Contents

CHAPTER-I

INTRODUCTION

Coordination Chemistry - An Overview

The closing years of nineteenth century and the beginning of last century saw a number of remarkable discoveries in the domain of physics, which had their necessary impact on chemical ideas. When the coordination theory was enunciated, the electron had not been discovered. Electron later became the basis of all theories of chemical bonding. The elucidation of geometry and bonding which were based mainly on preparative procedures received a theoretical foundation from the electronic theory of valency. This was followed by the concept of valence bond theory and electron pair repulsion theory given by *Sidgwick-Powell*, which is still used extensively, though the ideas have undergone a significant change. The controversy over the extent to which *d*-orbital participate in □-bonding has been widely discussed but the *Gillespie-Nyholm* -concept of d-orbital participation in hybridization is still useful for interpreting the geometry of simple inorganic compounds. The molecular orbital theory for explaining the bonding involved appears to have a better future with the availability of modern computational operations.

Syntheses of coordination compounds provide a challenge to inorganic chemists. This formed the basis of Werner's original work and that of his predecessors including S.M.J□rgensen. In fact the renaissance of inorganic chemistry in the post Second World War period is closely associated with the renewed interest in coordination chemistry. A survey of literature in inorganic chemistry reveals that at least 70% of the published

articles deal with coordination compounds. They provide stimulating problems to be resolved particularly in the context of their stereochemistries.

The burgeoning area of bioinorganic chemistry is centered on the presence of coordination compounds in living systems such as haemoglobins, cytochromes, vitamin B_{12} etc. Certain metal complexes including those formed by prophyrin act as oxygen carriers and are utilized in the biological transport and storage of molecular oxygen.

Coordination compounds are known to play a vital role in the field of medicine since the discovery of *cis*-platin and carboplatin as anticancer agents. A variety of related platinum (II) and platinum (IV) complexes containing primary and secondary amines were also found to be clinically active. The N-H bonds in these complexes appear to play a crucial role in their mechanism of action. Other complexes of Pt (II) with biologically active N-donor heterocyclic ligands have shown cytotoxicity. The precise action of the drug is not known but it is probable that platinum binds to DNA with guanosine as a base replacing the chloride ions. There are large numbers of transition and non-transition metal ions associated with DNA while the four elements, Na, K, Mg and Ca are always involved; the concentrations of the first two elements ensure electrolyte balance in the cell and serve as major counter ions of DNA.

Another class of compounds is Schiff bases which have been the subject of significant interest in the last three decades in view of their pharmacological importance. They possess remarkable antitumor, antiviral, and antimalarial activities, which are reported to be enhanced on chelating.

The discovery of such compounds and other chelating agents capable of eliminating excessive intake of metal ions from the human body has made important contributions in chelate therapy.

The physicist designs the sophisticated instruments but it is the chemist who derives advantage by making use of them as analytical tools especially for structural elucidations. X-ray crystallography, multinuclear NMR, ESR, Raman Spectroscopy, and SQUID (Superconducting Quantum Interference Device) are some of the dominant structural techniques used by coordination chemists. The cluster chemistry could not have been developed without such instrumental techniques

Though compounds containing metal-metal bonds are known for a long time, the chemistry of metal cluster compounds has grown in the last 30 years at a phenomenal rate. They offer a wide range of polynuclear carbonyls, nitrosyls, lower halides, oxides and related compounds. Interest in this area arises from the fact that important iron storage proteins like ferritin and hemosiderin comprise large iron oxide clusters, which are assembled step by step with a specific mechanism and requires full understanding. The progress in this area is very rapid and during the last few years several promising synthetic techniques have been developed.

An area termed supramolecular coordination chemistry has emerged recently and is shaping well and progressing with great vigor. Supramolecular chemistry has been defined by Lehn as “the chemistry of molecular assemblies and intermolecular bond’, or “Chemistry beyond the molecule”, bearing organized entries of higher complexity that result from the association of two or more chemical species held together by

intermolecular forces". Thus, supramolecular chemistry may be considered to represent a generalized coordination chemistry extending beyond the coordination of transition metal ions by organic and inorganic ligands to the binding of all kinds of substrates [1].

The coordination chemists are interested mainly in stereo chemical, thermodynamic, kinetic, spectral and magnetic properties of coordination compounds. Recently, there has been a growing interest in the role of metal ions and their complexes play in biological systems. Despite these developments, the coordination compounds still provide many stimulating problems to be resolved.

The nature of coordination compound depends on the metal ion, the donor atom, the structure of the ligand and the metal-ligand interactions [2]. Generally, a metal ion does not form bonds of equal strength with two different donor atoms and a given donor atom does not form bonds of equal strength with different metal ions.

The present work was undertaken to select potentially biologically active ligand, synthesize and investigate the chemistry of their complexes with cobalt (II), nickel (II), copper (II) and zinc (II). The thiosemicarbazone ligand selected for studies mainly contain O, N, S donor atoms and functional groups such as >C=N, -OH, >C=S or –SH and -NH_2 which are carefully designed to produce mono- and multinuclear complexes.

The first row transition metals are characterized by their ability to form a wide range of coordination compounds in which the octahedral, tetrahedral, and square-planar stereochemistry are predominant. The

cobalt (II), nickel (II), and copper (II) ions are typical transition metal ions in respect of the formation the coordination compounds.

Cobalt

Cobalt exhibits various oxidation states ranging from 1 to +5. The most common oxidation states are +2 and +3. The coordination compounds of cobalt (II) and cobalt (III) are large in number and exhibit diversity in coordination number, geometry, lability and stability as well as in many other aspects of their chemistry. Numerous studies have been directed towards understanding and application of these important substances.

The chemistry of cobalt(II) is associated with three distinct stereochemical configuration s and possibly a forth. These are tetrahedral, octahedral, square-planar, trigonal bipyramidal and square pyramidal. The stereochemical varieties of cobalt (II) compounds are more often discussed in terms of magnetic and spectral data than on the basis of isomerism. Biological importance of cobalt compounds has been reviewed by Nicholls[3a].

The complexes of cobalt(III) are exceedingly numerous. Because they generally undergo ligand-exchange reactions relatively slowly, they have, from the days of Werner and Jorgensen, been extensively studied and a large fraction of our knowledge of the isomerism, modes of reaction, and general properties of octahedral complexes as a class is based on studies of Co(III) complexes. Almost all discrete Co(III) complexes are octahedral, though a few cases of tetrahedral, planar and square antiprismatic complexes are known. Cobalt(III) complexes are synthesized in several steps beginning with one in which the aqua Co(II) ion is oxidized in solution,

typically by O_2 or H_2O_2 and often a surface-active catalyst such as activated charcoal, in the presence of the ligands [3b].

Nickel

Nickel, the member of the first transition series having atomic number 28, and $3d^8,4s^2$ outer electronic configuration, was isolated in 1751 by A.F.Cronsted from some ores in the cobalt mines of Helsingland, Sweden. Nickel compounds have been found to occur with the metal in oxidation states ranging from –1 to +4. However, comparatively very few compounds correspond to the lowest (-1) and to the higher (+3 and +4) oxidation states. Most of the nickel compounds in the solid state and almost all in aqueous solution contain the metal in the oxidation state +2, which, by consequence, can be considered the ordinary oxidation state for the nickel in its compounds. The most stable electronic configuration of the free Ni(II) ion is $[Ar]3d^8$ which is also the ground state configuration in its complexes. The majority of nickel (II) complex have coordination number of four, five [5- 8] and six. Complexes with coordination number of three, seven and eight still quite rare [4].

Nickel is now recognized as an essential trace element for bacteria, plants, animals and humans. While the role of this metal in animal biochemistry is still not well defined, to date four bacterial enzymes have been found to be Ni dependent; Crease(also found in plants), carbon monoxide dehydrogenase (CODH), hydrogenase (H2-ase), and methyl-S-coenzyme-M methylreductase (MCR), which employs a Ni. containing prosthetic group(factor 430) [9].

Copper

Copper has a single electron outside a completed 3d shell. It exhibits oxidation states +1, +2, and +3. The di-positive state is the most important one for copper. The $3d^9$ configuration makes copper (II) susceptible to Jahn-Teller distortion when placed in an environment of cubic symmetry (i.e. regular octahedral or tetrahedral), and this has profound effect on its stereochemistries. With one possible exception, *viz*. $K_2Pb[Cu(NO_2)_6]$ [10], in which regular octahedral arrangement of the nitrogen atoms around copper(II) ion has been established by neutron diffraction data, no example of a copper (II) complex involving a completely regular octahedral or tetrahedral geometry has yet been found. In six-coordinated octahedral geometry, octahedron is severely distorted. The typical distortion is an elongation along one fourfold axis, so that there is planar array of four short Cu-L bonds and two trans long ones. This kind of distortion may lead to a situation where an octahedral geometry becomes indistinguishable from square planar coordination. Hence the cases of tetragonally distorted octahedral coordination and square coordination cannot be easily differentiated.

All the hexa-coodinated copper (II) complexes, structures of which have been determined by X-ray technique [11], are shown to suffer from tetragonal distortion due to Jahn-Teller effect.

The predominant coordination numbers observed with copper (II) ion are 4, 5 and 6, but variations of each structure occur through bond-length or bond-angle distortions. Another major factor, which is significantly responsible for the distortions, is the steric effect.

Copper is also known to form complexes in mono- and trivalent states. The copper(III) ion is isoelectronic with nickel (II) ion. However, these oxidation states are not so common as bivalent copper.

Copper compounds have applications in organic chemistry for oxidations, coupling reactions, halogenations etc. [12]. Oxidation of phenol by copper-amine complexes [13] provide model for phenol-oxidizing enzymes.

Copper is also round to play a significant role in biological processes. For instance, dimethylglyoxime (DMG) alone is not active, but the $Cu(DMG)_2$ shows some activity against cancer [14] and shows increasing life span to the extent of 200 – 300%.

Zinc

Zinc, the last member of the first transition series, having atomic number 30 and electronic configuration as [Ar] $3d^{10}$ $4s^2$ have attracted the chemist in one or the other way from last few years. Even though it exhibits two oxidation states +1 and +2, it will appear in +2 state in its coordination compounds as a predominant one and its +1 state is not possible under normal conditions except as a spectroscopic species.

Usually zinc(II) will form complexes with various organic ligands which are essentially diamagnetic due to completed d-orbital, i.e. d^{10} – configuration. But the complexes of zinc(II) may be of tetrahedral, square pyramidal or trigonal bipyramidal and octahedral when coordination number is 4, 5, and 6 respectively.

But it is invariably seen that zinc in its +2 state forms only tetrahedral complexes with coordination number 4. Many polymeric structures

involving bridging group are reported. Certain complexes show even coordination number seven.

Regarding its biological aspects, zinc has roles that are second only to iron in importance [15]. One of the roles of zinc in biology is as a structural component in proteins. This role was first proposed in 1983 for the protein transcription factor IIIA, which has zinc based domains called fingers [16].

Binuclear complexes with N, O as donor atoms in ligands are of current interest since such system of two zinc atoms at a distance less than $3.4A^0$ are known to exist at the active site of some zinc containing enzymes such as phospholipage C from Bacillus cereus [17] and bovine lens leucine amino peptidase [18,19]. The chemistry of zinc complexes with tri-, and tetradentate N_xS_y ligands is well developed. This fact is clear from various publications [20 – 23] in which the design of N_2S and NS_2 ligands, Zn-complexes and their structural models from the related zinc-enzymes have been reported.

In the last few years a variety of Zn(II) complexes with synthetic ligands have been used in biomimetic zinc[24]chemistry. Binuleating phenol based ligands are suitable to stabilize binuclear metal cores and widely used to mimic bimetallic biosites[25,26].

The present dissertation comprises investigations on coordination compounds of Co(II), Ni(II), Cu(II) and Zn(II) with different aryl substituted thiosemicarbazone Schiff bases derived from 2-hydroxy-3-formyl quinoline .

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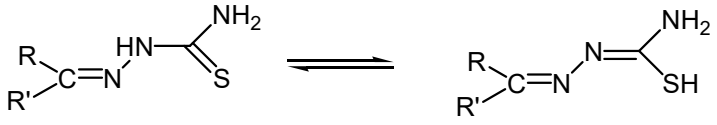
CHAPTER-II

Review of literature

The sulphur donor compounds like thiosemicarbazides, thiocarbazones, thioureas, dithiophosphates, dithiocarbamates, dithiolates, dithio-β-diketones and dithioxamides or xanthates occupy an important position among organic reagents due to their wide applications in analytical chemistry [3-12], medicine [13-15] and industry [16-19]. Thiosemicarbazones are obtained by condensing thiosemicarbazide with suitable carbonyl compound (aldedyde or ketone).

In solution thiosemicarbazones probably consist of an equilibrium mixture of thioamide **(Fig-1)** (1) and thioimidol (2) tautomers.



(1) (2)

Fig-1

Ligand in thione form act as a neutral bidentate, while in the thiol form it acts as monobasic bidentate fashion [20]. Therefore, depending upon preparative conditions (pH), the complex unit can be cationic, neutral or anionic.

The literature survey reveals that large amount of work has been done on transition metal complexes thiosemicarbazones, which is evident

by a large number of publications. In this section, recent work on thiosemicarbazones with various transition metal ions is discussed.

Quinoline derivatives represent the major class of heterocycles, and a number of preparations have been known since the late1980 onwards. The quinoline ring occurs in various natural products, especially in alkaloids. The quinoline skeleton is often used for the design of many synthetic compounds with diverse pharmacological properties.

The study of transition metal quinoline complexes is an area of great current interest. Meth Cohn *et. al.* [21] has reported the synthesis of 2-chloro3-formylquinolines which on acid hydrolysis form 2-hydroxy3-formylquinolines. Ambika Srivastava *et al* in 2005 [22] have reported the synthesis of 2-chloro 3-formylquinolines by the action of Vilsmeir reagent on acetanilide in dimethylformamide and subsequent conversion into 3-formyl-2(1H)-quinolones. These compounds containing the functional groups –OH / =O and –CHO at the appropriate positions the ring may serve as precursors for the synthesis of ligands and their metal complexes. Further, these precursors may also form Schiff bases, which function as ligands. Schiff bases are known to posses many pharmacological activities such as tuberculostatic, fungicidal, anti-inflammatory, antitumor, antiviral, and antimicrobial activities [23].Nitrogen heterocyclic compounds have been used widely in the pharmaceutical industry, medicine, and agriculture for their biological activity because of their antimicrobial, antipyretic, anti-inflammatory, and anticancer properties.

Motivated by the potential antitumour activity of quinones, which are presently in use in clinical practices [24], S. Padhye *et al*.[25]., in 1992 synthesized napthoquinone-thiosemicarbazone hybrid molecules by combining structural feature of both the groups with retention of their antitumour properties and reported in *BioMetals* (**Fig.2**). Such hybrid antitumour agents involving *cis*-platin and doxorubicin moieties have been found to be possessed lower therapeutic dosages, minimal cytotoxicities and reasonable kidney clearance [26].

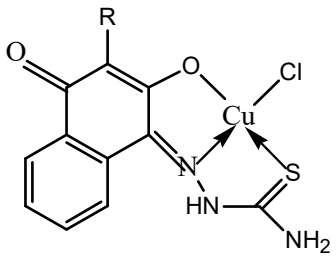


Fig-2

Anupa Murugkar *et al* in 1999 [27] synthesized and characterized the copper and platinum complexes of testosterone acetate thiosemicarbazone. They studied in vitro activity of these compounds against human breast cancer cell line MCF-7.

Cu(II) complexes of 5-phenylazo-3-methoxy salcylidine thiosemicarbazone and ^{4}N substituted thiosemicarbazones were reported by Patil *et al*. [28]. One representative complex has been screened *in vitro* and *in vivo* against P388 lymphocytic leukema cells sensitive and resistant to adriamycin (P388/S and P388/R) **(Fig-3)**

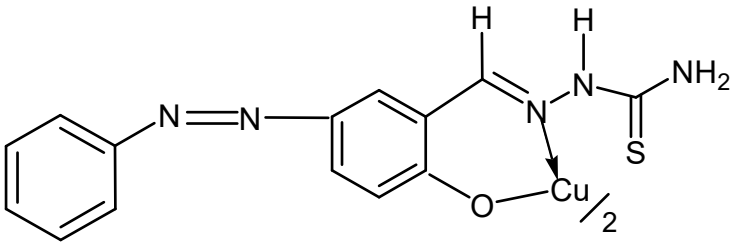


Fig-3

Shreelekha Adsule *et al* [29] in 2006, published a paper in *Journal of Medicinal Chemistry.,* under the heading "**Novel Schiff Base Copper Complexes of Quinoline-2 Carboxaldehyde as Proteasome Inhibitors in Human Prostate Cancer Cells".** They described the synthesis and structural characterization of novel copper (II) quinoline-2-carboxaldehyde thiosemicarbazone complexes **(Fig-4)**. Synthesized Schiff base compounds were different with respect to their various functional groups attached to the quinoline moiety.

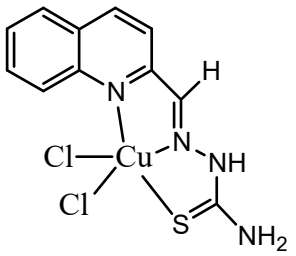


Fig-4

A. A. Osowole in 2008, [30] synthesized and characterized VO(IV), Ni(II) and Cu(II) complexes of the asymmetric Schiff base and their heteroleptic analogues with triphenyl phosphine and 2,2'-bipyridine.

Kulkarni, Naveen V *et al* [31] synthesized and characterized metal complexes of thiosemicarbzones with quinoline core. They evaluated for

their antimicrobial activity against bacteria Escherichia coli and Pseudomonas aeruginosa and fungi Aspergillus niger and Cladosporidium.

Hence the present investigation involves the clubbing of quinoline and thiosemicarbazide moieties through schiff base formation followed by complex preparation, characterization and study of their antimicrobial properties.

CHAPTER III

Experimental, Results and discussion

Experimental

The chemicals used were of reagent grade. Purified solvents were used for the synthesis of ligand and complexes.

I. **Synthesis of ligand**

II. **Synthesis of complexes**

I. Synthesis of ligand:

The synthesis of ligand involves two steps.

a. Synthesis of quinoline compounds
b. Synthesis of thiosemicarbazone (Ligands)

a. Synthesis of quinoline precursors

Synthesis of 2–chloro3–formylquinoline was carried out according to the method reported by Otto Meth-Cohn [32- 34].

Dimethylformamide (9.13 g, 9.6ml, 0.125mol) was cooled to 0^0 C in a round bottom flask equipped with a drying tube. Phosphoryl chloride (53.7g, 32.2ml, 0.35 mol) was added drop wise with stirring and the solution turns to white solid. This is called as Vilsmeier-Hack reagent or adduct. To this was added the acetanilide (0.05 mol) and after 5 min the solution was heated to reflux for 16.5 hrs on water bath.

The reaction mixture was then poured into ice-water (300ml) and stirred for 30 min at 0—10^0 C. The 2–chloro3–formylquinoline was washed well with water, dried and recrystallized with ethyl acetate to get yellow needles. M.P 148 - 149^0 C. Yield 68%. (Fig-1)

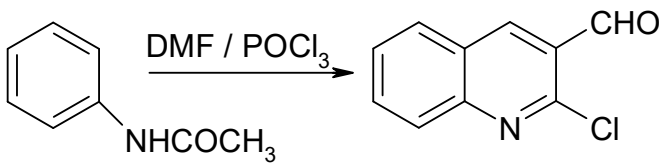


Fig-1

1. Synthesis of 3–formyl-2(1*H*)-quinolone

2–chloro3–formylquinoline (1 mmole) in 70% acetic acid (10 ml) was heated under reflux for 4-6 hr. The completion of the reaction was checked by TLC. Upon cooling the reaction mixture a solid product precipitated out which was filtered, washed well with water, dried and purified by re-crystallization from DMF. M.P 303-304^0 C. Yield 93%. (Fig-2).

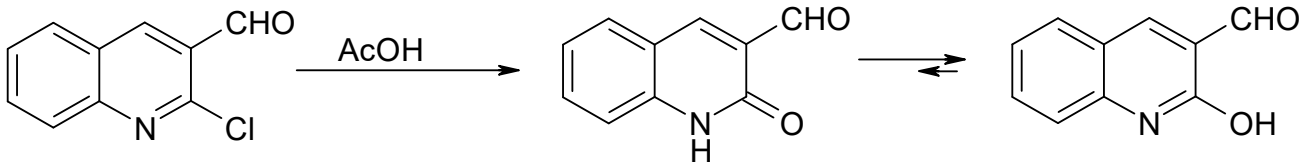


Fig-2

2. Synthesis of 3–formylquinoline-2(1*H*)-thione

To the solution of 2–chloro3–formylquinoline (1 mmole) in dry DMF (5 ml), sodium sulphide
(1.5 mmoles, fused flakes) was added and (monitored by TLC), the reaction mixture was poured into ice-water (*ca*. 15 ml) and made acidic with acetic acid. The product was filtered off, washed well with water, dried and was pure enough for further use. M.P. 285-286^{0}C. Yield 84%.[22] (Fig-3).

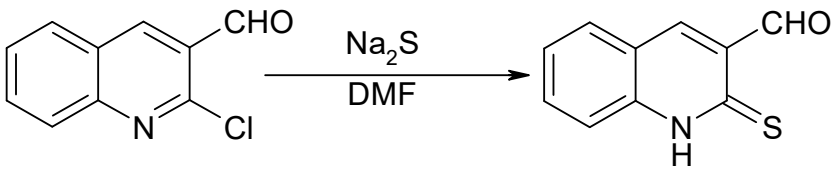
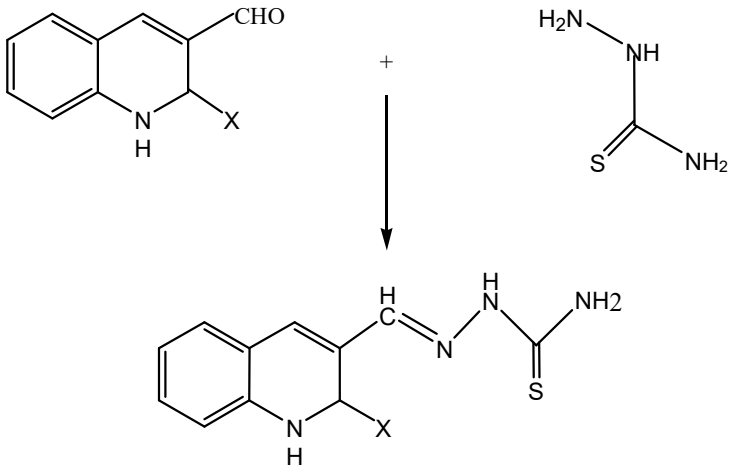


Fig-3

b. Synthesis of thiosemicarbazone (Ligands)

Aryl thiosemicarbazide (0.01mol) in ethanol (100ml) was treated with 3–formyl-2(1*H*)-quinolone and 3–formylquinoline-2(1*H*)-thione (0.01mol) separately. The reaction mixtures were refluxed for 3-4 hours. Yellow solids separated were filtered, washed with ethanol 2-3 times and dried. Yield 70-80% (Fig-4).



H_2L^1 X = O: H_2L^2 X = S,

Fig-4

The formula and structure of ligand prepared is given in the **Table-1**.

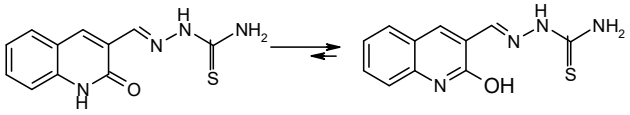
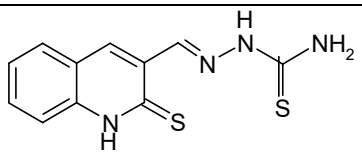
Code	Ligand Structure	Formula	Mp(^{0}c)
H_2L^1		$C_{11}H_{10}N_4OS$	> 300^{0}C
H_2L^2		$C_{11}H_{10}N_4S_2$	> 300^{0}C

Table-1.

2. Synthesis of complexes

Ligand (0.002 mol) was taken in 35-40 ml of hot ethanol. To this, hot ethanolic solution of metal acetate (0.002 mol) (for multinuclear complexes excess metal salts were added) was added drop wise with stirring at 60-65^{0}C. After complete addition of metal salt solution, the reaction mixture was stirred for another 30-40 minutes at the same temperature and refluxed for 3-4 hours on water bath. The isolated complexes were filtered in hot condition, washed with hot ethanol and dried.

Analysis of complexes

The elemental analysis of complexes for metal and halogen was carried out by the following standard methods [35].

Estimation of Cobalt

An accurately weighed (~ 0.100 g) complex was decomposed with a mixture of perchloric acid and concentrated hydrochloric acid (20 ml 1:1 v/v) on a sand bath. The solution was evaporated till the dense white fumes appeared and cooled to room temperature. The solution was diluted with

distilled water (~ 50 ml) and transferred into conical flask. Three drops of xylenol orange indicator were added followed by very dilute H_2SO_4 until colour changes from red to yellow. Powdered hexamine was added with shaking until the deep-red colour is restored (*p*H-6). The solution was warmed to 60°C and titrated against standard EDTA. Colour change red to yellow-orange.

% Co = BR × Molarity of EDTA × 0.05894 × 100 / Wt of Complex

Estimation of Nickel

An accurately weighed complex was decomposed and diluted as discussed in the estimation of cobalt. Freshly prepared murexide indicator (5-6 drops) was added followed by 10 ml of 1*M* ammonium chloride solutions. Concentrated ammonia solution was added drop wise until the *p*H of the solution reached to 7, which was indicated by the yellow color of the solution. The solution was titrated against standard EDTA until the end point is approached and the solution was made strongly alkaline by addition of 10 ml of concentrated ammonia solution and then the titration was continued until the color changes from yellow to bluish-violet.

% Ni = BR × Molarity of EDTA × 0.05871 × 100 / Wt of Complex

Estimation of Copper

An accurately weighed complex was decomposed and diluted as discussed in the estimation of cobalt. To the solution 5 ml of concentrated NH_3 and 5 drops of Fast-sulphon Black f indicator solution were added. The resulting solution was titrated against standard EDTA solution until the color changed from blue to dark green.

$$\% \text{ Cu} = \text{BR} \times \text{Molarity of EDTA} \times 0.06354 \times 100 / \text{Wt of Complex}$$

Estimation of Zinc by EDTA titration

An accurately weighed (0.1g) complex was taken and organic matter was destroyed as above. The resulting solution was diluted up to the mark in 100ml volumetric flask. Then 10 or 25 ml of this homogeneous solution was pipette into a clean conical flask and diluted with 30ml of water and titrated against standard EDTA solution using Erichrom-black-T indicator with 2ml of buffer of 10 pH. Color change is from wine-red to blue.

$$\% \text{ Zn} = \frac{\text{BR X Molarity of EDTA X } 0.06539}{\text{Wt of complex decomposed}} \text{ X } 100$$

Where B.R. = burette reading.

Gravimetric estimation of chloride

An accurately weighed (~ 0.1 g) complex was treated with 30 ml of dilute HNO_3 (1:1 v/v) on water bath for 1h. The solution was filtered through Whatman 40 filter paper to remove unwanted organic matter. Thus obtained solution was diluted to 100 ml and treated with $AgNO_3$ solution. The solution was heated nearly to boiling and allowed to stand for 2 h for complete coagulation. The process of precipitation and coagulation were performed in subdued light. The precipitate was filter through previously weighed sintered glass crucible (G-4) and washed with very dilute HNO_3 and dried at 130-140 °C. Further the percentage of chloride was determined by the formula given below.

$$\% \text{ Cl} = \frac{\text{Wt. of AgCl} \times 0.2474}{\text{Wt. of Complex.}} \times 100$$

Physical measurements

C, H and N analyses were carried out on Thermo quest elemental analyzer at USIC Karnatak University Dharwad. **The magnetic susceptibility** measurements were carried out at room temperature using Faraday balance at Institute Instrumentation Center, Indian Institute of Technology Roorkee, The results were given as magnetic moments x 10^{-2} emu. The magnetic susceptibility was calculated by the relation

χ_g = magnetic moment (emu) / weight of the sample x H (applied field in oersteds 'Oe').

The effective magnetic moment was calculated from the expression $\mu = 2.828(\chi_m T)^{1/2}$, where χ_m is the molar magnetic susceptibility per metal atom corrected for diamagnetism.

The electronic spectra of the complexes were recorded on a Hitachi 150–20 in the range of 1100-200 nm spectrophotometer. IR spectra were recorded in KBr matrix using Impact-410 Nicolet (USA) FT-IR spectrometer in the range 4000 – 400 cm^{-1}.

The ^{1}H-NMR spectra of ligand and its Zinc(II) and Cobalt(III) complexes along with D_2O exchange were recorded in the range of 0-15 ppm in DMSO-d_6 solvent on a 'Bruker 300 MHz spectrometer' at room temperature using TMS as internal reference.

The molar conductance measurements were made on an ELICO–CM–82 conductivity bridge provided with a dip type conductivity cell fitted with platinum electrodes. The cell constant of the electrode is 0.51cm^{-1}.

Molar conductivities of the complexes were measured in DMSO solution with 10^{-3} M concentration. The molar conductance is calculated by using the relation,

Λ_M = [1000 × k × observed conductance (in mhos)] / C

Where, Λ_M = Molar conductance

K= cell constant (0.51).

C = Molar concentration (10^{-3}M).

The EPR spectra of the copper (II) complexes were recorded at room temperature, on Varian E–4 X-band EPR spectrometer, using TCNE as the <g> marker. All these EPR spectra were run at RSIC, I.I.T. Powai, Bombay. The $g_{II}$and $g_{\perp}$are compared with the position of TCNE. The $g_{II}$and $g_{\perp}$ values are calculated using the following equations,

g_{II}or $g_{\perp} = g_{TCNE}$ X H_{TCNE} / H

(g_{TCNE} = 2.0027)

$g_{av} = 1/3(g_{II} + 2g_{\perp})$

Scan range 5000G; Field set at 3000G.

Antifungal and antibacterial analysis was carried out in Biotech finishing school of M.M.Arts and Science College, Sirsi.

DNA Cleavage study complexes were carried out on *Escherichia coli* DNA by agarose gel electrophoresis in BioGenics Hubli .

Results and Discussion

The complexes obtained in the present study were non-hygroscopic and in the form of amorphous solids. They are insoluble in water, EtOH, MeOH but soluble in DMSO. Attempts to grow single crystals suitable for X-ray structure determination have not been successful due to their amorphous nature.

The compositional data of synthesized ligands and their complexes are compiled in **Table-2**. The interaction of metal salts with the ligands in 1:2, 3:2, 1:3, 1:1 and 2:2 molar ratios in ethanol yielded stable solid complexes.

Elemental analysis data of complexes.

Com	Empirical formula	C	H	N	M	Cl	Molar cond. Λ_M
H_2L^1	$C_{10}H_{10}N_4O_1S_1$	48.74 (48.56)	4.09 (4.48)	22.75 (22.89)	--	--	--
CoL^1	$[Co(C_{22}H_{18}N_8O_2S_2)]Cl$	45.17 (44.81)	3.10 (3.08)	19.16 (19.51)	10.07 (10.40)	6.06 (5.79)	85
NiL^1	$[Ni(C_{22}H_{20}N_8O_2S_2)Cl_2]$ $2H_2O$	40.14 (40.02)	3.68 (3.40)	17.02 (17.32)	8.92 (8.63)	10.77 (10.20)	23
CuL^1	$[Cu_2(C_{22}H_{18}N_8O_2S_2)Cl_2$ $(H_2O)_2].H_2O$	44.84 (45.08)	3.54 (3.48)	12.30 (12.16)	17.11 (17.39)	9.55 (9.13)	41
ZnL^1	$[Zn(C_{22}H_{20}N_8O_2S_2)Cl_2]$	42.02 (41.86)	3.21 (3.19)	17.82 (17.23)	10.40 (10.23)	11.27 (11.01)	18
H_2L^2	$C_{10}H_{10}N_4S_2$	45.74 (45.86)	3.84 (3.65)	21.34 (21.45)	--	--	--
CoL^2	$[Co(C_{30}H_{28}N_{12}S_6)]H_2O$	41.76 (42.02)	3.51 (3.87)	19.49 (19.67)	6.84 (7.04)	--	78
NiL^2	$[Ni(C_{10}H_{14}N4O_2S_2)Cl]$ Cl	28.04 (28.78)	3.29 (3.59)	13.08 (13.84)	14.20 (14.46)	16.09 (16.86)	105
CuL^2	$[Cu_2(C_{20}H_{28}N_8O_4S_4)]$ Cl_2	31.58 (32.02)	3.71 (3.86)	14.74 (14.96)	8.36 (8.78)	9.08 (9.56)	398
ZnL^2	$[Zn(C_{10}H_{12}N_4O_1S_2Cl_2)]$	31.43 (31.87)	3.17 (2.98)	14.67 (14.26)	17.13 (17.19)	18.07 (18.63)	72.4

Table-2

The metal complexes are soluble in DMSO, insoluble in ethanol, methanol, and chlorinated hydrocarbons. The metal complexes melt with decomposition above 300^0C. The Co (III) complexes are dark brown, Ni(II) complexes are light brown and CuL^1(II) complex is green and CuL^2(II) is dark brown in color.

Molar conductivity measurements

The molar conductance values of complexes (except NiL^2 and CuL^2 complexes)in DMSO at concentration 10^{-3} M fall in the range 11 - 15 mho cm^2 mol^{-1} **(Table-2).** These values are much less than that expected for 1:1 electrolytes (65-90 mho cm^2 mol^{-1}) and hence are non-electrolytic in nature [36]. While NiL^2(II) complex shows conductance values in the range 90 – 100 mho cm^2 mol^{-1} which indicates the 1:1 electrolyte and CuL^2 complex shows conductance as 398 mho cm^2 mol^{-1} which indicates 2:2 electrolyte nature to this complex[37-39].

I.R spectral studies

Infrared spectra of ligands and its complexes as KBr pellets were recorded in the range 4000-400 cm^{-1}. The important IR spectral bands of ligands and corresponding complexes along with assignments are presented in **Table–3.** The IR spectra of ligands and its complexes are shown in **Fig-5 (a-j)**.

The spectra of ligand shows two bands of medium intensity in the range of 3270 – 3310 cm^{-1} which are assigned to $\nu(^4NH)$ and band in the region 3140 – 3170 cm^{-1} assigned to hydrazine $\nu(^2NH)$ [40,41]. The possibility of thioamide – thioimidol tautomerism (H-N-C=S $\Leftrightarrow$ C=N-SH) in

the ligands have been ruled out, since there is no IR absorption band around 2500-2600 cm^{-1}, which is characteristic of thiol group.

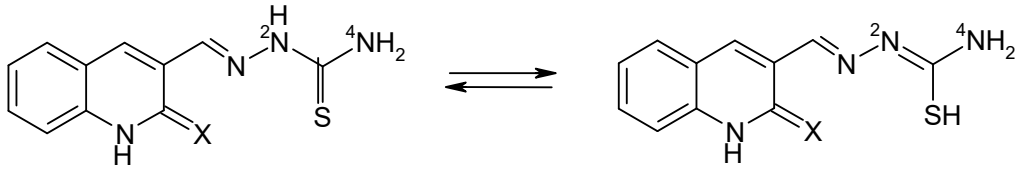


Fig-4 : H_2L^1;x = O , H_2L^2;x = S,

The phenolic *v* (OH) is found around 2900 – 2925 cm^{-1} as a weak band, appearance of this band indicates the predominance of hydroxyl form of the ligand H_2L^1 and disappearing of this band indicates the deprotonation and coordination of phenoxide group to the metal. This is further supported by the shift of phenolic *v*(C-O) around 1220 cm^{-1} in free ligand to higher frequency in complexes [42, 43]

The band around 2950 - 3050 cm^{-1} is assigned for *v* (CH) vibrations. The (N-N) stretching band is assigned in the range of 1040 – 1090 cm^{-1} in ligand and complexes [44, 45, 46]. The sharp band around 1651cm^{-1} is assigned to azomethine C=N group [40, 47, 48] in ligands. This band shifts to lower frequency [49] by ~ 20 – 30 cm^{-1} in all the complexes except in zinc complex (ZnL^1) where it shifts to lower frequency [50] by only 3 cm^{-1}. Interestingly, the shifting has been reported both to higher and lower energies. The shift of these bands depends on bond order of *v*(C=N) on coordination, which in turn depends on the group attached to azomethine function.

The coordination of azomethine nitrogen is also indicated by the shift of band chiefly assigned to the N–N stretch [51]. In the present spectra of complexes CuL^1 and ZnL^1 this band shows positive shift and the rest of the complexes show the negative shift.

Coupled vibration among thioamide bands I, II, III, and IV in the fingerprint region are distributed around 1540, 1486, 1374, and 945 cm^{-1} respectively [52- 54]. The appearance of four thioamide bands in the spectra of ligand is another support for the existence of thioketo (thione) form of ligand in the solid state.

In complexes CoL^1 and CuL^2 presence of only one band, assigned at higher energy side for ^{4}NH and disappearance of lower energy side band assigned for ^{2}NH around 3200 cm^{-1} in ligand, indicates deprotonation of ^{2}NH proton of ligand during complexation with metal ions via thioenolisation. This fact is supported by the positive shift of thioamide band II and considerable reduction in intensity of thioamide band III & IV (around 1350 & 950 cm^{-1}) which were assigned to the coupled vibration of *v*(C=S). Along with this, appearance of a weak band around 617 – 670 cm^{-1} due to *v*(C-S) confirms the deprotonation of ^{2}NH proton through thioenolization and subsequent coordination to metal through sulfur atom [45, 52].

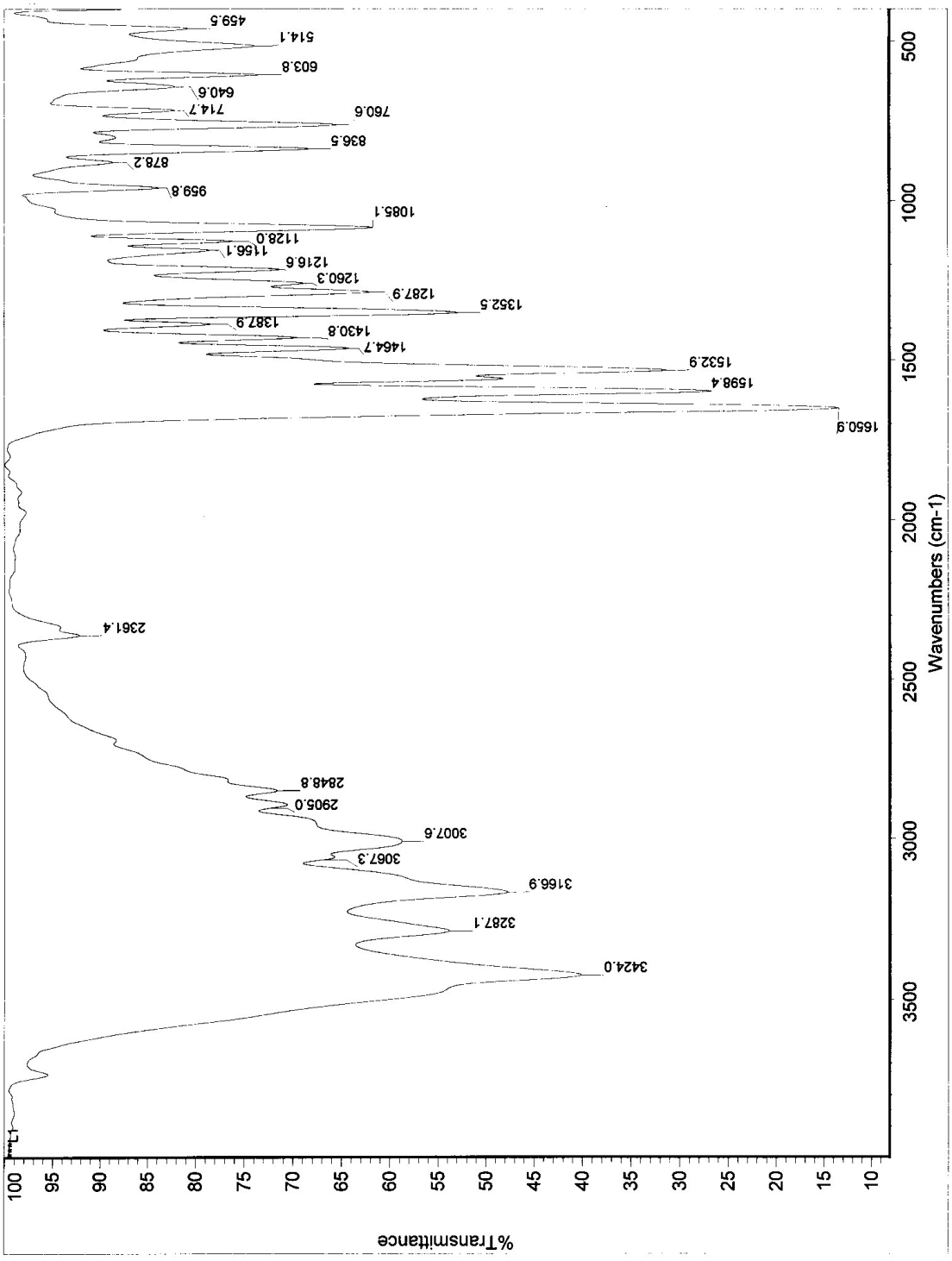


Fig5-a : IR Spectrum of Ligand H_2L^1: 2-oxo3-ormylquinolinethiosemicarbazone

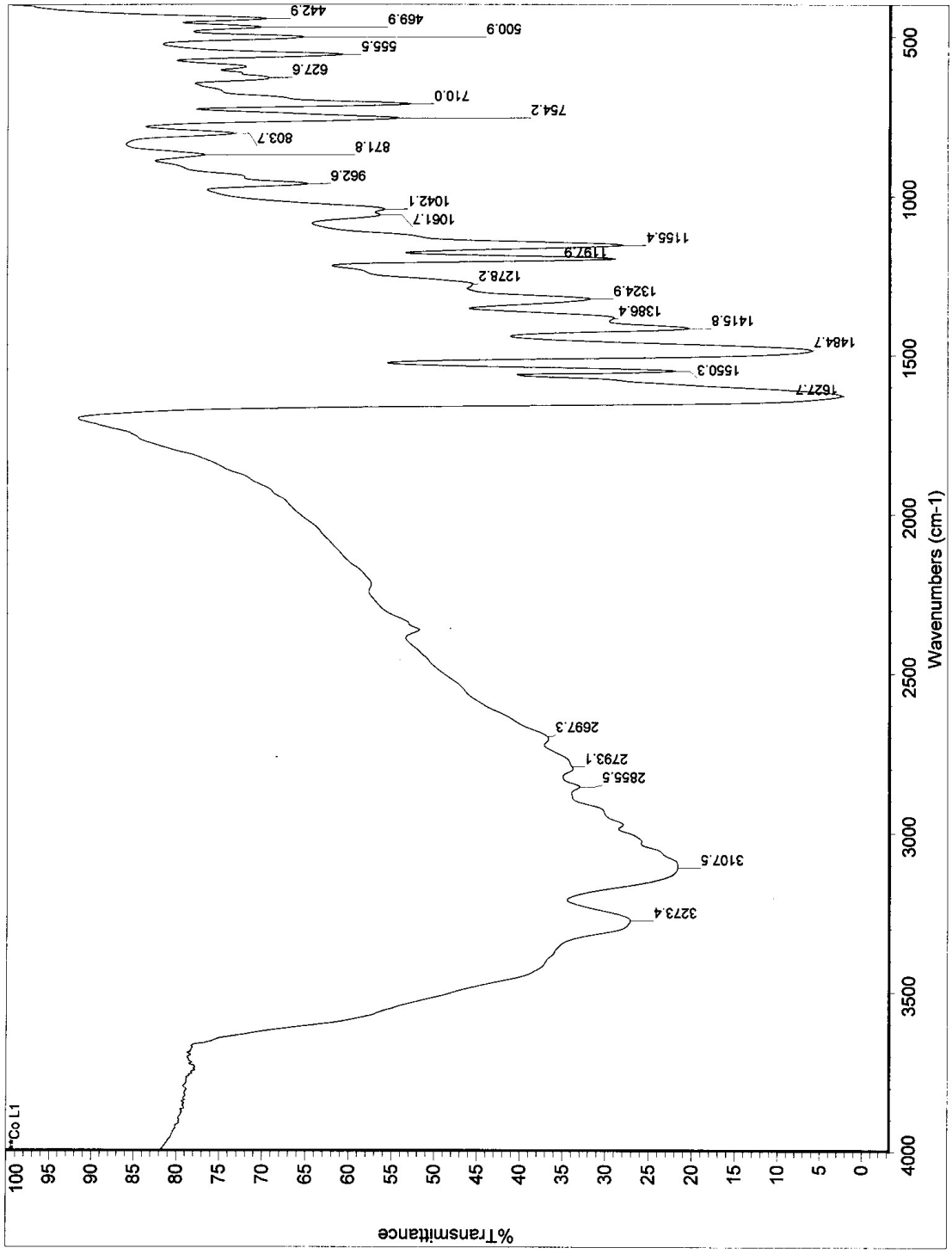


Fig5-b: IR Spectrum of Complex CoL^1: $[Co(HL^{-1})(HL^{-2})]$

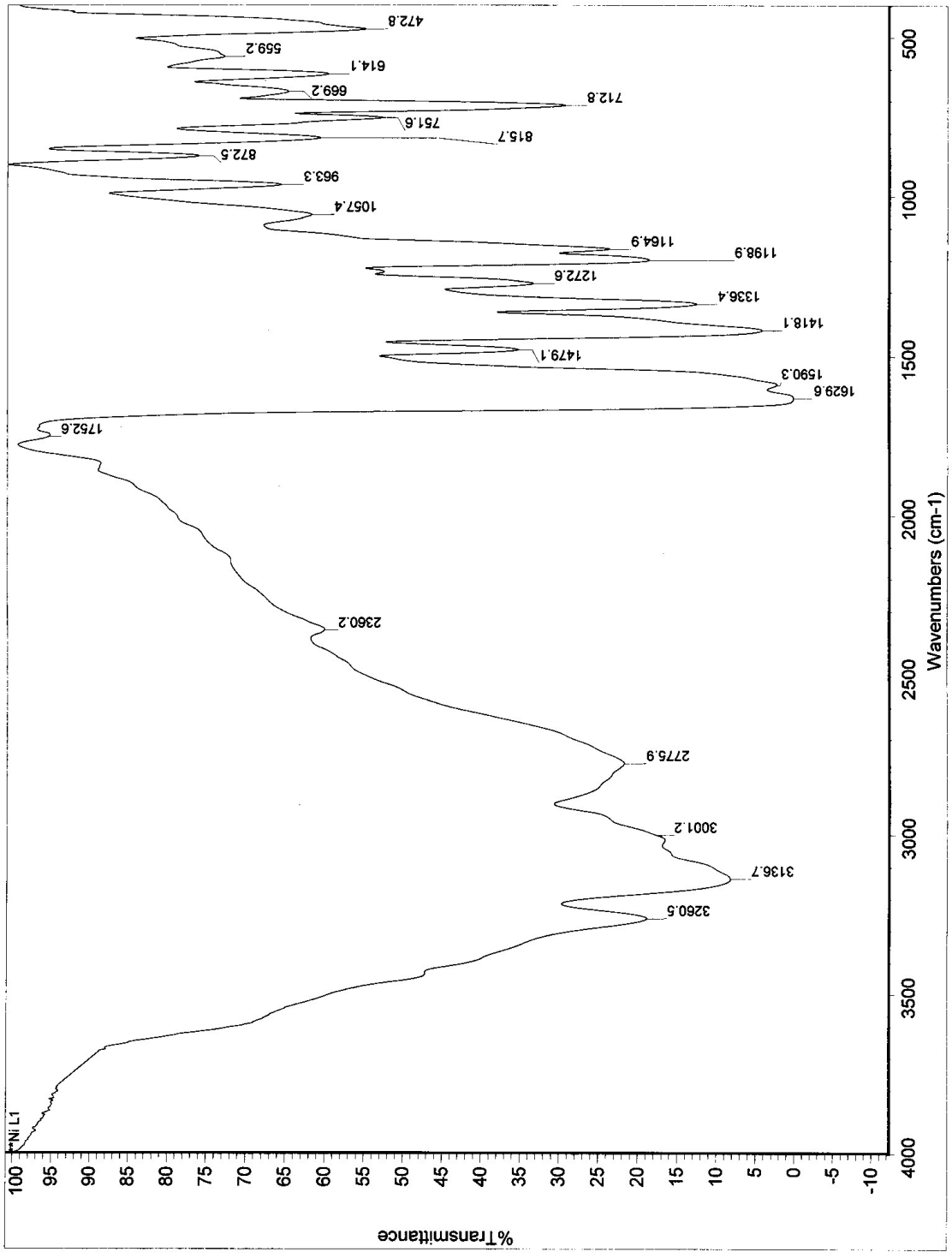


Fig5-c: IR Spectrum of Complex NiL^1: $[Ni(H_2L^1)_2Cl_2].2H_20$

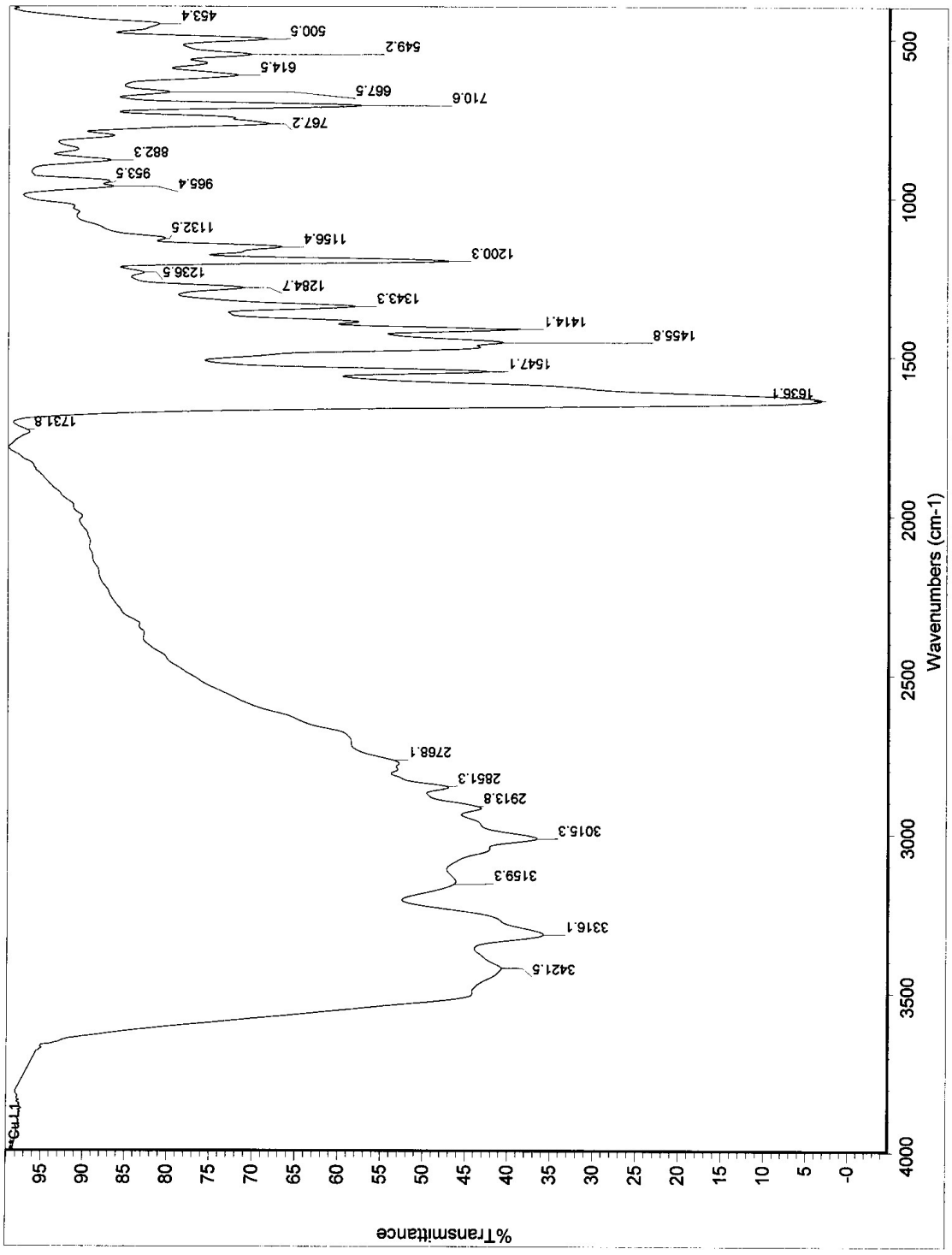


Fig 5-d : IR Spectrum of Complex CuL^1: $[Cu_2(HL^1)_2Cl_2(H_2O)_2]$

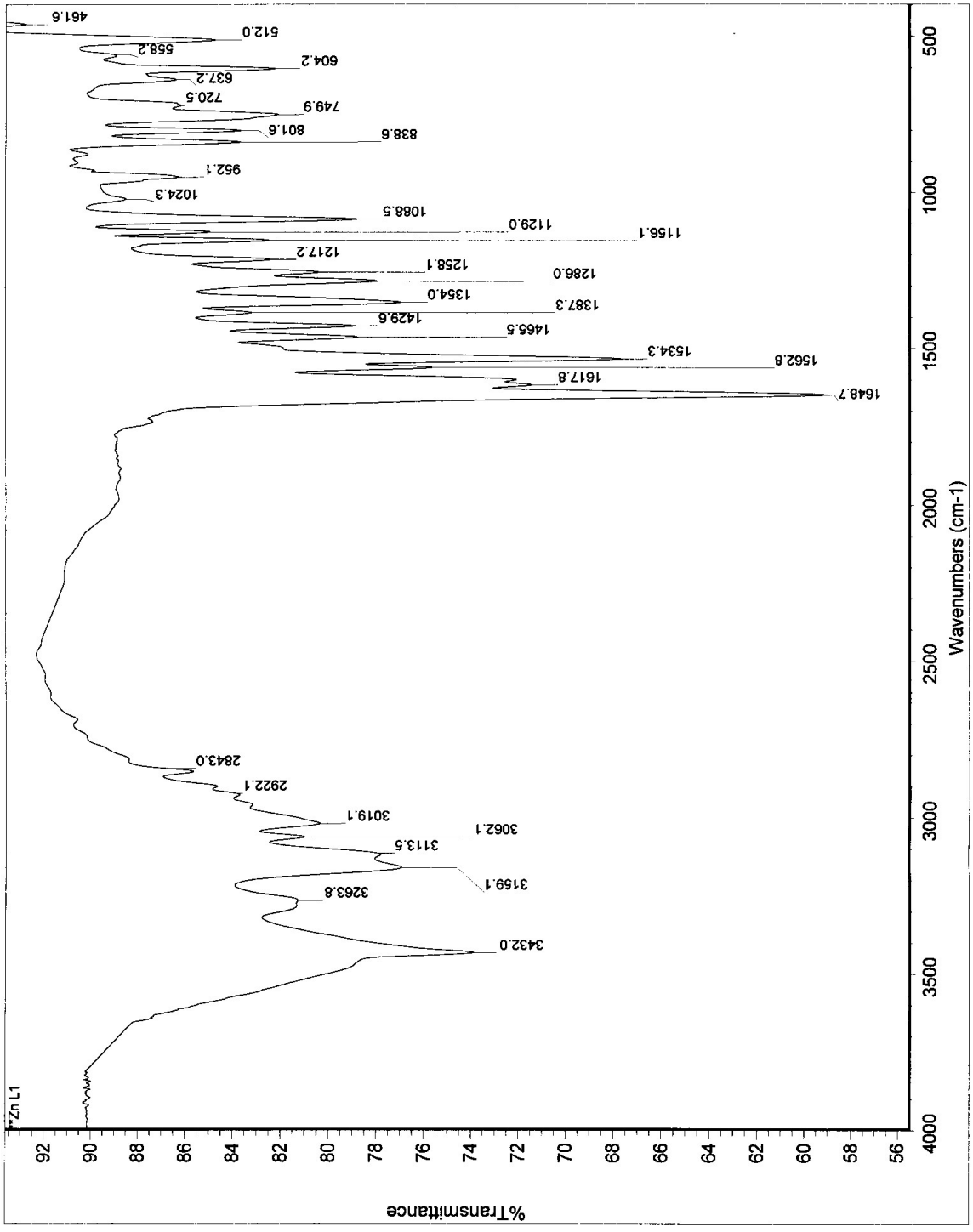


Fig5-e : IR Spectrum of Complex ZnL^1: $[Zn(H_2L^1)_2Cl_2]$

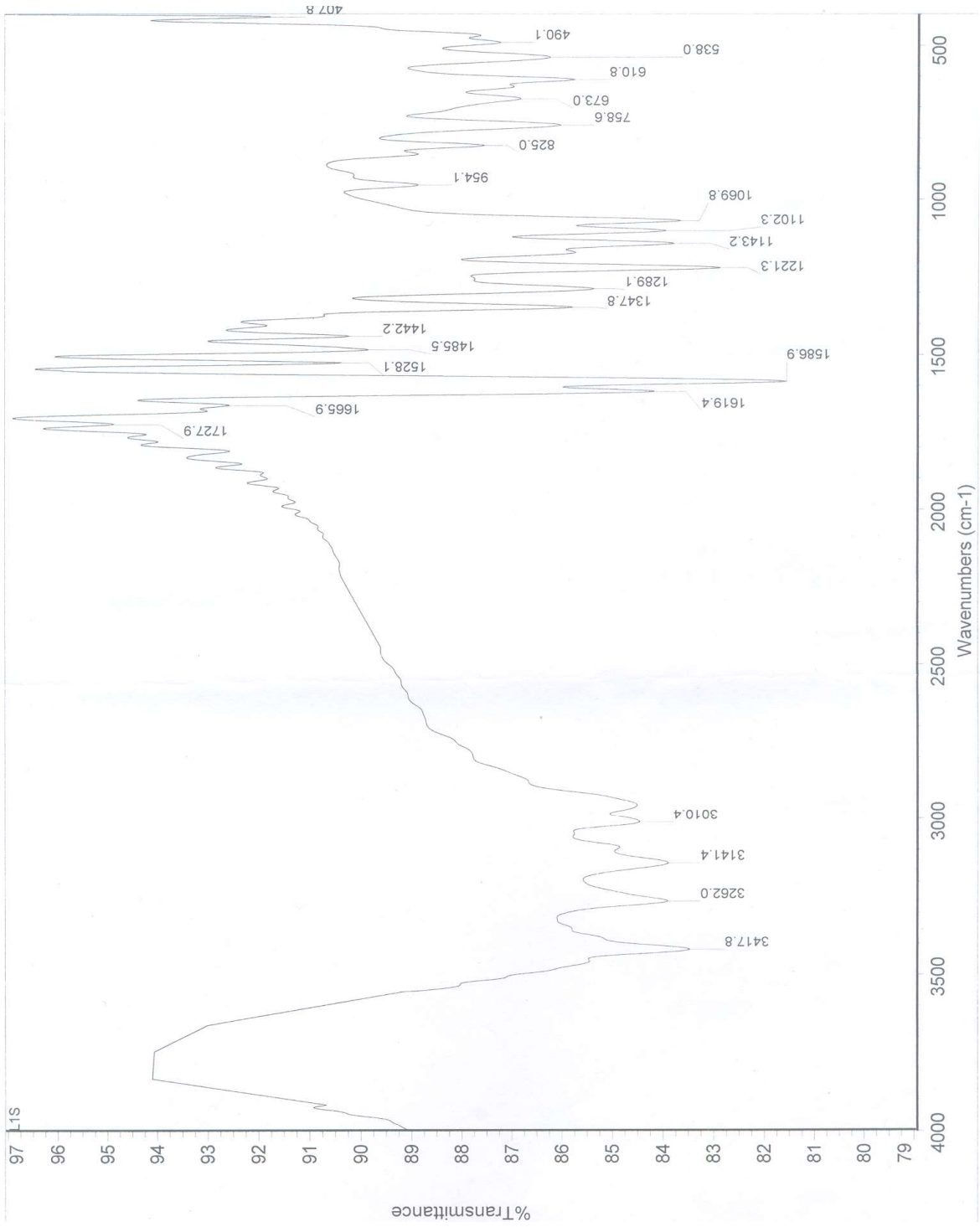


Fig5-f:IR Spectrum of Ligand H_2L^2: 2(1*H*)-thio-3–formylquinolinethiosemicarbazone

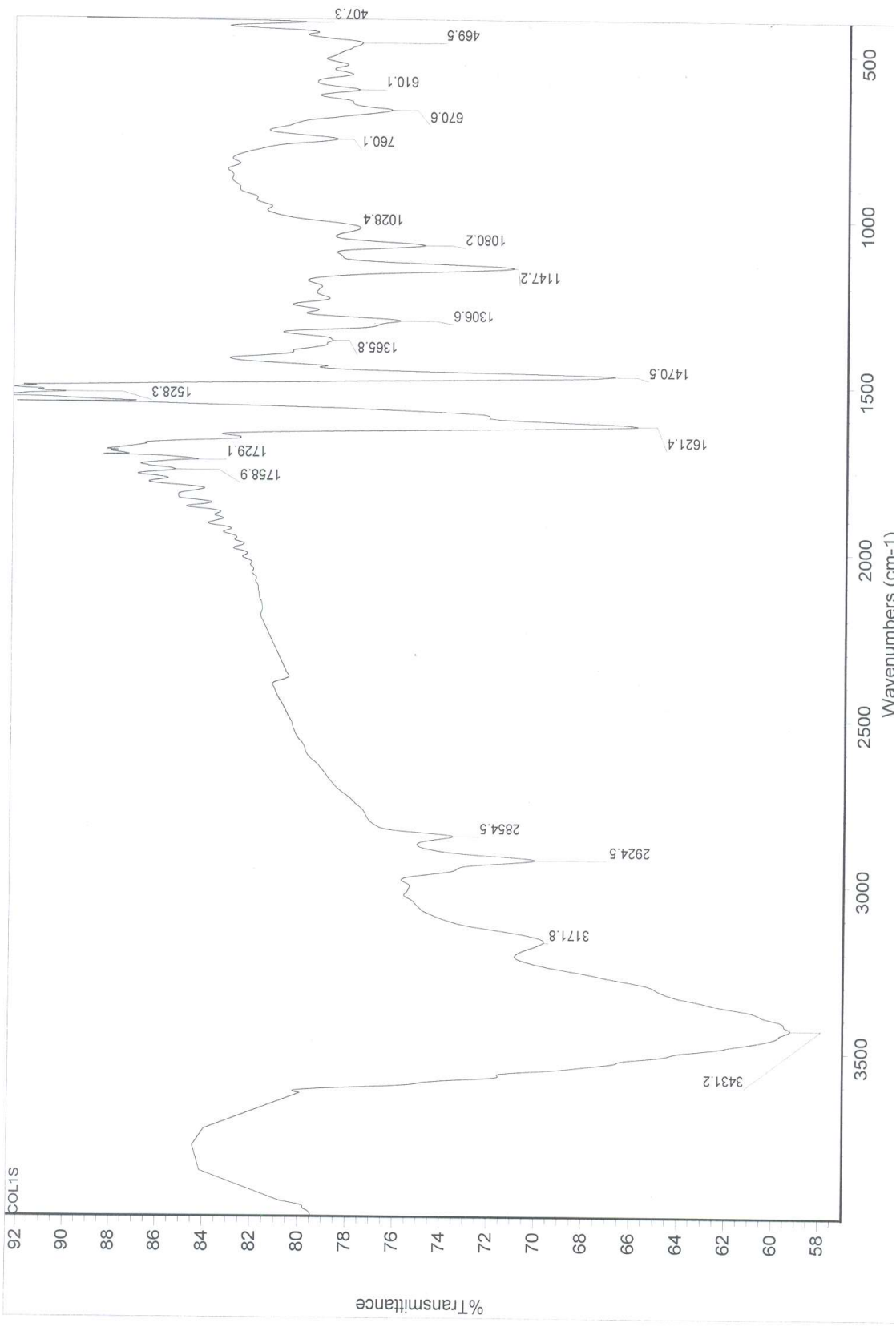


Fig5-g : IR Spectrum of Complex CoL^2: $[Co(H_2L^2)((HL^2)^{-1})_2].H2O$

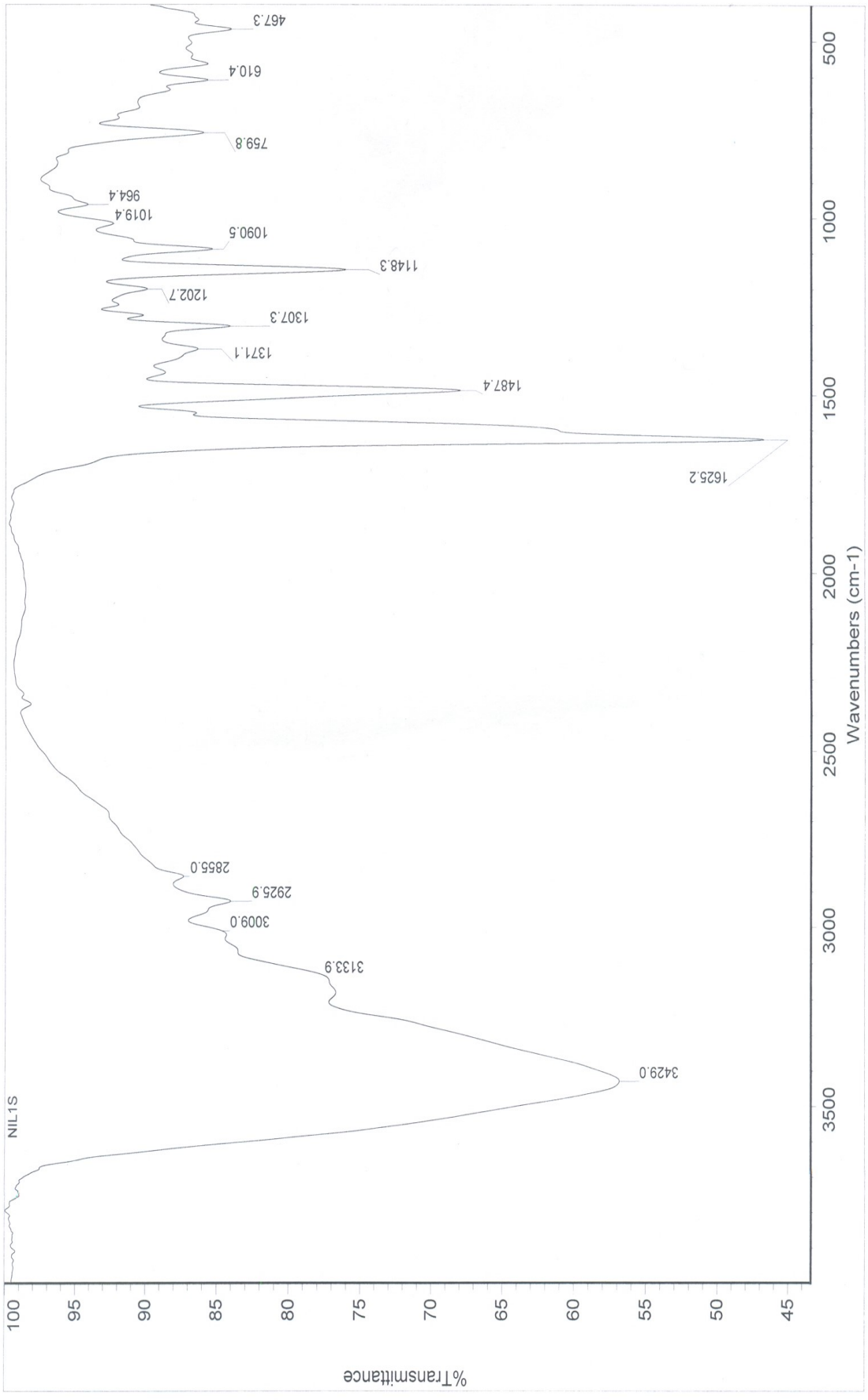


Fig5-h : IR Spectrum of Complex NiL^2: $[Ni(H_2L^2)(H_2O)_2Cl]Cl$

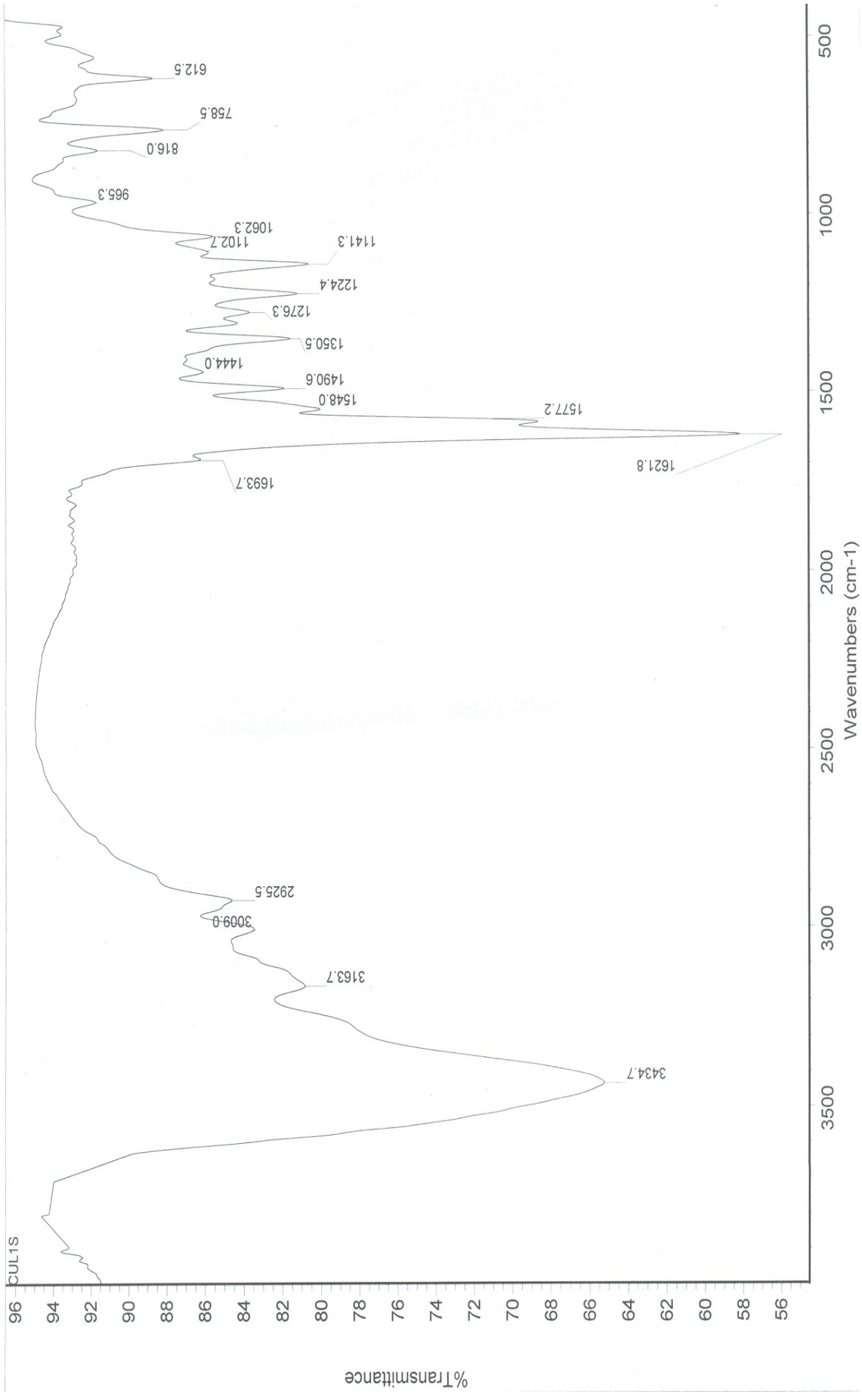


Fig5-i : IR Spectrum of Complex CuL^2: $[Cu_2((HL^2)^{-1})_2(H_2O)_4]Cl_2$

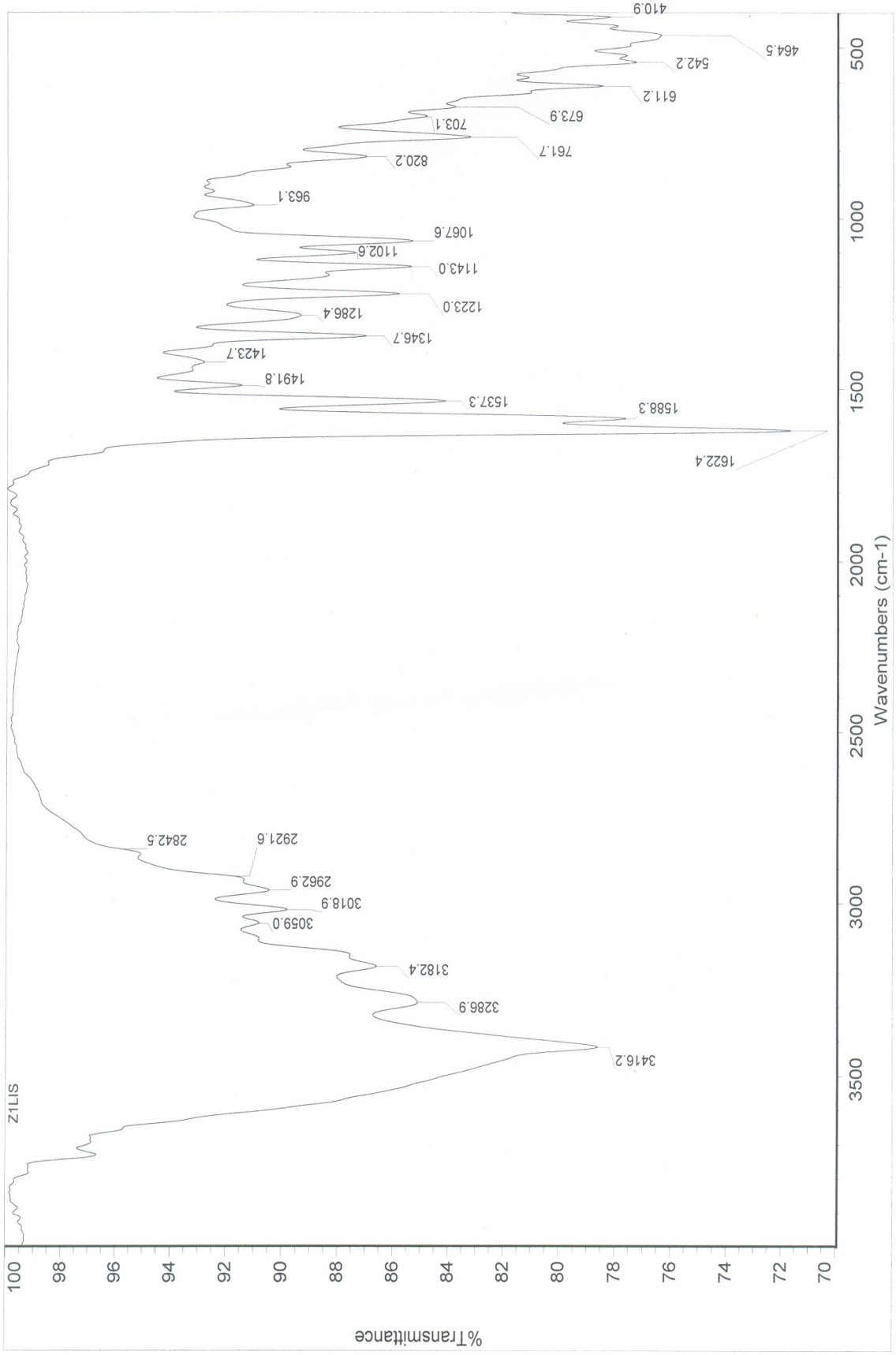


Fig5-j : IR Spectrum of Complex ZnL^2: $[Zn(H_2L^2)(H_2O)Cl_2]$

Table-3. IR data of ligand and complexes V(O-H)P =Phenolic OH

Com	V (OH)	v(^{4}NH)	V (^{2}NH)	*V* C=N	*Thioamide bands*				*V* (O-H)P	v(N-N)	V (C-S)	V (C-O)	V (MN)
					I	*II*	*III*	*IV*					
H_2L^1	3424	3287	3167 s	1651	1598 s	1464 m	1352 s	960 m	3007	1085 m	___	1288	___
CoL_1	__	3273	__	1627	1550	1484	1325	962	__	1042	628 m	1155	500
NiL^1	___	3260	3136	1629	1590	1478	1336	963	__	1057	___	1199	472
CuL_1	3421	3316	3159	1636	1547 w	1455	1343	953 w	___	1156	___	1200	500
ZnL^1	3432	3263 w	3159	1648	1562	1465	1354	952	2985	1088	__	1286	512
H_2L^2	--	3417	3262s	1665	1586 s	1485 m	1348 s	954 m	--	1102 m	--	--	--
CoL_2	3431	--	3171	1621	1528	1470	1365	1028	--	1080	610 m	--	469
NiL^2	3429	--	3134	1625	1625	1487	1371	964	--	1090	--	--	467
CuL_2	3434	--	3163	1622	1577 w	1491	1350	965 w	--	1062	612	--	--
ZnL^2	3416	3287 w	3182	1622	1588	1492	1347	963	--	1068	--	--	542

After complex formation the ^{4}NH band shifted towards higher energy side. In most of the complexes this band is superimposed by uncoordinated water molecule band and hence assignment of this band is difficult. Some intense bands occurring at 3421(CuL^1), 3421(NiL^2) and 3434(CuL^2) are assigned for coordinated water molecules.

The spectra are rather complex in the region below 400 cm^{-1}, where the various M-L bond-stretching vibrations are often found in combination with other bands. Non-ligand low frequency bands in the 523 – 500 cm^{-1} and 420 497 cm^{-1} regions are assigned to *v*(M-N) and *v*(M-O) respectively [52-58]

Magneto chemistry

The experimentally determined room temperature magnetic moments of all the complexes are given in the **Table-5**.

The **Copper (II) complexes** shows the effective magnetic moment as 1.56 and 1.25 BM. Considerably lower magnetic moment than the spin only value (1.73 B.M) for Cu (II) complexes is attributed for the anti-ferromagnetic coupling interaction between metal ions. These values are consistent with the di-nuclear complexes CuL^1, which is further confirmed from the EPR study.

The difference between the coordinating sites of CuL^1 and CuL^2 is reflected in the magnetic moments. The CuL^1 complex shows μ_{eff} as 1.56 B.M, the square pyramidal chloro bridged CuL^1 complex do not contain sulphur coordination, while CuL^2 contains thiolate sulphur as bridging atom and exhibit fairly lesser effective magnetic moment per metal atom than

the above value, which indicates the stronger magnetic interaction for S-bonded complexes than others. Similar observations have been made by Seleem *et al* [59-61], where they have compared the magnetic moment values of sulphur coordinated complexes with oxygen ligated complexes.

Nickel (II) complexes:

The magnetic moment value of Ni (II) complex gives valuable information regarding its stereochemistry. This is due to favorable changes occurring in the number of unpaired electrons and the orbital contribution to the magnetic moments, when stereochemistry around Ni (II) ion is changed.

From the magnetic point of view, most of the Ni (II) complexes may be divided into three categories.

1. Six coordinated octahedral paramagnetic complexes with $^3A_{2g}$ ground state.

2. Four coordinate tetrahedral paramagnetic complexes with $^3T_1$ ground state.

3. Four coordinated square planar diamagnetic complexes with spin singlet ground state $^1A_{1g}$.

The octahedral complexes have $^3A_{2g}$ ground state and hence the orbital contribution to the magnetic moment due to orbital degeneracy is absent. However octahedral nickel (II) complexes show the effective magnetic moments that are more than the spin-only value of 2.83 B.M. This is because the excited state $^3T_{2g}$ carry the orbital magnetic moment. The

spin-orbit coupling brings about some mixing of ground state with excited state, thus forcing some orbital contribution. The spin-orbit coupling constant λ, which is given by the relation. $\mu_{eff} = \mu_{so}[1- \alpha \lambda /10 Dq]$, where α=4 increases the magnetic moment for about 10% than the 'spin–only' value of 2.83 B.M. Therefore, a magnetic moment ranging from 2.93-3.01B.M indicates an octahedral geometry around nickel (II) ion. It follows from the above equation that the greater the 10 Dq, the smaller the mixing effect, and hence lesser the orbital contribution, i.e., a strong donor ligand likely to reduce the orbital contribution. The loss of degeneracy of the orbitals affects the unrestricted motion of electrons about the nucleus. In a stereochemistry of a low symmetry, e.g., a teragonally distorted octahedral complex, a trigonal bipyramidal complex, and a square pyramidal complex; d orbitals lose their degeneracy to a significant extent. In such cases the magnetic moment is close to μ_s [62]. Naik *et al*., [63] have reported magnetic moment values in the range of 2.62 – 2.91 B.M. for Ni(II) octahedral complexes. Biradar *et al*.,[64] reported 2.5 – 3.4 B.M. for octahedral Ni(II) complexes. In the present investigation the observed magnetic moment value for Ni (II) complexes are found to be 2.90 and 2.96 B.M. which are in the range expected for octahedral geometry around Ni (II) ion.

The **cobalt complex** of H_2L^1 is found to be diamagnetic, which suggests that the complex is in the +3 oxidation state and have low spin octahedral structure even though cobalt (II) salt is used for the synthesis [65 - 70]. The complex CoL^2 exhibits the magnetic moment 1.84 B.M. indicating the presence of one unpaired electron and forming low spin complex.

^{1}H NMR studies

^{1}H NMR of ligand and its complexes were recorded in DMSO-d_6-solvent on 300 MHz instrument in 0 – 18 ppm range. Magnetic study revealed that cobalt complex is diamagnetic, which enabled us to study the NMR spectra of this complex. Diamagnetic zinc complex has also been studied.

Chemical shifts of all prominent peaks of ligand and their complexes are tabulated in **Table 4.** All spectra are presented in the **Fig8-a-f.** Proton NMR spectra of the precursor of thiosemicarbazone ligand i.e., 2-hydroxy3-formylquinoline shows resonance of formyl proton at 10.24 ppm and quinoline OH proton at 12.23 ppm. These peaks were shifted to (azomethine) 8.75 and 12.00 ppm in the thiosemicarbazone ligand, indicating the expected Schiff-base formation.

The spectrum of ligand shows resonances at 7.19 – 8.09, 8.27, 8.75, 11.63 and 12.00 ppm. Of these absorptions, a multiplet ranging from 7.19 – 8.09 ppm is assigned for aromatic protons. The simple NH_2 group of thiosemicarbazide part in ligand H_2L^1 resonates at 8.27 ppm and the azomethine proton is observed as a singlet at 8.75 ppm. The hydrazine ^{2}NH protons resonate as singlets at 11.63 ppm [71]. This peak disappeared on D_2O exchange. Along with this, the examination of the spectrum of ligand shows no signal around 4 ppm, which may be ascribed for S-H proton [72]. The proton of hydroxy group in quinoline ring absorbs at 12.00 ppm., which is further confirmed by D_2O exchange. Thus appearance of both -NH signal implies that the thiol form (II) is presumably not present in DMSO solution and the ligand exist in thione or keto form (I).

Comparative study of ^{1}H NMR data of **cobalt (III) complex** with their corresponding ligand H_2L^1 supported our expectation of octahedral coordination sphere around cobalt (III) metal ion. In the spectrum of complex the singlet observed at12.00 □ ppm due to quinoline OH in ligand is absent. A new singlet around 13.96 □ ppm appeared in the complex. The proton resonating in this region is highly de-shielded due to its strong acidic nature. All hydroxyquinolines are known to exist in tautomeric equilibrium with the corresponding quinolones as shown in **Fig-6,** which probably favors the coordination to cobalt (III) ion [73a, 73b].

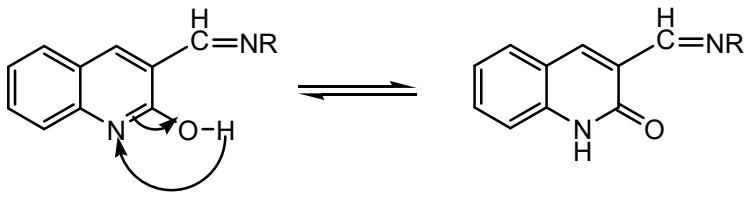


Fig-6

Due to the resonance the proton bonded to nitrogen in quinolone becomes highly acidic. This proton is responsible for the appearance of new deshielded peak at 13.96 □ ppm.

Of the two separate singlet signals appeared around 9.42 – 10.20 and 11.63 – 12.05 □ ppm, due to $^{4}NH_2$ and hydrazine ^{2}NH proton respectively, the peak due to hydrazine ^{2}NH proton disappeared and peak due to $^{4}NH_2$ proton is observed at up field in all four spectra of cobalt complexes. The presence of $^{4}NH_2$ proton, in all complexes, was confirmed by observing disappearance of this peak on D_2O exchange. This observation clearly supports the involvement of >C=S chromophore through thioenolization during complexation. The singlet appeared at 8.75 □ ppm, which accounts

for the azomethine proton in uncomplexed ligand, suffered downfield shift to 8.85 ppm. This shift indicates the coordination of azomethine nitrogen to metal ion during complex formation.

Thus from the ^{1}H NMR study, it is concluded that the cobalt (III) metal ion is coordinated by thiolate sulphur, azomethine nitrogen and quinone oxygen atoms.

^{1}H NMR spectra of Zinc (II) complexes are tabulated in **Table-4**. Comparative study of spectra of zinc complex with its ligand shows very little shifting of peaks on complexation with ligand. The spectrum of zinc complex shows all peaks that were present in their corresponding ligand.

The presence of singlet at 13.87 ppm in the ligand (H_2L^2) itself clearly indicates the thione form of the ligand.(Fig.-7)

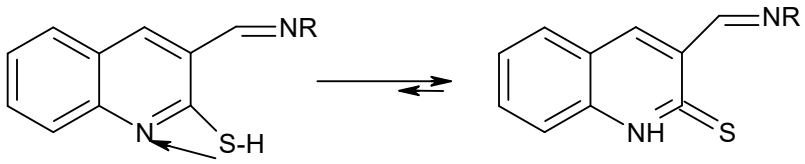


Fig.-7

There is no considerable shift of bands observed in the zinc complex of L^2 ligand.

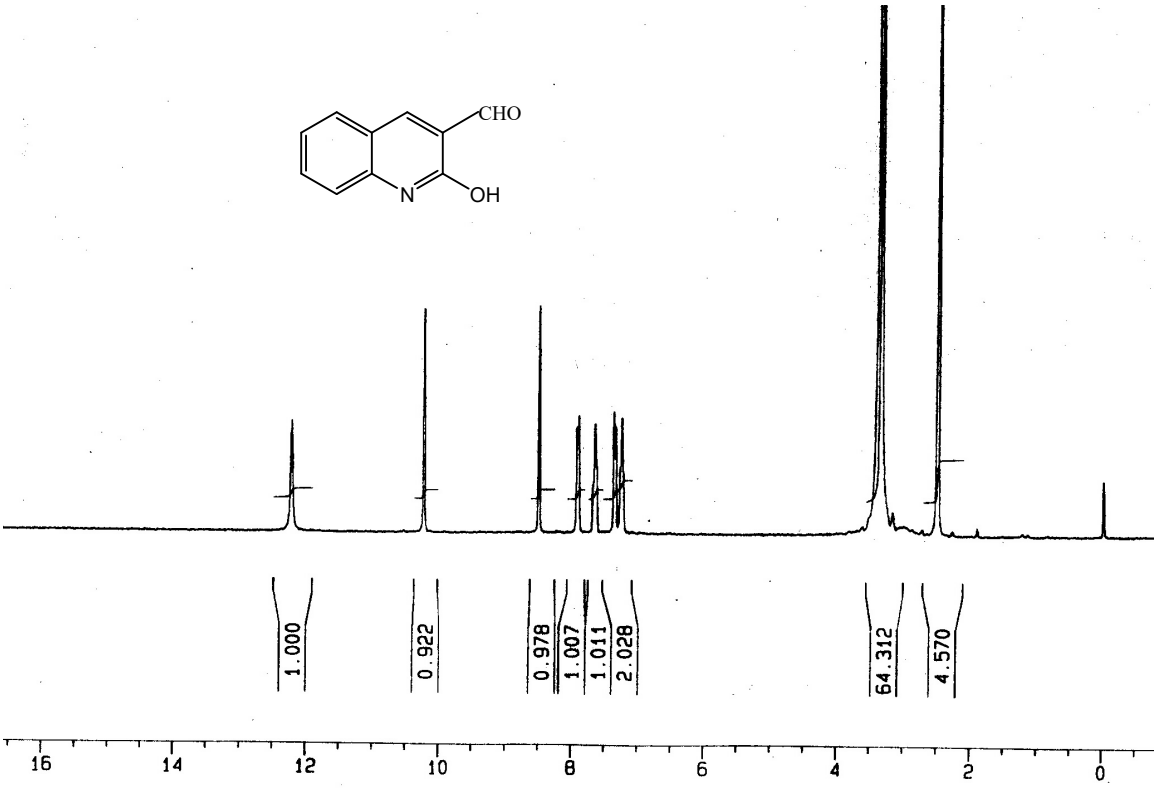


Fig8-a: ^{1}H NMR Spectrum of 2-hydroxy3-formylquinoline

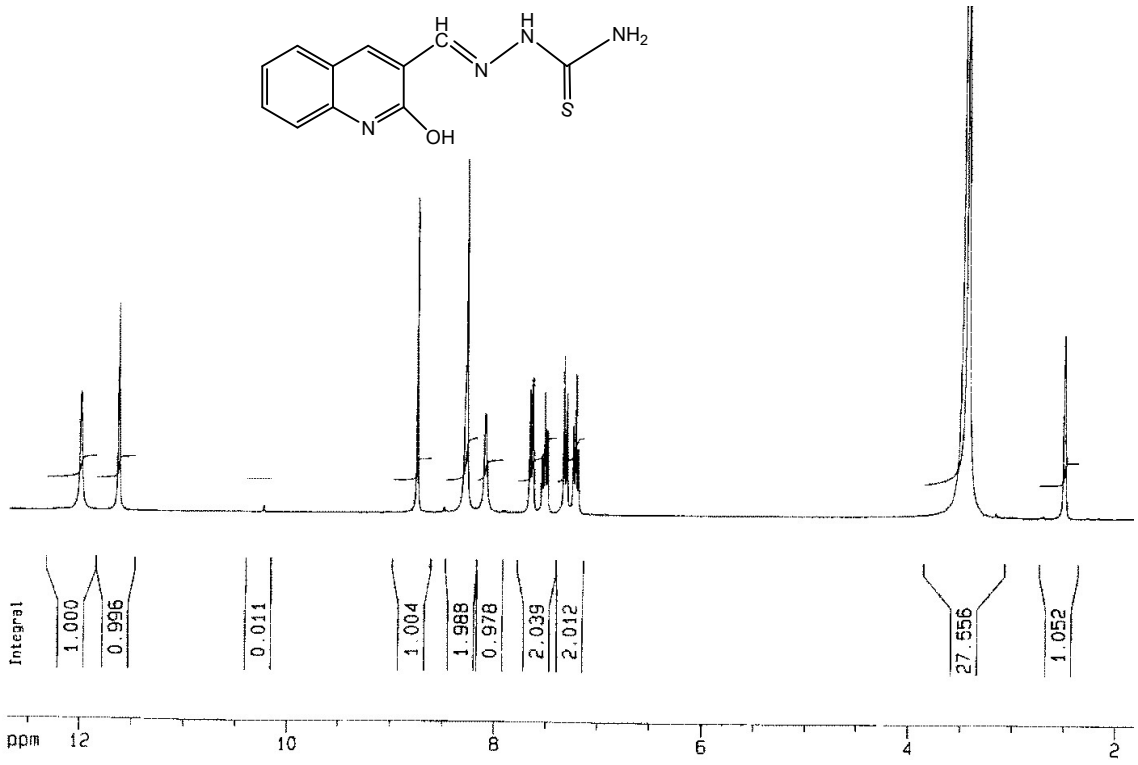


Fig8-b: ^{1}H NMR Spectrum of Ligand H_2L^1

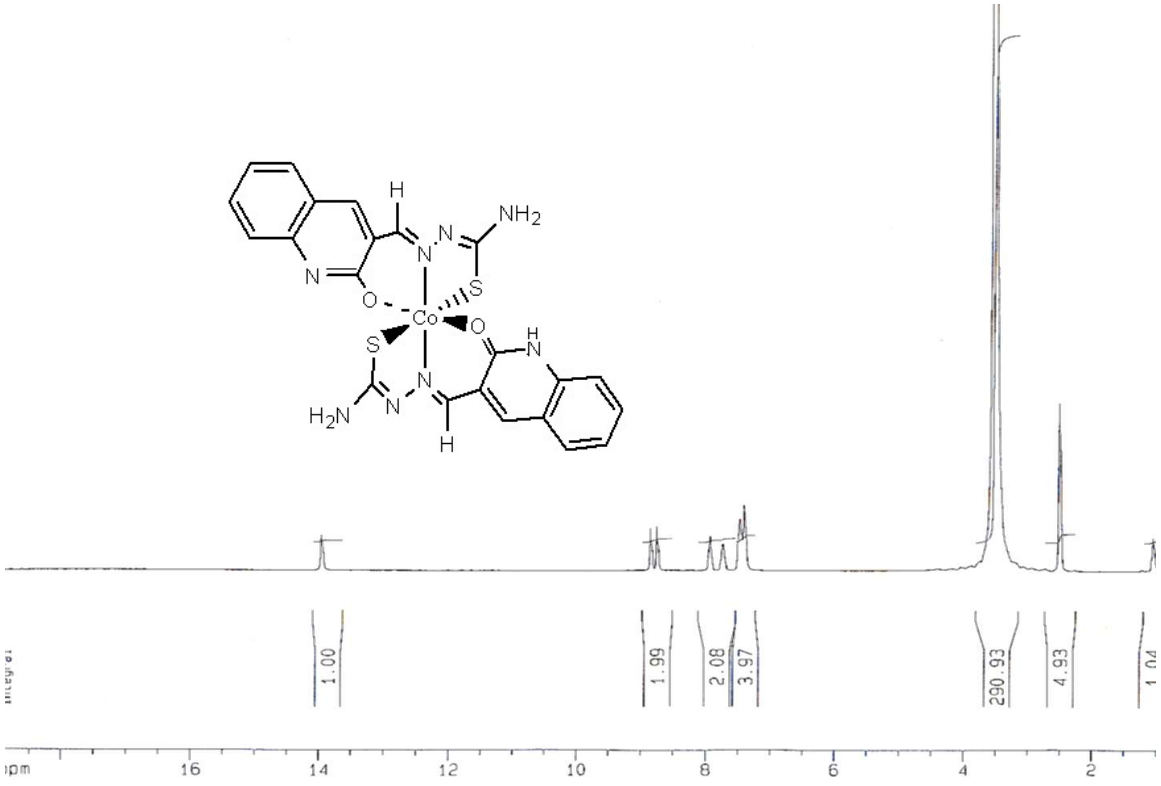


Fig8-c: ^{1}H NMR Spectrum of Complex CoL^1

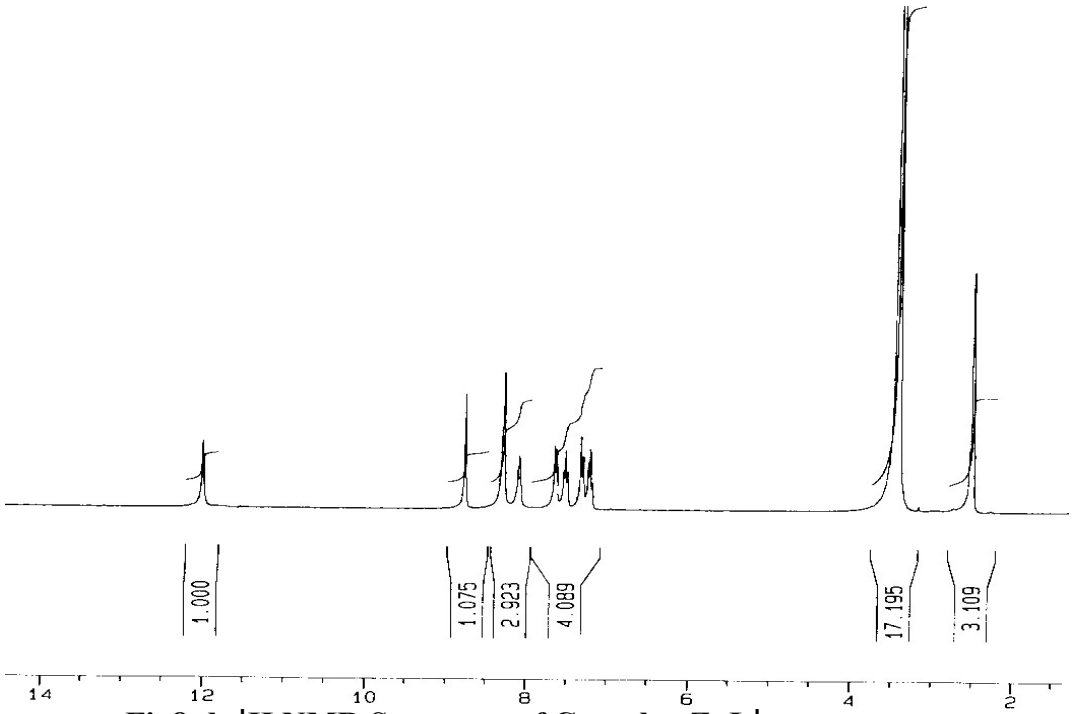


Fig8-d: ^{1}H NMR Spectrum of Complex ZnL^{1}

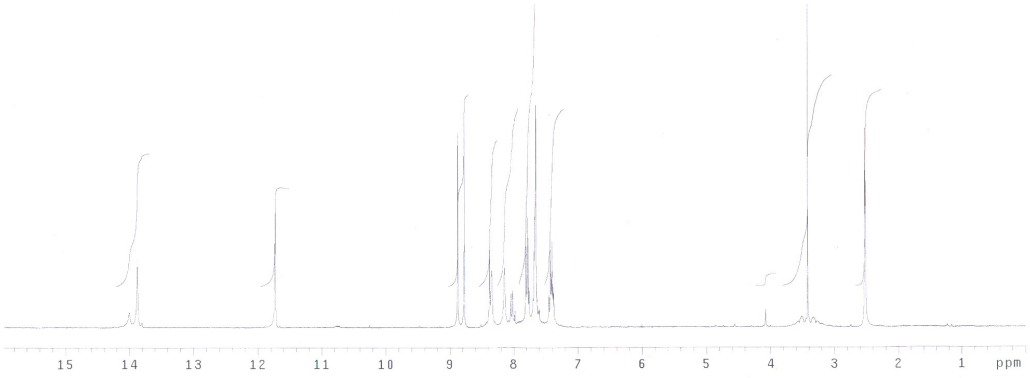


Fig8-e: ^{1}HNMR spectrum of H_2L^2

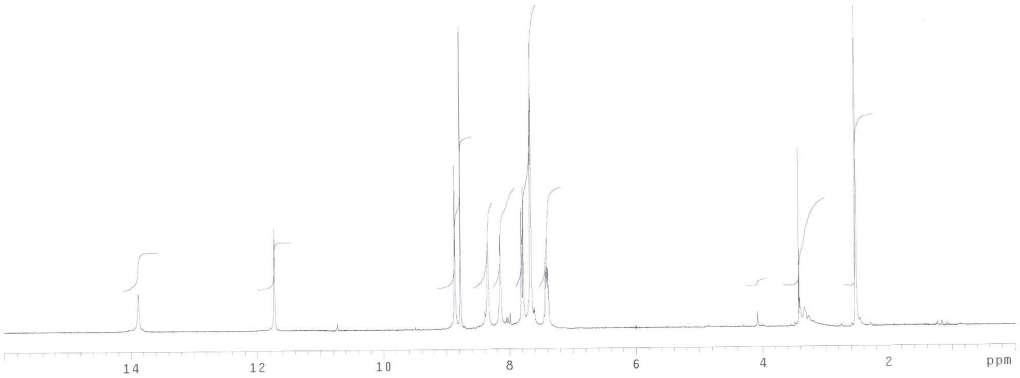


Fig8-f: ^{1}HNMR spectrum of ZnL^2

Comp	*Ar-H*	**-HC=N**	**Quinoline OH**	**Hydrazine NH**	*-NH_2*	**Quin. NH**
HFQ	7.26-8.51	**CHO**10.2	12.23*	__	__	__
H_2L^1	7.19-8.09	8.75	12.00*	11.63*	8.27	__
CoL^1	7.40-8.85	8.85	--	--	7.93	13.96*
ZnL^1	7.19-8.09	8.76	--	11.62*	8.27	__
H_2L^2	7.35-8.20	8.77	--	11.73*	8.34	13.87
ZnL^2	7.38-8.14	8.78	--	11.72*	8.34	13.88

Table- 4

- * Disappeared on D_2O exchange
- -- Disappeared on complex formation

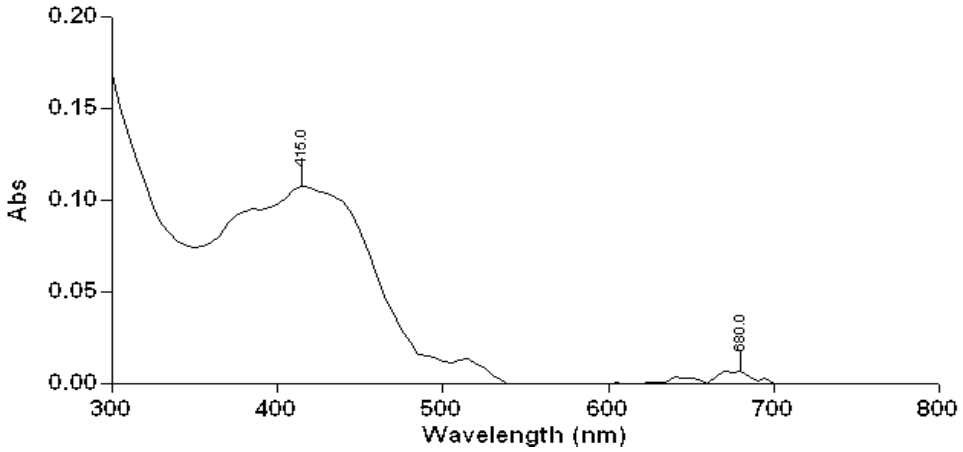
The fact that the chemical shifts of the azomethine protons change not in an assessable size is caused by the back-donation of the azomethine system for coordination. Since the □ electrons of the azomethine group are not affected, the chemical environment of the proton is not changed.

Thus in ZnL^1, azomethine –N and quinoline –O (deprotonated -OH) are utilized in coordination bond to metal atom.

Electronic spectral studies

The electronic spectra of the ligand and its complexes are recorded in Dimeyhylsulphoxide and data are summarized in **Table-5.** The representative spectra are shown in the **Fig-9.**

Both the ligands exhibit UV-Visible absorption bands around 220 and 240 – 260 nm. The intense band around 260 nm is assigned to intra ligand $\pi \rightarrow \pi^*$ transition. This band is almost unchanged in the spectra of complexes. The ligand also shows a broad band at 385-420 nm with a shoulder on low energy side, due to $n \rightarrow \pi^*$ transition associated with azomethine linkage. This band in all complexes have shown slight red shift due to the donation of lone pair of electron to the metal and hence the coordination of azomethine.



Electronic spectra of representative complex: CoL^1

Fig-9

Compound	λ_{max} (nm)	μ_{eff} (B.M.
H_2L^1	205, 243, 260, 385	----
H_2L^2	356, 371, 420	----
CoL^1	240, 380, 415, 515, 680, 915	Diamagnetic
CoL^2	280, 340, 366	1.84
CuL^1	225, 260, 370, 685, 770	1.56
CuL^2	308, 376	1.25
NiL^1	215, 252, 392, 676, 911	2.96
NiL^2	261, 330	2.90
ZnL^1	218, 225, 256, 390	Diamagnetic
ZnL^2	287, 367	Diamagnetic

Table-5. **Electronic spectra and magnetic moment data**

Octahedral Cobalt (III) complex

Cobalt (III) complexes are diamagnetic, hence Co(III) ion must have low spin d^6 configuration. Therefore, the right hand side of the cross-over region in the Tanabe-Sugano diagram should be considered for electronic transition. The strong field ground state electron configuration $(t_{2g})^6$ transforms as $^1A_{1g}$. Excitation of an electron to the e_g orbital yields the configuration $t_{2g}^5 e_g^1$ which spans $^3T_{1g} + {}^3T_{2g} + {}^1T_{1g} + {}^1T_{2g}$ with the spin-triplet states lying at lower energy than the singlets.

Two principal spin allowed absorption bands are to be expected corresponding to transitions from the $^1A_{1g}$ ground state to the $^1T_{1g}$ and $^1T_{2g}$ excited states. In addition, two weak bands assigned to the spin

forbidden singlet-triplet transitions may be observed at lower energies than the spin allowed transitions.

The energies of these transitions [74] are given by

$E\,[^1T_{1g,} \leftarrow {}^1A_{1g}] = 10\,Dq - C + 86\,B^2 / 10Dq$

$E\,[^1T_{2g,} \leftarrow {}^1A_{1g}] = 10\,Dq + 16B - C + 2\,B^2 / 10Dq$

$E\,[^3T_{1g,} \leftarrow {}^1A_{1g}] = 10\,Dq - 3C + 50\,B^2 / 10Dq$

$E\,[^3T_{2g,} \leftarrow {}^1A_{1g}] = 10\,Dq + 8B - 3C + 14\,B^2 / 10Dq$

In view of the large values of $10Dq$ and small values of B commonly observed in Co(III) system, the final $kB^2 / 10Dq$ factor may generally be ignored. When only spin allowed bands are observed, the customary assumption that $C = 4B$ may be used to solve the equations for B and $10\,Dq$. The intensities of the ligand field bands of octahedral Cobalt(III) complexes are comparatively high (□□□□10-10^2 l cm^{-1} mol^{-1}□□which may loosely be ascribed to the higher degree of covalency in these complexes relative to d^6 metal ions of oxidation state II. In D_{4h} symmetry, due to tetragonal ligand field the $^1T_{1g}$ state of the octahedral complex splits into $^1A_{2g}$ and ^1E_g states. While $^1T_{2g,}$ splits into ^1E_g and $^1B_{2g}$, is shown in **Fig-10.**

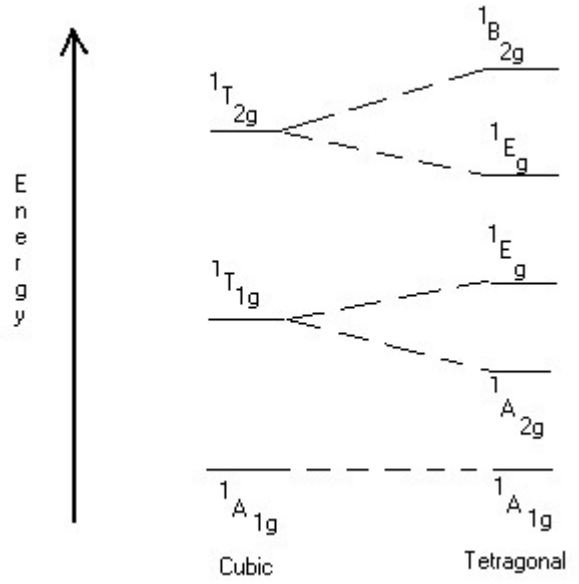


Fig-10: Cobalt(III) in Cubic and Tetragonal field

Electronic spectra of present cobalt (III) complex exhibits bands at 380, 420, 510, 675 and 915 nm, representative spectrum is shown in (**Fig**-**11**). First two bands show high molar extinction coefficient (□□>5000 *l* cm^{-1} mol^{-1}), and hence are assigned to ligand to metal charge transfer transitions.

Bands around 510, 675 and 915 nanometers because of their low □ □values (~ 100 *l* cm^{-1} mol^{-1}), are essentially d-d transitions and are intuitively assigned as $^1T_{2g} \leftarrow {}^1A_{1g}$, $(^1T_{1g})\ ^1E_{1g} \leftarrow {}^1A_{1g}$ and $^1A_{2g} \leftarrow {}^1A_{1g}$ respectively. Splitting of $^1T_{2g}$ level is not observed, which appears adjacent to the LMCT band and has gained the intensity. Low energy spin forbidden transitions to triplet "T" states are not observed. Because of the tetragonal distortion and merging of LMCT bands with d-d bands the 10*Dq* values could not be calculated [74].

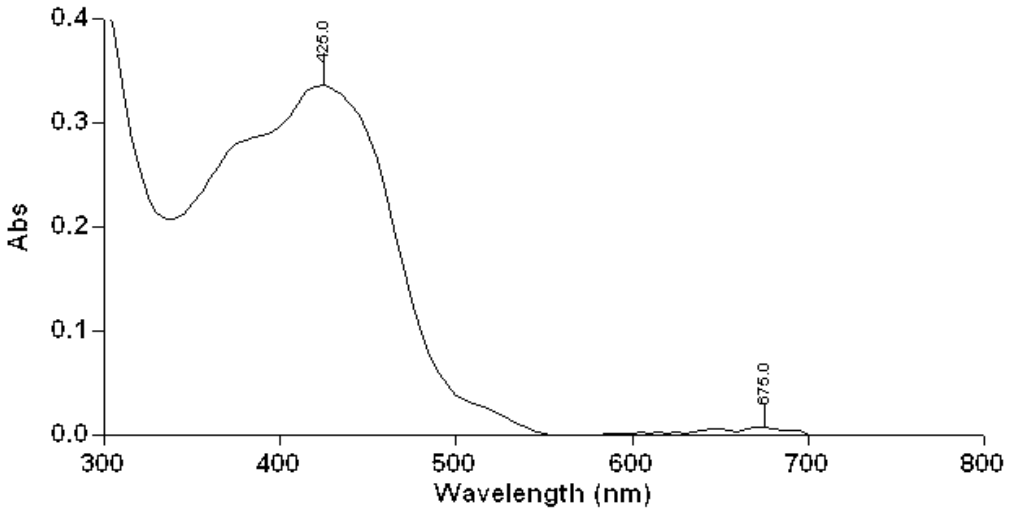


Fig 11: UV spectra of CoL^1

Octahedral Nickel (II) complexes:

The electronic spectra of nickel (II) (d^8) generally have three spin-allowed transitions in O_h symmetry. The assignments of those bands are as follows, $^3T_{2g} \leftarrow {}^3A_{2g}(\nu_1)$, $^3T_{1g} \leftarrow {}^3A_{2g}(\nu_2)$ and $^3T_{2g}(P) \leftarrow {}^3A_{2g}(\nu_3)$.

The electronic spectra of Ni(II) complexes exhibits the λ_{max} values at 297, 340,402The first two bands can be assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of the ligand. The third band around 402 nm is assigned to S$\rightarrow$ Ni(II) ligand to metal charge transfer transition (LMCT) with molar extinction coefficient around 15000 *l* cm^{-1} mol^{-1}. Because of the low solubility of Ni (II) complex d-d absorption bands cannot be observed and hence ligand field parameters such as *Dq,* B, v_2/ v_1 and LFSE are not calculated.

Copper (II) complex

The electronic spectra of copper (II) complexes exhibit the λ_{max} values at 260, 295 and 308 nm. The first two bands can be assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of the ligand. The third band around 368 nm is assigned to S→ Cu(II) ligand to metal charge transfer transition (LMCT) with molar extinction coefficient around 25000 *l* cm^{-1} mol^{-1}

Because of the Jahn–Teller distortion and the low symmetry of the environment around Cu(II) d^9, detailed interpretations of the spectra and magnetic properties are somewhat complicated [75].

In **Zinc (II)** complexes band in the region 390 – 394 nm with around 25000 *l* cm^{-1} mol^{-1} is accounted for ligand to metal charge transfer transition [76]. The other bands appeared around 260 nm and above are attributed to ligand bands.

EPR spectral studies

EPR is useful method to investigate geometry around the metal ions and to determine the ground state of electrons in metal ions. The fundamental principles of EPR are essentially same as those of NMR. In EPR a transition between two different electrons spin energy states occurs upon absorption of quantum radiation in the microwave region. The energy of the transition is given by,

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

Where ν = frequency of radiation

h = Plank's constant

g = Spectroscopic splitting factor

β = Bohr magneton

H = Magnetic field

The EPR instruments are operated in the region of 9000 MHz with the corresponding field intensity ~3000Gauss. Owing to the orbital moment contribution, the value of "*g*" will differ from 2.0027. The value of *g* in any arbitrary direction can be expressed as the resultant of the tensor component g_X, g_Y and g_Z corresponding to the direction of the X, Y and Z-axis. The average value (g_{av}) is given by the relation.

$g^2_{av} = 1/3 (g_X^2 + g_Y^2 + g_Z^2)$

The g_{II} and $g_{\perp}$ values are compared with resonance position of tetracyanoethylene (TCNE) radical. The g_{II} and $g_{\perp}$ values are calculated according to the procedure indicated by Peisach and Blumberg [77].

g_{II} or $g_{\perp} = g_{TCNE} \times H_{TCNE} / H$

($g_{TCNE} = 2.0027$)

$g_{av} = 1/3(g_{II} + 2g_{\perp})$

The EPR spectra are recorded for copper complexes in powder form and the results are given in the **Table-6** and the spectra are also presented. The present EPR study of copper(II) complexes of newly synthesized thiosemicarbazones is intended to

- To determine the geometry around Cu(II) ion
- To know the ground state of unpaired electron
- To investigate whether the EPR spectra show evidence of metal-metal interactions.

In axial symmetry the g values are related by the expression [78,79] $G= (g_{II}–2)/(g_{\perp} -2)$, which measures the exchange interaction between copper centers in the polycrystalline solid. According to Hathway [80-82], if the value of G is greater than four, the exchange interaction is negligible, where as when the value of G is less than four considerable exchange interaction is indicated in the solid complex.

On the basis of the relation between g_{II} and $g_{\perp}$, one can determine the ground state term for the unpaired electron on Cu(II) complex. For Cu(II) ion, its six coordinated compounds cannot achieve the highest symmetry O_h, because of the Jahn-Teller effect; it can only have D_{4h} or lower symmetry, if some other unsymmetrical factors exists. If the unpaired electron of Cu(II) occupies the $d_{x^2-y^2}$ orbital as the ground state, there would be elongated distortion of the electron density of Cu(II) ion and EPR spectra would show $g_{II} > g_{\perp}$. On the other hand if d_{Z^2} is the ground state, there would be compressed distortion and the EPR would show $g_{II} < g_{\perp}$.

For Cu(II) ion in a crystal field, the magnetic moment is calculated by the first approximation method [83] i.e. $\mu^2 = (3/4)\, g_{av}^2$.

Comp	***g_{II}**		***$g_{\perp}$**	**g_{av}**
	g_1	**g_2**	**g_3**	
CuL^1	*2.15		*2.05	2.12
CuL^2	2.21	2.10	2.03	2.11

Table-6

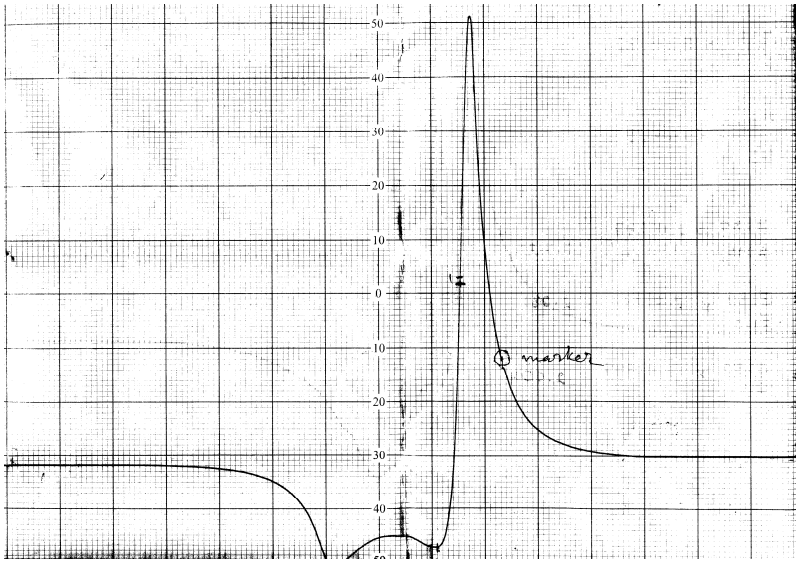


Fig.-12-a : EPR spectrum of complex: CuL^1

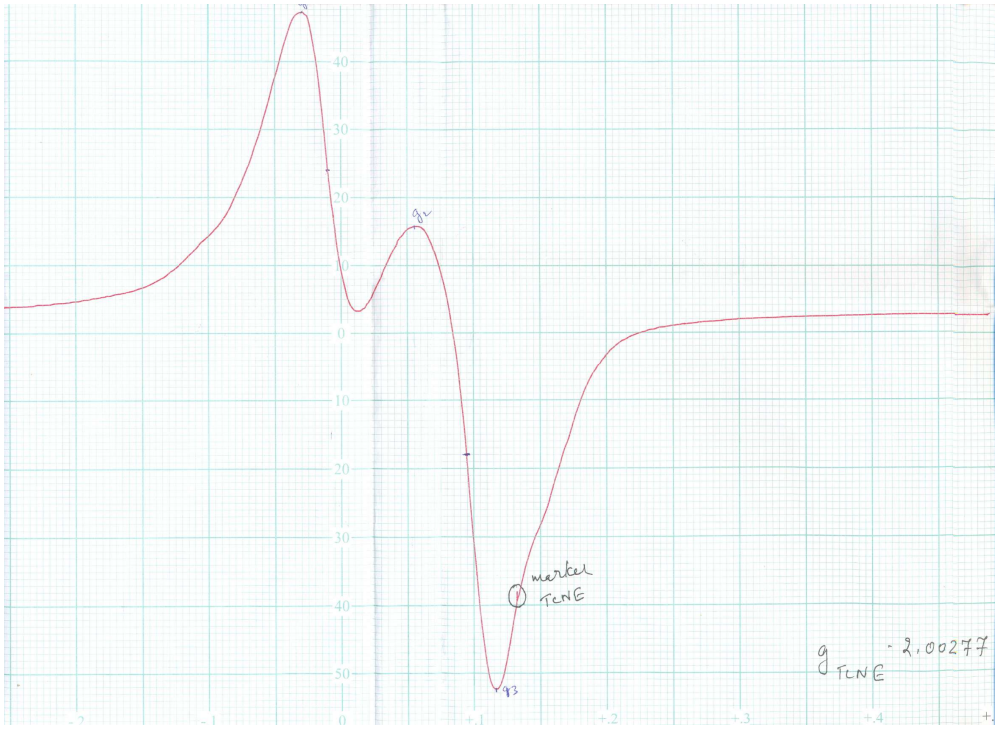


Fig.-12-b: EPR spectrum of complex: CuL^2

Kivelson and Nieman [84 59] have shown that g_{II} is moderately sensitive function of metal – ligand covalency. For ionic environment g_{II} is normally 2.3 or larger and for more covalent environments it is less than 2.3.

Complexes CuL^1 exhibits two g values and CuL^2 exhibits anisotropic signals giving three g values. These values indicate the distortion in the highest-fold rotation axis. From the observed g values of CuL^1, g_{II} (2.15) > $g_{\perp}$ (2.05) > g_e (2.00277), it is evident that the unpaired electron lies predominately in the $d_{x^2-y^2}$ orbital with the possibility of some d_{z^2} character being mixed with it because of low symmetry [80]. The g_{II} values i.e g_{II} (2.15) < 2.3 indicates the larger percentage of covalency [84] in metal – ligand bonds. The shape of the EPR line indicates that the present complex may have either a square pyramidal or elongated octahedral geometry.

The complex CuL^2 exhibited rhombic EPR spectrum [85] with g_1 = 2.21, g_2 = 2.10 and g_3 = 2.03. Three lines with different g values in this complex not only imply about the magnetic anisotropy but also indicate the rhombic distortion in complex.

The lowest g_{av} value of CuL^2 compared to CuL^1 complex is attributed to the two thiolate sulphur bridge present in this bimetallic rhombic complex. Similar comparison is made between S-bonded and O-bonded complexes by Seleem *et al* [59-61], They observed a decrease of 0.144 in g_{eff} values of the S-bonded complexes compared to the O-bonded complexes, and concluded that the EPR parameters are dependent on the coordinating atoms. This type of behavior has been observed for Schiff-base complexes [60,61] and is attributed to (a) higher covalency of Cu–S compared to Cu–O bonds and (b) higher spin–orbit coupling constants for S

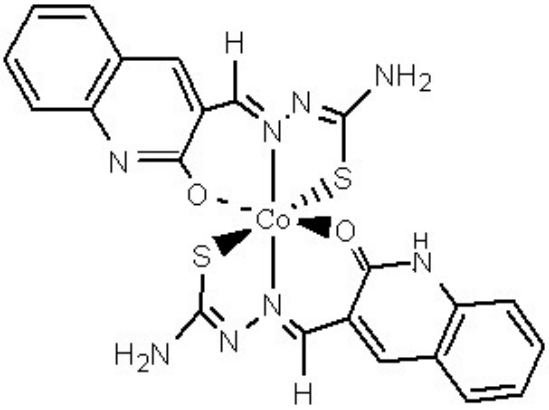
than for O. Both factors reduce the spin–orbit contribution of the Cu(II) ion to the g-tensor, decreasing the g-values [61]. Hence the bimetallic CuL^1 complex, which does not contain any sulphur coordination, shows slightly higher g_{av} value compared to CuL^2 that contains sulphur coordination.

From EPR study of above complexes, following conclusions were made.

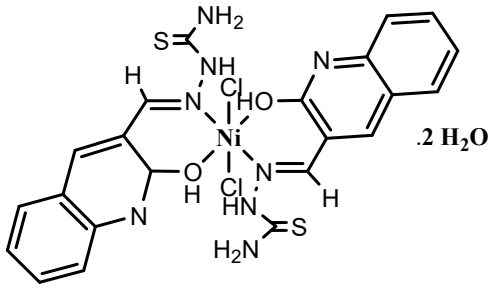
- The complex CuL^1 shows the axial distortion.(square pyramidal geometry).
- The complex CuL^2 exhibits rhombic geometry.

Conclusion:

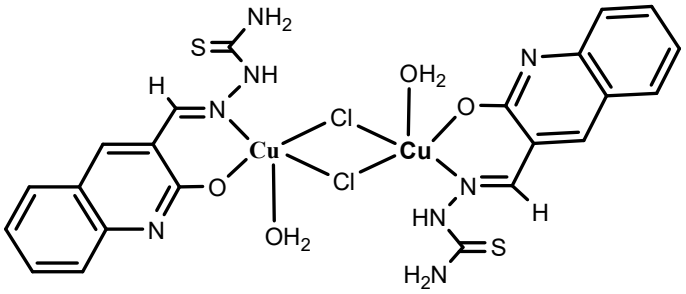
From the result of elemental analysis and various spectral studies, we have proposed octahedral geometry for all cobalt, nickel and zinc complexes. Binuclear CuL^1 complex contain two square pyramidal sites. Tentative structures for all these complexes are shown below.



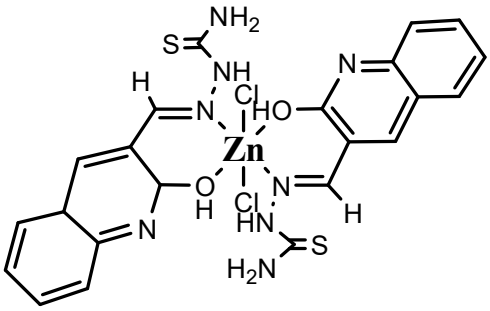
CoL^1: [Co (HL^{-1})(HL^{-2})]



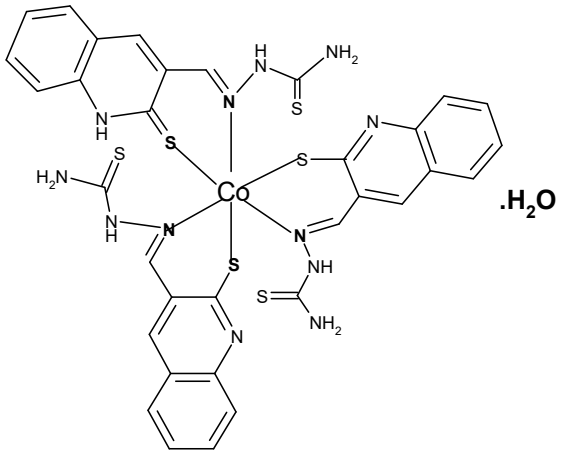
NiL^1: [Ni (H_2L^1)$_2$ Cl_2].2H_2O



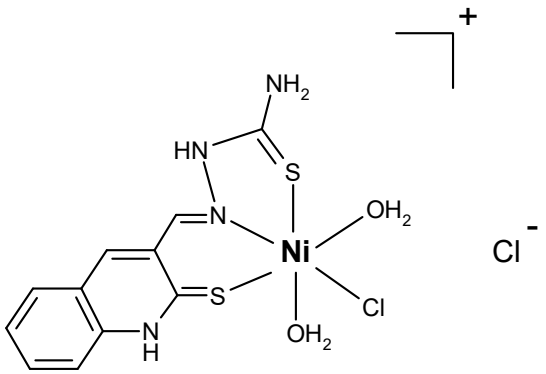
CuL^1 :$[Cu_2(HL^1)_2(H_2O)_2Cl_2].H_2$



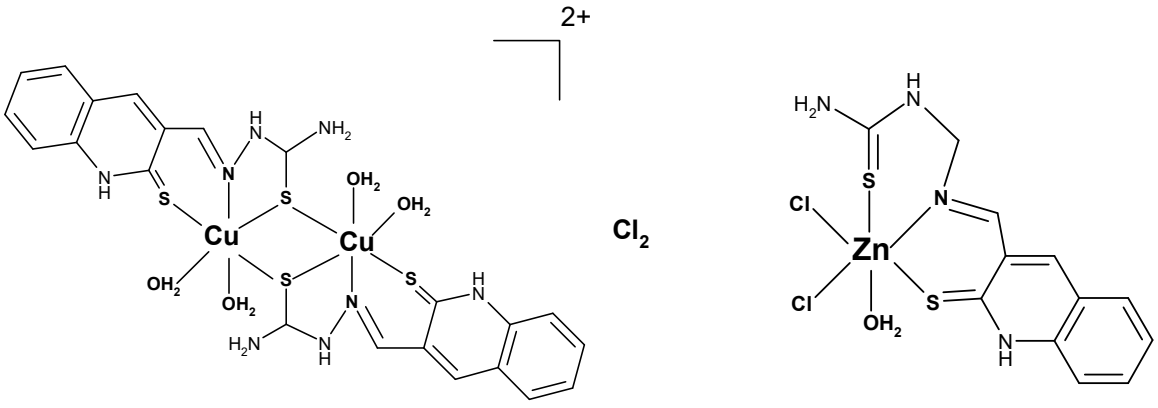
ZnL^1: $[Zn(H_2L^1)_2Cl_2]$



$[Co(H_2L^2)((HL^2)^{-1})_2].H2O$



$[Ni(H_2L^2)(H_2O)_2Cl]Cl$



$[Cu_2((HL^2)^{-1})_2(H_2O)_4]Cl_2$ $[Zn(H_2L^2)(H_2O)Cl_2]$

Thus from the present investigation of physico-chemical properties of 3d metal (II) complexes, derived from thiosemicarbazone ligand, it is observed that the coordination mode of ligand is of dibasic tridentate and monobasic tridentate in cobalt (III) complex and involves the utility of N(azomethine nitrogen), S(thiol) & O(quinone) coordination sites to yield six coordinated distorted octahedral complex(CoL^1). The mode of coordination in NiL^1 and ZnL^1complexes is of monobasic bidentate involving -N & -OH coordination sites to form distorted octahedral complexes. The ligand behaves as monobasic bidentate in CuL^1 complex utilizing azomethine –N and -O (deprotonated quinoline OH) resulting in the square pyramidal complex.

Where as in cobalt complex of L^2, the ligand behaves as neutral bidentate and monobasic bidentate utilizing azomethine –N, and thiolate –S for coordination, to yield mononuclear octahedral complex.

NiL^2 shows octahedral geometry involving neutral tridentate ligand coordinating through S, N, S donor atoms, it involves two water molecules and a chloride ion as coordinating sites leading to 1:1 ionic complex.

In di-nuclear CuL^2 complex, the ligand behaves as monobasic tridentate coordinating through S, N, S donor atoms where thiolate S acts as bridging donor site. There are two coordinated water molecules leading to distorted octahedral ionic complex with 2:2 ionic ratio.

The ligand in ZnL^2 complex acts as neutral tridentates utilizing thione-S, azomethine-N and thione-S of thiosemicarbazide part as donor atoms. There is one coordinated water molecule and two chloride ions to compensate the charge on the metal ion leading to neutral octahedral complex.

CHAPTER-IV

Antimicrobial activity studies:

Preparation of media:

Nutrient agar is selected for growing bacterial cultures and for demonstration of antimicrobial activity.

Preparation of plates by cup-bore method

Appropriate quantity of nutrient agar medium were poured into separate sterile Petri plates and allowed to solidify in the laminar air flow. After the perfect solidification of agar medium in the plate, 0.1 ml of bacterial suspension were poured and spread throughout the plate. While spreading special care was take to spread uniformly all over the plate. With the help of sterilized cork borer uniform wells were bored in agar dish in which known volumes of extracts were added and allowed to stand at room temperature for stabilization [86].

Incubation and microbial activity:

The bacterial plates were incubated at 37º C for 24 hours in bacteriological incubator. The antimicrobial activity is demonstrated by zone of inhibition surrounding the well containing the plant extracts.

Standard drugs:

“Streptomycin” is used as standard dug to compare the activity of extract. The potency of extract was studied by comparing the zones of inhibition with that of standard drug on two bacterial strains.

Micro organisms used for the present work:

Microorganisms used in the present study were from our college collection centre. Names of the microorganisms are as follows:

Escherichia coli

Escherichia coli is a Gram-negative, rod-shaped bacterium that is commonly found in the lower intestine of warm-blooded organisms. Most *E. coli* strains are harmless, but some serotypes can cause serious food poisoning in humans, and are occasionally responsible for product recalls. The harmless strains are part of the normal flora of the gut, and can benefit their hosts by producing vitamin K_2, and by preventing the establishment of pathogenic bacteria within the intestine.

Streptococci

The streptococci are facultative anaerobes which produce a small gray colony after 24 hour incubation at 35°C on sheep blood agar. Unlike the staphylococci, streptococcal colonies grown under anaerobic conditions are larger than those grown aerobically. Also, the streptococci are catalase-negative, while the staphylococci are not (see the discussion concerning weak positive catalase reactions exhibited by enterococci. Microscopically, Gram-positive cocci occurring in chains or pairs with individual cells being somewhat elongated can be presumed to be streptococci or enterococci, and the pneumococcus itself has a distinctive microscopic morphology occurring as lancet-shaped pairs.

Chaetomium

is a genus of fungi in theChaetomiaceae family. It is a dematiaceous (dark-walled) mold normally found in soil, air, and plant debris. As well as being a contaminant, *Chaetomium* spp. are also encountered as causative agents of infections in humans. A few cases of fatal deep infections due to *Chaetomium atrobrunneum* have been reported in the

immunocompromised host. Other clinical syndromes include brain abscess,peritonitis, and onychomycosis.

Chaetomium infections in humans can be avoided by proper hygiene habits. For instance, the Sohnian Kittah strain's presence can often be eliminated entirely with household products.

Sl No.	Compounds used	Media	Method	Standard used	Organisms used			Zone of inhibition
					Bacteria	Bacteria	Fungi	
1	L^2	Nutrient Agar	Bore method	Streptomycin	*Streptococcus sps*			No zone
						E. coli		No zone
							Chaetomium (fungi)	No zone
2	CoL^2	Nutrient Agar	Bore method	Streptomycin	*Streptococcus sps*			No zone
						E. coli		No zone
							Chaetomium	No zone
3	NiL^2	Nutrient Agar	Bore method	Streptomycin	*Streptococcus sps*			No zone
						E. coli		No zone
							Chaetomium (fungi)	No zone
4	CuL^2	Nutrient Agar	Bore method	Streptomycin	*Streptococcus sps*			No zone
						E. coli		3 mm
							Chaetomium (fungi)	6 mm
5	ZnL^2	Nutrient Agar	Bore method	Streptomycin	*Streptococcus sps*			No zone
						E. coli		No zone
							Chaetomium (fungi)	3 mm

Conclusion:

The Ligand H_2L^1 and all its complexes did not show any activity against the above microbes and fungus. The ligand L^2 and complexes CoL^2 & NiL^2 did not show any activity. However, CuL^2 found active against E. coli

and Chaetomium(fungi) where as the complex ZnL^2 shown activity against Chaetomium(fungi) only.

DNA Cleavage activity analysis

Methodology:

Culture media

Nutrient broth was used for the growth of the organism. The 50 ml media was prepared, autoclaved for 15 min at 121^0C, 15 lb pressure. The autoclaved media were inoculated with the seed culture and incubated at 37^0C for 24 h

Isolation of DNA

DNA was isolated using the procedure mentioned below (Sambrook et al., 1989)[87].

1. Centrifuge the fresh bacterial culture (1.5 ml) to obtain the pellet. Dissolve the pellet in 0.5 ml of lysis buffer (100 mM tris pH 8.0, 50 mM EDTA, 50 mM lysozyme)
2. Add 0.5 ml of saturated phenol and incubate at 55^0C for 10 min
3. Centrifuge at 10,000rpm for 10 min and to the supernatant add equal volume of Chloroform: isoamyl alcohol (24.:1) and $1/20^{th}$ volume of 3M sodium acetate (pH 4.8)
4. Centrifuge at 10,000rpm for 10 min and to the supernatant add 3 volumes of chilled absolute alcohol.
5. Separate the precipitated DNA by centrifugation. Dry the pellet and dissolve in Tris buffer (10 mM tris pH 8.0) and store in cool.

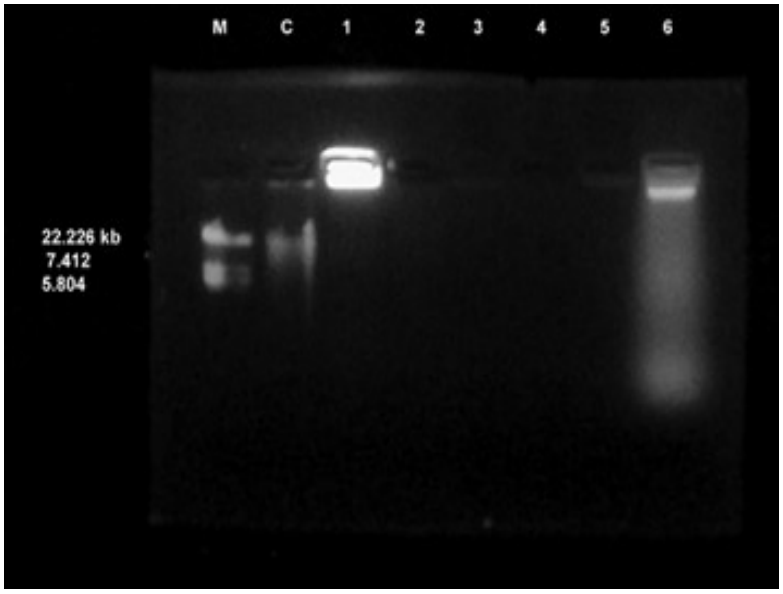
Treatment of DNA with the samples

The synthetic compounds were added separately to the DNA sample. The samples mixtures were incubated at 37ºC for 2 h

Agarose gel electrophoresis

Following the treatment of DNA samples, the electrophoresis of the samples were done according to the following procedure (Sambrook et al., 1989)[87].

1. Weigh 250mg of agarose and dissolve it in 25 ml of TAE buffer (4.84 g Tris base, pH 8.0, 0.5 M EDTA/1 ltr) by boiling.
2. When the gel attains ~55^{0}C, pour it into the gel cassette fitted with comb. Let the gel to solidify
3. Carefully remove the comb, place the gel in the electrophoresis chamber flooded with TAE buffer.
4. Load 20 µl of DNA sample (mixed with bromophenol blue dye @ 1:1 ratio), carefully into the wells, along with standard DNA marker and pass the constant 50 V of electricity for around 45 min
5. Remove the gel and carefully stain with ETBR solution (10 µg/ml) for 10-15 min and observe the bands under UV transilluminator.



Gel picture showing the DNA cleavage activity

[In the photograph M- Standard DNA molecular weight marker (λ DNA EcoRI digest, Banglore Genei, Bangalore),

C- Control *E. coli* DNA (untreated sample)

1-6 are L^2, CoL^2, NiL^2 (10 µg), NiL^2 (100 µg), CuL^2, ZnL^2]

Conclusion:

All the samples, except CuL^2 have shown complete cleavage of DNA. Partial cleavage of DNA was observed with ZnL^2.

Scope for future work

Metal complexes of thiosemicarbazide & quinoline moieties and their Schiff bases were found to have many biological activities including anti cancer properties as revealed by the literature review, hence there is scope for further investigation regarding biological activities of complexes we prepared.

The present work will be communicated for publication in reputed journals.

CHAPTER-V

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