)
Z	4
Calculated density (ρ), mg^3	1.466
Absorption coefficient (μ) mm^{-1}	0.111
F(000)	584
Crystal size	0.46 X 0.20 X 0.12 mm
θ Range for data collection	3.06 to 28.27 deg.
Limiting indices	$-13 \le h \le 16$, $-10 \le k \le 10$, $-17 \le l \le 14$
Reflections collected/ unique	7773 / 3103 [R(int) = 0.0330]
Completeness to θ	28.27, 99.4 %
Absorption correction	Empirical
Max and min transmission	0.9868 and 0.9508
Refinement method	Full-matrix least-squares on F^2
Data/ restraints/ parameters	3103 / 0 / 241
Goodness-of-fit on F^2	1.056
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0614, wR2 = 0.1388
R indices (all data)	R1 = 0.0984, wR2 = 0.1568
Largest diff peak and hole	0.243 and -0.334 e.$Å^{-3}$

Table 2. 3. Selected Bond lengths (Å) and Bond angles (deg) of Compound A

O(1)-C(13)	1.273(3)	C(2)-C(1)-C(6)	118.3(2)
O(2)-C(13)	1.250(3)	C(2)-C(1)-C(13)	121.0(2)
O(3)-C(6)	1.353(2)	C(6)-C(1)-C(13)	120.54(19)
N(1)-C(9)	1.319(3)	C(4)-C(5)-C(6)	118.76(19)
N(1)-C(8)	1.387(3)	O(3)-C(6)-C(5)	118.40(18)
N(2)-C(9)	1.339(3)	O(3)-C(6)-C(1)	121.10(19)
N(2)-C(10)	1.366(3)	C(5)-C(7)-N(3)	108.30(17)
N(3)-C(12)	1.501(3)	C(10)-C(8)-N(1)	110.38(19)
N(3)-C(7)	1.520(3)	C(10)-C(8)-C(7)	124.16(19)
C(1)-C(2)	1.394(3)	N(1)-C(8)-C(7)	125.45(18)
C(1)-C(6)	1.409(3)	N(1)-C(9)-N(2)	113.3(2)
C(1)-C(13)	1.501(3)	C(8)-C(10)-N(2)	106.14(19)
C(2)-C(3)	1.373(3)	C(8)-C(10)-C(11)	126.4(2)
C(3)-C(4)	1.385(3)	N(2)-C(10)-C(11)	127.4(2)
C(4)-C(5)	1.386(3)	C(10)-C(11)-C(12)	108.61(19)
C(5)-C(6)	1.400(3)	O(2)-C(13)-O(1)	123.8(2)
C(5)-C(7)	1.516(3)	O(2)-C(13)-C(1)	119.6(2)
C(7)-C(8)	1.492(3)	O(1)-C(13)-C(1)	116.59(19)
C(8)-C(10)	1.358(3)	C(9)-N(1)-C(8)	103.54(19)
C(10)-C(11)	1.488(3)	C(9)-N(2)-C(10)	106.60(19)
C(11)-C(12)	1.521(3)	C(12)-N(3)-C(7)	114.49(17)

Table 4. Hydrogen bonding, π-π and C-H- π interaction parameters of compound A

D-H---A	D-H (Å)	H---A (Å)	D---A (Å)	∠D-H---A
N2-H2A....O1W	0.92 (3)	1.87 (3)	2.783 (3)	178 (2)
N3-H3A....O1^{i}	1.02 (3)	1.71 (3)	2.720 (2)	174 (2)
N3 H3A...O2^{ii}	0.89 (2)	2.02(2)	2.864 (2)	175(3)
O1W1-HIWI...O2^{iii}	0.76 (4)	2.14 (4)	2.897 (3)	171 (3)
O1W1-H2WI...N1^{iv}	0.89 (3)	1.96 (3)	2.844 (3)	170 (4)
O3-H103...O1	0.90 (3)	1.64 (3)	2.513 (2)	161 (3)
C12-H12A...O1^{iv}	0.98 (3)	2.48 (3)	3.325 (3)	145 (2)
C12-H12B...O3^{v}	0.96 (2)	2.51 (2)	3.447 (3)	166 (2)

Symmetry codes:

(i) 2-x, 1-y, 1-z (ii) x, ½-y, ½+z (iii) x, y, 1+z (iv) x, 2/3-y, ½+z, (v) 2-x, y-1/2, 3/2-z

π-π interactions	Centroid	Cg-Cg (Å)	Cg(1) N1, C8, C10, N2, C9
Cg(i)-Res[i]-Cg(i)	Cg1 [1]- Cg3	3.8817	Cg(3) C1, C2, C3, C4, C5, C6

Symmetry codes:x,3/2-y,-1/2+z

C-H- π interactions	H...Cg(Å)	D-H...Cg(°)	D...Cg(Å)
C11-H1CB[1]- Cg3	2.7917	164.14	3.7764

Symmetry codes: x,1/2-y,-1/2+z

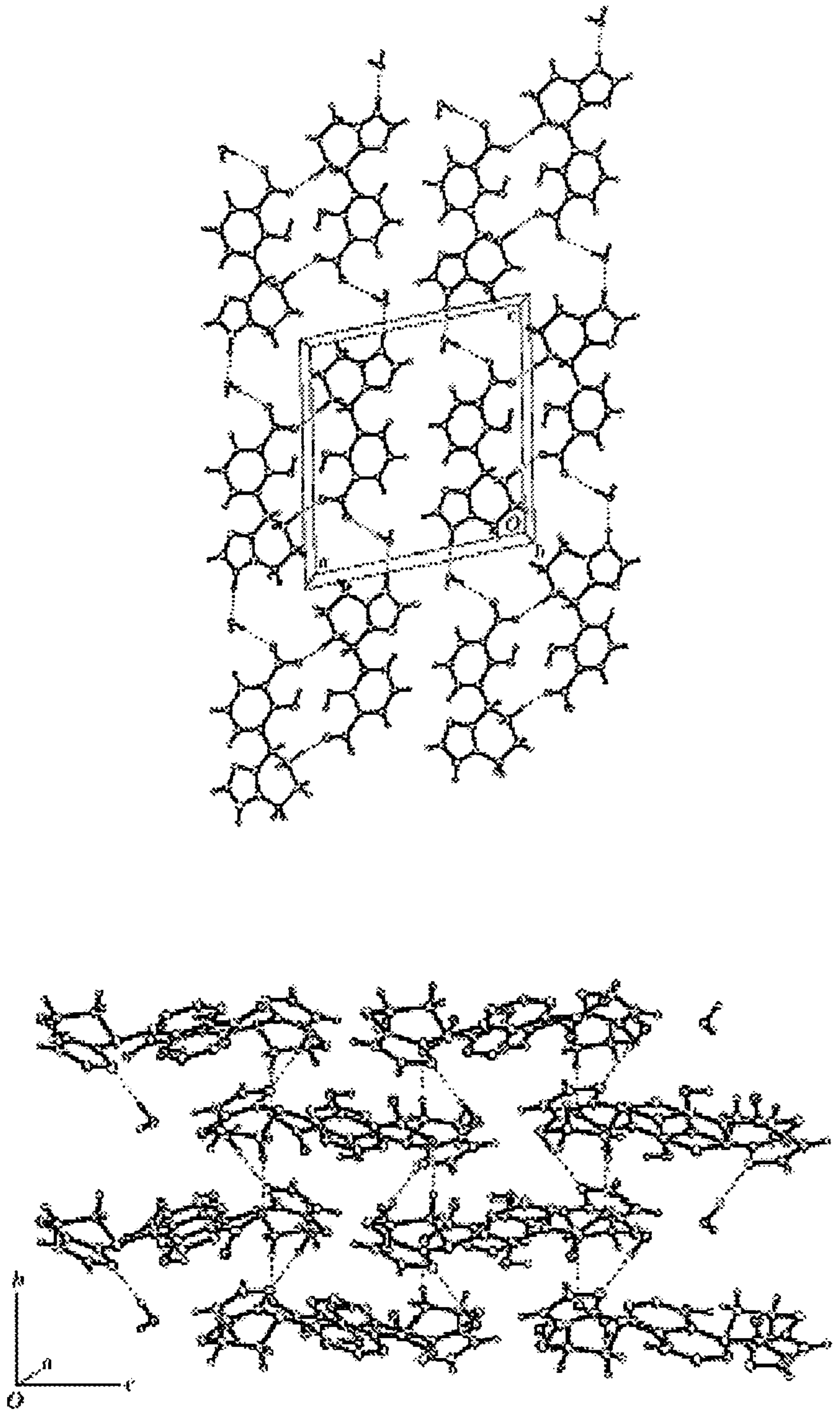
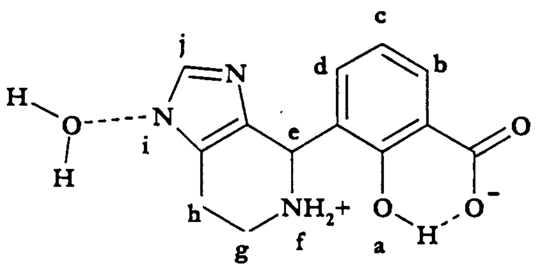


Figure 2.2. Packing of the compound A in a unit cell, views along a axis

2.3.2. ^{1}H NMR spectral studies:

NMR spectroscopy is a spectroscopic method that allows the examination of the properties of nuclei that have nonzero spin numbers. The technique is directly applicable to the nuclei that are commonly present in organic molecules and used to examine the environment of protons and carbons. The tentative assignments of the peaks in the spectrum of compound A was assigned on the basis of different NMR experiments, based on the couplings and connectivities of the signals observed. The ^{1}H resonances were assigned on the basis of chemical shifts, multiplicities and coupling constants from ^{1}H NMR and ^{1}H-^{1}H COSY experiments. Figure 2.3 shows a schematic contour plot of the ^{1}H-^{1}H COSY experiment. Both dimensions represent the ^{1}H chemical shift scale; they are identical so that the spectrum is symmetrical with respect to the diagonal. The ^{1}H NMR spectrum appears on the diagonal where as the off diagonal peaks prove the existence of spin-spin couplings. The coupling parameters were identified by drawing horizontal and vertical lines to connect the diagonal and cross peaks. The complete assignment of the 1-H NMR resonances were done by making use of the multiplicities and ^{1}H-^{1}H correlation.[58]



Actual signal positions along with coupling constants were assigned as follows: H_a (s, 12.01 ppm); H_c (s, 6.51 ppm); H_b (s, 6.48 ppm); H_d (s, 7.70 ppm); H_e (s,5.70 ppm); H_f (s, br.9.10 ppm); H_g (s, 3.15 ppm); H_h (s, 2.87 ppm), H_i(s, 9.29 ppm); H_j (s,5.70 ppm).

Signals at δ =12.01, 9.29, and 9.10 ppm are assigned to OH, NH, and $^+NH_2$ protons respectively. All these protons are attached to hetero atoms and so differ from protons on a carbon atom in that,

1. They are exchangeable.
2. They are subjected to hydrogen bonding and
3. They are subject to partial or complete decoupling by electrical quadrupole effects of the heteroatom

The high value of OH proton is due to the presence of carbonyl group at the ortho position. A carbonyl group in the ortho position shifts the phenolic proton to downfield by intra molecular hydrogen bonding. The peak of the proton on nitrogen nucleus induces a moderately efficient spin relaxation and resulting in an intermediate lifetime for spin states of the nitrogen nucleus. The protons thus see three spin states of nitrogen nucleus that are changing at a moderate rate and they respond by giving a broad peak. Aromatic proton exhibit signals in the region 7.8 ppm-6.51 ppm. The signals at 2.50 ppm and 3.15 ppm are attributed to the CH_2 group of the heterocyclic six membered ring. The signal at 5.7 ppm is attributed to H_e.[83-84]

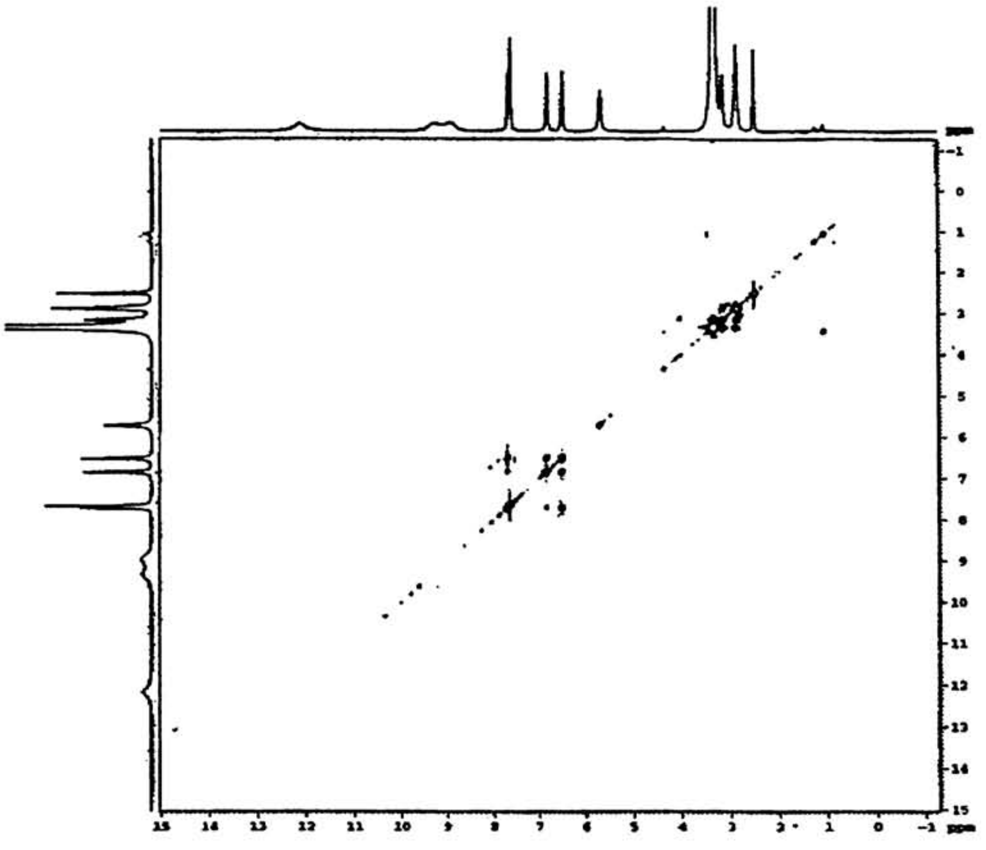


Figure 2.3. ^1H-^1H **Correlation spectrum of compound A.**

2.3.3. IR spectra

The significant IR spectral bands of compound A and three complexes are given in Table 2.5.

The IR spectrum of compound A shows a broad band at 3452 cm^{-1}, which can be attributed to the ν_{OH} stretching. This decrease in wavenumber is due to hydrogen bonding present in the compound. A strong $^+NH_2$-stretching band is obtained at 3038 cm^{-1}. Aliphatic ν_{CH} stretching superimposed on NH is seen at 2836 cm^{-1}. A weak asymmetric $^+NH_2$ bending band is obtained at 1676 cm^{-1}. The carboxylate ion absorbs strongly at 1615 cm^{-1} and weakly at 1448 cm^{-1}, resulting from the asymmetrical and symmetrical stretching of C ($-O_2$), respectively.

Absence of a strong band in region near to 1640 cm^{-1} suggests the absence of azomethine linkage. This suggests a cyclisation of the product, which is confirmed from crystal data. Prominent bands in the range 900-675 cm^{-1} are attributed to the out of plane bending of the aromatic ring C-H bonds.

Table 2.5. Selected IR spectral bands (cm^{-1}) of the compound A and complexes

Compound	ν_{OH}	ν_{CN}	ν_{CO}	ν_{MO}	ν_{MN}
A	3452	-	1615	-	-
MnHLOAc(1)	3367	1631	1564	384	456
Ni_2L_2(2)	3416	1642	1577	351	414
$[Cu_3L_2]Cl_2$(3)	-	1633	1572	394	401

The IR bands of the complexes show a new band in the region 1645-1630 cm^{-1} that corresponds to ν_{CN} of azomethine group. This gives information regarding coordination of azomethine group[58-59] which suggests that during complexation, cyclisation of the ligand does not occur. A broad and strong band was found in the region 1560-1575 cm^{-1} which was observed at 1615 cm^{-1} in the ligand. In general, the $\nu_{c=o}$ mode of carbonyl shifts to lower frequency by coordination.[59]

In the case of complexes of 3-formylsalicylic acid[9] and its Schiff bases,[10] the C=O stretching was around 1550 cm^{-1}. Therefore it seems reasonable to assign the band at region 1560-1570 cm^{-1} to the coordinated carboxylate group.

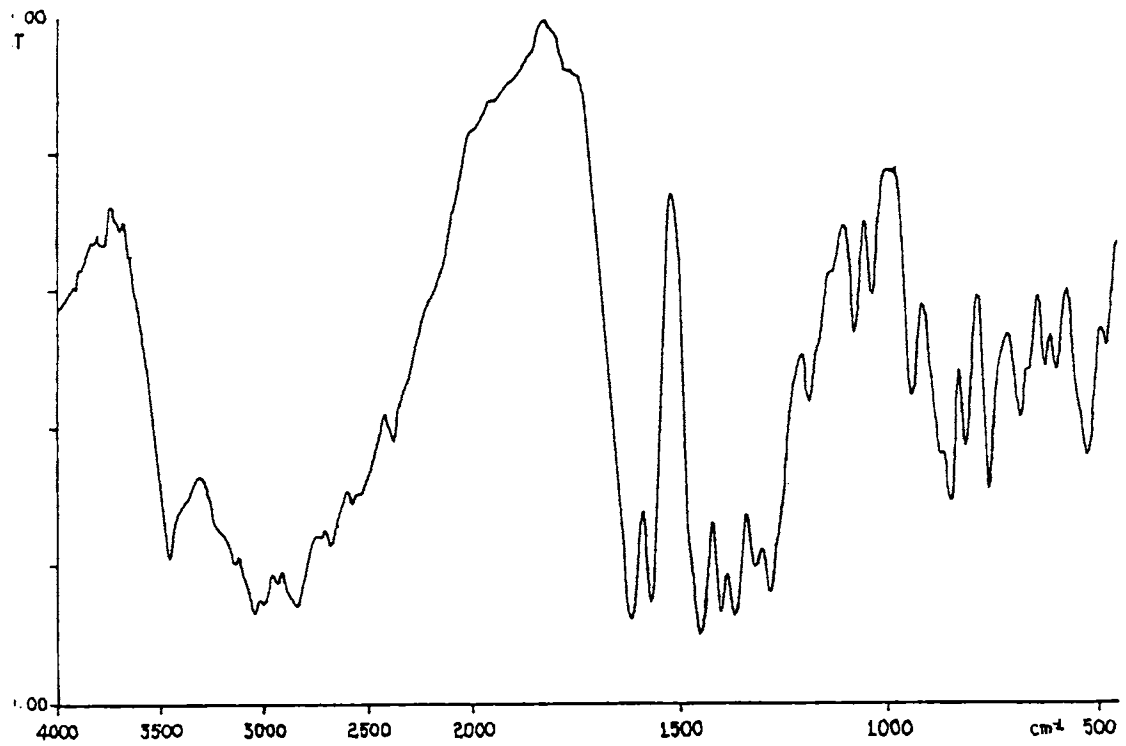
The IR spectral bands of complexes show a new band in the region 1645-1630 cm^{-1} that corresponding to $\nu_{C=N}$ of azomethine group. This gives information regarding coordination of azomethine group.[61] A broad absorption bands at 3400 cm^{-1} in the spectrum of Mn(II) complex indicate the presence of a nondeprotonated and uncoordinated OH group of 3-formylsalicylic acid moiety. Figure 2.4 shows the IR spectra of compound A, Cu(II) and Mn(II) complexes.

2.3.4. Magnetic Studies

Due to the additional stability of half filled *d* shell, manganese (II) generally forms high spin complexes, which have an orbitally degenerate ^6S ground state term. A spin only magnetic moment of 5.92 B.M is expected which will be independent of the temperature and of stereochemistry.[60] The manganese complex has a magnetic moment value of 5.05 B.M., which shows the presence of five unpaired electrons. So the complexes will be of high spin type.

The maximum spin-only magnetic moment for a multinuclear system is given by $\mu^2_{eff} = n\ (n+2)$, where n is the number of unpaired electrons in the cluster. Hence for Cu(II), n =1 per copper atom, thus for a three copper system $\mu^2_{eff} = 3\ (3+2) = 15$. μ^2 per Cu atom is equal to 5 and hence magnetic moment was expected to be 2.24 B.M. In view of this, the magnetic moment of 2.08 B.M suggest that this complex contains three copper atoms.[61]

The spin only magnetic moment value calculated for nickel complex is 2.94 BM. Ni(II) having a coordination number of four in accordance with the data. Usually due to inherent orbital angular moment, regular tetrahedral complex should have high magnetic moment than spin only value. But for distorted complexes, the moments are in same range as in the six-coordinated complexes[5]



IR Spectrum of Compound A

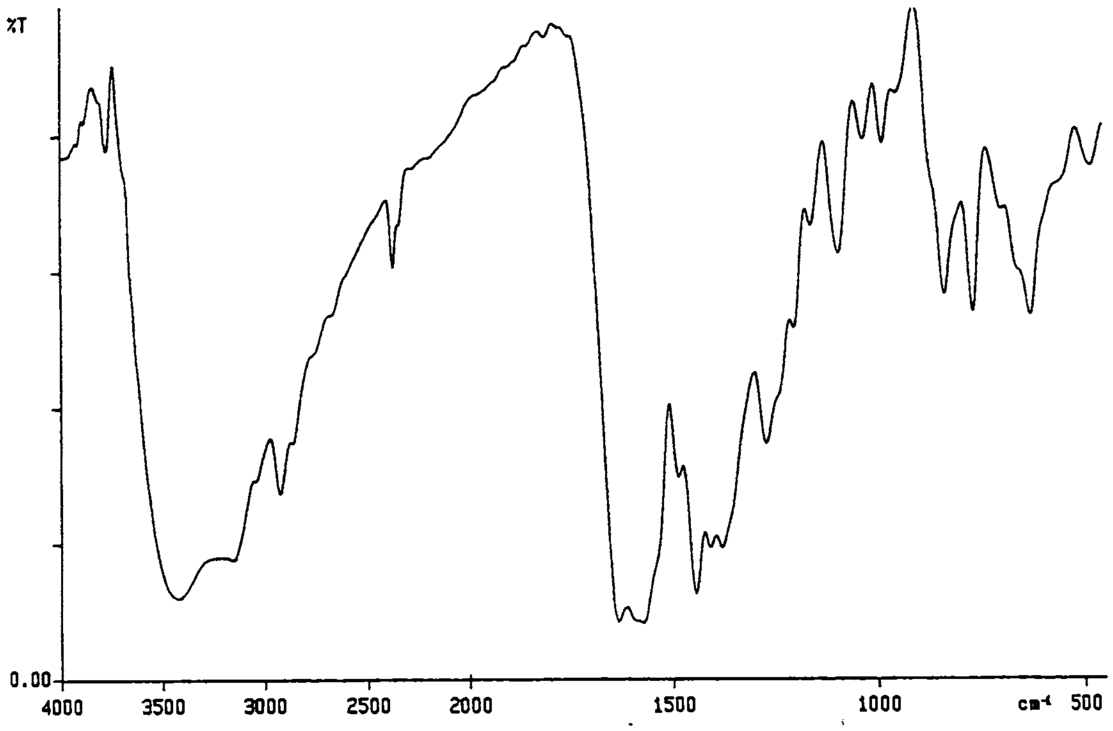


Figure 2.4. IR Spectra of Compound A and 1

2.3.5. EPR spectra of Mn(II) and Cu(II) complexes

2.3.5.1. Manganese(II) complex (1)

EPR spectrum of the complex is shown in the Figure 2.5. The interpretation of the electron spin resonance spectra observed for high spin d^5 complexes has been made in detail but it is important to mention a few of the principles. For the compound under study the spectra could be fitted for an axial Hamiltonian. The high spin manganese(II) has an orbital $^6S_{5/2}$ ground state term which should not interact with the electric field in first order case. However, the combined action of the electric field gradient and the spin-spin interaction produces splitting of energy levels due to second order spin orbit coupling between the $^6A_1$ ground state and the lowest level of the manifold $^4A_{2g}$ state.[62]

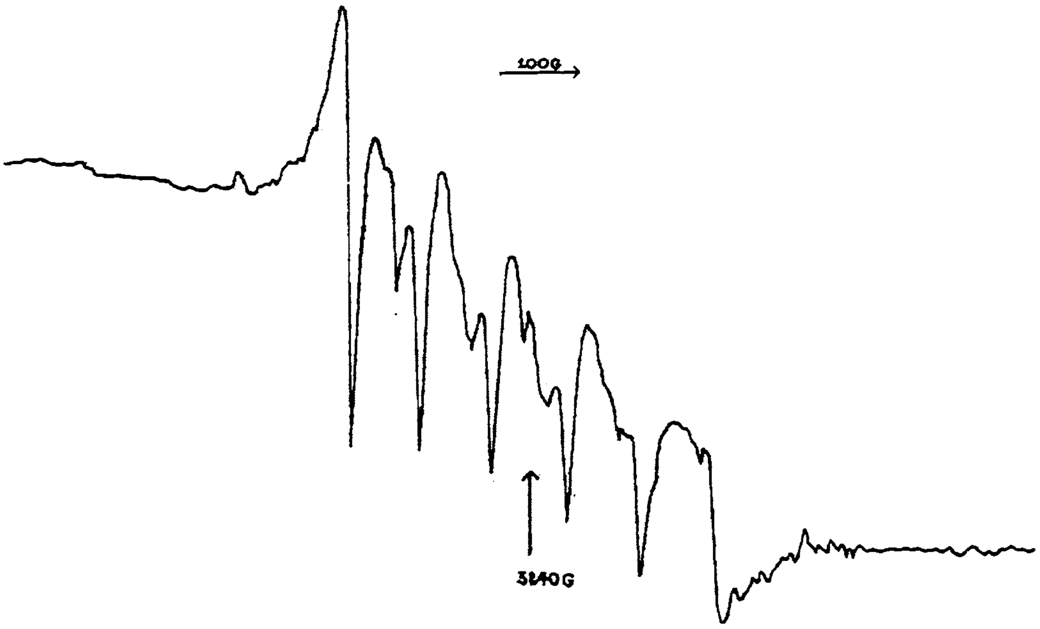


Figure 2.5. EPR spectrum of Mn(II) complex in DMF solution at 77 K

Axial field splitting parameter *D* in the case of an axially distorted octahedral field expects the magnitude of zero-field splitting. The spin Hamiltonian for manganese(II) can be defined as:

$$\hat{H} = g\beta H\cdot s + D[s_z^2 - 1/3\ s(s+1) + A\ s \cdot I$$

where, H is the magnetic field vector,

g is the spectroscopic splitting factor,

β is the Bohr magneton,

A is the manganese hyperfine splitting constant,

s is the electron spin vector and s is equal to 5/2,

I is the nuclear spin vector,

s_z is the diagonal spin operator

For s = 5/2 and noting the selection rule $\Delta m_s = \pm 1$, the allowed transitions should arise when field separations are dependent on θ, the angle between the applied magnetic field and the symmetry axis. These transitions are:

$\Delta m_s = \pm 5/2 \leftrightarrow 3/2$; $H = Ho \pm 2D\ (3\cos^2\theta - 1)$

$\Delta m_s = \pm 3/2 \leftrightarrow 1/2$: $H = Ho \pm D\ (3\cos^2 - 1)$

$\Delta m_s = \pm 1/2 \leftrightarrow -1/2$: $H = Ho$

where, $Ho = h\nu/\beta$ and θ is the angle between the applied magnetic field and direction of the axial distortion.

When the complex is very nearly octahedral only central $\Delta m_s = \pm 1/2 \leftrightarrow 1/2$ transition will be observed since it has only a second order dependence on *D*. Thus central line will of course be split into a sextet due to electron spin nuclear spin hyperfine coupling (^{55}Mn, I = 5/2). If, however, the zero-field splitting is appreciable, then the other electronic transitions will appear in the powder spectrum and the value of zero-field splitting can be evaluated. In addition to these allowed transitions the frozen solution spectra give low intensity pair forbidden lines between each pair of allowed lines. These lines are due to simultaneous change of both the electron and nuclear spin by ±1.

The electron spin nuclear spin hyperfine coupling constant A in the present study has been calculated by taking the average of all the observed lines. From the EPR spectra the values of g =2.014 and A = 184 G have been calculated .The observed values are consistent with the values obtained for chromophores like MnO_6, MnN_2O_4. It is seen that the A values are some what lower than that of the pure ionic compounds and also when manganese(II) is coordinated to oxygen the metal ligand bond seems to be more covalent as reflected by A values.[63]

2.3.5.2. Copper(II) complex (3)

The EPR spectra of copper complex was recorded in DMF solution at room temperature and 77 K (Figure. 2.6). The spin Hamiltonian parameters of the complexes were calculated and summarized in Table 2.6.

The solution spectrum at room temperature (Figure 2.7) shows is isotropic due to the tumbling motion of the molecules. However, this complex in frozen state at 77 K shows four well-resolved peaks of low intensities in the low field and one intense peak in the high field region. No band corresponding to $\Delta m_s = \pm 2$ transition was observed in the spectrum, ruling out any Cu-Cu interaction. The *g* tensor values can used to derive the ground state. In tetragonal and square planar complexes, the unpaired electron lies in the $d_{x^2-y^2}$ orbital giving $^2B_{1g}$ as the ground state with the $g_{\|} > g_{\perp}$. From the observed values, it is clear that $g_{\|} > g_{\perp}$ (2.28 > 2.076), which suggests square planar geometry. Also it is supported by the fact that the unpaired electron lies predominantly in the $d_{x^2-y^2}$ orbital. Molecular orbital coefficients α^2 in plane sigma bonding parameter and β^2 in plane pi bonding parameters are calculated using the following equations:

$$\alpha^2 = A/0.036 + (g_{\|} - 2.0023) + 3/7\,(g_{\perp} - 2.0023) + 0.04$$

$$\beta^2 = (g_{\|} - 2.0023)\,E\,/\,-8\lambda_0\alpha^2.$$

Table 2.6. Spin Hamiltonian and bonding parameters of copper(II) complex

In DMF(298 K)	g_{iso}= 2.14	
In DMF (77 K)	$g_{\|}$-	2.284
	$g_{\perp}$	2.076
	g_{av}	2.145
	$A_{\|}$	195
	$A_{\perp}$	12.8
	A_{av}	69.83
	G (77 K)	3.74
	α^2	0.8636
	β^2	0.9497
	γ^2	0.9232
	$K_{\|}$	0.779
	$K_{\perp}$	0.7973
	f	117.2

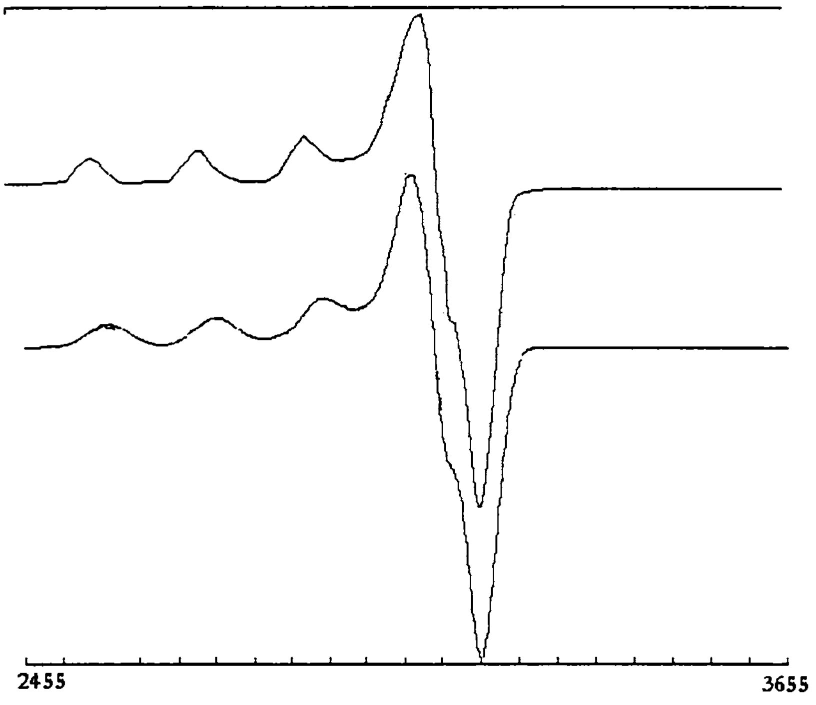


Figure 2.6.Experimental and simulated best fit pairs of the EPR spectrum at 77 K of the copper(II) complex DMF

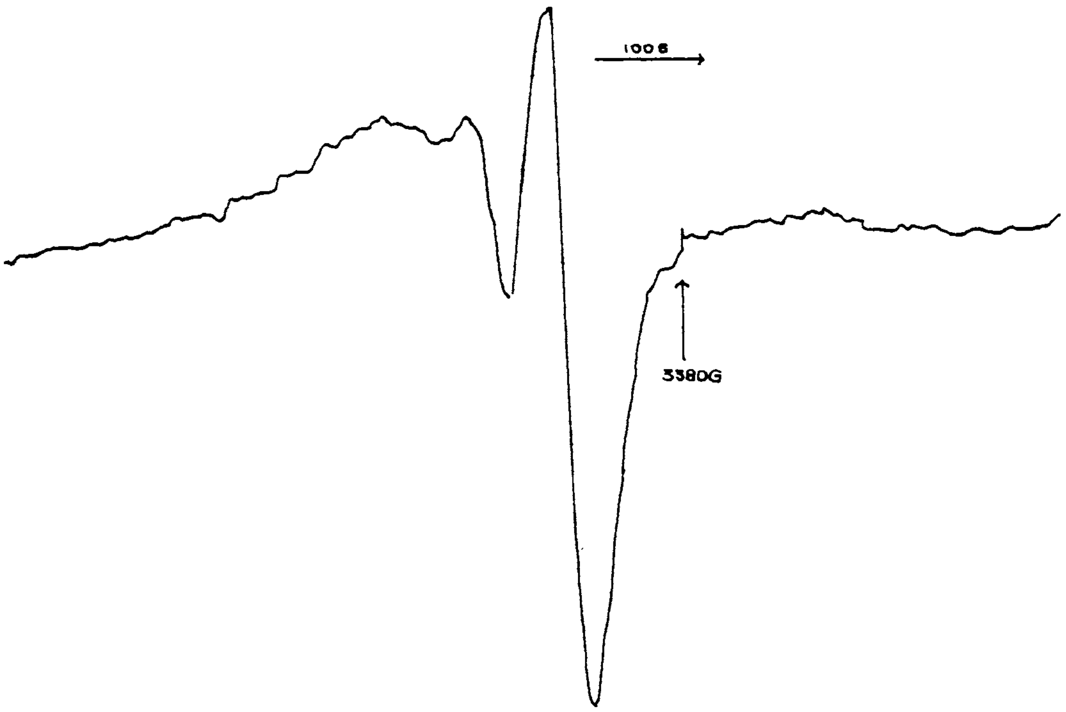


Figure 2.7. EPR spectrum of the copper(II) complex at 298 K

2.3.6. Electronic spectral studies

Table 2.7. lists the band maxima of solid state and solution electronic transitions for A and the complexes.

The bands at 263, 293 and 373 nm can be attributed to the n→π*and two π→π* transitions. The diffuse reflectance spectrum (DRS) of copper(II) complex has shown asymmetric broad bands at 550 and 700 nm whcic can be assigned respectively to the transitions $^2B_{2g}\leftarrow{}^2B_{1g}$ and $^2E_g\leftarrow{}^2B_{1g}$ of square planar structure. Broad band centered at 485 nm is a characteristic of square planar geometry

The electronic reflectance spectra of the Cu(II)-Schiff base complexes show a group of identical asymmetric broad bands with λ_{max} at 720-725 nm. The general shape and position of such bands are closely similar.[64]

Table 2.7. Electronic spectral bands (nm) of the compound A and complexes

Compound	Mode	d-d	CT	n→π*	π→π*
A	DRS	-		286	266 ,373
$[Cu_3L_2]Cl_2$	DRS	700	367	270	241
	H_2O	650	373	298	239
Ni_2L_2	DRS	682, 552	383		240
	DMSO	730, 537	382		241
MnHLOAc	DRS	542, 431, 359,345	363	267	235

Therefore, it could be safely concluded that Cu(II)-schiff base complexes might be present in the same geometrical coordination. Accordingly, the absorption band may be assigned to the transition $^2B_{1g}\leftarrow{}^2E_g$ within the energy level diagram of Cu(II) by considering a highly distorted arrangement (tetragonal elongation-square planar) due to the strong splitting of Jahn-Teller unstable octahedral ground state term ^2E_g. Moreover, it was suggested that such a highly split ^2E_g ground state and consequently an overlapping with the splitting term $^2T_{2g}$ are characteristic of square planar coordination, i.e., D_h symmetry.[65]

Mn(II) has a ^6S electronic ground state. Under octahedral symmetry the ground term of the high spin complexes is $^6A_{1g}$. There are no excited levels of the same multiplicity and the observed absorption bands are spin forbidden transitions to the upper quartet and doublet levels. The bands at 542, 431, 359 and 345 nm are attributed to d-d transition of manganese, which are consistent with octahedral manganese complexes.

In tetrahedral symmetry the d^8 configuration gives to a $^3T_1(F)$ ground state. The transition from this to $^3T_1(P)$ state occur in the visible region. Solid state reflectance showed a strong peak around 524nm. This can be attributed to the transition $^3T_1(F) \rightarrow {}^3T_1(P)$.

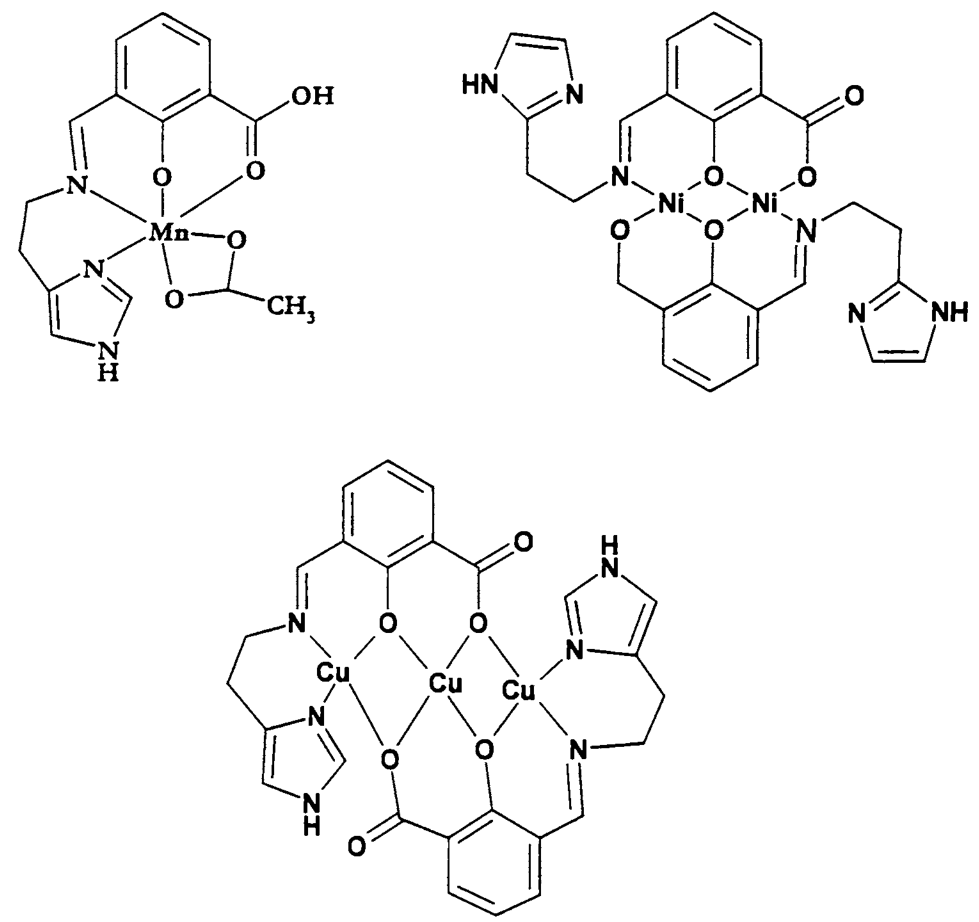


Figure 2.8. Tentative structures of Mn(II), Ni(II) and Cu(II) complexes

SYNTHESIS AND SPECTRAL CHARACTERIZATION OF Zn(II), Cd(II) AND Co(II) COMPLEXES OF SCHIFF BASE DERIVED FROM 3-FORMYLSALICYLIC ACID AND 1,3-DIAMINOPROPANE.

3.1. INTRODUCTION

The concept of binucleating ligands has been developed three decades ago.[66-68] Various ligands of this type have been synthesized with the aim to stabilize dinuclear metal complexes. The class of binucleating ligands comprises compounds providing bridging atoms such as alkoxo or phenoxo oxygen that held the metal ions in close proximity and compounds having isolated donor sets.[69] Bimetallic cores are versatile at active sites of many metalloenzymes and play essential role in biological systems by interplay of a pair of metal ions. Synthetic simple dinuclear metal complexes are important to understand the mutual influence of two metal centers on the electronic, magnetic and electrochemical properties of such bimetallic cores. Compartmental macrocyclic ligands, having two phenolic oxygens have been developed for this purpose, because they bind two metal centres in close proximity relevant to the active sites of bimetallic enzymes.[70] Here we have prepared binuclear zinc, cadmium and cobalt complexes of N_2O_4 donor derived from 3-formylsalicylic acid and 1,3-diaminopropane. In these complexes the phenolic oxygen and the imino nitrogen coordinate to metal ion and phenolic oxygen act as bridging group.

Geometrical requirement of the ligands results in the formation of a cis-conformation complex with respect to imino nitrogens and carboxylate oxygens.

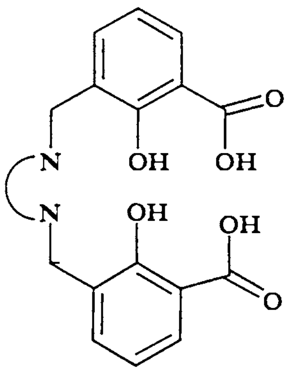


Figure 3.1.

Therefore, the inside coordination site has N_2O_2-coordinating atoms while the outside coordination site has O_4- coordinating atoms (Figure 3.1).

3.2. Experimental

3.2.1. Materials

3- Formylsalicylic acid was prepared according to the reported method of Duff and Bills.[55] Ligand was prepared via reaction of 3-formylsalicylic acid with 1,3 diaminopropane. All reagents used are of analar grade. Solvents are used after purifying by standard methods. 1,3 Diaminopropane was purchased from Sigma-Aldrich and used without further purification.

3.2.2. Zinc(II) and Cadmium(II) Complexes (Compound 4 and 5)

The zinc and cadmium complex were obtained as yellow powder by the reaction of 3-formylsalicylic acid (1.92 mmol) with 1,3-diaminopropane (0.96 mmol) and corresponding metal chlorides (0.96 mmol) in methanol-water (5:1, 30 ml) at room temperature overnight. The precipitate was filtered, washed with water, alcohol and ether. and dried *in vacuo*.

3.2.3. Cobalt(II) complex

To an aqueous solution of 3-formylsalicylic acid (2 mmol) and 0.102 g sodium carbonate, 1,3-diaminopropane (1 mmol) was added, stirred at room temperature for 20 minutes. To this 1 mmol of cobalt acetate in 20 ml water was added and stirred for 2 hrs. Dark green precipitate obtained was filtered, washed with water, alcohol and ether and dried *in vacuo*.

3.3. Results and discussion

Metal complexes of Schiff bases are generally prepared by the single step condensation of an aldehyde with an amine in presence of metal ion.[71]

The partial elemental analyses, colours and magnetic moments are given in Table 3.1. Compounds 4 and 6 contain uncoordinated water in lattice, whereas 5 contains two molecules of uncoordinated ethanol. These complexes are soluble in DMF and conductivity measurements were done which indicate that all are nonconductors. Magnetic moment indicates the diamagnetic nature of zinc(II) and cadmium(II) complexes. However, the cobalt complex showed a room temperature magnetic moment per atom in the range 4 - 4.5 B.M. (4.08 B.M.) indicating coordination geometry of cobalt(II) complexes to be distorted tetrahedral. This value agrees well with reported values of several tetrahedral Schiff bases of Co(II) complexes.[72-75]

Table 3.1. Colour, partial elemental analyses and magnetic moments of the complexes

Compound	Color	Elemental analysis Found (Calculated)			Magnetic moments (BM)
		Carbon%	Hydrogen%	Nitrogen%	
$Zn_2L_2^2$ (4)	Yellow	44.3 (44.1)	3.13 (3.11)	5.44 (5.02)	Diamagnetic
$Cd_2L_2^2$ (5)	Yellow	40.78 (40.43)	3.29 (3.84)	4.02 (4.10)	Diamagnetic
$Co_2L_2^2$ (6)	Green	45.03 (44.64)	3.99 (3.35)	4.9 (5.48)	4.08

3.3.1. IR spectroscopy

The infrared spectral data of ligand and its metal(II) complexes are given in Table 3.2. The ligand shows a band around 1683 cm^{-1}due to the presence of azomethine group as reported earlier. Upon coordination the ν_{CN} frequency undergoes a negative shift of about 50-70 cm^{-1}, showing a decrease in the C=N bond order due to the coordinate bond of the metal with the azomethine lone pair.[76-79] The broad and strong band found around 1550 cm^{-1}, is attributed to the coordinated carboxylate group. The characteristic ring breathing bands of benzene is found in the region 990-600 cm^{-1}.

The weak O-H stretching frequency near 2572 cm^{-1} is absent in the spectra of coordinated ligand, as expected. In the ligand the free O-H stretching frequency was expected around 3300–3800 cm^{-1} region. However, there is a shift due to the hydrogen bonding and these bands are very board.[80] The ligands are planar with adequate distance for hydrogen bonding. The strong and medium band near 1290 cm^{-1} are assigned to the C-O stretching frequency, which is within the 1280–1340 cm^{-1} range.[81]

Table 3.2. The infrared spectral data (cm^{-1}) of ligand and its metal(II) complexes

Compounds	ν_{OH}	ν_{CN}	$\nu_{C\text{-}O}$	$\nu_{carboxylate}$	ν_{OH}	ν_{MO}
H_2L^2	2572	1683	1290	1658	3452	-
$Zn_2L_2^2$ (4)	-	1630	1290	1546	3447	586
$Cd_2L_2^2$ (5)	-	1616	1290	1559	3429	-
$Co_2L_2^2$ (6)	-	1640	1990	1555	3445	550

3.3.2. NMR spectra

The 1D and 2D NMR spectra have been used in the determination of the geometry of zinc(II) and cadmium(II) complex with hexadentate ligand containing N and O atoms. NMR spectra were recorded on a Brucker DRX 500 instrument using DMSO-d_6 and TMS as reference. There are three types of easily accessible information available in NMR spectroscopy

1. *Chemical shift* which provides information about the average effective magnetic field present at various locations within a molecule,
2. *Spin –spin coupling* (coupling constants and multiplicities) which derives from bond interaction between spin active nuclei and
3. Signal intensity measured as the integral of the signal, which derives the number of equivalent nuclei present.

Two dimensional correlation spectroscopy assist in determining the connectivity of a molecule, showing proton-proton (HOMOCOSY) as well as carbon-proton coupling (HMQC). Tentative assignments of the ^1H and ^{13}C NMR spectra of the ligand and complexes are given in the Table 3.3.

^{13}C NMR Data

It reveals three well resolved signals for phenyl moiety with typical values of coupling constant, two doublet and a triplet.[82] In the spectrum of ligand two singlets at δ 12.8 ppm and 10.35 ppm can be attributed to the exchangeable OH and COOH protons whose intensity decreases on addition of D_2O. The absence of these peaks in the spectra of complexes 4 and 5 indicates the coordination of metal through phenolate and carboxylate ion. The proton attached to the azomethine carbon H7 shows a singlet at δ 8.8 ppm, which shifts to lower frequency in complex. This is a clear evidence of coordination of nitrogen to metal, which reduces the electronegativity. The aliphatic protons H9 and H10 show only unresolved singlet peaks. However, COSY shows a

Table 3.3 Tentative assignments of the ^1H and ^{13}C NMR spectra of ligand and complexes

Compound	Assignments of peak along with coupling constants					
	H3	H4	H5	H7	H9	H10
H_2L	8.08 (d, J 7.4 Hz)	6.68 (t, J 7.8 Hz)	7.64 (d d, J 7.8 & 1.7 Hz)	8.80, (s)	3.82(s)	3.82 (s)
Zn_2L_2 4	7.98 (d, J 7.5 Hz)	6.07 (t, J 7.5 Hz)	7.57, (d, J 7.4 Hz)	8.39 (s)	3.90 (s)	1.99 (s)
Cd_2L_2 5	7.93 (d, J 7.5Hz)	6.70 (t,J 7.5 Hz)	7.52 (d,J 6.8 Hz)	8.31 (s)	3.88 (s)	1.97 (s)

Compound	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
Zn_2L_2.4	139.51	118.47	135.39	115.42	138.56	120.85	169.79	171.38	62.05	29.70
Cd_2L_2.5	139.65	123.74	131.45	115.27	137.79	121.61	169.401	171.124	64.59	33.17

correlation between these adjacent H atoms. The structure and ^{1}H NMR spectrum of complex 4 is given in Figure3.2.

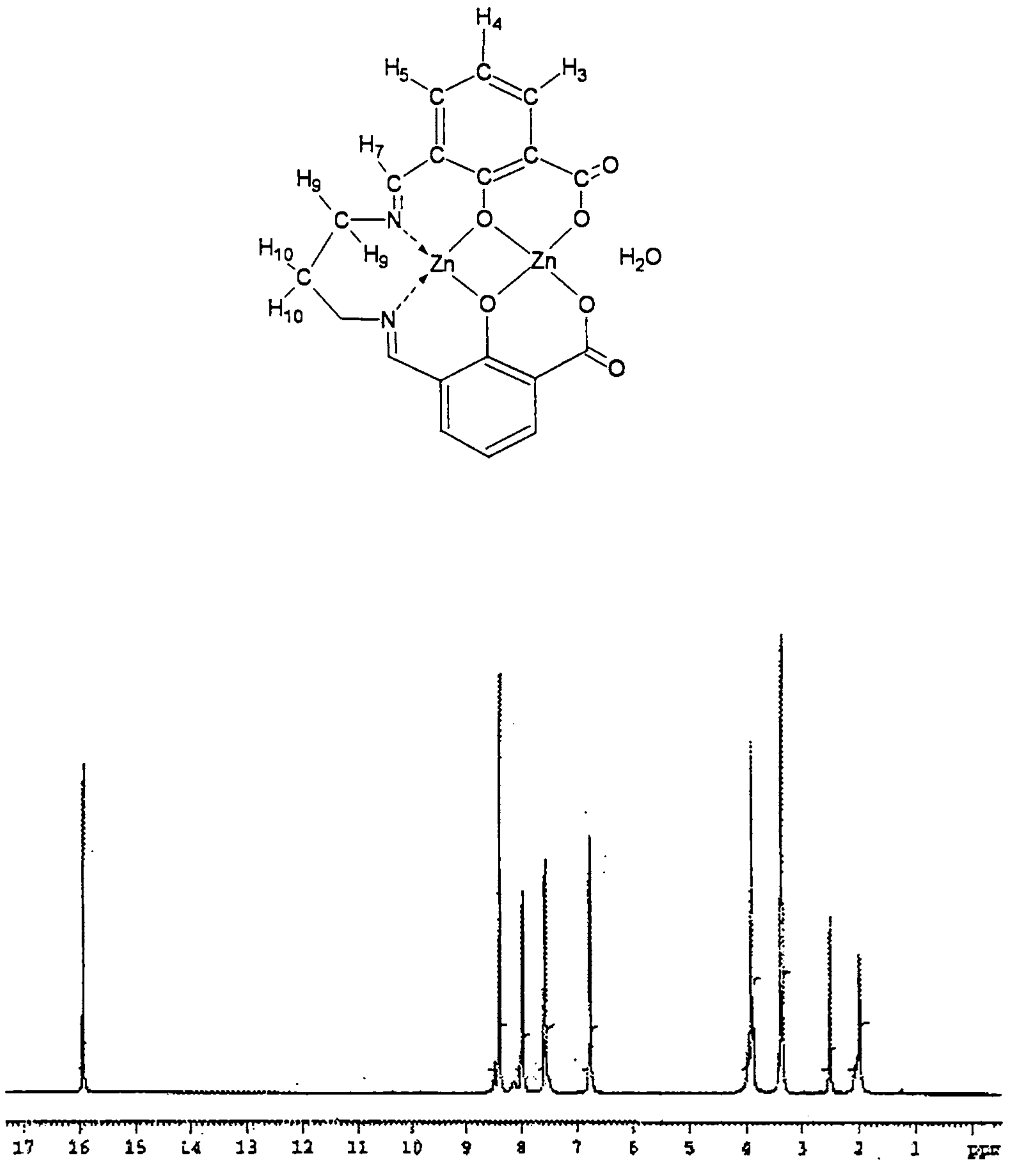


Figure3.2.Structure and ^{1}H NMR spectrum of complex 4

In the 2D experiment, there are two coordinate axes. The signal is represented as a function of chemical shift. The data is plotted as a grid; one axis represents one chemical shift range, second represents second chemical shift range and third dimension constitutes the intensity of observed signal. The result is a form of contour peaks where contour lines correspond to the signal intensity. Off diagonal peaks denote splitting between protons on adjacent carbons.[82-83]

Figure 3.3 is the COSY spectrum of the zinc(II) complex. The COSYspectrum shows distinct spots on a diagonal, extending from the upper right corner of the spectrum to the lower left corner. By extending horizontal and vertical lines it will meet at the same spot on the diagonal. In the proton spectrum we have already identified the peak at δ 6.75 ppm as phenyl proton H_4. If we extend the horizontal and vertical line from the spot at 6.75 ppm, it will eventually encounter off diagonal spots at δ 7.9 and 7.6 ppm corresponding to H_5 and H_3 protons respectively. The presence of these two off diagonal spot shows the correlation between H_4 with H_3 and H_5. At the same time, spectral data indicate no correlation between H_4 and H_5. Similarly, two H_9 proton couples with neighboring two H_{10}, which are chemically and magnetically equivalent. Here the coupling is of vicinal type, *ie;* three bond coupling and coupling constant is ^3J.

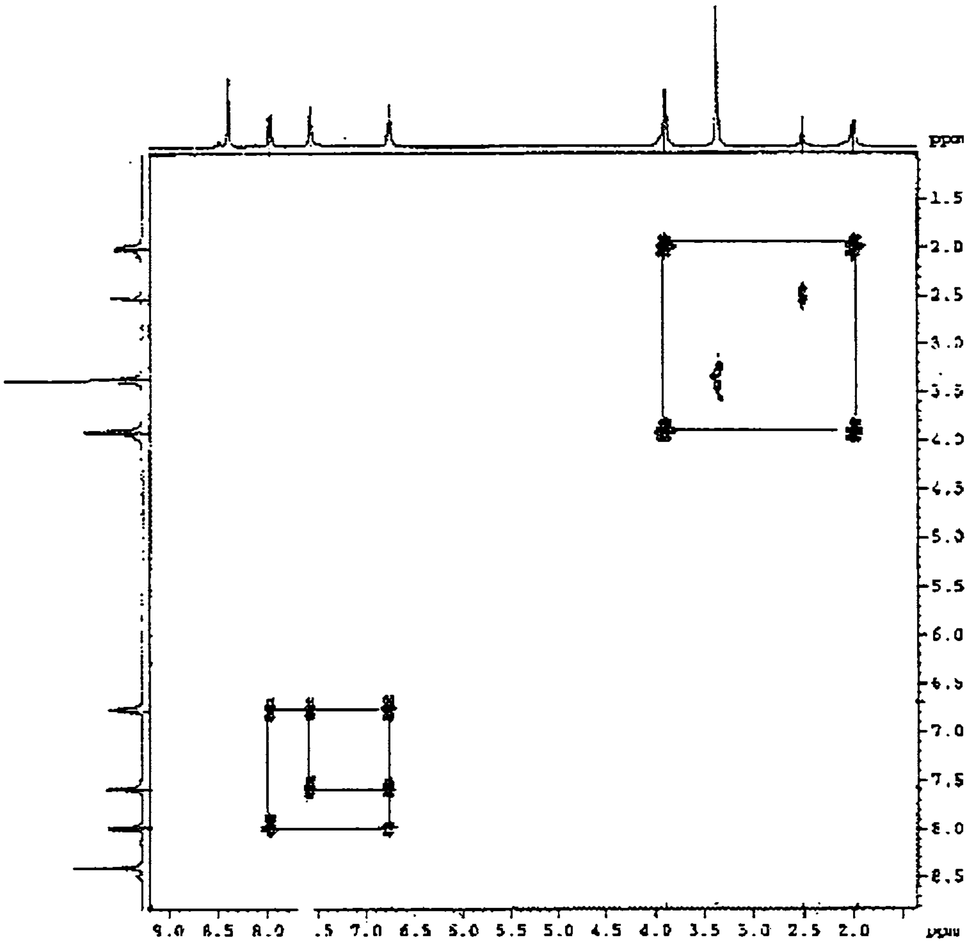
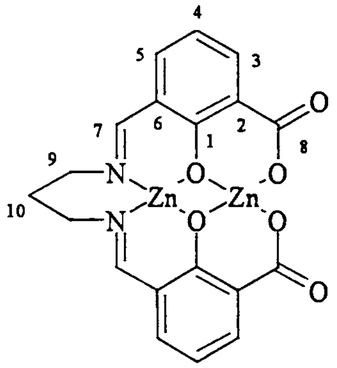


Figure3.3 ^{1}H-^{1}H correlation spectroscopy of compound 4

The carbon-13 spectrum was assigned on the basis of proton-decoupled ^{13}C spectrum and HMQC (Figures 3.4 and 3.5). The decoupled ^{13}C spectrum of the complex contain 10 peaks corresponding to ten magnetically unique atoms; Of course, the signal from ^{13}C is much weaker than that of the corresponding ^{1}H NMR because only 1.1% of all the carbon present in a molecule is ^{13}C. The balance is ^{12}C, which don't give an NMR signal. The carbon atom in close proximity to the electronegative atom appears extreme downfield. So the peaks at 171.38, 169.79 and 139.51 ppm were attributed to C8-O, C7=N and C1-O carbons. Aromatic carbons appear at C2 118.47, C3 135.39, C4 115.42,

C5 138.5 and C6 120.85 ppm. The two methylene carbon C9 and C10 give signals at 62.05 and 29.70 ppm respectively.

These assignments are confirmed by interpreting HMQC that gives correlation between carbon and proton. In Figure 3.5 the ^{1}H spectrum is plotted along X axis and carbon along Y-axis. Each spot of intensity on the two dimensional plot indicates a carbon atom bearing a proton. The spectrum shows that the proton at 7.98 ppm is attached to carbon at 135.39 ppm and belongs to the aromatic C3 moiety. Similarly the doublet at 7.43 ppm and triplet are attached to the carbon at 115.42 and 138.56 ppm respectively. The aromatic C8 carbons have no proton attached to it. H9 and H10 protons are attached to the carbons at 62.05 and 29.71 ppm. The Cadmium(II) complexes also show similar peak and coupling.



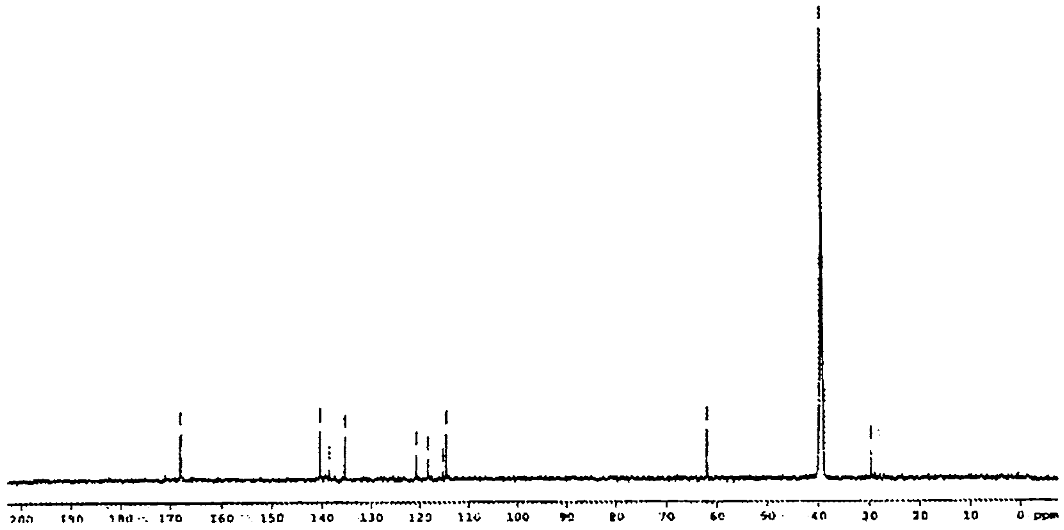


Figure 3.4. $^{13}C-\{^1H\}$-NMR of compound 4

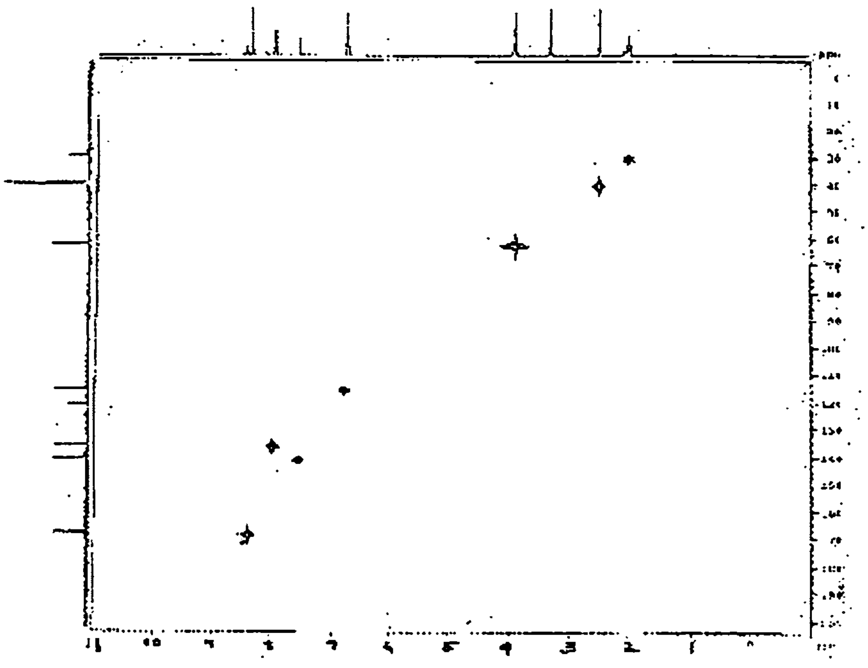


Figure 3.5. HMQC of Compound 4

3.3.3 Thermo gravimetric Analysis

Thermal stability of complexes can be studied by thermo gravimetric analysis. In this technique change in physical and chemical properties of a substance is measured as a function of temperature. The TG was taken up to 1200°C .in an inert atmosphere. It shows a slight decrease in weight due to the presence of ethanol as an impurity in the complex. The first stage of the decomposition starts at 245.24°C, giving a weight loss of 7.97%. The second stage of decomposition starts at 360.09°C. It continues till 782.35°C. The TG curve of the compound $Cd_2L_2^2$ is shown in Figure 3.6.

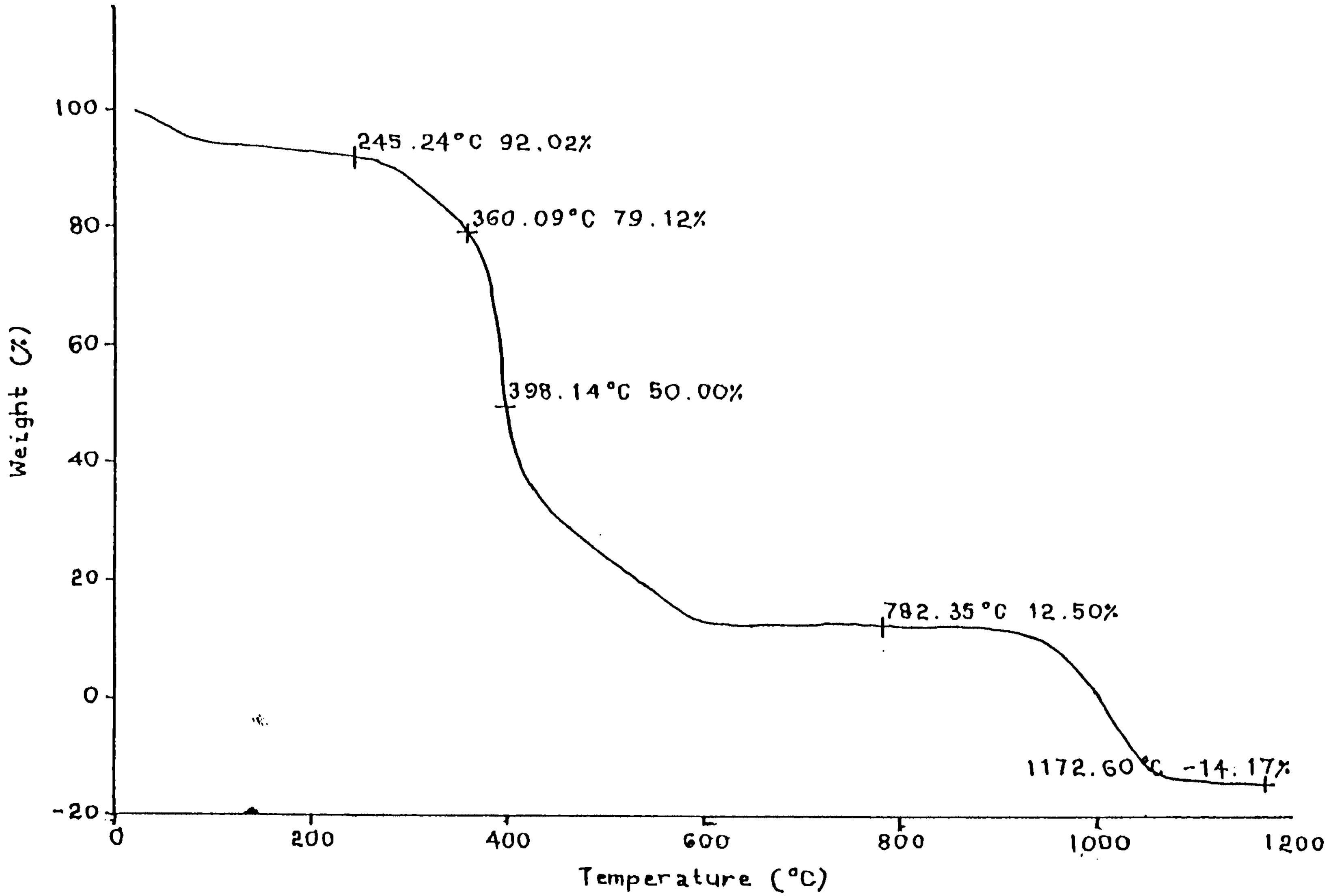


Figure 3.6 T. G. Curve of the compound $Cd2L_2^2$

SYNTHESIS AND SPECTRAL STUDIES OF COPPER(II) COMPLEXES OF 2-HYDROXYACETOPHENONE ^4N-PHENYL SEMICARBAZONE

Copper and its complexes remain outstanding reagents or catalysts in the reaction of organic compounds. The importance of copper(II) species in oxygenation reactions has been reviewed [85]. The question of copper promoted reactions in aromatic chemistry and the role of organometallic complexes in organic reactions has been widely investigated. In general the role of copper is intimately involved and related to the presence of copper(I) and copper(II) oxidation states, although there is little or no information on the stereochemistry of various copper(I) and copper(II) complexes or of their mechanism of involvement. Copper is the third most abundant transition metal element in biological systems, with an occurrence of 80-120 mg in human body. A great deal of scientific work worldwide has been devoted to the search for derivatives of semicarbazides. These materials are often used as drugs whose action is attributed to their ability to form metal complexes. Several ligands and metal complexes have been the subject of chemical and structural studies. They are used mainly as anticancer and antiviral agents since quite a long time.[86-88] We have prepared some copper(II) complexes with Schiff base derived from ^4N-phenyl semicarbazone and 2-hydroxyacetophenone and heterocyclic bases like 1,10-phenanthroline, 2,2'-bipyridyl.

4.1. EXPERIMENTAL

4.1.1. Materials

Copper(II) acetate (Reagent grade Qualigens Fine) was purified by standard methods. The bases such as 1, 10-phenanthroline, 2, 2'-bipyridyl and 4-phenyl semicarbazide (Fluka) were used as received. The solvents were purified by standard methods.

4.1.1.1. Synthesis of ligand

The ligand was prepared in methanol solution from 4-phenylsemicarbazide and 2-hydroxyacetophenone in acid medium. A mixture of 4-phenylsemicarbazide (1.5117 mg, 1 mmol) and 2-hydroxyacetophenone (1.3615mg 1mmol) in methanol was refluxed for 3 hours on water bath. To this few drops of dilute acetic acid was also added to change the pH. On cooling very pale yellow colour crystals were separated out. Yield was 70%. Melting point 188-190.

4.1.1.2. Synthesis of complexes

The mixed ligand complexes have been prepared by mixing of the appropriate heterocyclic base (2 mmol) in MeOH to a hot solution of semicarbazone (2 mmol) in methanol. To this hot solution of copper acetate (2 mmol) in 30 ml methanol was added with constant stirring. The mixture was heated under reflux for 5-8 hrs. The complex precipitated was filtered, washed with water, ethanol and ether respectively and dried *in vacuo.*

The thiocyanate and azido complex were prepared by stirring 0.5 mmol of copper acetate and a hot ethanolic solution of semicarbazone (2 mmol). After 15 minutes solid sodium azide or potassium thiocyanate (0.75 mmol) was added and stirring continued for half an hour. The complex precipitated was filtered washed with water, ethanol and ether and dried *in vacuo.*

4.2. RESULTS AND DISCUSSION

The elemental analyses, colors and magnetic moments are given in Table 4.1. Elemental analyses data of compounds 7 and 8 suggest a formulation of MLB where B is the heterocyclic bases 1,10-phenanthroline and 2,2' bipyridyl. The compounds 9 and 10 have the formula CuHLX with X as thiocyanate or azide.

We have attempted to prepare complexes of formula MLB with various heterocyclic bases like piperidine, pyrrolidine etc. But, contrary to our expectations, we got the dimers. (compound 11). The same product was also obtained when we took the ligand to metal salt ratio as 1:2 (compound 12). Both the compounds 11 & 12 were identical, i.e., of same color and composition, except that latter contains 1.5 molecule of uncoordinated water in lattice. All the complexes have pale green colour. They are all soluble in DMF in which conductivity was measured and all are found to be non conductors.[89] The elemental analyses data are given in the Table.4.1

Table 4.1. Colour, Partial elemental analysis and magnetic moments of the complexes.

Compound	Colour	Elemental analysis found(calcd)(%)			Magnetic moments
		C	H	N	
CuLphen(7)	Green	59.48(59.28)	3.94(4.61)	12.94(12.80)	2.00
CuL bipy(8)	Green	59.46(59.05)	4.59(4.30)	13.87(13.37)	1.97
CuHLNCS.H_2O(9)	Green	45.24(44.58)	3.45 (4.84)	11.84 (12.23)	1.92
CuHLN_3 .H_2O(10)	Green	46.61(45.97)	4.07 (4.12)	21.9 (21.45)	1.95
Cu_2L_2.1.5H_2O (11)	Green	52.24(52.24)	4.20 (4.38)	11.9 (12.9)	2.08
Cu_2L_2(12)	Green	54.61(54.46)	4.21 (3.96)	12.71 (12.70)	2.09

4.2.1.Magnetic moments

The room temperature magnetic moments of the copper(II) complexes in polycrystalline state fall in range 1.9 - 2.2 B.M, which are very close to the spin only value for d^9. There is no magnetic evidence for any copper –copper interaction in the case of compound 11.

4.2.2 IR spectra

The IR spectra of the free ligand show bands at 3227 and 3040 cm-^{1} assignable to the –NH stretching modes in N-NH-CO-NH-C_6H_5 residue.[90] In the 1700-1500 cm^{-1} range the spectrum exhibit bands (1621 and 1644 cm^{-1}) which may be attributed to $\nu_{C=O}$ and $\nu_{C=N}$ modes. The spectrum has a series of bands due to phenyl ring at around 900 to 600 cm^{-1}. The vibrational spectra of the copper complexes showed a pronounced shift of about 50 cm^{-1} (around1593 cm^{-1}) in stretching frequency modes of C=N vibrations. On complexation the azomethine bond weakened and as a result it shifts to lower frequency.[91] A board at 3440 cm^{-1} in ligand due to OH stretching disappears due to deprotonation and $\nu_{C\text{-}O\ \mathrm{shifts}}$ to lower frequency by 40-50 cm^{-1} . A new band is found around 1550 cm^{-1} in complexes 7,8,11 and 12 due to the $\nu_{C=N}$ which is formed during complexation due to enolisation. The disappearance of the ν_{NH} band t 3040 cm^{-1} in the complex spectrum also supports the enolisation, which brings about additional stability, which is thermodynamically favored. In the vibrational spectra of the complexes 9 and 10, the ν_{NH} band is present showing that here the coordination is through amide oxygen. There is slight shift in $\nu_{C=O}$ band from 1644 to 1626 cm$^{-1\cdot}$ These complexes show new bands at 2157 cm^{-1} and 2047 cm^{-1} corresponding to the NCS moiety and azide moiety. The Table 4.2 shows different IR band frequencies.

Table 4.2. I. R. Spectral bands of the copper (II) complexes.

Compound	νC=N	νN=C	νC=O	νC-O	νOH	νNH	Bands due to other groups
H_2L^3	1621		1644	1200	3440	3227,3040	
CuLphen	1593	1542	-	1141	-	3247	phen 1233, 007
CuL bp	1595	1563	-	1150	-		bipy 1439, 1083
CuHLNCS	1573	-	1626	1145	-	3210,3049	ν_{NCS} 2157
CuHLN3	1605	-	1626	1146	-	3200,3049	ν_{N3} 2047
Cu_2L_2	1595	1564	-	1149	-	3242	
Cu_2L_2	1597	1575	-	1156	-	3245	

4.2.3 Electronic Spectra

The semicarbazone has two bands centered about 256 and 330 nm due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. These are seen in both DRS (Figure and in solution spectra. In solution , a slight shift towards longer wavelength is observed. It may be due to solvent interaction or due to slow displacement of ligand by solvents. The complexes show corresponding $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions in the region 312 and 344 nm. The complexes show a strong intense band around 435 nm and may be assigned to ligand to metal charge transfer transitions. The band in 400- 475 nm ranges is assignable to phenoxy O→Cu(II) transitions.[92] The d-d bands of square pyramidal copper(II) complexes fall in the range 500–700 nm. The complexes 9 and 10 show peaks in the region 609 nm indicating that these complexes are square planar.[93] The complexes 7 and 8 show bands around 690 nm, which is characteristic of five coordinated copper complexes having square pyramidal geometry.

4.2.4 EPR spectra

The EPR parameters of Cu(II) complexes obtained for four complexes in DMF at 77 K are presented in the Table 4.4. The compound 1 does not give well-resolved spectra. Others show typical axial spectra with four hyperfine lines, which is characteristic of monomeric copper(II) complexes. The *g* and *A* values are obtained from the simulated spectrum given in Figure 4.1. In all the cases $g_{||}$ is found to be greater than $g_{\perp}$ This predicts a square pyramidal geometry to five coordinated complex rather than a trigonal bipyramidal structure which would be expected to have $g_{\perp}$ greater than $g_{||}$. Thus the compounds (8) comprises of coordination of two bipyridyl nitrogens, azomethine nitrogen, enolate oxygen and phenolate oxygen. The $g_{||}$ values are almost same for all compounds, which indicate more or less axial symmetry for all complexes

EPR parameters $g_{||}$, $g_{\perp}$, g_{av}, $A_{||}$ and $A_{\perp}$ and energies of d-d transition were used to evaluate the bonding parameters α^2 , β^2 and γ^2, which may be regarded as measures of the covalency of in plane σ bond and in plane and out of plane π bond respectively. The β^2 are usually so close to unity. The value of α^2 usually lie in the range 0.75 to 0.990 for most copper complexes. This relatively small range of value explains that sigma bond is quite covalent in nature since the bond is delocalised over both the copper and ligand orbitals. If $\alpha^2 = 1$ the bond would be completely ionic and if the overlap integral is very small and $\alpha^2 = 0.5$ the bond will be completely covalent. Therefore smaller the value of α^2, greater will be the covalent nature of compounds. α^2 is calculated using the formula

$$\alpha^2 = -(A/P) + (g_{\parallel} - 2.0023) + 3/7\,(g_{\perp} - 2.0023) + 0.04$$

The orbital reduction factors, $K_{\parallel}$ and $K_{\perp}$ are calculated using the formula

$$K_{\parallel} = [(g_{\parallel} - 2.0023) / 8\lambda_o\,]\,\Delta E_{dx2\text{-}y2}$$

$$K_{\perp} = [(g_{\perp} - 2.0023) / 2\lambda_o\,]\,\Delta E_{dx2\text{-}y2}$$

Where λ_o is spin orbital coupling constant for the free copper ion.

$$K_{\parallel} = \alpha^2\beta^2$$

$$K_{\perp} == \alpha^2\gamma^2$$

According to Hathaway, $K_{\parallel} = K_{\perp}$ for pure sigma bonding.

$K_{\parallel} < K_{\perp}$ for in plane pie bonding

$K_{\parallel} > K_{\perp}$ stronger in plane pie bonding

Ko, fermi contact hyperfine interaction term is a measure of contribution of s electrons to hyperfine interaction and given by the equation

$Ko = A_{iso} / P\ \beta^2 + (gav - 2.0023) / \beta^2$ and have a value of 0.3

Table 4. 3. Spin Hamiltonian and bonding parameters of copper(II) complexes

compounds	8	9	11
$g_{\|}$	2.2504	2.277	2.2504
$g_{\perp}$	2.0505	2.067	2.0569
g_{av}	2.11	2.137	2.807
$A_{\|}$	175.2	187.94	177.6
$A_{\perp}$	13.81	13.81	13.2
A_{av}	64.73	68.13	64.74
G(77 K)	4.9	4.134	4.4
α^2	.8296	0.86393	0.8048
β^2	0.8880	0.9039	0.9744
γ^2	0.7827	0.87737	0.9142
$K_{\|}$	0.73675	0.7809	0.78423
$K_{\perp}$	0.64948	0.75799	0.7358
F	126.7	121.5	126.7

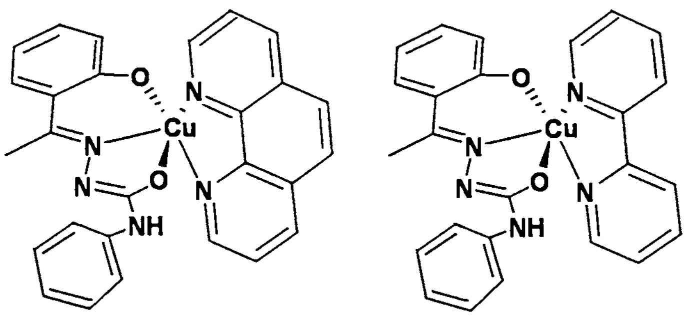


Figure 4.2 Tentative structures of the complexes 8 and 9

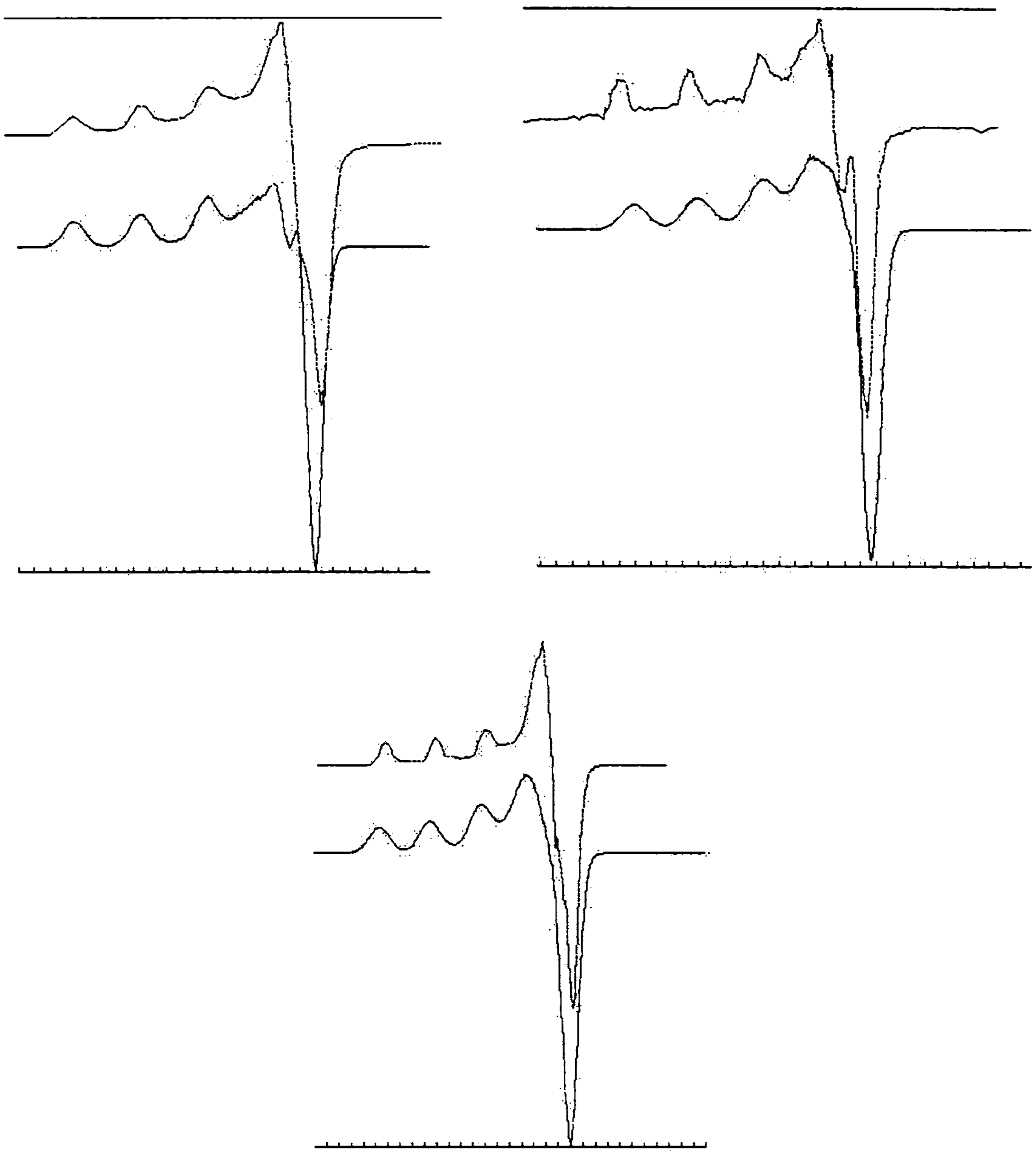


Figure 4.1.Experimental and simulated best fit pairs of the EPR spectrum at 77 K of the copper(II) complexes in DMF.

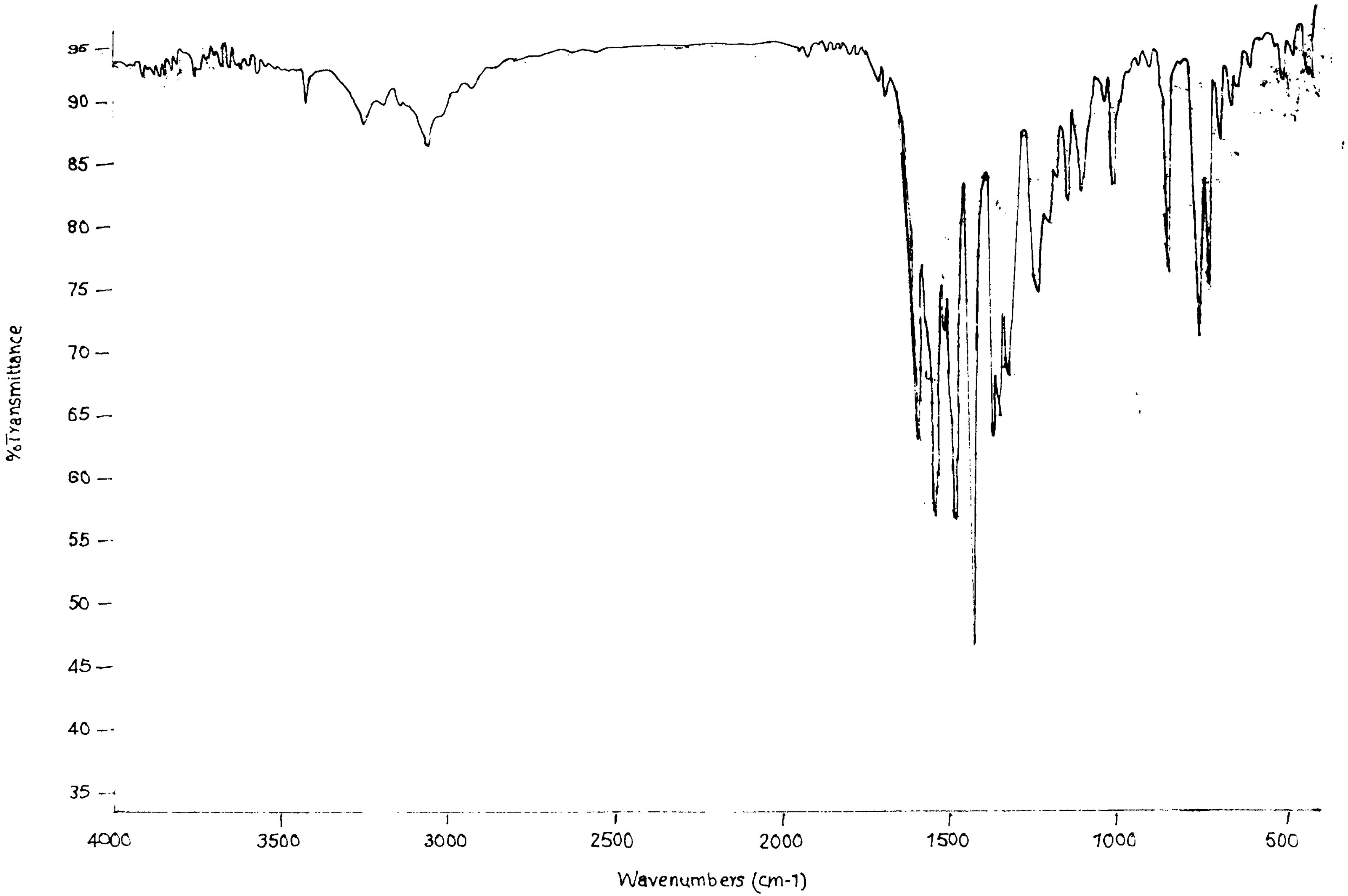


Figure 4.3 IR spectra of compound CuI.Phen. (7)

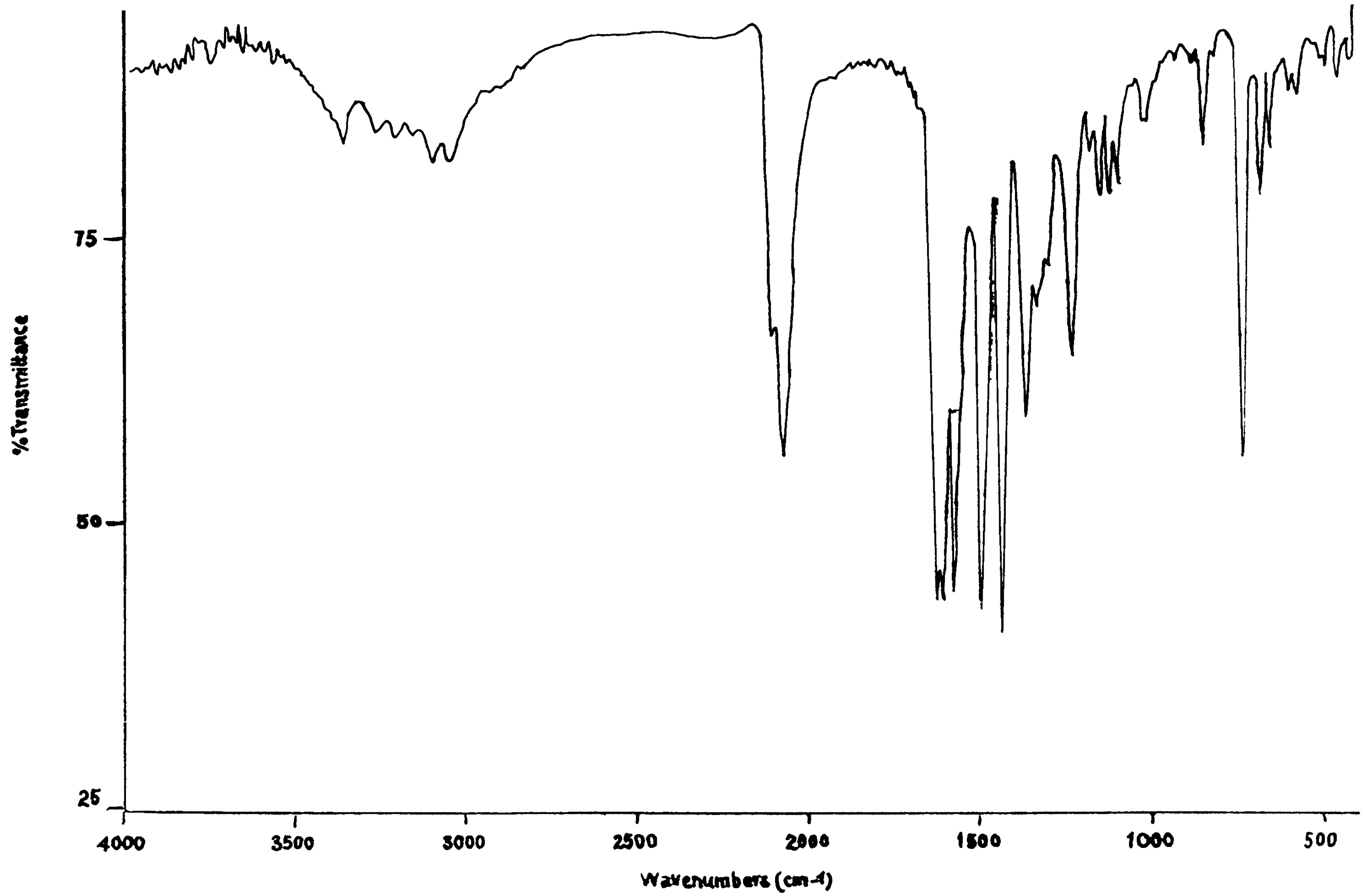


Figure.4.4 IR spectra of compound CuHLNCS (9)

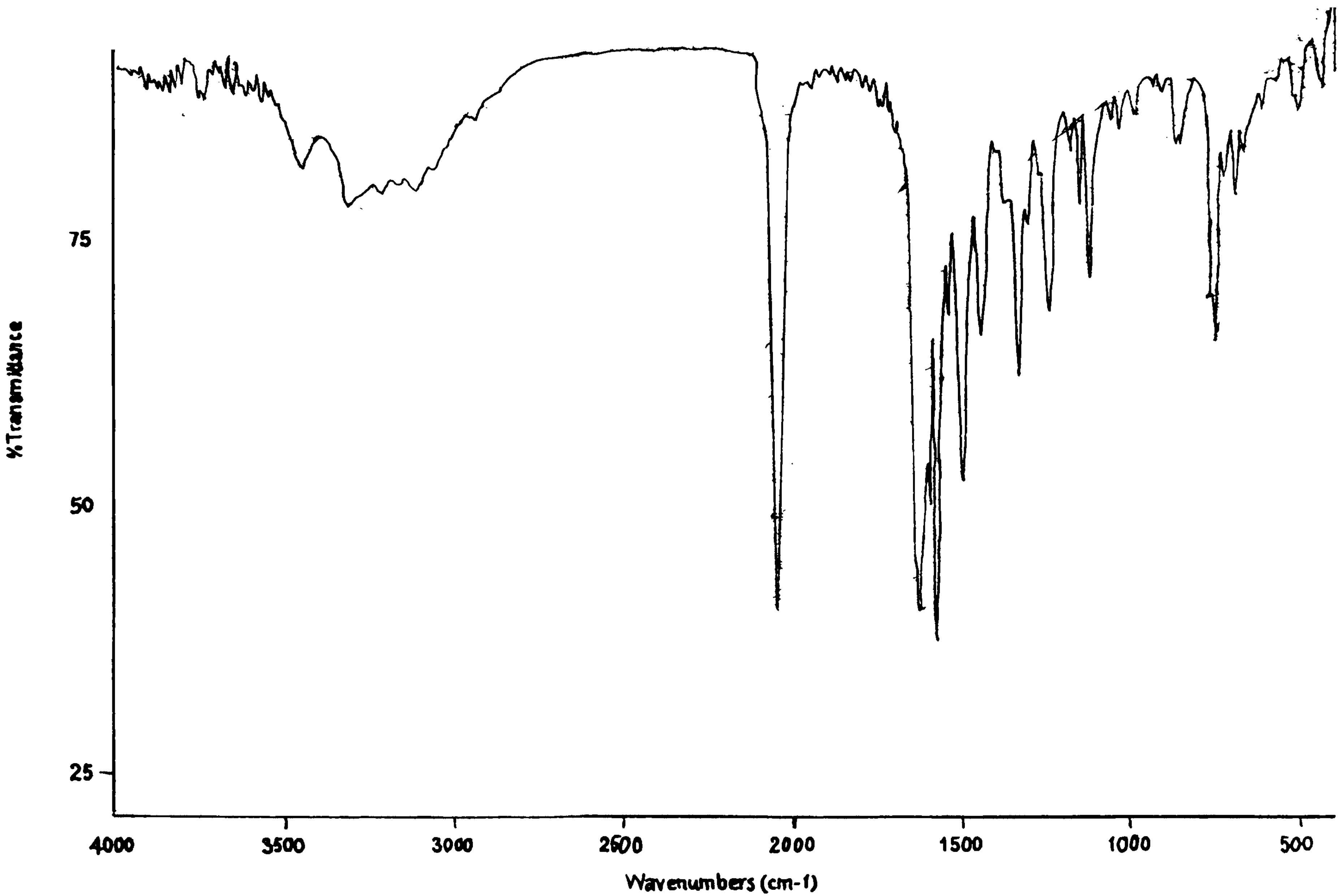


Figure 4.5 IR spectra of compound $CuHLN_3$ (10).

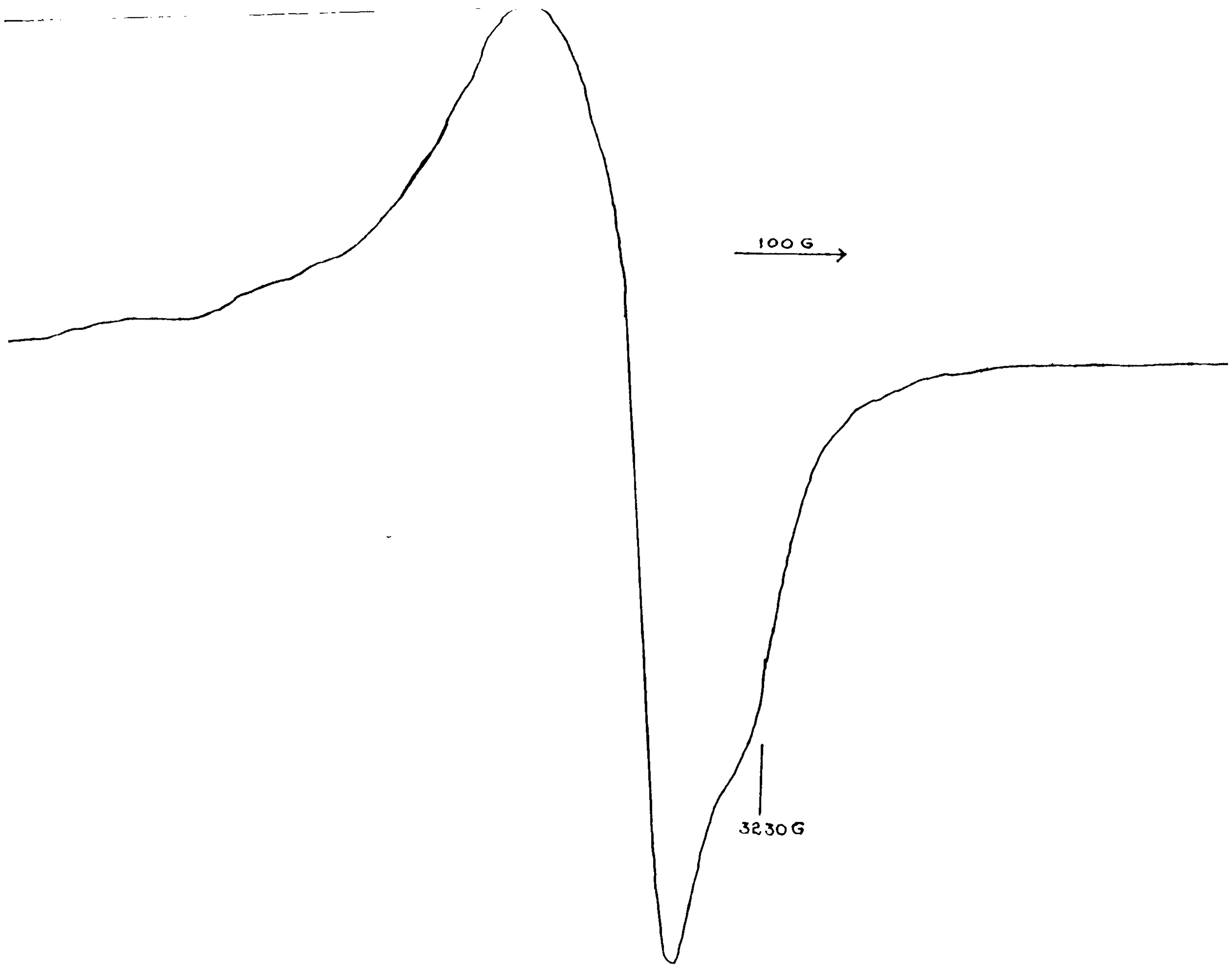


Figure 4.6. EPR spectrum of CuLphen at 298 K

SYNTHESIS AND SPECTRAL CHARACTERIZATION OF Co(III) COMPLEXES OF SALICYLALDEHYDE ^4N- PHENYLTHIOSEMICARBAZONE

5.1 INTRODUCTION

The investigations of metal complexes with sulfur containing Schiff bases is a subject of current and growing interest and many of the complexes has been shown to be anticancer active.[94-95] Thiosemicarbazones (TSCs) have attracted attention as potential drugs in the early years of twentieth century. They were found to be effective against a variety of diseases. There are many reports regarding the biological activity of this class of compounds.

The general method of preparation of this class of compounds involves condensation of a ketone or an aldehyde with the TSC moiety or with that of a ^{4}N substituted one. Depending upon the nature of the ketone or aldehyde the nature of resulting thiosemicarbazone may vary.

Metal complexes of thiosemicarbazone have been extensively studied and have been the subject of several reviews. Cobalt complexes are of great interest because of their antitumour, antimicrobial and electric properties.[96-97]

This chapter describes the preparation and characterization of cobalt(III) complexes of salicylaldehyde ^4N-phenylthiosemicarbazone containing heterocyclic bases.

5.2 EXPERIMENTAL

5.2.1. Materials

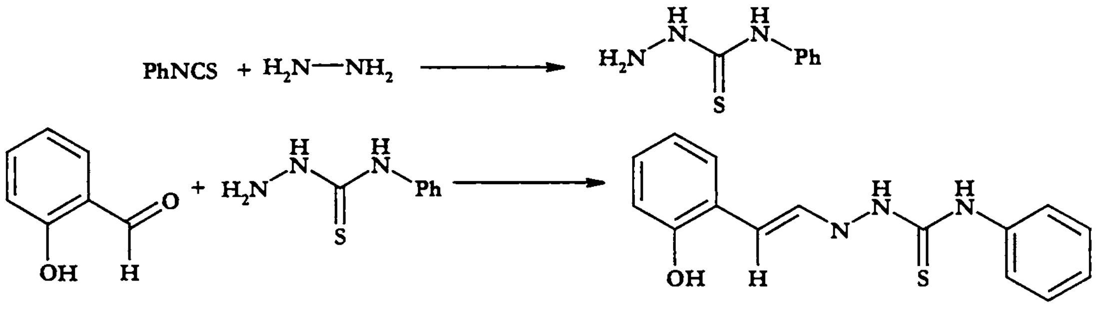
All the chemicals are purchased from Sigma-Aldrich and used as such. The solvents are purified by standard method.Reagent grade sodium azide (Merck), KCNS, heterocyclic bases, viz 1,10-phenanthroline and 2,2'-bipyridyl were used as such. Co(II) acetatetetrahydrate (BDH) was purified by recrystallisation before complexation.

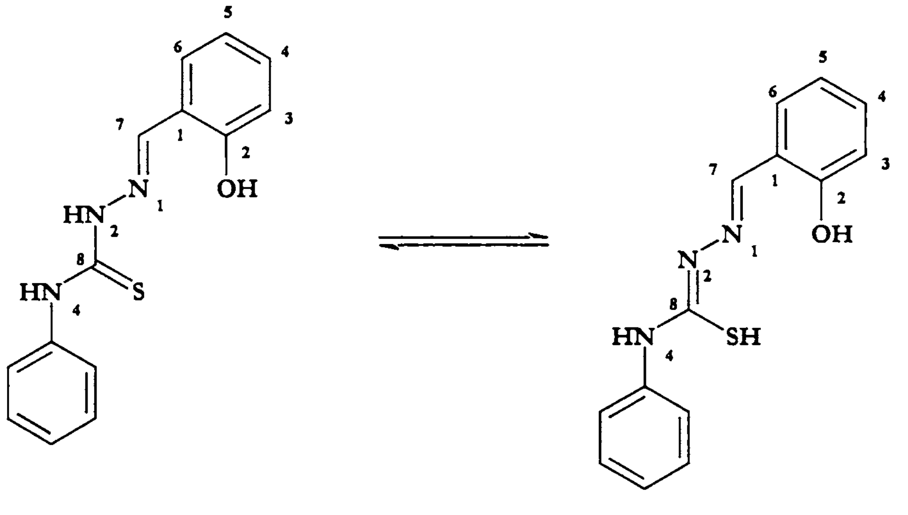
5.2.2. Synthesis of ligands:

Salicylaldehyde ^{4}N-phenyl thiosemicarbazone (H_2L) was prepared as follows: Phenyl isothiocyanate (100 mmol) dissolved in 40 ml of ethanol and hydrazine hydrate (100 mmol) in 20 ml of ethanol was added slowly with constant stirring to the above solution. After the completion of the addition of hydrazine hydrate, the resulting solution was kept in stirred condition for 0.5 hr. A white product formed was collected and washed subsequently with water and little ethanol and dried over P_4O_{10} *in vacuo*. The ^{4}*N*-phenylthiosemicarbazone thus obtained was condensed with salicylaldehyde to get salicylaldehyde ^{4}N-substituted thiosemicarbazone.

^{4}*N*-Phenylthiosemicarbazone (2 mmol) was dissolved in 25 ml of hot ethanol. To this hot solution, salicylaldehyde (2 mmol) in ethanol (20 ml) was added with constant stirring, and the resulting solution was refluxed for 0.5 hr. The pale yellow crystals separated were filtered, washed with 40% ethanol, recrystallised from ethanol and dried over P_4O_{10} in *vacuo*.

The melting point was found to be 178°C.





Keto (thione) form

Enol (thiol) form

Figure 5.1. Tautomers of Salicylaldehyde thiosemicarbazone.

5.2.3. Synthesis of complexes

Heterocyclic base (0.5 mmol) in solid form was added to thiosemicarbazone (0.5 mmol) dissolved in 20 ml of ethanol. The mixture was slightly warmed to ensure complete dissolution of the ligand. To the above mixture 10 ml of methanolic solution of cobalt(II) acetate (0.5 mmol) was added. The solution was warmed for about 15 minutes. When it turned to a deep brown solution, solid sodium azide or potassium thiocyanate (0.75 mmol) was added to obtain compounds 13, 14, 16 and 17 respectively. For 15 and 18, cobalt perchlorate (0.5 mmol) was added instead of cobalt(II) acetate.

5.3. RESULTS AND DISCUSSION

It has been found that the Co(II) ion undergo oxidation in the presence of methanol or chloroform. All complexes are found to be brown in colour.

The elemental analyses data of compounds suggests a formulation of [CoLBX]. However, compound **15** and **16** contains one molecule and half molecule of uncoordinated water respectively. All complexes are found to be diamagnetic. This confirms the +3 oxidation state of cobalt, corresponding to d^6configuration in strong field. Colours and elemental analyses are given in the Table 5.1.

Table. 5.1. Colours, and partial elemental analyses of cobalt(III) complexes

		Elemental analysis Found (Calcd) %		
Compound	Colour	C	H	N
CoLphenNCS (13)	Brown	56.17 (56.84)	3.43 (4.06)	14.40 (14.73)
CoLphenN$_3$ (14)	Brown	56.57 (56.87)	3.72 (4.22)	16.50 (16.57)
CoLphenClO$_4$ (15)	Brown	50.32 (50.45)	3.02 (3.58)	11.84 (11.32)
CoLbipyNCS(16)	Brown	53.38 (53.76)	4.12 (3.7)	14.94 (14.92)
CoLbipyN$_3$ (17)	Brown	54.40 (54.26)	4.01 (4.42)	21.20 (21.26)
CoLbipyClO$_4$ (18)	Brown	46.46 (46.35)	4.05 (3.7)	11.15 (10.19)

5.3.1. IR Spectroscopy

The significant IR bands are compiled and presented in Table 5.2, along with their tentative assignments. This indicates that the ligand acts as binegative anion and useful for determining the mode of coordination.

The absence of any band in 2600-2800 cm^{-1} region of the spectrum of H$_2$L suggests the absence of thiol tautomer in the solid state. On coordination, $\nu_{C=N}$ shifts to lower wave number by 5-10 cm^{-1} *i.e.*, 1597-1595 cm^{-1} from the corresponding peak at 1622 cm^{-1} in the uncoordinated thiosemicarbazone spectrum. Coordination of azomethine nitrogen is confirmed with the presence of a new band at 431-440 cm^{-1}, assignable to Co-N bond.

An increase in the $\nu_{N\text{-}N}$ in the spectra of complexes can be attributed due to the increase in the double bond character compensating the loss of electron density via donation to the metal. This again confirms the coordination of the ligand through azomethine nitrogen atom. There is a decrease in the wave number of thioamide band $\nu_{C=S}$ at 1335 and 792 cm^{-1} by 30-60 cm^{-1} which shows coordination by thiolate sulfur.[98] A new medium band observed at 1500-1490 cm^{-1} is due to the stretching vibration of newly formed N=C bond. This indicates enolisation of the ligand during complexation

The thiocyanato complexes **13** and **17** have very strong bands at 2103 and 2117 cm^{-1}. A strong band in the range 700 cm^{-1} is also attributed to the CS stretching frequencies. These two bands show that the NCS moiety is bonded to complex through S atom.

The azido complexes **14** and **17** show strong band around 2018 cm^{-1}. The perchlorato complexes **16** and **19** show a band at 1025 cm^{-1} corresponding to perchlorate stretching frequencies.

Table 5.2. IR spectral assignments (cm^{-1}) for the salicylaldehyde ^{4}N-phenyl thiosemicarbazone and its cobalt(III) complexes.

	C=N	N=C	C-O	C-S	Heterocyclic base	Co-N
H_2L	1622		1259	1335, 792		
13	1597	1500	1198	1314, 751	1437, 721	440
14	1596	1496	1197	1313, 751	1435, 721	432
15	1595	1500	1199	1313, 751	1435, 721	431
16	1595	1500	1199	1436, 730	1434, 719	439
17	1597	1500	1200	1437, 725	1436, 736	445
18	1595	1500	1210	1435, 719	1440, 727	429

5.3.2. Electronic spectra

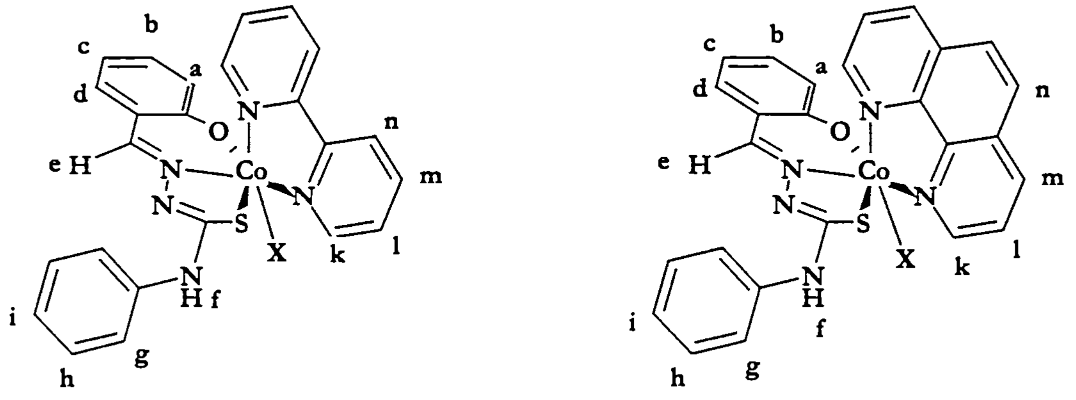
Here the cobalt is having d^6 configuration. Co(II) d^6 complexes generally form low spin complexes giving rise to spin allowed transitions $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$. However, the high energy band due to $^1A_{1g} \rightarrow {}^1T_{2g}$ transition get masked by the charge transfer band around 400 nm. The electronic spectra show broad bands in the visible region about 485-495 nm. The charge-transfer bands are too board as they are the combination of both S → Co and O → Co charge transfer transitions.[99] The significant peaks of ligand and complexes are tentatively assigned and shown in Table.5.3.

Table 5.3. Electronic spectral assignments (nm)

Compound	d-d	LMCT	$n \rightarrow \pi^*$	$\pi \rightarrow \pi^*$
13	604	450	372, 317	248
14	600	453	374, 317	248
15	580	426	390, 371	249
16	599	427	394, 330,	252
17	604	430	394, 320	253
18	600	453	381, 320	249

5.3.3. ^{1}H NMR spectra

The ^{1}H NMR spectra of complexes were taken in DMSO-d_6. The spectra look complicated as all the signals comes in the aromatic region. The signals due to OH and NH groups are absent in the spectra of complexes indicating complexation after double deprotonation.[100] This supports the evidence from IR spectra that the thiosemicarbazone coordinates as dibasic tridentate ligand existing in the thiol form. The protons corresponding to the heterocyclic base show separate signals, which indicate lose of symmetry for the base on coordination due to imposition of rigid geometry around metal ion. This suggests that the complex indicate signals corresponding to the heterocyclic bases and thiosemicarbazone moiety.[101] The chemical shifts of some of the protons near to coordinated sites are shifted downfield, which are evidences for coordination of L^{-2} to cobalt(III). The structure (Figure 5·4) and assignment of ^1H NMR data are shown in the Table. 5 4.



Compound 16

Compound 13

Figure 5·4·

Table 5.4. ^1H assignments of compound 16 and 13

	CoLbipyNCS(16)	CoLphenNCS (13)
H_a	6.45	6.39
H_b	6.88	6.85
H_c	6.45	6.40
H_d	7.39	7.75
H_e	9.45	9.53
H_f	10.40	9.80
H_g	7.31	7.50
H_h	6.90	6.95
H_i	6.91	7.1
H_k	7.6	7.70
H_l	7.9	8.05
H_m	8.05	8.15
H_n	8.60	8.45

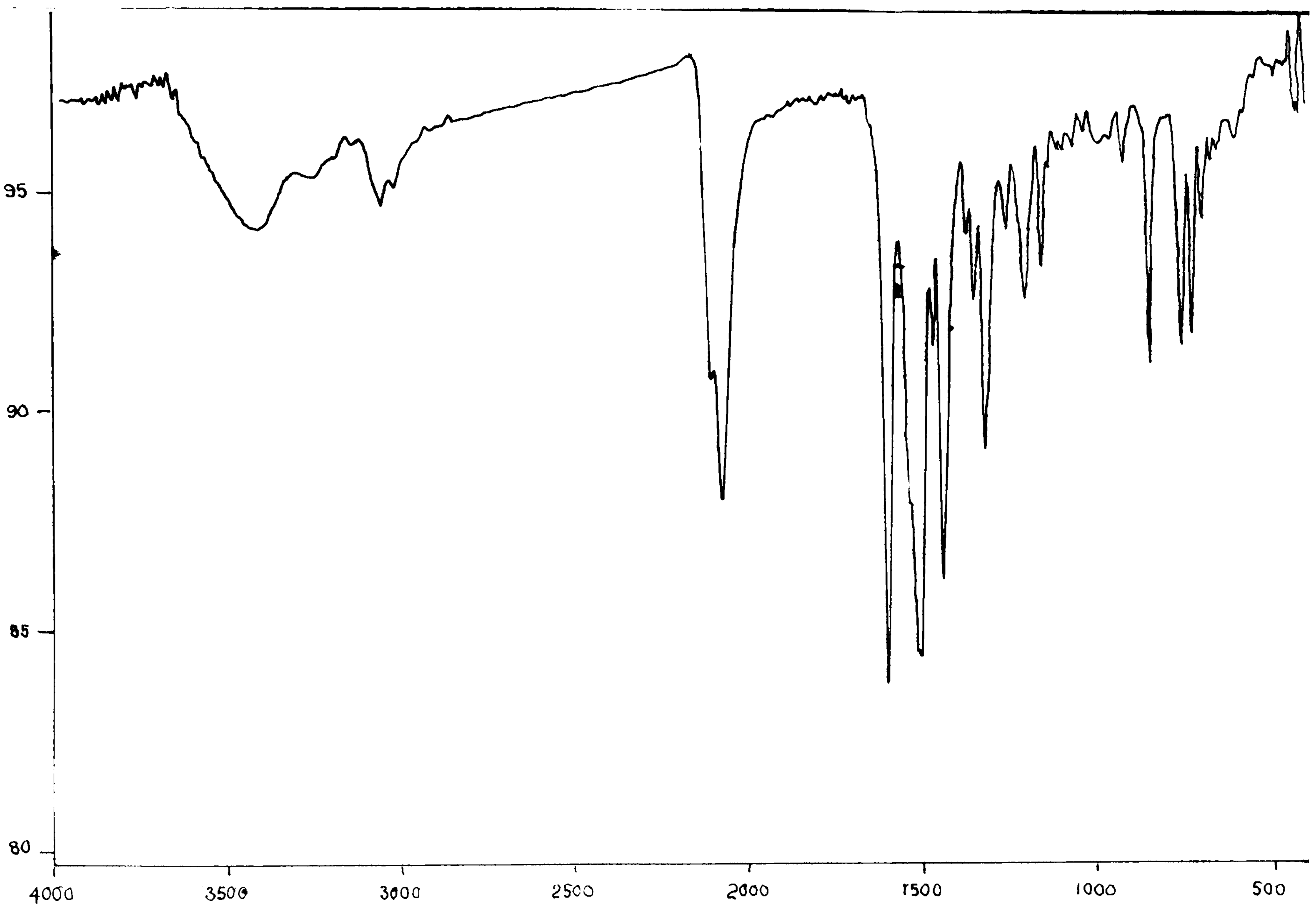


Figure 5.1 IR spectra of compound CoL.PhenNCS .(13).

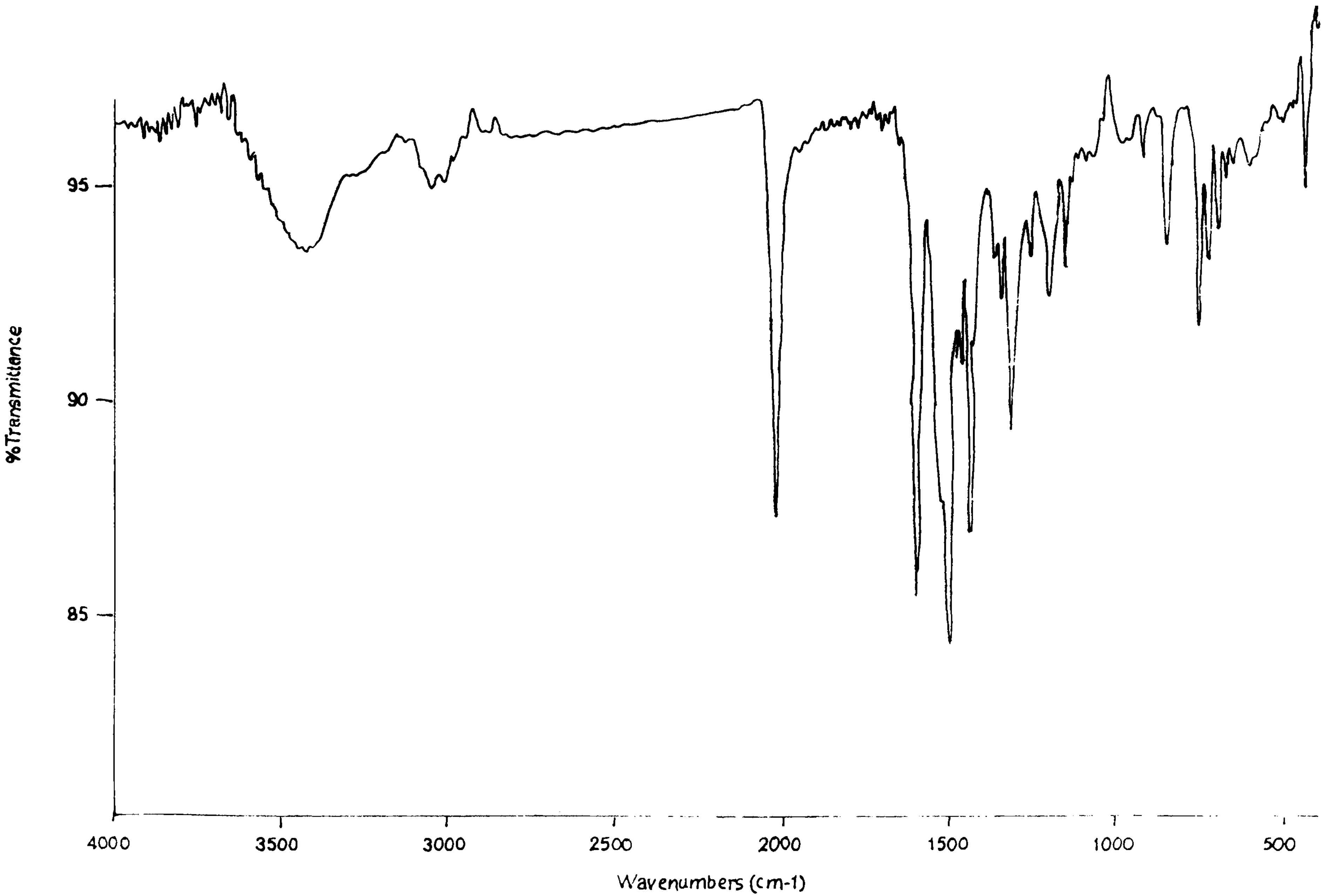


Figure 5.2 IR spectra of compound CoLPhenN$_3$ (14).

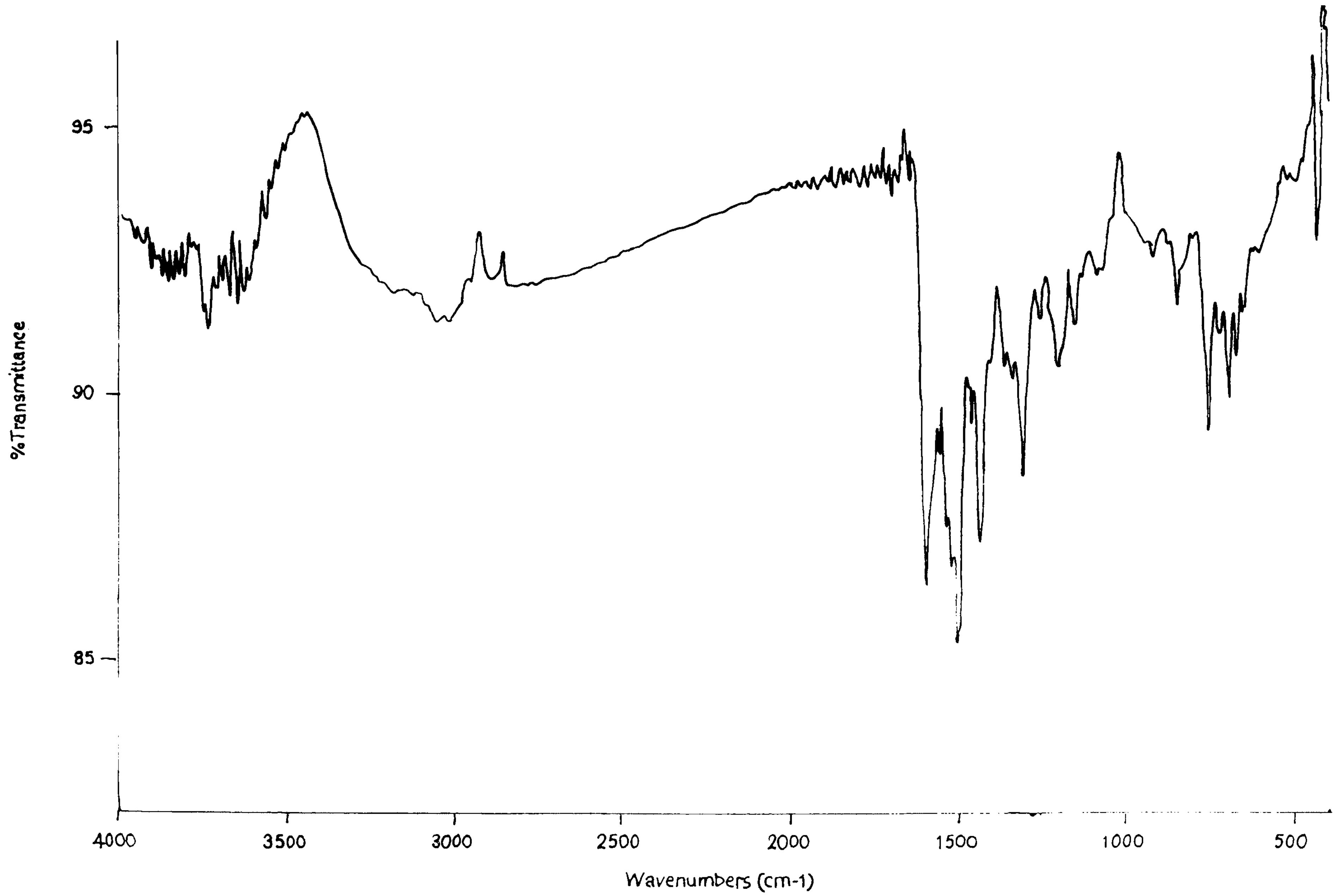


Figure5.3 IR spectra of compound CoLPhenClO_4 (15).

SUMMARY AND CONCLUSION

The thesis deals with the synthesis and spectral characterization of transition metal complexes derived from four different Schiff bases .The entire thesis is divided into five chapters.

Chapter one deals with general introduction about the coordination chemistry, Schiffbases, physical methods and objective and scope of the present work.

Chapter two deals with synthesis and structural characterization of pyridial imidazolyl derivative obtained during the condensation of 3-formylsalicylic acid and histamine base. Copper(II), manganese(II) and nickel(II) complexes of this Schiff were prepared. The structure of the compound was obtained from X-ray diffraction studies. Complexes were characterized by IR,UV-Visible, DRS and EPR studies. The copper(II) complex is a trinuclear square planar complex whereas other two, manganese and nickel complexes are mono and dinuclear respectively with octahedral and tetrahedral geometry. Magnetic moment measurements were done for all the three complexes. EPR spectra were recorded at 77K and at 298K. EPR simulations were carried out to obtain accurate magnetic parameters.

Chapter three deals with synthesis of zinc(II) ,cadmium(II) and cobalt(II) complexes derived from 3-formyl salicylic acid and 1,3-diaminopropane. The Prepared complexes were analysed by UV-Visible, IR and NMR spectroscopy.The geometry of the zinc and cadmium complexes were assigned with help of 1D and 2D NMR techniques. Thus predicting a square planar geometry to the zinc and cadmium complexes and a terahedral structure to cobalt complexes.

Chapter four deals with synthesis of copper(II) complexes of 2-hydroxyacetophenone ^4N-phenylsemicarbazone. We have prepared about six copper complexes. Two were dimers . I.R and EPR studies were done. Based on the EPR simulation programme all parameters have been calculated .The *g* values, calculated for four complex show that the unpaired electron is in the $d_{x^2-y^2}$ orbital. The magnetical and spectroscopic studies suggest a square planar structure for four coordinate system and square pyramidal geometry for five coordinate system.

Chapter five gives details about the synthesis and characterization of Co(III) complexes of Salicylaldehyde ^4N-phenylthiosemicarbazone, heterocyclic bases like 1,10-Phenanthroline or 2,2'bypyridial and thiocyanite or azide or chloride as ions. Octahedral structure is assigned to all the complexes. NMR spectra was also taken.

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Publications

1. 2-Hydroxy-3-(4,5,6,7-tetrahydro-1H-imidazo[4,5-c]pyridin-5-ium-4-yl) benzoate monohydrate, A. Usman, , C. R. Nayar, P.A. Unnikrishnan, P. B. Sreeja, M. R. P. Kurup, H.K.Fun, , *Acta.Cryst, C Cryst. Struc. Commun*, ***58***,o724, **2002**.
2. Synthesis, spectral studies and structure of 2-hydroxyacetophenone nicotinic acid hydrazone, P. B. Sreeja, A. Sreekanth, C. R. Nayar, M. R. P. Kurup, A. Usman, I. A. Razak, S. Chantrapromma and H. K. Fun; *J. Mol. Struct.* in press

Papers presented

1. Synthesis and Characterization of Binuclear Zinc(II) Complexes, Chandini R. Nayar and M.R.P.Kurup, *SIF users' symposium*, May 2, 2002, Sophisticated Instruments Facility, Indian Institute of Science, Bangalore 560012.