Abstract

There are several ways for preparing Schiff bases. The most common way is the condensation reaction between amines and aldehydes.

The Schiff bases were prepared by the reaction of cyclohexylamine with piperonaldehyde and reaction of 2,4-dichloroaniline with salicylaldehyde with mole ratio 1:1 to prepare ligand [L_A] (Piperonaldehyde cyclohexylimine) and ligand [L_B] (Salicylidene-2,4-dichloroaniline) respectively.

Also the reaction of dithiooxamide with salicylaldehyde and reaction of o-phenylenediamine with salicylaldehyde with mole ratio 1:2 to prepare ligand [L_C] (bis salicylidene-dithiooxamide) and ligand [L_D] (bis salicylidene -o-phenylenediamine) respectively.

The prepared ligands were characterized by TLC technique, melting points measurement, F.T.IR and UV-Vis spectroscopy

The [L_A, L_B, L_C and L_D] have been used as ligands to prepare a number of transition metal complexes, which include [Cu (II), Co (II) and Rh (III)] ions.

The preparation of complexes of [Cu(II), Co(II) and Rh(III)] with [L_A] and complexes of [Cu(II), Co(II) and Rh(III)] with [L_B] were done with mole ratio 1:2 (metal : ligand)

While the preparation of complexes of [Cu (II), Co (II) and Rh (III)] with [L_C] and complexes of [Cu(II), Co(II) and Rh(III)] with [L_D] were done in mole ratio 1:1 (metal : ligand)

The metal complexes of the prepared ligands have been obtained in solid state. They were characterized by F.T.IR, UV-Vis spectroscopy, metal analysis spectrophotometer, conductivity and magnetic susceptibility measurements.

According to the result of the above measurements, the following formula for new complexes were suggested

1) The structural formula of complexes of Cu(II), Co(II) and Rh(III) ions with [L_A] were as follows:

$[Cu_2(L_A)_4(NO_3)_2]\ (NO_3)_2\ .6H_2O$

$[Co(L_A)_2(ONO_2)_2\ (H_2O)_2].2H_2O$

$[Rh(L_A)_2(Cl)_2(H_2O)_2]\ Cl.3H_2O$

2) The structural formula of complexes of Cu(II), Co(II) and Rh(III) ions with [L_B] were as follows:

$[Cu(L_B)_2(H_2O)_2]$

$[Co(L_B)_2(H_2O)_2].3H_2O$

$[Rh_2(L_B)_4(Cl)_2].4H_2O$

3) The structural formula of complexes of Cu(II), Co(II) and Rh(III) ions with [L_C] were as follows:

$[CuL_C(H_2O)_2].2H_2O$

$[CoL_C(H_2O)_2].6H_2O$

$[RhL_C(H_2O)Cl].4H_2O$

4) The structural formula of complexes of Cu(II), Co(II) and Rh(III) ions with [L_D] were as follows:

$[CuL_D(H_2O)_2]$

$[CoL_D(H_2O)_2].6H_2O$

$[Rh_2(L_D)_2(Cl)_2].3H_2O$

Different bonding and structural behavior were related during the study of coordination chemistry of the different new complexes. The **Racah** and other ligand field parameters which illustrate the bonding nature between metal ion and donor atoms of the ligand were calculated for Co (II) and Rh (III) complexes using (Tanabe-Sugano) diagram.

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تحضير ودراسة معقدات الكوبلت(II)، النحاس(II) والروديوم(III) مع مزيج من الليكندات

Chapter one

Introduction

(1-1) The basics of coordination complexes:-

A coordination compound, or complex, is formed when a Lewis base (ligand) is attached to a Lewis acid (acceptor) by means of a"lone-pair"of electrons where the ligand is composed of a number of atoms; the one which is directly attached to the acceptor is called the "donor atom".

Ligands are most conveniently classified according to the number of donor atoms which they contain and are known as uni-, bi-, ter-, quadri-, quinqi-, and sexa-dentate. Unidentate ligands may be simple monatomic ions, or polyatomic ions or molecules which contain a donor atom. When formation of complexes, differing numbers of ligands (coordination numbers) can associate with a central transition metal ion and the resulting complexes can assume any of several possible geometric configurations (1).

The more important factors determining the most favorable coordination number for a particular metal and ligand are summarized below.

If electrostatic forces are dominating the attraction between the metal and the ligands should exceed the destabilizing repulsions between the ligands, the attraction is proportional to the product of the charges on the metal and the ligand whereas the repulsions are proportional to the square of the ligand charge.

The concept of the coordinate bond as an interaction between a cation and anion or molecule possessing a lone pair of electrons can be accepted before specifying nature of the interaction indeed; it is now evident that in different complexes the bond can span the whole range from electrostatic to covalent character (2).

One of the earliest correlations was the Irving-Williams series of stability (3). For a given ligand, the stability of complexes with dipositive metal ion follows the order $Ba^{+2} < Sr^{+2} < Ca^{+2} < Mg^{+2} < Mn^{+2} < Fe^{+2} < Co^{+2} < Ni^{+2} < Cu^{+2} > Zn^{+2}$

This order arises in part from decreases in size across the series and in part from the ligand field effects.

A second observation is that certain ligands form their most stable complexes with metal ions such as Ag^{+} , Hg^{+2} , and Pt^{+2} but other ligands seem to prefers ions such as Al^{+3} , Ti^{+4},and Co^{+3}. Ligands and metal ions were classified (4) as belonging to type (a) or (b) according to their preferential bonding. Class (a) metal ions include those of alkali metals, and lighter transition metal in higher oxidation states such as Ti^{+4}, Cr^{+3}, and hydrogen ion, H^{+}.

Class (b) metal ions include those of heaver transition metals, and those in lower oxidation states such as Cu^{+}, Ag^{+}, Hg^{+}, Hg^{+2}, Pd^{+2} and Pt^{+2} (5).

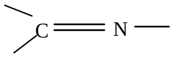
The increase of the positive charge on the central transition metal ion strengthens the metal-ligand bonds.

The metal ion prefer to bind with atoms of high electron density such as N^{-3}, O^{-2}, P^{-3}, S^{-2} and C^{-4}

The ligand should have certain characteristic properties to make it convenient to form stable complex with transition metal ions. The size, geometrical shape, number and geometrical arrangement of ligand donor atoms play the important role in stability of the resultant complex (6).

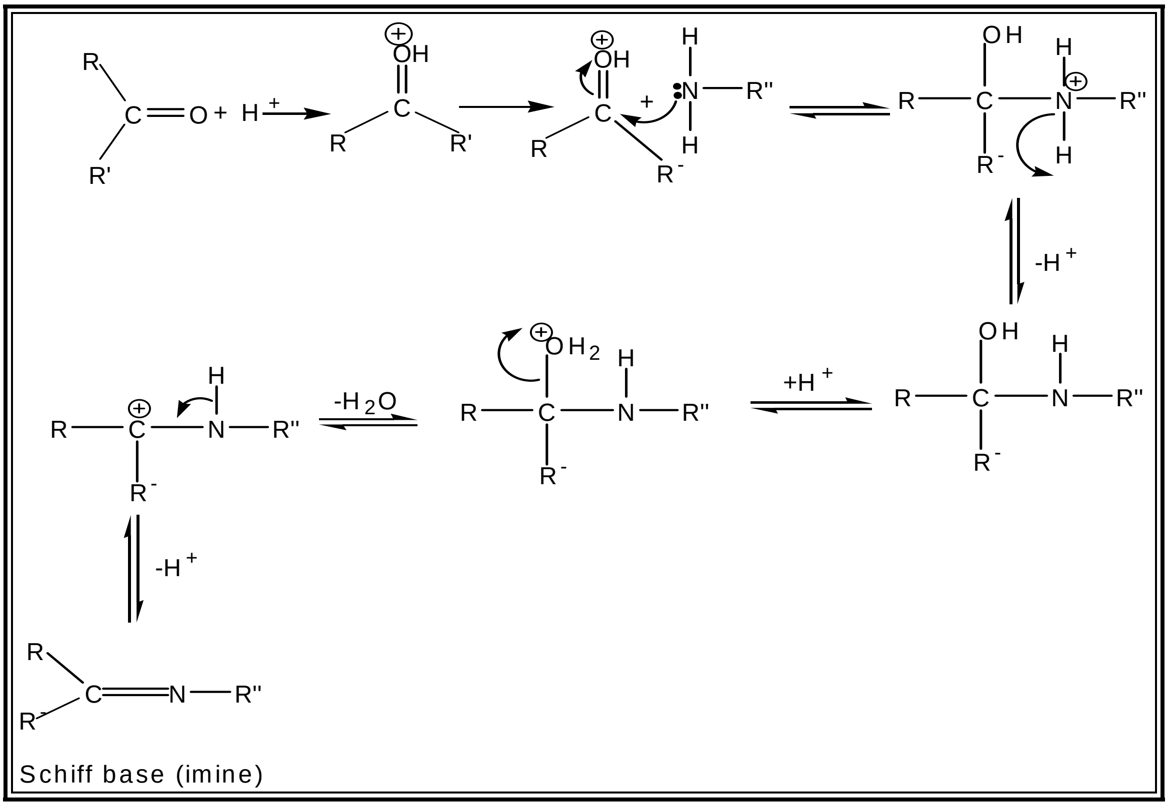
Metals centers, begin positively charged, are favored to bind to negatively charged biomolecules, the constituents of proteins and nucleic acid offer excellent ligands for binding to metals ions (7).

(1-2) Schiff bases:-

The term "Schiff bases" was firstly used to define those organic compounds which contain the functional groups(), these Schiff bases have several names; anils, azomethines, benzanils and benzylideneaniline (8) , these compounds were firstly prepared by Schiff in (1864) (9), from a simple condensation reaction of aldehydes or ketones with primary amines and for this reason, these imines were called Schiff bases.

Schiff bases are rapidly decomposed in aqueous solution of acidic media, but are they stable in aqueous solution of basic media (10).

The addition of proton to the carbonyl group yields the conjugated acid in which the carbon of the carbonyl group is more electrophilic, thus facilitating the attack of the amine on the carbonyl group. The added acid will enhance elimination of water molecule to give the final product Schiff bases. The general mechanism of the Schiff base (11) shown in Scheme (1-1).



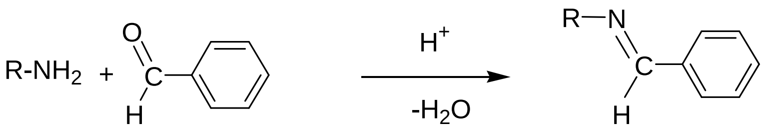
Scheme (1-1): Mechanism of Schiff base

These bases can also be prepared by refluxing of equimolar quantities of aldehyde or ketone with amine without solvent or by slow melting for 10 minutes and then isolating and purifying the product by recrystallization or sublimation under reduced pressure (12).

(1-3)Preparation of Schiff bases:

Schiff bases prepared by several ways.

1-Reaction of primary aliphatic or aromatic amines with carbonyl group of the aldehyde or ketone to give imines or Schiff bases the speed of reaction increases by added few drops of glacial acetic acid as catalyst (10).



--- (1-1)

R=(CH_3-, CH_3CH_2-, C_6H_5-, $CH_3C_6H_4$-, 2-Cl-C_6H_4-, 2-Br-C_6H_4-, 2-I-C_6H_4-, 2,6-$(CH_3)_2C_6H_3$-, 3-Cl-C_6H_4-, 3-Br-C_6H_4-)

The stability of the final product depends on the nature of the aldehyde and the amine. It can be concluded that stable Schiff bases may be prepared from the following types of compounds (13), as shown in Figure (1-1)

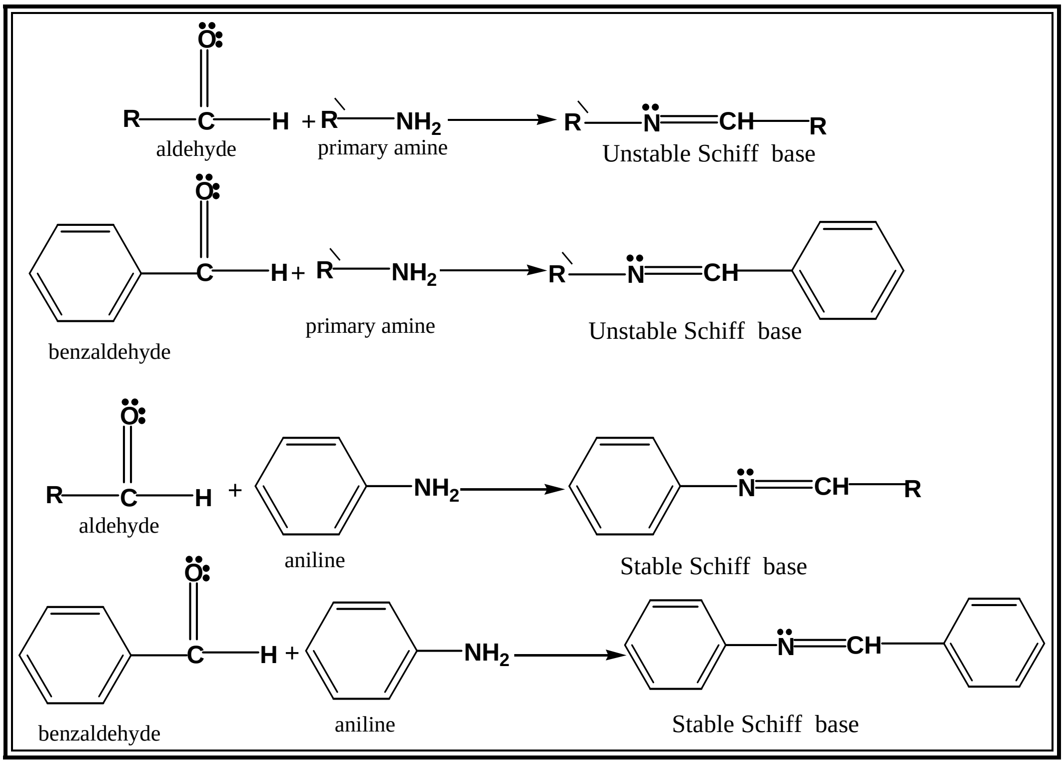
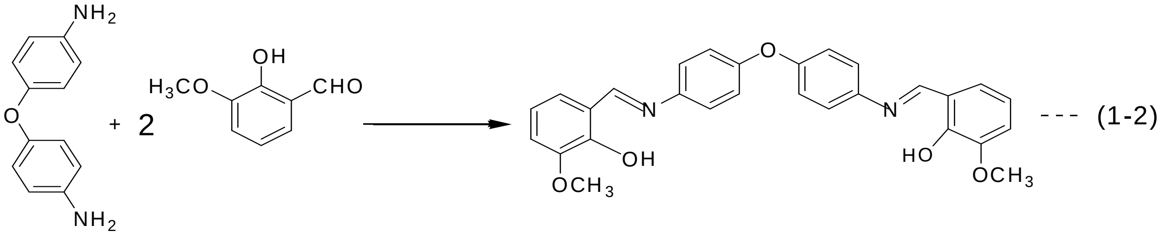
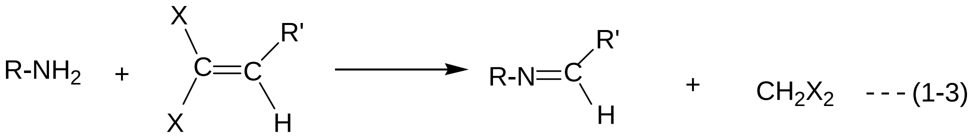


Figure (1-1): Condensation between aldehyde and amine

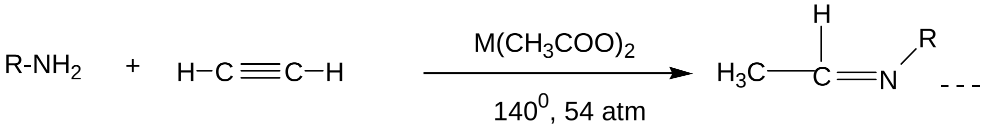
Or reaction of aldehyde or ketone with diamino compounds (14) :



2-Reation of primary amines with dihalide alkene (15):



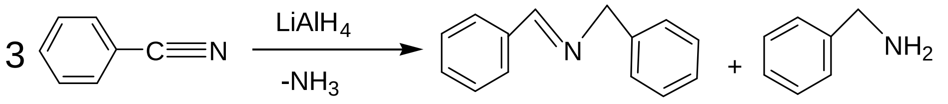
3-Reaction of primary amines with acetylenes in cadmium or zinc acetate (16):



- - - (1-4)

M^{II} = Zn, Cd

4-Redaction of nitriles by (Lithium Aluminum Hydride) ($LiAlH_4$) (17)



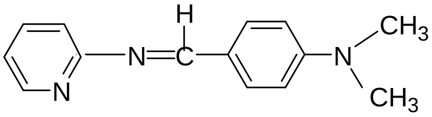
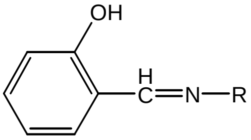
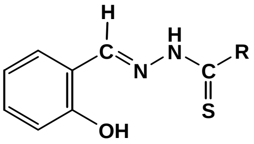
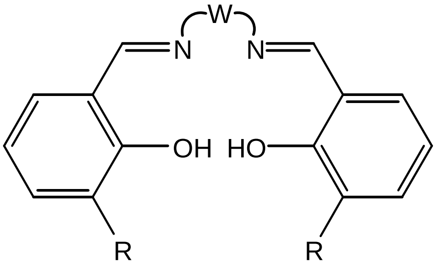
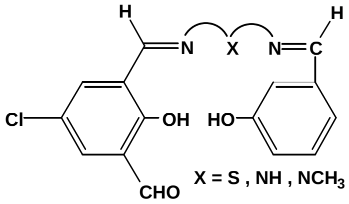
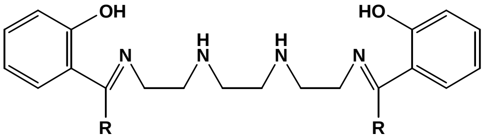
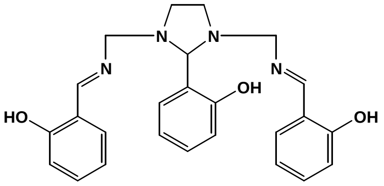
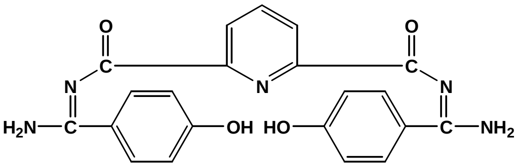
- - - (1-5)

(1-4) Classification of Schiff bases :-

Schiff bases can be classified according to the number of coordinating sites, type of bonding, type of donor atom (rather than azomethin nitrogen), number of donated electron pairs and other method of ligand classification.

Of these methods the one which depend on the coordination site is considered to be the most important. Table (1-1) shows examples of Schiff bases classified according to this method.

Table (1-1): Some Schiff bases with different donor atoms

Compound	Donor atoms	Type of donor	Ref
	N	Monodentate	**18**
 R = ph , 2-MeC_6H_4 , 3-C_6H_4 4-MeC_6H_4		Bidentate	**18**
	NSO	Tridentate	**19**
 R = H , OMe W= $(CH_2)_2$, $(CHMeCH_2)$, $(CH_2)_4$	ONNO	Quadridentate	**18**
 X = S , NH , NCH_3	NNNOO, NNOOS	Pentadentate	**20**
	NNNNOO	Hexadentate	**21**
	NNNNOOO	Heptadentate	**22**
	NNNNNOOOO	Nanodentate	**23**

(1-5) Complexation of ligands with metal ions:-

In 1968 Harris and Sinn(24) were prepared Cu(II) complexes which appears in Figure (1-2).

These complexes have been characterized by the magnetic susceptibility measurements, I.R and U.V spectroscopy methods, the proposed chemical structure for these complexes were square planar with distorted towards the tetrahedral structure.

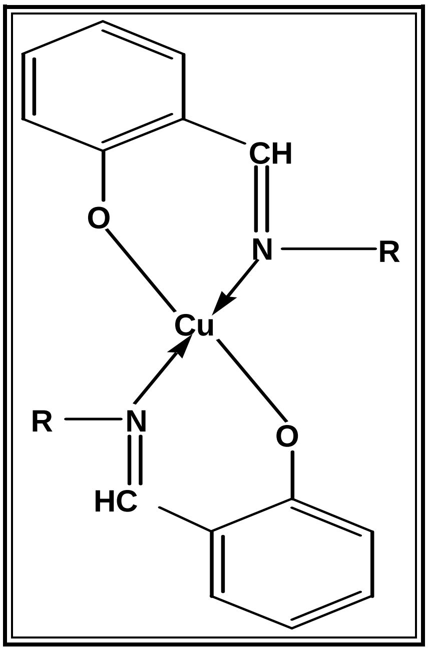
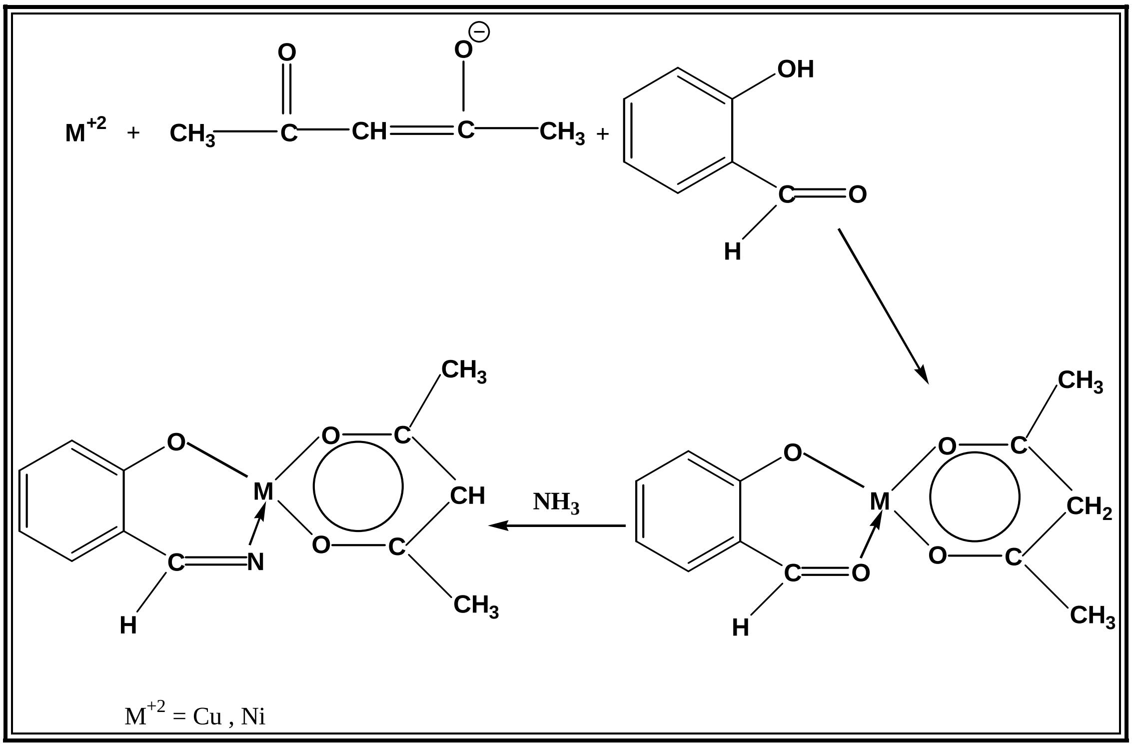


Figure (1-2): Complex of Cu (II) ion with alkyl salicyldehyde

Where:

R= Methyl, Ethyl, n-propyl, n-butyl, n-hexyl, n-octyl, isobutyl, isopropyl, Cyclohexyl, t-butyl and phenyl.

In (1975) U. Doraswarmy and Bhattacharya (25) were prepared complexes of Ni (II) and Cu (II), through react them with acetyl acetone and salicyldehyde, and after that the complexes were reacted with aqueous solution of (NH_3) to prepared (MML^-) complex. The proposed structure for these complexes were square planer, the reaction for the complex is shown in Figure (1-3).



M^{+2} = Cu , Ni

Figure (1-3): Complex of (MML^-) with Cu (II) and Ni (II) ions.

In 1998 Pavel Kopel and co-worker (26) were synthesized binuclear Fe (III) complexes with combination of Schiff bases N,N`- bis (salicylidene) ethylenediamine (salen $H_2$) or N,N`- bis (salicylidene) o- phenylenediamine (saloph) with 6- methyl-2,4-pyridine dicarboxylic acid (mdicarpy H_2) or 3,5- pyrazole dicarboxylic acid (pyrdica H_2), have been characterized using elemental analysis, I.R spectroscopy, conductivity measurements and variable temperatures magneto chemical measurements. The proposed structures of two of them are depicted in Figures (1-4) and (1-5).

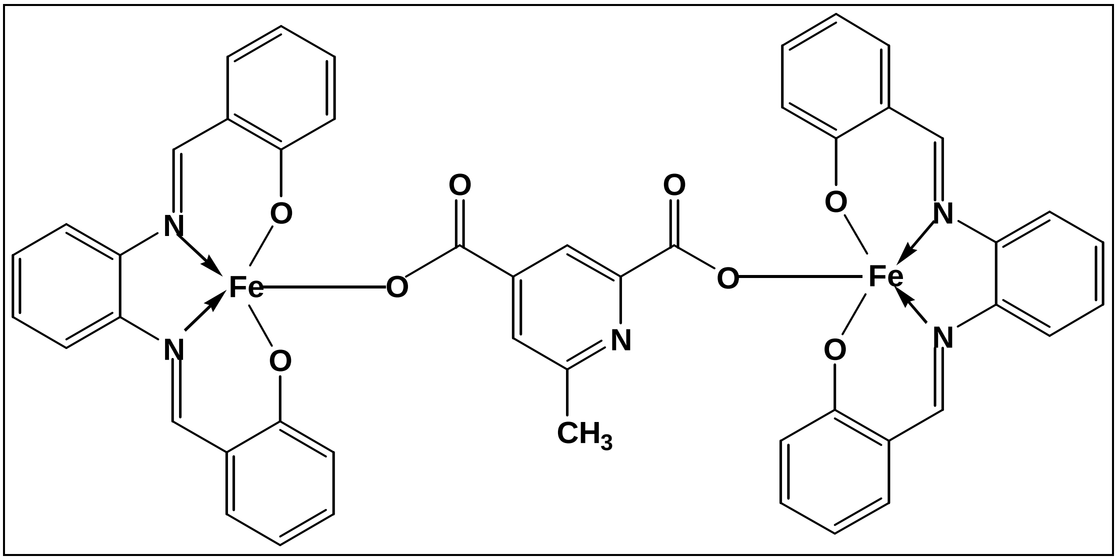


Figure (1-4): Proposed structure of [{Fe(saloph)}$_2$(mdicarpy)]

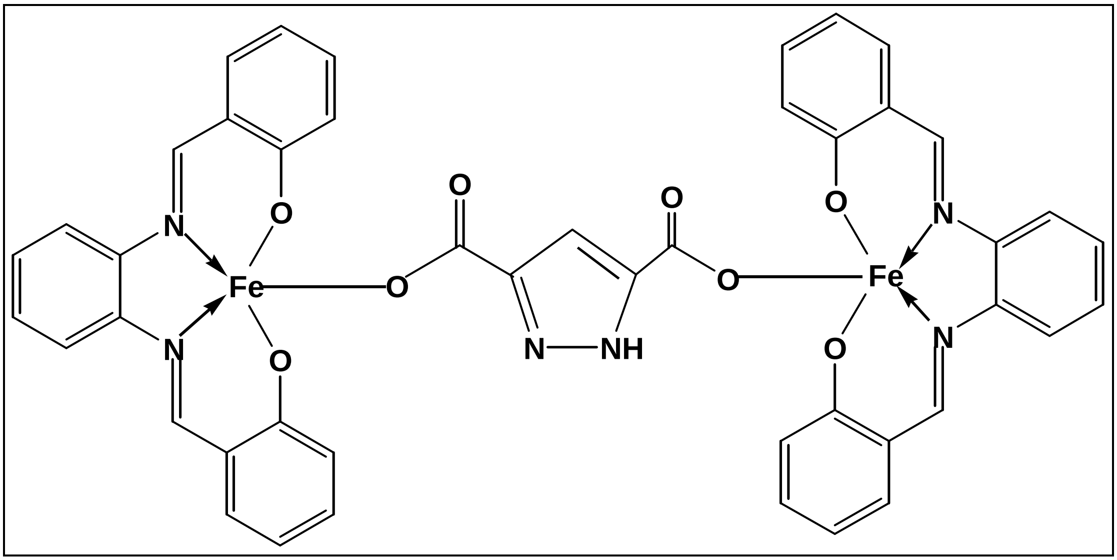


Figure (1-5): Proposed structure of [{Fe(saloph)}$_2$(pyrdica)]

In 1999 Antony F. Marinovich and co-workers (27) were reported the crystal structure of N,N-1,2-phenylene-bis (Salicylideneiminato) Copper (II). The complexes have been characterized by x-ray structural analysis. Two crystallographically distinct but similar molecules are found in the asymmetric unit. The copper atoms of the two molecules both exhibit distorted square planar coordination geometry with two Nitrogen and two Oxygen donor atoms.

In (2000) A. Z. El-Sonbatai and co-worker (28) were prepared several new coordination compounds of copper (II), nickel (II), cobalt (II), manganese (II), iron (II), tin (II), mercury (II), dioxouranium (VI) and iron (III) with Schiff base derived from 7-forml-8-hydroxyquinoline(oxine) and 2-aminophenol(H_2L^1) or 2-aminopyridine(HL^2), these ligands are shown in Figure (1-6), and its complexes are shown in Figure (1-7). The ligand and the complexes have been characterized by elemental analysis, IR, UV, ^{1}H-NMR and ^{13}C-NMR spectra, with magnetic susceptibility measurements.

Chemical properties of quinoline and its derivatives are of interest due to their biological activity (29), coordination capacity (30) and their use as metal extracting agents (31).

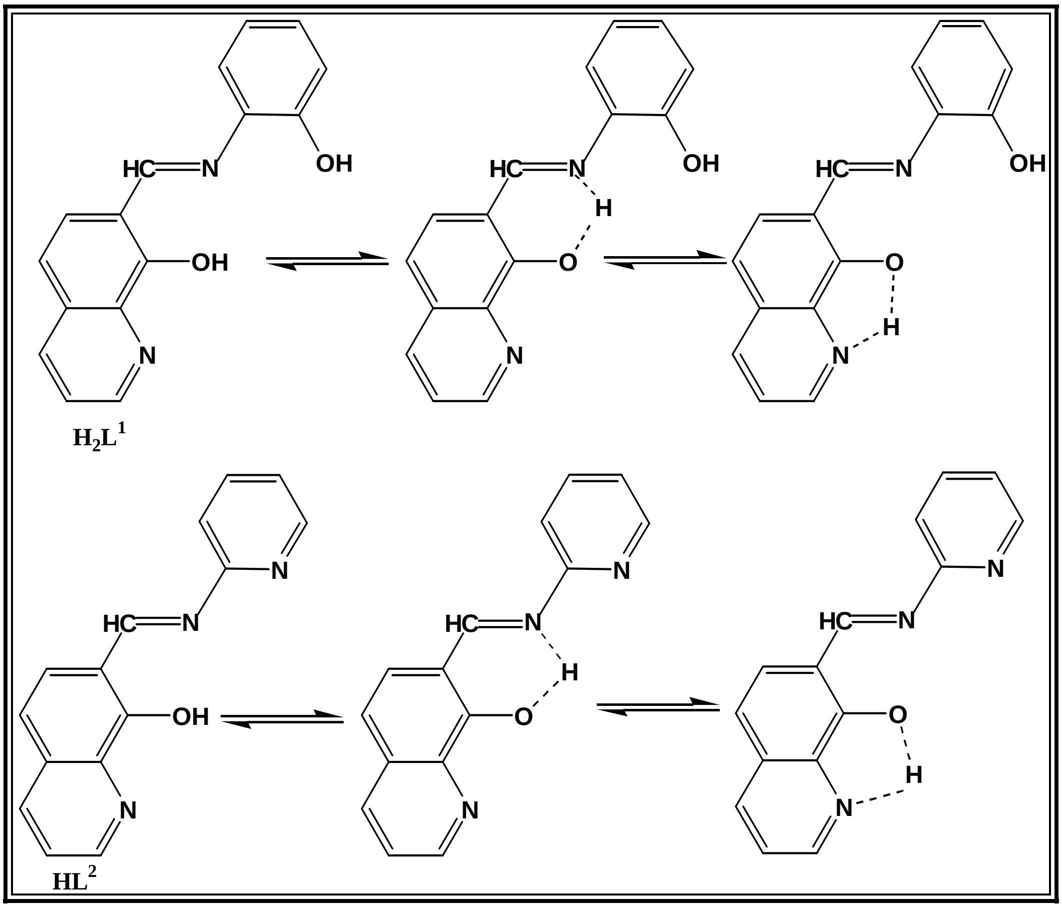
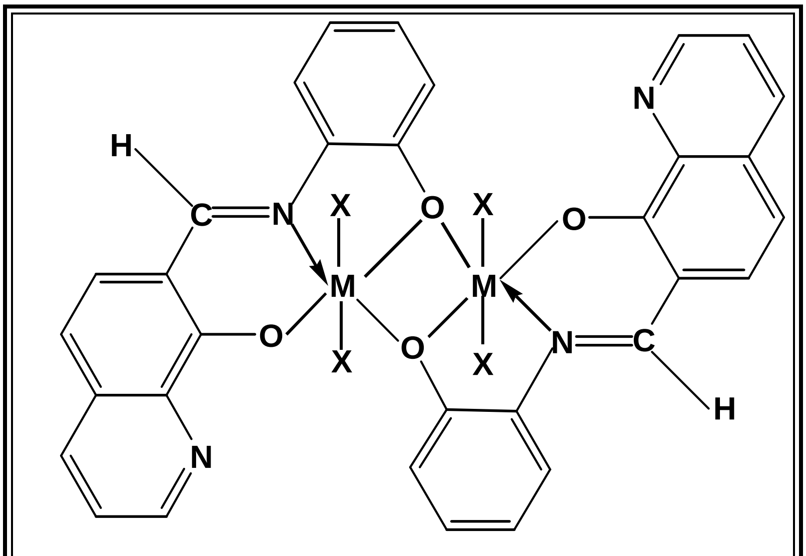


Figure (1-6): (H_2L^1), (HL^2) ligands



M= Cu or UO_2 X= nil

M=Mn, Fe, Co, Hg or Ni X= H_2O

Figure (1-7): Complexes of (H_2L^1), (HL^2)

In 2004 N. Raman and co-worker (32) synthesized new Schiff base chalets of Cu(II), Co(II), Ni(II) and Zn(II) derived from benzil-2,4-dinitrophenylhydrazone with aniline. These complexes are shown in Figure (1-8).

Micro analytical data, molar conductance, and magnetic susceptibility values have been obtained, and IR, ^{1}H NMR, ^{13}C NMR, and UV-Vis, spectral studies have been carried out to suggest tentative structures for the complexes. The Schiff base coordinates through its azomethine nitrogen's to the metal ion and acts as a neutral bidentate ligand. All the complexes exhibit octahedral geometry.

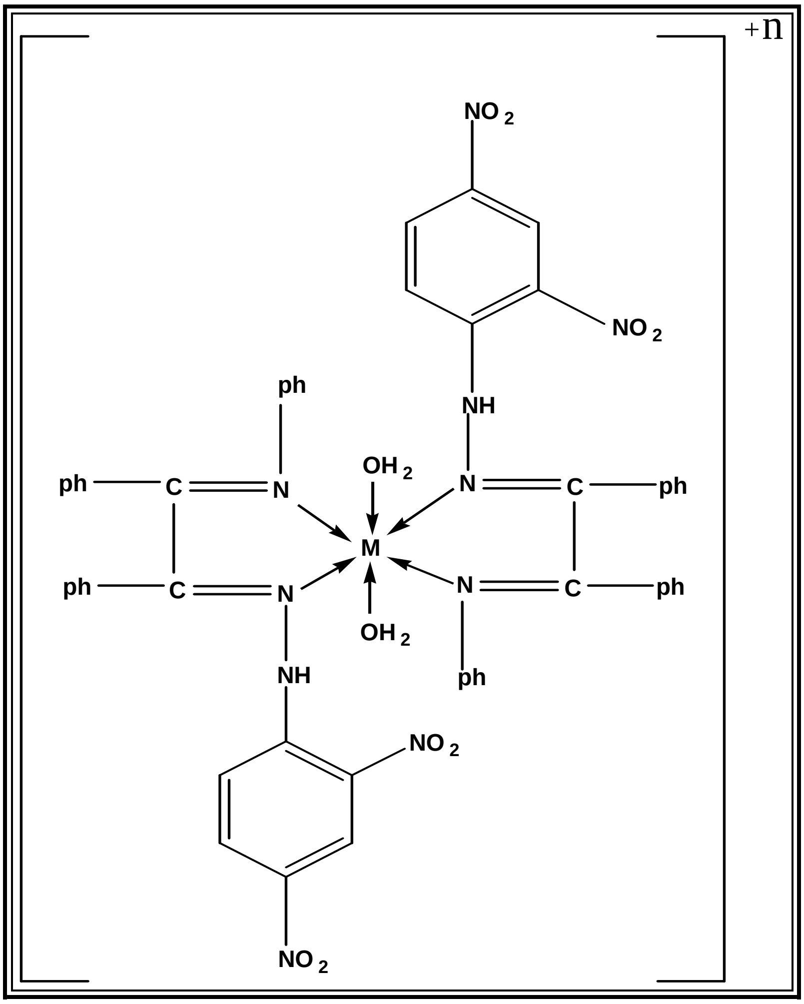


Figure (1-8): Proposed structure of Cu (II), Co (II), and Zn (II) and Ni (II) complexes

In 2005 J. Iqbal and co-workers (33) were reported a novel Schiff bases ligand derived from P-chloro aniline with salicylaldehyde and its transition metal complexes with Cu (II) and Co (II) have been synthesized. The reaction of this Schiff base ligand is shown in Figure (1- 9).

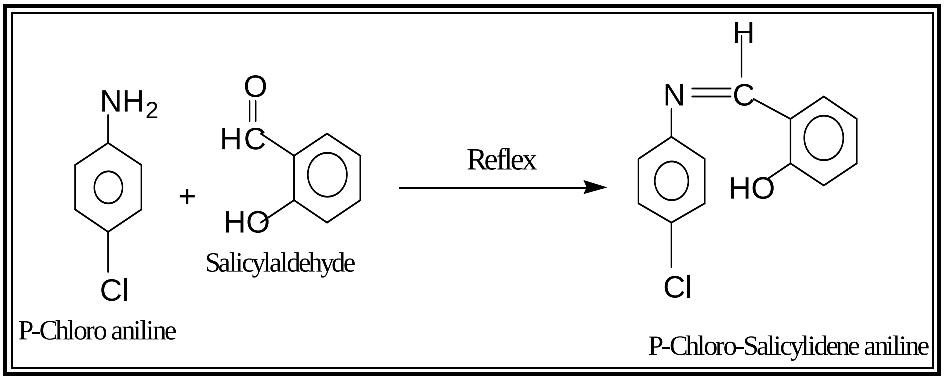


Figure (1-9): Preparation of Schiff base ligand

The proposed chemical structure for the transition metal complexes are shown in Figure (1-10)

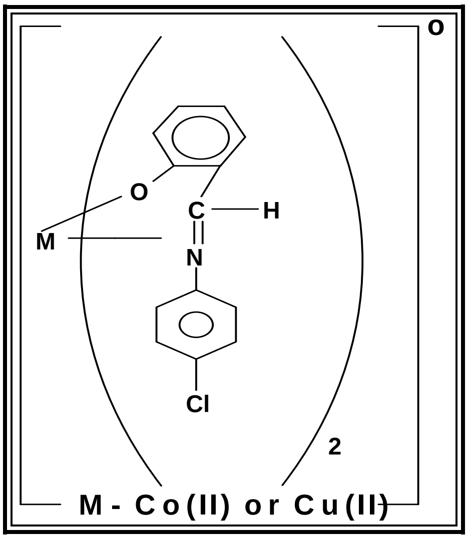


Figure (1-10): Complexes of chloro-salicylidene aniline with Co(II) and Cu(II).

These prepared complexes screened for antibacterial activity against several bacterial strains, namely *Escherichia coli*, *Staphylococcus aureus* and *Pseudomonas aeruginosa*. The metal complexes showed enhanced antibacterial activity compared to uncomplexed ligands.

In 2006 Tudor Rosu and co-worker (34) synthesized Cu(II) complexes derived from Schiff base ligands obtained by the condensation of 2-hydroxybenzaldehyde or terephtalic aldehyde with (4-amino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one) to form ligand (a) and (b) respectively . The structure of Schiff base ligands are shown in Figure (1-11).

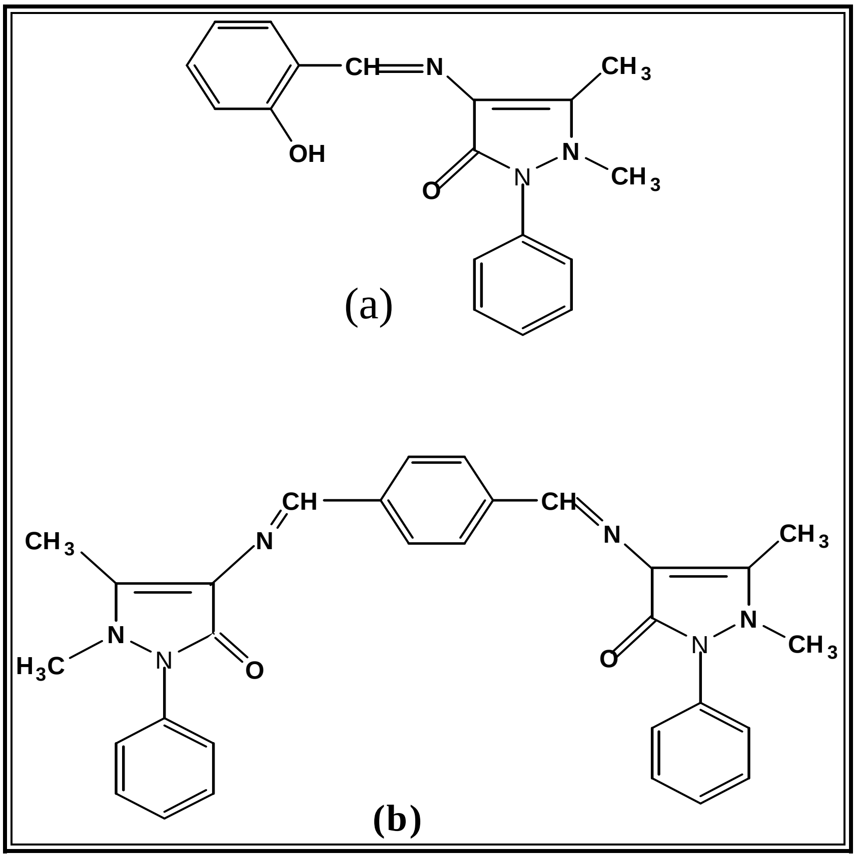
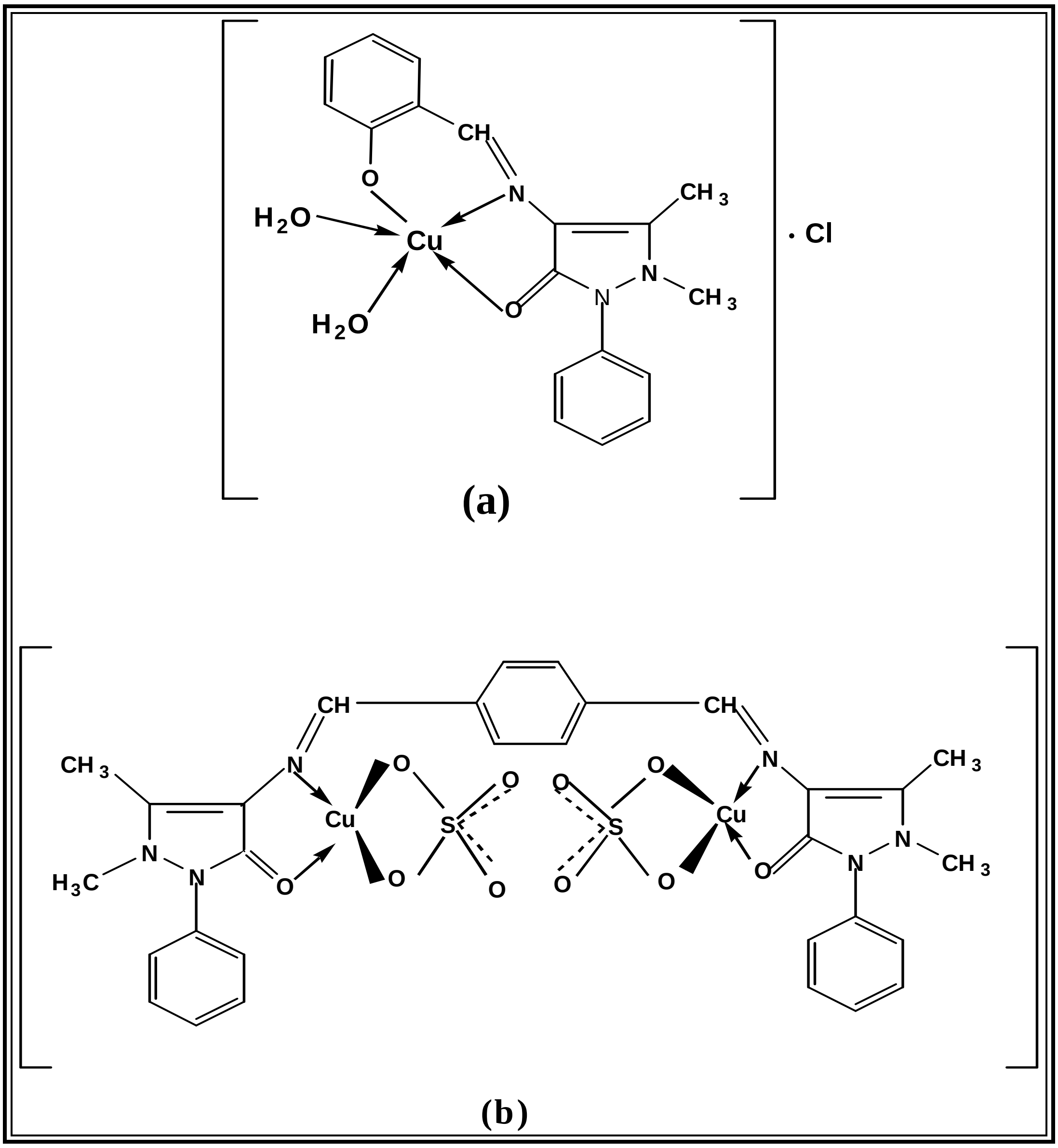


Figure (1-11): Chemical structure of Schiff bases ligand

The newly prepared compounds were characterized by ^{1}H-NMR, UV-VIS, IR and ESR spectroscopy which shown that the Cu^{2+} ion of the ligand (a) is form pentacoordinated complex with a C_2v symmetry, while in the ligand (b) the Cu^{2+} ion has a deformed tetrahedral geometry. Figure (1-12) shown the structures of complexes (**a**). $[Cu(C_{18}H_{16}N_3O_2)(H_2O)_2]Cl$ and (**b**). $[Cu_2\ (C_{30}H_{28}N_6O_2)\ (SO_4)_2]$.



(a)

(b)

Figure (1-12): Propos structures of Cu (II) complexes.

In 2007 A. A. Ahmed and co-worker (35) synthesis new Schiff base ligands by condensation of benzoylacetone and ethylenediamine, o-phenylenediamine and 1,6- hexanediamine to gives H_2L^1= $C_{22}H_{24}N_2O$, [N,N_ bis(benzoylacetone)ethylenediamine]; H_2L^2= $C_{26}H_{24}N_2O_2$ [N,N_(benzoylacetone)-ophenylenediamine] and H_2L^3= $C_{26}H_{32}N_2O_2$, [N,N_bis (benzoylacetone)-1,6- hexanediamine] respectively. The fourth ligand is formed by the condensation of benzoin and o-phenylenediamine H_2L^4=$C_{34}H_{28}N_2O_2$,[N,N_bis(Benzoin)-ophenylenediamine**].** The structure of Schiff base ligands are shown in Figure (1-13).

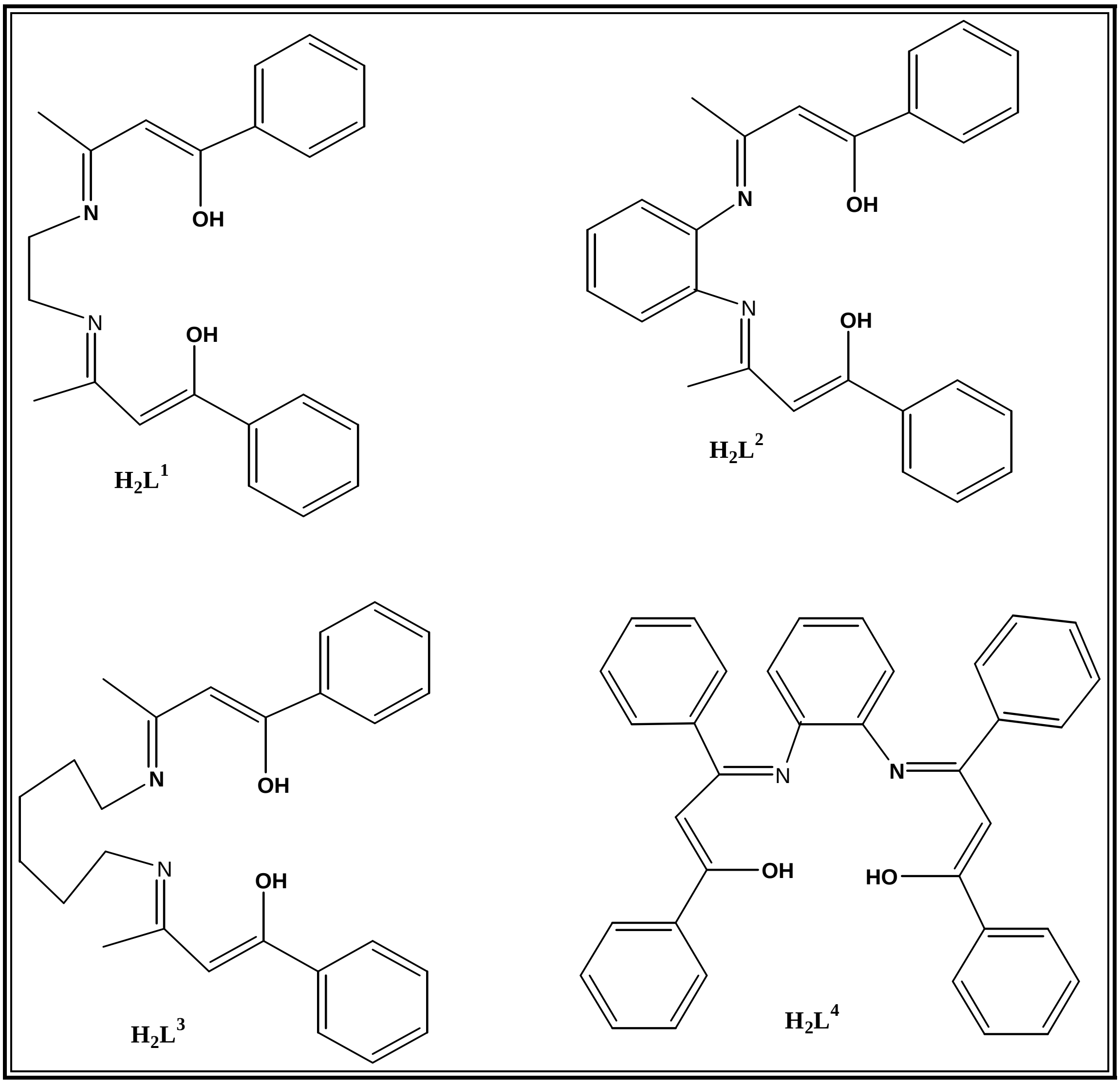


Figure (1-13): Chemical structure of imine ligand.

The Schiff base ligands and their complexes of divalent metals of Ni(II), Co(II) and Cu(II) were investigated in terms of synthesis, elemental analysis, molar conductivity, thermal analysis, infrared spectra, ultraviolet-visible and magnetic susceptibility measurements. Some of complexes structures are shown in Figure (1-14).

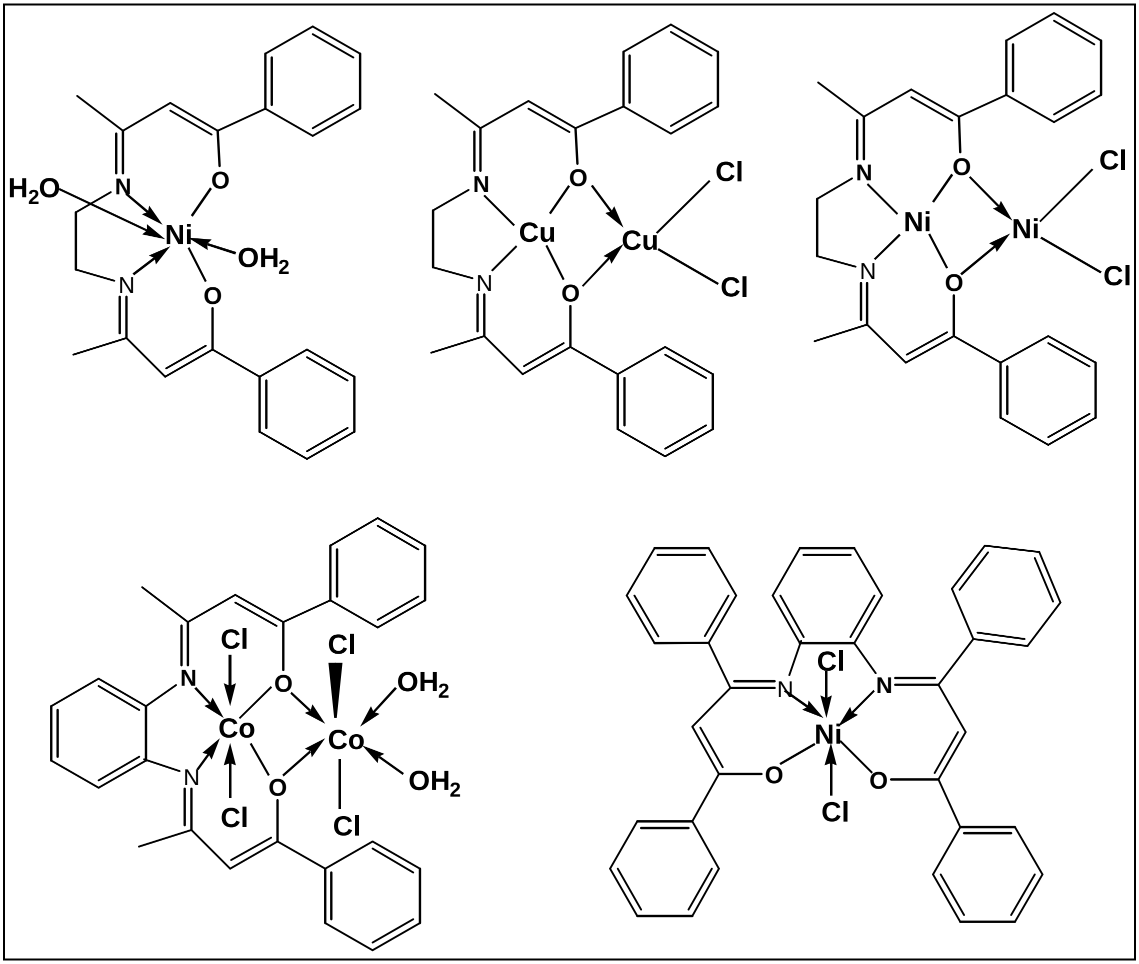


Figure (1-14): Schiff bases Complexes with Ni (II), Co (II) and Cu (II) ions

(1-6) Infrared spectra of Schiff bases and their metal complexes:-

* The IR spectra of Schiff bases have the characteristic ($-\overset{|}{C}=N-$) absorption band at (1610-1680 cm^{-1}) with weak or moderate intensity depending on their molecular structure, presences of aromatic or heterocyclic rings or other multiple bonds (36).

* A strong band at 1600 cm^{-1} was corresponded to υ($>C=N-$) (37) in some Schiff base derived from 2-furylglyoxal and 2-aminopyridine. This band was shifted to lower frequencies in the spectra of the Mn(II), Co(II), Ni(II) and Cu(II) complexes indicating the involvement of azomethine nitrogen in coordination(38).

* A strong band appeared around 1590 cm^{-1} is assigned to the ($>C=N-$) stretching of the free Schiff bases, bis (vanillin) ethylenediimine, bis (vanillin) propylenediimine, bis (vanillin) *o*-phenylenediimine, it was found in the region (1675-1665)cm^{-1} for their complexes with Cu(II)(39).

* Coordination of chain polymers of Schiff bases derived from *o*-animobenzoic acid and terephthalaldehyde shows ($>C=N-$) stretching at 1625cm^{-1} and is shifted to (1620-1612) cm^{-1} on complex formation, indicating the involvement of azomethine nitrogen in coordination (40).

* The IR spectrum give absorption band in the region (1640-1630) cm^{-1} for υ(C=N) of free tetraimine Schiff bases macrocycles derived from the condensation of 1,3-diamino-2-hydroxypropane with pyrrole-2,5-dicarbaldehyde and with thiophene-2,5-dicarbaldehyde(41).

(1-7) Electronic spectra of Schiff bases:

Nothing is interested in the electronic spectra of aliphatic Schiff bases because they absorb light below 200 nm.

The electronic spectra of the unsubstituted aromatic Schiff's base molecule: N-benzylidene benzene amine has four absorption bands:

* An absorption band at (314 nm) due to the electronic transfer $\pi \rightarrow \pi^*$ characteristic of the structure (42, 43).

* An absorption band at (262 nm) due to the electronic transfer $\pi \rightarrow \pi^*$ characteristic of the structure C_6H_5–C (42, 44, 43).

* An absorption band at (236 nm) due to the electronic transfer $n \rightarrow \pi^*$ which caused by local excitation of the part C_6H_5–N where there is an overlap of the electron pair on the nitrogen atom with π electrons of the ring. The position of the band varies when donating or drawing with electron groups are present on the ring (45, 46) their position also varies with solvent.

* An absorption band at (218 nm) due to the electronic transfer $\pi \rightarrow \pi^*$ which is caused by local excitation of the part C_6H_5–C. The position of the band absorption is varies when donating or drawing with electron groups are present on the ring (42, 43, 46). Their position also varies with solvent. The two band at (314 nm) and (262 nm) are displaced towards longer wavelength and shorter frequency as the number of double bonds is increased towards part C_6H_5–N or C_6H_5–C. In both cases, the co-planarity of the molecule is increased with the increase number of the double bonds (44).

(1-8) Applications of Schiff bases and its complexes:

Schiff bases and its complexes have many applications in difference fields summarize as following:

1-Analytical application:-

Many of Schiff bases are found as ligands poly-chelating colored form complexes with many of metals ions, and that make them to be selective and sensitive methods to determine the metals (47).

2- Biological applications:-

Schiff bases have biological activity, therefore use in prepare of some drugs like isonicotinyl hydrazide , appearance anti phthisis activity, the amino group show toxicity in application as follow figure (1-15) :

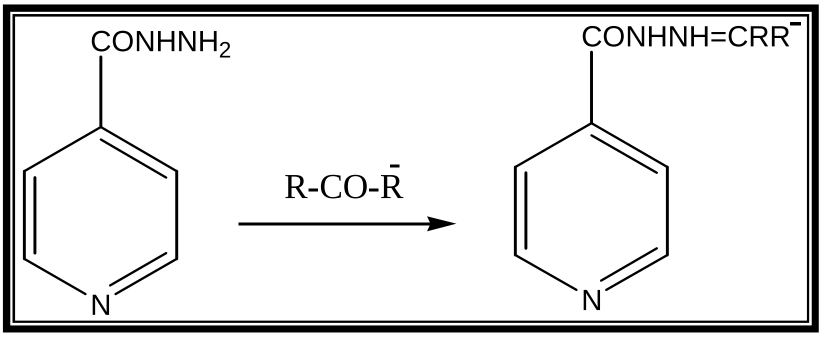


Figure (1-15): Isonicotinyl hydrazide

The toxicity removed by conversion of the compound to the Schiff bases by condensation with ketones or aldehydes (48, 49). However, the use of some Schiff bases in (visual process) (50) and reactions involved imine group (non-enzymatic transition reaction) (51, 52) and some accelerated reactions by vitamin (B_6) (53) and some of Schiff bases have activity against cancer disease (54).

3- Industrial applications:-

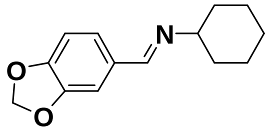
When some Schiff bases mixed with oxidized agent (oxygen molecules, organic hydro peroxide and benzene iodide) by certain ratio , the product conforms active system use as catalytic agent which can not make that alone , e.g: (Col) complex which is Schiff base of ethylene bis salicylideneiminato which uses as catalytic agent to oxidize the hydrazone to diazo compound which uses in organic preparation involved the peptides(55) , oxidation of asymmetric sulphide to sulphoxide also by using organic hydroxides using amount of one of optical active compounds like vanadium Schiff bases complex (56) . Manganese complexes used with Schiff bases catalytic agents in epoxidation of olefins by mixed with benzene iodide as oxidation agent (57)

(1-9) Aim of the present work:-

Because of the importance of Schiff bases and their coordination compounds which have played a great importance in medicine, industry and biochemistry. So the aim of this work could be summarized as follows.

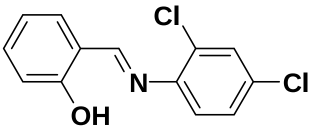
1- Synthesis of four shiff base ligands with different donor atoms.

a)



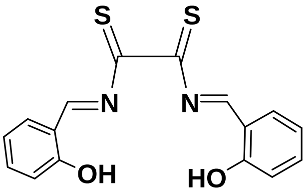
Piperonaldehyde cyclohexylimine (L_A)

b)



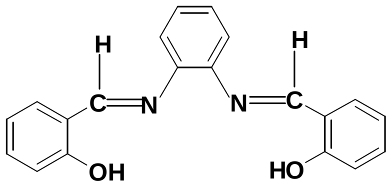
Salicylidene-2,4-dichloroaniline (L_B)

c)



bis salicylidene-dithiooxamide (L_C)

d)



bis salicylidene-o-phenylenediamine (L_D)

2- Complexes of these ligands with transition metals ions Cu (II), Co (II) and Rh (III) are to be synthesized.

3- Characterization of these ligands and complexes using different suitable techniques.

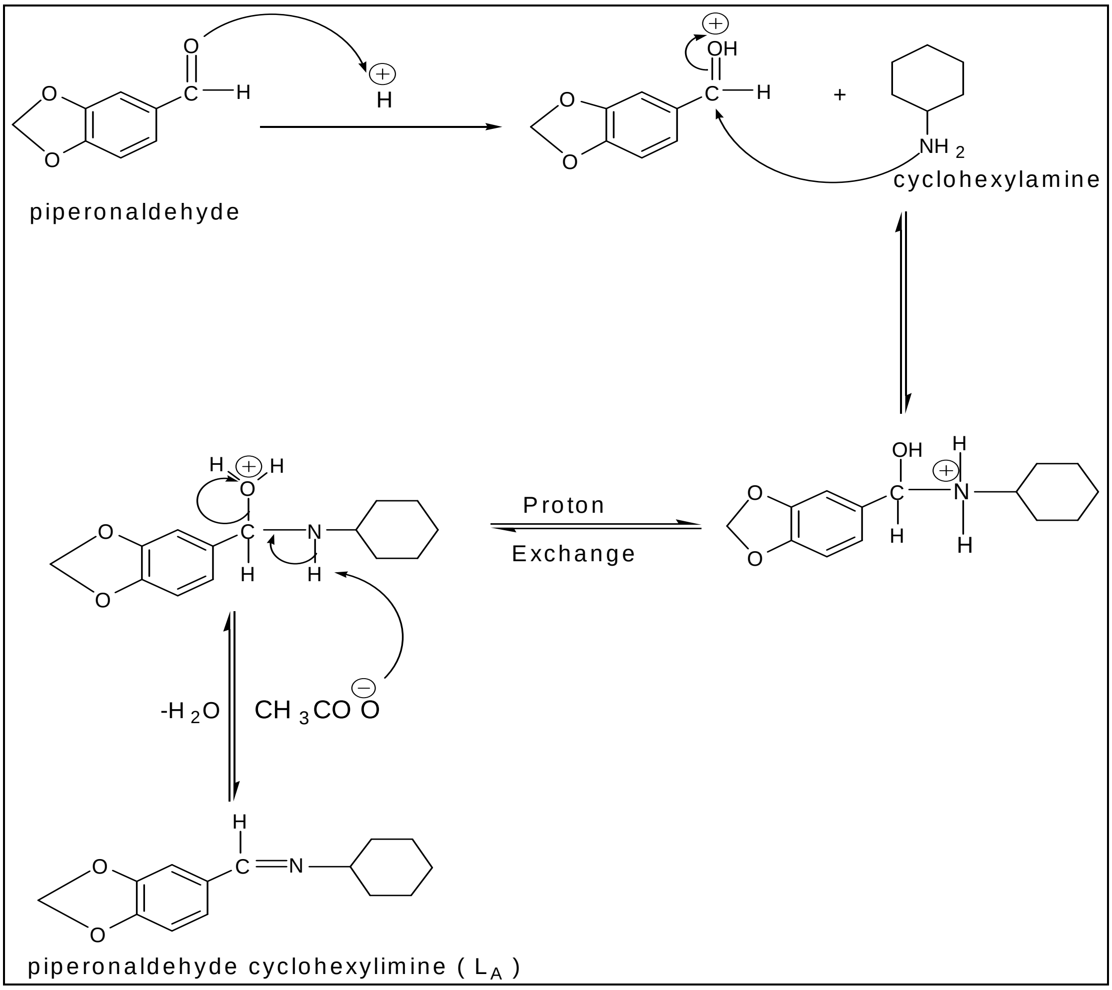
Chapter three

Results and Discussion

(3-1)Synthesis and Characterization of Ligands and their Metals Complexes:-

(3-1-1) Synthesis and Characterization of L_A and Its Metals Complexes:

This ligand was prepared by fusion of Cyclohexylamine with Piperonaldehyde in [1:1] ratio in the presence of glacial acetic acid as catalyst. The reaction can be postulated according to the general mechanism (11) shown in Scheme (3-1).



Scheme (3-1): Mechanism of synthesis of ligand (L_A)

The end of the reaction was confirmed by thin layer chromatography (TLC) technique. Higher yield product with higher purity of [**L_A**]. Recrystallization solvent was ethanol for **[L_A].**

Then reaction of [**L_A]** with copper (II), cobalt (II) as nitrate salts and with Rhodium (III) as chloride salt. Using absolute ethanol as solvent.

All reactions were carried out under reflux conditions at least (3 hours) to ensure completion of reaction. New fine crystalline complexes were obtained; recrystallization solvent was absolute ethanol for all reactions of complexes**.**

The physical data for the prepared ligand [**L_A**] and their complexes are shown in Table (3-1). Which show different melting points. The colours of the complexes were useful in structural determination.

Identification and study of these complexes were carried out by metal analysis using flame atomic absorption, infrared spectroscopy, ultra-violet visible spectrophotometery, magnetic susceptibility and electric conductivity measurements. According to these measurements the chemical formulas of the prepared complexes have been suggested as given in Table (3-15).

Table (3-1): Physical properties for [L_A] and their metal complexes

Symbol	Colour	m.p.(C°)	Yield (%)	Metal analysis (%)	
				Calc.	Found
L_A	Deep brown	64	75.8	-	-
L_A Cu(II)	Brownish-Green	138-140	72	9.02	9.52
L_A Co(II)	Gray	110 Dec.	70	8.22	8.94
L_A Rh(III)	Reddish brown	198 Dec.	73.5	13.52	13.85

Dec. = Decompose

Table (3-2) shows the solubility of the prepared ligand **[L_A]** and its metals complexes in different solvents.

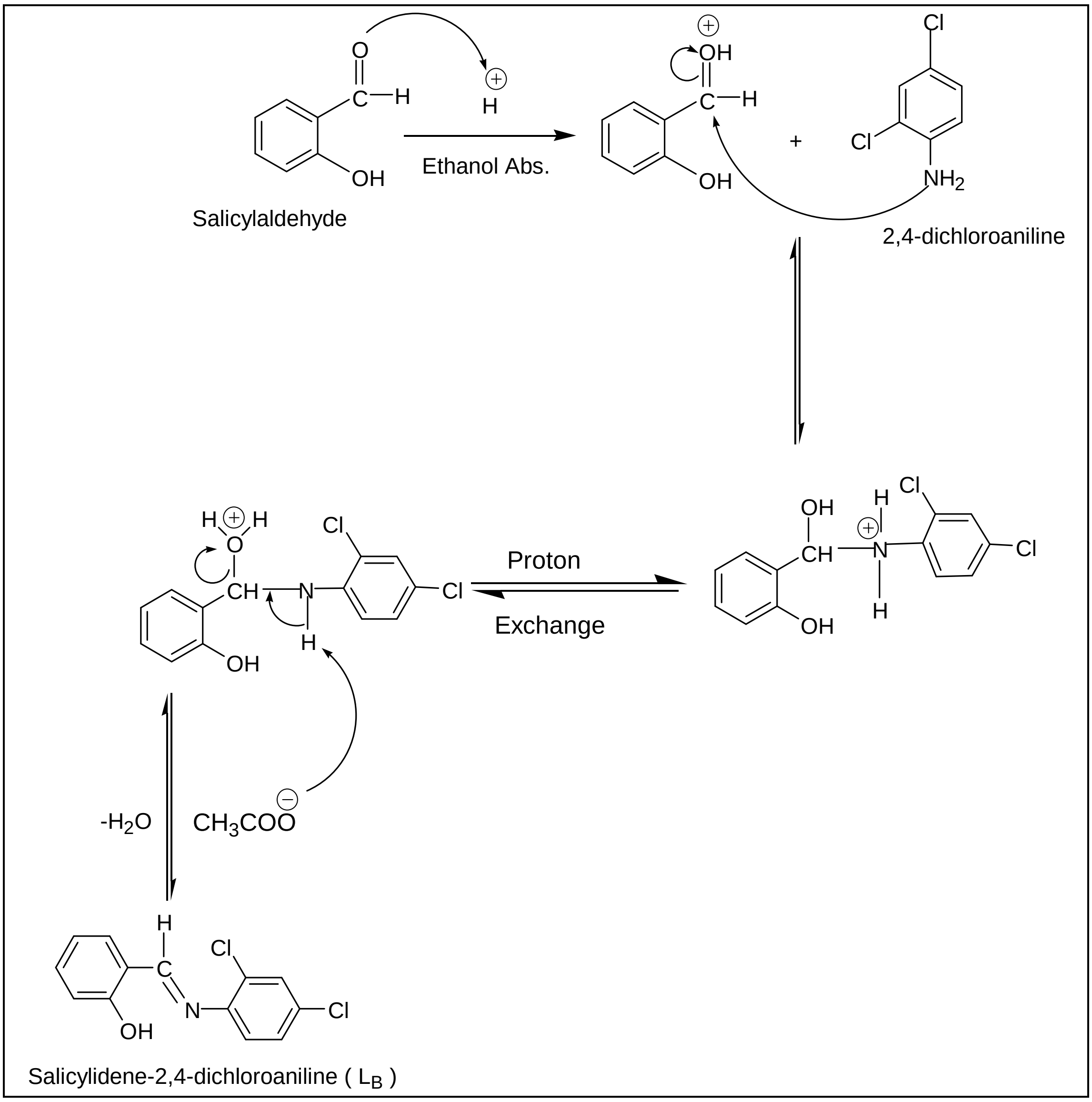
Table (3-2) Solubility of the [L_A] and their metals complexes in different solvents at room temperature.

Symbol	DMF	DMSO	H_2O	Acetone	CH_3OH	CH_2Cl_2	$CHCl_3$	C_6H_6	CCl_4
L_A	+	+	-	-	+	+	+	+	+
L_A Cu(II)	+	+	-	-	+	-	+	-	-
L_A Co(II)	+	+	-	+	+	-	-	-	-
L_A Rh(III)	+	+	-	-	+	-	+	-	-

Where (+) Soluble
(-) Insoluble

(3-1-2) Synthesis and Characterization of L_B and Its Metals Complexes:

The condensation reaction of 2,4-dichloroaniline with salicylaldehyde in [1:1] ratio in the presence of glacial acetic acid as catalyst., resulted in the preparation of the ligand [L_B]. The reaction can be postulated according to the general mechanism (11) shown in Scheme (3-2).



Scheme (3-2): Mechanism of synthesis of ligand (L_B)

The end of the reaction was confirmed by thin layer chromatography (TLC) technique. Higher yield product with higher purity of [$\mathbf{L_B}$]. Recrystallization solvent was absolute ethanol for [$\mathbf{L_B}$].

Then reaction of [$\mathbf{L_B}$] with copper (II), cobalt (II) as nitrate salts and with Rhodium (III) as chloride salt, using hot absolute ethanol as solvent, with addition of few drops of pH buffer (9).

All reactions were carried out under reflux conditions at least 3 hours to ensure completion of reaction. New fine crystalline complexes were obtained; recrystallization solvent was absolute ethanol for all reactions.

The physical data for the prepared ligand [$\mathbf{L_B}$] and their complexes are shown in Table (3-3). Which show different melting points. The colours of the complexes were useful in structural determination.

Identification and study of these complexes were carried out by metal analysis using flame atomic absorption, infrared spectroscopy, ultra-violet visible spectrophotometery, magnetic susceptibility and electric conductivity measurements. According to these measurements the chemical formula of the prepared complexes has been suggested as given in Table (3-15).

Table (3-3): Physical properties for [L_B] and their metal complexes

Symbol	Colour	m.p.(C^o)	Yield (%)	Metal analysis (%)	
				Calc.	Found
L_B	Pale green	75	77	-	-
L_B Cu(II)	Brown	190 - 192	74	10.06	10.85
L_B Co(II)	Yellowish green	150 - 152	80	8.66	9.45
L_B Rh(III)	Red	210 - 212	76	14.57	14.95

Table (3-4) shows the solubility of the prepared ligand [$\mathbf{L_B}$] and its metals complexes in different solvents.

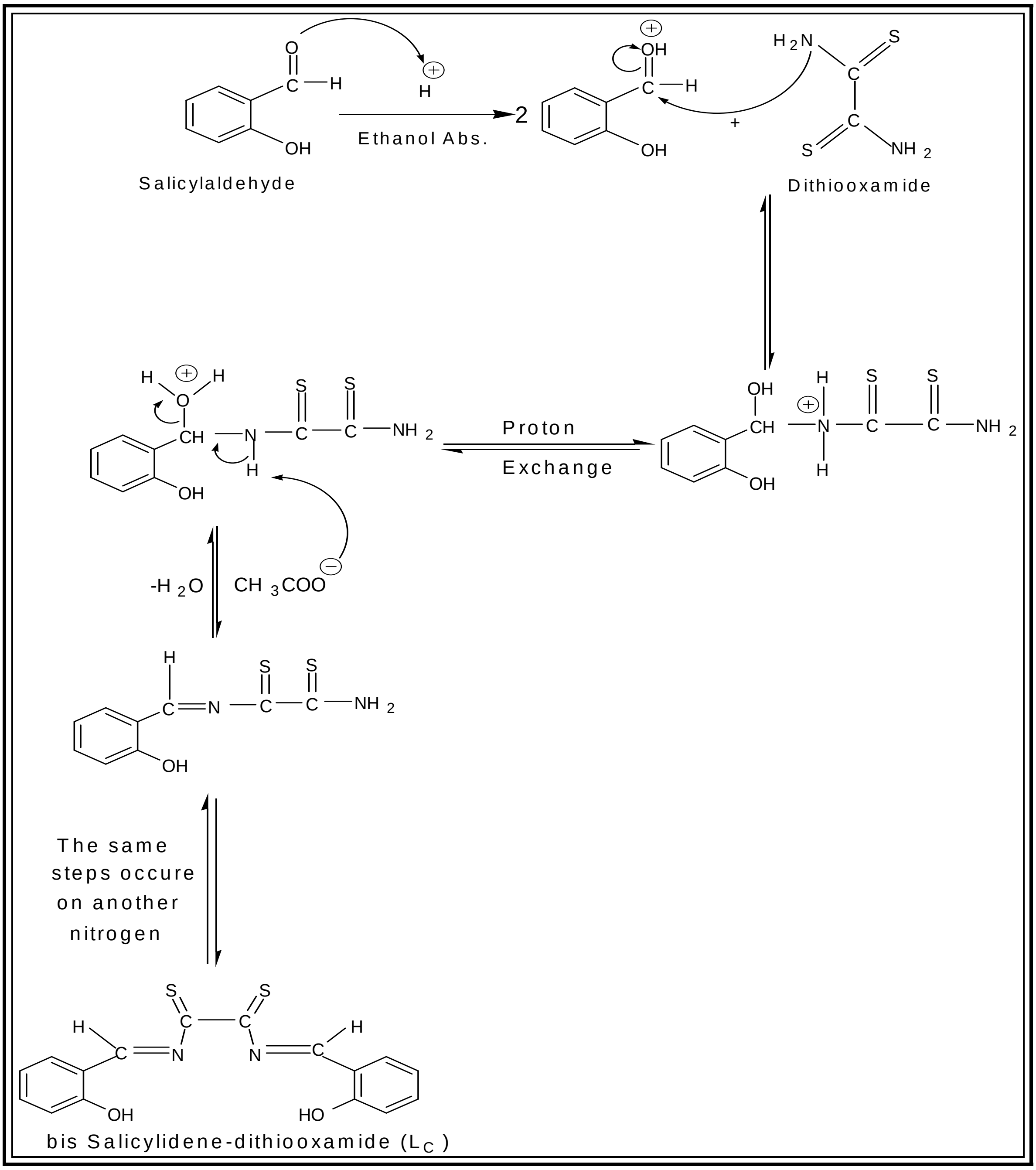
Table (3-4) Solubility of the [L_B] and their metals complexes in different solvents at room temperature.

Symbol	DMF	DMSO	H_2O	Acetone	CH_3OH	CH_2Cl_2	$CHCl_3$	C_6H_6	CCl_4
L_B	+	+	-	+	+	+	+	+	+
L_B Cu(II)	+	+	-	+	-	+	+	-	+
L_B Co(II)	+	+	-	-	-	-	-	-	-
L_B Rh(III)	+	+	-	+	-	-	-	-	-

Where (+) Soluble
(-) Insoluble

(3-1-3) Synthesis and Characterization of L_C and Its Metals Complexes:

The condensation reaction of dithiooxamide with salicylaldehyde in [1:2] ratio in the presence of glacial acetic acid as catalyst. Resulted in the preparation of the ligand [L_C]. The reaction can be postulated according to the general mechanism (11) shown in Scheme (3-3).



Scheme (3-3): Mechanism of synthesis of ligand (L_C)

The end of the reaction was confirmed by thin layer chromatography (TLC) technique. Higher yield product with higher purity of [**L_C**]. Recrystallization solvent was absolute ethanol for [**L_C**].

Then reaction of [**L_C**] with copper (II), cobalt (II) as nitrate salts and with rhodium (III) as chloride salt, using hot absolute ethanol as solvent, with addition of few drops of pH buffer (9).

All reactions were carried out under reflux conditions at least 3 hours to ensure completion of reaction. New fine crystalline complexes were obtained; recrystallization solvent was absolute ethanol for all reactions of complexes.

The physical data for the prepared ligand **[L_C**] and their complexes are shown in Table (3-5). Which show different melting points. The colours of the complexes were useful in structural determination.

Identification and study of these complexes were carried out by metal analysis by using flame atomic absorption, infrared spectroscopy, ultra-violet visible spectrophotometery, magnetic susceptibility and electric conductivity measurements. According to these measurements the chemical formulas of the prepared complexes have been suggested as given in Table (3-15).

Table (3-5): Physical properties for [L_C] and their metal complexes

Symbol	Colour	m.p.(C^o)	Yield (%)	Metal analysis (%)	
				Calc.	Found
L_C	Yellowish brown	260 Dec.	62	-	-
L_C Cu(II)	Deep brown	280 Dec.	75	13.59	13.35
L_C Co(II)	Yellowish green	270 Dec.	78	11.02	10.85
L_C Rh(III)	Deep brown	290 Dec.	72	18.36	18.11

Dec. = Decompose

Table (3-6) shows the solubility of the prepared ligand [L_C] and its metals complexes in different solvents.

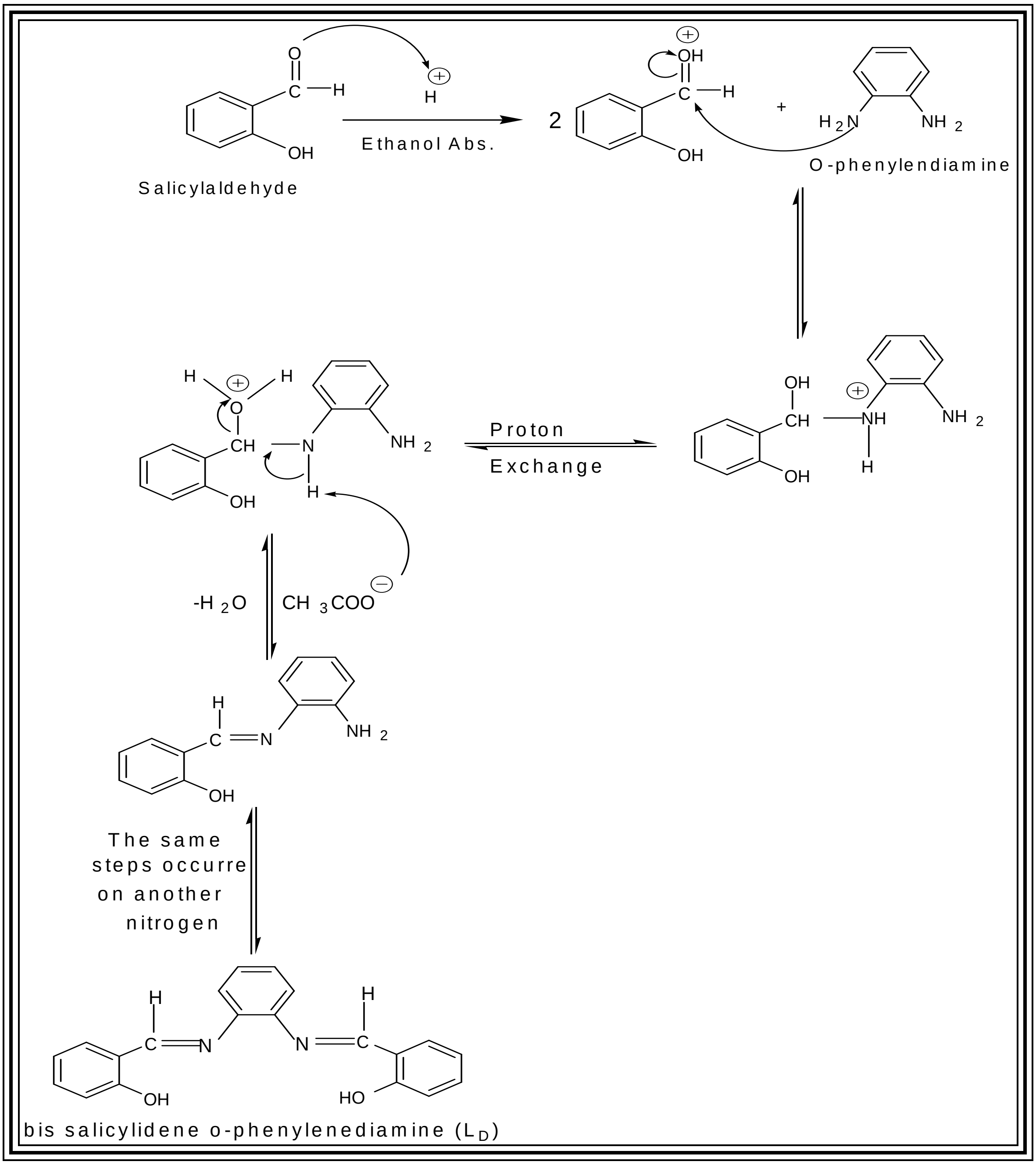
Table (3-6) Solubility of the [L_C] and their metals complexes in different solvents at room temperature.

Symbol	DMF	DMSO	H_2O	Acetone	CH_3OH	CH_2Cl_2	$CHCl_3$	C_6H_6	CCl_4
L_C	+	+	-	-	-	+	+	-	-
L_C Cu(II)	+	+	-	-	-	-	+	+	-
L_C Co(II)	+	+	-	+	-	-	+	+	-
L_C Rh(III)	+	+	-	-	+	-	+	+	+

Where (+) Soluble
(-) Insoluble

(3-1-4) Synthesis and Characterization of L_D and Its Metals Complexes:

The condensation reaction of o-phenylenediamine with salicylaldehyde in [1:2] ratio in the presence of glacial acetic acid as catalyst resulted in the preparation of the ligand [L_D]. The reaction can be postulated according to the general mechanism (11) shown in Scheme (3-4).



Scheme (3-4): Mechanism of synthesis of ligand (L_D).

The end of the reaction was confirmed by thin layer chromatography (TLC) technique. Higher yield product with higher purity of [$\mathbf{L_D}$]. Recrystallization solvent was absolute ethanol for [$\mathbf{L_D}$]**.**

Then reaction of [$\mathbf{L_D}$**]** with copper (II), cobalt (II) as nitrate salts and with rhodium (III) as chloride salt, using hot absolute ethanol as solvent, with addition few drops of pH buffer (9).

All reactions were carried out under reflux conditions at least 3 hours to ensure completion of reaction. New fine crystalline complexes were obtained recrystallization solvent was absolute ethanol for all reactions of complexes**.**

The physical data for the prepared ligand **[**$\mathbf{L_D}$] and its complexes in Table (3-7). Which show different melting points. The colours of the complexes were useful in structural determination.

Identification and study of these complexes were carried out by metal analysis by using flame atomic absorption, infrared spectroscopy, ultra-violet visible spectrophotometery, magnetic susceptibility and electric conductivity measurements. According to these measurements the chemical formulas of the prepared complexes have been suggested as given in Table (3-15).

Table (3-7): Physical properties for [L_D] and their metal complexes

Symbol	Colour	m.p.(C^o)	Yield (%)	Metal analysis (%)	
				Calc.	Found
L_D	Yellow range	164-166	90	-	-
L_D Cu(II)	Brown	290	85	15.29	14.96
L_D Co(II)	Bright green	283	79	11.36	12.42
L_D Rh(III)	Red	>300	87	11.97	11.58

Table (3-8) shows the solubility of the prepared ligand **[L_D]** and its metals complexes in different solvents.

Table (3-8) Solubility of the [L_D] and their metals complexes in different solvents at room temperature.

Symbol	DMF	DMSO	H_2O	Acetone	CH_3OH	CH_2Cl_2	$CHCl_3$	C_6H_6	CCl_4
L_D	+	+	-	+	+	+	+	+	-
L_D Cu(II)	+	+	-	-	+	-	+	+	-
L_D Co(II)	+	+	-	-	+	-	-	-	-
L_D Rh(III)	+	+	-	+	+	-	-	-	-

Where (+) Soluble
(-) Insoluble

(3-2) Infra-Red spectra:-

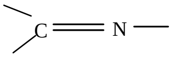
The FT-IR spectra were taken for the prepared complexes and compared with those of their respective ligands. The measurements were carried out for each compound in solid state as KBr disc in the range (4000-400) cm^{-1}.

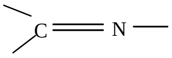
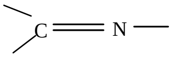
(3-2-1) The FT-IR spectra of [L_A] and their metal Complexes:-

The ligand [L_A] has the azomethine group. In general azomethine group ($>C=N-$) absorption occurs in the region (1610-1680) cm^{-1} depending on the nature of groups linked to it (36).

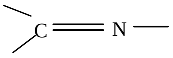
The F.T.IR spectra of the ligand [L_A], Figure(3-1), Table(3-9), showed the absence of the band at (1690 cm^{-1}) due to the carbonyl υ(C=O) also absence two bands at (3400 cm^{-1}) and (3340 cm^{-1}) due to asymmetrical and symmetrical of υ(NH_2) stretching vibration(62) of starting material, and a strong new band appeared at (1639 cm^{-1}) assigned to azomethin υ($>C=N-$) linkage. The bands appeared at (2821 cm^{-1}) and (1396 cm^{-1}) were due to υ(C-H) aldehyed stretching and bending vibration frequency respectively (62).

The band at υ (1600 cm^{-1}) was assigned to the υ(C=C) of aromatic ring stretching frequency (63). Other band shown at (2925 cm^{-1}) was assigned to the aromatic υ(C-H) stretching frequency, the out of plane υ(C-H) bending vibration was appeared at (723 cm^{-1})(64). Another set of bands were also observed at (1255 cm^{-1}) and (1035 cm^{-1}) due to the asymmetrical and symmetrical υ(C-O-C) stretching vibrations respectively (62). And the bands at (2850cm^{-1}) and (1444 cm^{-1}) refer to the υ(C-H) of cyclohexyl ring stretching and bending vibration frequency respectively (65).

The compound containing azomethine group show basic coordination behavior toward metal ions coordinating via the nitrogen atoms, this coordination shifts the stretching frequency of () group either toward higher frequency in some complexes (66, 67), or toward lower frequency in others (68, 69).

The increase in frequency may be due to the simultaneous strengthening of the () bond due to an increase in both sigma overlap and electrostatic attraction which is possible on account of the coordination of the azomethine nitrogen to metal ion (70). The decrease in frequency indicates a decrease in the stretching force constant of () group as a consequence of the coordination through azomethine nitrogen. The double bond character between carbon and nitrogen is reduced (71).

A- Spectrum of the Copper (II) Complex [L_ACu (II)]:-

The F.T.IR spectrum of [L_ACu(II)] complex, is shown in Figure (3-2), The strong band of υ() stretching band in the free ligand [L_A] at (1639) cm^{-1} for the azomethine group was splitted and shifted to lower frequency and appeared at (1608cm^{-1})(72, 76) when formation of complex, This means that coordination may took place through nitrogen of azomethine group(75, 82).

The three bands were absorbs at (1379, 1328 and 995) cm^{-1} refer to unidentate nitrate group (NO_3^-) to the metal atoms, and sharp band appeared at (1762 cm^{-1}) indicate the presence of nitrate ion (NO_3^-) out of the coordination sphere in the structure (73), Furthermore, new bands have been observed around (511, 426) cm^{-1} which are due to ν (Cu-N), ν (Cu-O)(73, 63), respectively, A medium sharp band which appeared at (784 cm^{-1}) indicate the presence of H_2O in the lattice molecules of the structure ν (Cu-OH_2) (73) .

Also broad band which appeared at (3539 cm^{-1}) refer to the presence of water molecules out of the coordination sphere in the structure of [L_ACu(II)] complex(73, 74). Table (3-9) shows the most characteristic band of [L_ACu (II)].

B- Spectrum of the Cobalt (II) Complex [L_ACo(II)]:-

The F.T.IR spectrum of [L_ACo(II)] complex, is shown in Figure (3-3), The stretching frequency of azomethine group was splitted and shifted to a lower frequency by (31 cm^{-1}) and appeared at (1608 cm^{-1}) (72, 76). Indicating the coordination through nitrogen of azomethine group (75, 82).

Furthermore the appearance of new weak low frequency band at (451 cm^{-1}), this was assigned to ν (Co-N) vibration and the observation at (406 cm^{-1}) indicated the participation of oxygen in the complex (Co-O) (73, 75). The bands at (1446, 1313 and 925) cm^{-1} referred to unidentate nitrate group (73).

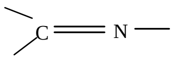
A medium sharp band which appeared at (846 cm^{-1}) indicates the presence of H_2O in the lattice molecules of the structure ν ($Co\text{-}OH_2$) (73). Also broad band which appeared at (3606 cm^{-1}) refer to the presence of water molecules out of the coordination sphere in the structure of [L_ACo(II)] complex(73, 74). Table (3-9) shows the most characteristic band of [L_ACo (II)].

C- Spectrum of the Rhodium (III) Complex [L_ARh (III)]:-

The F.T.IR spectrum of [L_ARh(III)] complex, is shown in Figure (3-4) which shows the shifting of azomethine band to a lower frequency and appeared at (1616 cm^{-1}) (72,76). This indicates the participation of azomethine-nitrogen with Rh (III) ion (75, 82).

A strong sharp band which appeared at (887 cm^{-1}) indicates the presence of H_2O in the lattice molecules of the structure ν (Rh-OH_2) (73). Also abroad band which appeared at (3483 cm^{-1}) refer to the presence of water molecules out of the coordination sphere in the structure of [L_ARh(III)] complex(73, 74)*.* The new band at (547 cm^{-1}) can be attributed to ν (Rh-N) (77). And another band observation at (457 cm^{-1}) indicated the participation of oxygen in the complex (Rh-O) (73). Table (3-9) shows the most characteristic band of [L_ARh(III)].

<u>*(3-2-2) The FT-IR spectra of [L_B] and their metal Complexes:-*</u>

The F.T.IR spectrum of [L_B] is shown in Figure (3-5), which shows the following characteristic bands: A broad band appearing at (3456 cm^{-1}) has been assigned to stretching vibration of the hydrogen bonded of (OH) group in the ligand [L_B]. A broad band was observed at (665 cm^{-1}) assigned to the hydrogen bonded out-of the plane of (O-H) bending vibration (80, 62). The medium to strong intensity bands appear at (1280 cm^{-1}) which assigned to the phenolic (C-O) (81, 62) stretching mode. The band at (1614 cm^{-1}) is due to () azomethine group stretching and (1554 cm^{-1}) due to the presence of (C=C) of aromatic system (63). The two strong band at (788 and 819) cm^{-1} are due to the ortho and para substitution respectively (78).

The ν(C-H) of the aromatic moiety appeared around (2758 cm^{-1}) in the free ligand (79), The out of plane υ(C-H) aromatic bending vibration was appeared at (748 cm^{-1})(64).

The bands appeared at (2320 cm^{-1}) and (1396 cm^{-1}) are due to υ(C-H) aldehyed stretching and bending vibrations frequency respectively (62). Table (3-10) shows the most characteristic bands of [L_B].

A- Spectrum of the Copper (II) Complex [L_BCu(II)]:-

The most significant difference between the F.T.IR spectrum of [L_B] ligand and the complex, as shown in Figure (3-6), was the shift of (C=N) stretching frequency to lower frequency by (10 cm^{-1}) and appear at (1604 cm^{-1}) (72, 76) due to metal-ligand coordination (75, 82). The ν(C-O) frequency which was changed from (1280cm^{-1}) to (1325cm^{-1}) after complexation with central metal ion(28, 83) this indicates displacement the metal ion by the hydrogen-phenol (75) and improves comes from no bands were observed at (667 and 3454) cm^{-1}, which are due to out of plane O-H bending and O-H stretching vibration.

The strong sharp band at (829 cm^{-1}) indicates the presence of H_2O molecules ν (Cu-H_2O) in the coordination of [L_BCu(II)] complex (73).

The new bands which have been observed around (530 and 455) cm^{-1} were attributed to ν (Cu-N), ν (Cu-O) respectively (84), Table (3-10) shows the most characteristic bands of [L_BCu (II)].

B- Spectrum of the Cobalt (II) Complex [L_BCo (II)]:-

The F.T.IR spectrum of complex [L_BCo (II)] is shown in Figure (3-7), Shows the shifting of ν(C=N) to a lower frequency by (10 cm^{-1}) and appear at (1604 cm^{-1}) (72, 76) indicating the coordination through nitrogen of azomethine group (75, 82). The ν(C-O) frequency which was changed from (1280cm^{-1}) to (1325cm^{-1}) after complexation with central metal ion(28, 83) this indicates displacement the metal ion by the hydrogen-phenol (75). These observations indicated the participation of both oxygen and nitrogen in the complex (75).

A strong sharp band which appeared at (729 cm^{-1}) indicates the presence of H_2O in the lattice molecules of the structure ν (Co-OH_2) (73). Also abroad band which appeared at (3421 cm^{-1}) refer to the presence of water molecules out of the coordination sphere in the structure of [L_BCo(II)] complex(73, 74)

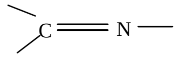
The bands at (524 and 450) cm^{-1} can be attributed to ν (Co-N) and ν (Co-O) respectively (73). Table (3-10) contains the most characteristic bands of [L_BCo (II)].

C- Spectrum of the Rhodium (III) Complex [L_BRh(III)]:-

In the spectrum of [L_BRh (III)], is shown in Figure (3-8), azomethine group ν(C=N) absorption frequency was shifted to a lower frequency and appear at (1604 cm^{-1}) (72, 76), indicating the coordination through azomethine nitrogen(75, 82). The ν(C-O) frequency which was changed from (1280cm^{-1}) to (1330cm^{-1}) after complexation with central metal ion(28, 83) this indicates displacement the metal ion by the hydrogen-phenol, these observations indicated the participation of both oxygen and nitrogen in the complex (75). The two bands corresponding to O-H bending and O-H stretching frequencies disappeared in the [L_BRh(III)] spectrum. The bands at (570 and 447) cm^{-1}can are attributed to ν (Rh-N) (77), (Rh-O)(73) respectively. A broad band which appeared at (3422 cm^{-1}) refer to the presence of water molecules out of the coordination sphere in the structure of [L_BRh(III)] complex (73, 74) respectively. Table (3-10) contains the most characteristic bands of [L_BRh (III)].

(3-2-3) The FT-IR spectra of [L_C] and their metal Complexes:-

The F.T.IR spectrum of [L_C] is shown in Figure (3-9), which shows the following characteristic bands: A broad band appearing at (3450 cm^{-1}) has been assigned to stretching vibration of the hydrogen bonded of (OH) group in the ligand [L_C]. Also the band observed at (651 cm^{-1}) was assigned to the hydrogen bonded out-of the plane of (O-H) bending vibration (80, 62).

The strong band at (1622 cm^{-1}) is due to azomethine group ν() stretching frequency and the bands appear at (1566, 1494 and 1475) cm^{-1}refer to υ(C=C) aromatic ring bands (63). The important absorption at (1585, 1598 cm^{-1}) in spectrum of ligand was assigned to thioamide band (I) [ν(C=N) (major) + δ (NH)](85). The thioamide band (II) due to [ν (CN) (major) + ν (C=S)] which appeared around (1463- 1468) cm^{-1} in the free ligand and its metal complexes. The thioamide band (III) is strong band appeared at (1178 cm^{-1}) due to υ(C=S) stretching frequency which was shifted to higher frequency up on complex formation (86). The thioamide band (IV) appeared at (705 cm^{-1}) was due to ν(C-S) (87) in free [LC] ligand. Also the assign about (908 cm^{-1}) which was attributed to the (N-C-S) group (88, 89) in free [LC] ligand. The ν (C-H) of the aromatic moiety appeared around (3056 cm^{-1}) in the free ligand(79), The out of plane υ(C-H) aromatic bending vibration was appeared at (738 cm^{-1})(64). The medium intensity band appear at (1278 cm^{-1}) which assigned to the phenolic (C-O) (62, 81) stretching mode. The sharp strong band at (752 cm^{-1}) is due to the ortho substitution (78). The bands appeared at (2852 and 2900) cm^{-1} stretching vibration frequency due to υ(C-H) aldehyede and at (1407 cm^{-1}) due to bending vibration frequency of the same band (62). Table (3-11) shows the most characteristic bands of [L_C].

A- Spectrum of the Copper (II) Complex [L_CCu (II)]:-

The F.T.IR spectrum of [L_CCu(II)] complex, is shown in Figure (3-10) which show the shifting of azomethine ν(C=N) band to a lower frequency and appeared at (1604 cm^{-1})(72, 76) this was indicating the coordination through of azomethine-nitrogen with Cu (II) ion (75, 82).The ν(C-O) frequency which was changed from (1278 cm^{-1}) to (1355 cm^{-1}) after complexation with central metal ion(28, 83) this indicates displacement the metal ion by the hydrogen-phenol (75), which indicates the coordination of the oxygen with the Cu (II) ion (75).

The presence of new weak band observed at (557 cm^{-1}) and (457 cm^{-1}) which assigned to υ (Cu-N) and υ (Cu-O) respectively (84).

A medium band which appeared at (622 cm^{-1}) indicates the presence of H_2O in the lattice molecules of the structure ν (Cu-OH_2) (73). And another abroad band which appeared at (3396 cm^{-1}) refer to the presence of water molecules out of the coordination sphere in the structure of [L_CCu(II)] complex(73, 74) . Table (3-11) shows the most characteristic bands of [L_CCu(II)].

B- Spectrum of the Cobalt (II) Complex [L_CCo (II)]:-

The spectrum of [L_CCo (II)] complex, is shown in Figure (3-11), which show the azomethine ν(C=N) band to be shifted to lower frequency by (22) cm^{-1} and appeared at (1600 cm^{-1}) (72, 76). Indicating the interaction of the metal ion with the azomethine-nitrogen (75, 82). The ν(C-O) frequency which was changed from (1278 cm^{-1}) to (1325 cm^{-1}) after complexation with central metal ion(28, 83) this indicates displacement the metal ion by the hydrogen-phenol, which indicates the coordination of the oxygen with the Co (II) ion (75).

The presence of two new weak band observed at (565 and 460) cm^{-1} refer to υ(Co-N) and υ(Co-O) bands respectively (73, 75).

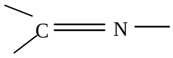
A medium band which appeared at (630 cm^{-1}) indicates the presence of H_2O in the lattice molecules of the structure ν (Co-OH_2) (73). And another abroad band which appeared at (3218 cm^{-1}) refer to the presence of water molecules out of the coordination sphere in the structure of [L_CCo(II)] complex(73, 74). Table (3-11) shows the most characteristic bands of [L_CCo (II)].

C- Spectrum of the Rhodium (III) Complex [L_C Rh (III)]:-

In the spectrum of [L_CRh(III)], is shown in Figure (3-12), which shows the azomethine absorption frequency was shifted to (1610 cm^{-1}) (72, 76), indicating the coordination through nitrogen atom of azomethine group (75, 82). The ν (C-O) frequency was changed from (1249 cm^{-1}) to (1348 cm^{-1}) (28, 83), this blue shift indicates the coordination through oxygen of phenolic group (75), and this improved disappearing the two bands corresponding to O-H bending and O-H stretching frequencies in the [L_CRh (III)] spectrum. The new bands appeared at (520 and 460) cm^{-1}can are attributed to ν (Rh-N) (77), ν (Rh-O) (73) respectively. A medium sharp band which appeared at (667 cm^{-1}) indicates the presence of H_2O in the lattice molecules of the structure ν (Rh-OH_2) (73). And another abroad band which appeared at (3355 cm^{-1}) refer to the presence of water molecules out of the coordination sphere in the structure of [L_C Rh (III)] complex(73, 74). Table (3-11) contains the most characteristic bands of [L_C Rh (III)].

(3-2-4) The FT-IR spectra of L_D and their metal Complexes:

The F.T.IR spectrum of [L_D] is shown in Figure (3-13), which show the following characteristic bands: A broad band appearing at (3360 cm^{-1}) has been assigned to stretching vibration of the hydrogen bonded of (OH) group in the ligand [L_D]. A sharp band was observed at (630 cm^{-1}) assigned to the hydrogen bonded out-of the plane of (O-H) bending vibration (80, 62). The strong intensity band appear at (1276 cm^{-1}) which assigned to the phenolic ν (C-O) (81, 62) stretching vibration frequency.

The band at (1612 cm^{-1}) is due to ν () azomethine group stretching vibration frequency, the bands (1585, 1560 and 1481) cm^{-1} due to the presence of ν (C=C) of aromatic ring system (63). The strong band at (746 cm^{-1}) is due to the ortho substitution (78).

The ν (C-H) of the aromatic moiety appeared around (3053-3056) cm^{-1} in the free ligand and its metal complexes(79), The out of plane ν (C-H) aromatic bending vibration was appeared at (759 cm^{-1})(64).

The bands appeared at (2830 cm^{-1}) and (1361 cm^{-1}) due to ν (C-H) aldehyde stretching and bending vibration frequency respectively (62). Table (3-12) shows the most characteristic bands of [L_D].

A- Spectrum of the Copper (II) Complex [L_DCu (II)]:-

The F.T.IR spectrum of [L_DCu (II)] complex, is show in Figure (3-14), which show the stretching frequency of azomethine ν (C=N) group was shifted to lower frequency and appeared at (1608 cm^{-1}) (72, 76). this indicate the participation of azomethine nitrogen (75, 82),The ν (C-O) frequency was changed from (1276 cm^{-1}) to (1338 cm^{-1}) (28, 83), this blue shift indicates the coordination through oxygen of phenolic group (75), and this improved disappearing the two bands corresponding to O-H bending and O-H stretching frequencies in the [L_DCu (II)] spectrum.

The presence of new weak band observed at (536 cm^{-1}) and (441 cm^{-1}) which assigned to υ (Cu-N) and υ (Cu-O) respectively (87). A medium sharp band which appeared at (617 cm^{-1}) indicates the presence of H_2O in the lattice molecules of the structure of [L_DCu (II)] ν(Cu-OH_2) (73). Table (3-12) shows the most characteristic bands of [L_DCu (II)].

B- Spectrum of the Cobalt (II) Complex [L_D Co (II)]:-

The spectrum of [L_DCo (II)] complex, is shown in Figure (3-15), which show the azomethine ν (C=N) band to be shifted to lower frequency appeared at (1607 cm^{-1}) (72, 74). Indicating the interaction of the metal ion with the azomethine-nitrogen (75, 82). The ν(C-O) frequency which was changed from (1276 cm^{-1}) to (1330 cm^{-1}) after complexation with central metal ion(28, 83) this indicates displacement the metal ion by the hydrogen-phenol, which indicates the coordination of the oxygen with the Co (II) ion (75).

The presence of tow new weak band observed at (541 and 464) cm^{-1} refer to υ (Co-N) and υ (Co-O) bands respectively (73, 75).

A medium sharp band which appeared at (680 cm^{-1}) indicates the presence of H_2O in the lattice molecules of the structure ν (Co-OH_2) (73). And another abroad band which appeared at (3450 cm^{-1}) refer to the presence of water molecules out of the coordination sphere in the structure of [L_DCo(II)] complex(73, 74). Table (3-12) contains the most characteristic bands of [L_DCo (II)].

C- Spectrum of the Rhodium (III) Complex [L_D Rh (III)]:-

In the spectrum of [L_DRh (III)], is shown in Figure (3-16), which show the azomethine ν (C=N) band absorption frequency was shifted to (1604 cm^{-1}) (72, 76), indicating the coordination through nitrogen atom of azomethine group (75, 82). The ν(C-O) frequency which was changed from (1278 cm^{-1}) to (1319 cm^{-1}) after complexation with central metal ion(28, 83) this indicates displacement the metal ion by the hydrogen-phenol, which indicates the coordination of the oxygen with the Rh(III) ion (75), and this improved disappearing the two bands corresponding to O-H bending and O-H stretching frequencies in the [L_D Rh (III)] spectrum. The new bands appeared at (536 and 468) cm^{-1}can is attributed to ν (Rh-N) (77), (Rh-O) (73) respectively. A broad band which appeared at (3400 cm^{-1}) refers to the presence of water molecules out of the coordination sphere in the structure of [L_D Rh (III)] complex (73, 74). Table (3-12) contains the most characteristic bands of [L_D Rh (III)].

Table (3-9): The most significant bands of F.T.IR spectra of [L_A] and their metal complexes in (cm^{-1}):

Symbol	ν(C=N)	ν (C-O-C)	ν(C-H) Alkyl ring	ν(C=C) Arom.	ν(C-H) Arom.	ν(M-N)	ν(M-O)
L_A	1639	(1035) (1255)	2850	1600	2925	–	–
L_ACu(II)	1608	(1035) (1259)	2981	1525	3002	453	426
L_ACo(II)	1608	(1035) (1259)	2983	1525	3002	451	406
L_ARh(III)	1616	(1033) (1253)	3020	1596	3072	547	457

Table (3-10): The most significant bands of F.T.IR spectra of [L_B] and their metal complexes in (cm^{-1}):

Symbol	ν (O-H)	ν(C=N)	Phenolic ν (C-O)	ν(C=C) Arom.	ν (C-H) Arom.	Ortho sub. C-Cl	Para sub. C-Cl	ν M-N	ν(M-O)
L_B	3454	1614	1280	1554	2758	748	819	–	–
L_BCu(II)	-	1604	1325	1579	3012	754	829	530	455
L_BCo(II)	-	1604	1325	1531	2877	750	850	524	450
L_BRh(III)	-	1604	1330	1521	2923	756	827	570	447

Table (3-11): The most significant bands of F.T.IR spectra of [L_C] and their metal complexes in (cm^{-1}):

Symbol	Isomethane Bands ν (C=N)	Thioamide Band (I) ν(C=N)+δ(NH)	Thioamide Band (II) ν(C=S)+ν(C=N)	Thioamide Band (III) ν(C=S)	Thioamide Band (IV) ν (C-S)	Phenolic ν (C-O)	ν(M-N)	ν(M-O)
L_C	**1622**	**1585** **1598**	**1463**	**1178**	**705**	**1278**	**–**	**–**
L_CCu(II)	**1604**	**1586**	**1467**	**1220**	**703**	**1355**	**557**	**457**
L_CCo(II)	**1600**	**1583**	**1465**	**1188**	**706**	**1325**	**565**	**460**
L_CRh(III)	**1610**	**1589**	**1468**	**1207**	**707**	**1348**	**520**	**460**

Table (3-12): The most significant bands of F.T.IR spectra of [L_D] and their metal complexes in (cm^{-1}):

Symbol	ν (O-H)	ν(C=N)	Phenolic ν (C-O)	ν(C=C) Arom.	ν (C-H) Arom.	Ortho sub.	ν (M-N)	ν(M-O)
L_D	**3360**	**1612**	**1276**	**(1585)** **(1560)** **(1481)**	**3053**	**746**	**–**	**–**
L_DCu(II)	**-**	**1608**	**1338**	**(1577)** **(1523)** **(1488)**	**3053**	**746**	**536**	**441**
L_DCo(II)	**-**	**1607**	**1330**	**(1579)** **(1525)** **(1473)**	**3056**	**746**	**541**	**464**
L_DRh(III)	**-**	**1604**	**1319**	**(1521)** **(1473)** **(1458)**	**3053**	**752**	**536**	**468**

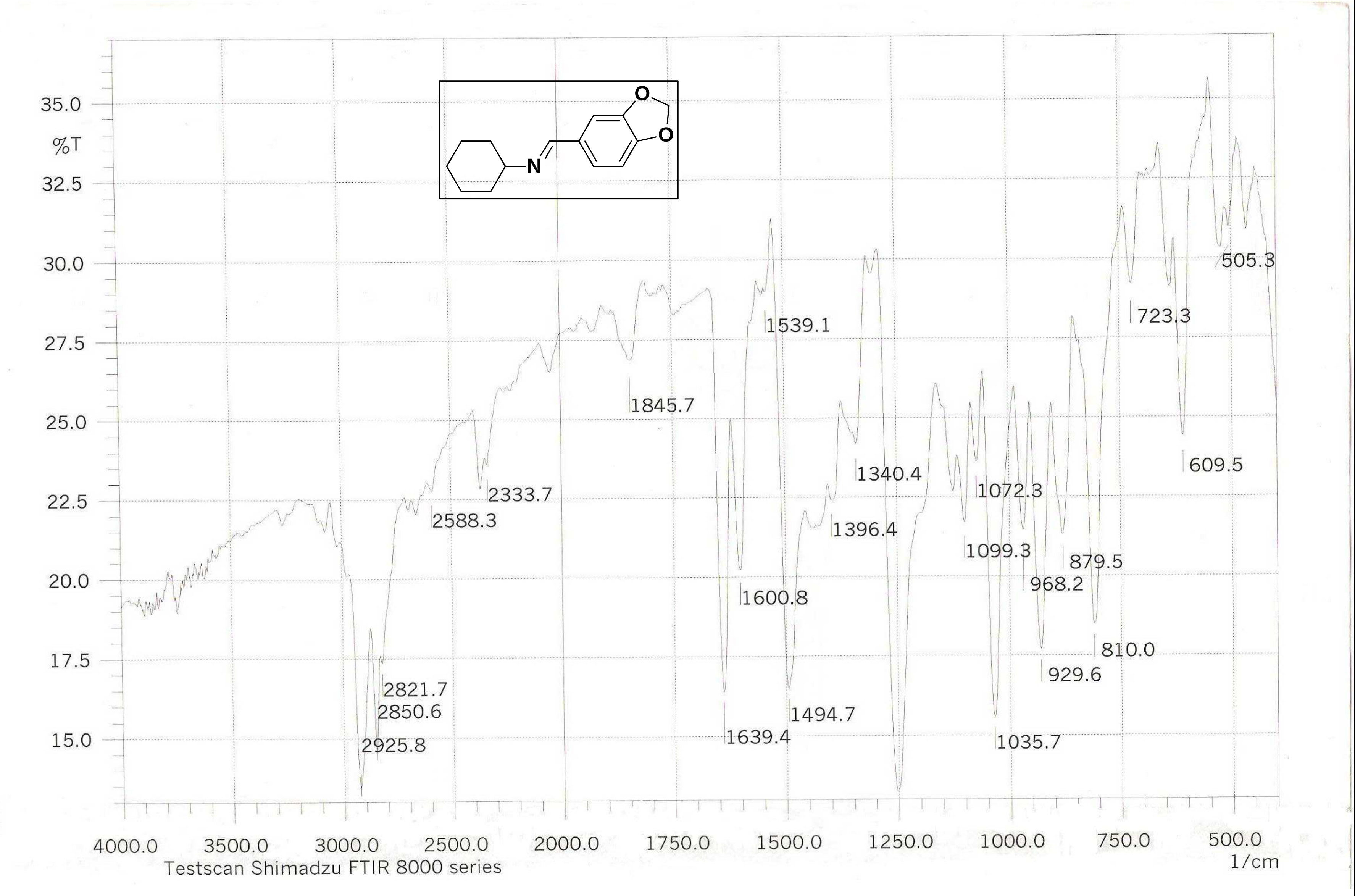


Figure (3-1): F.T.IR spectrum of [L_A].

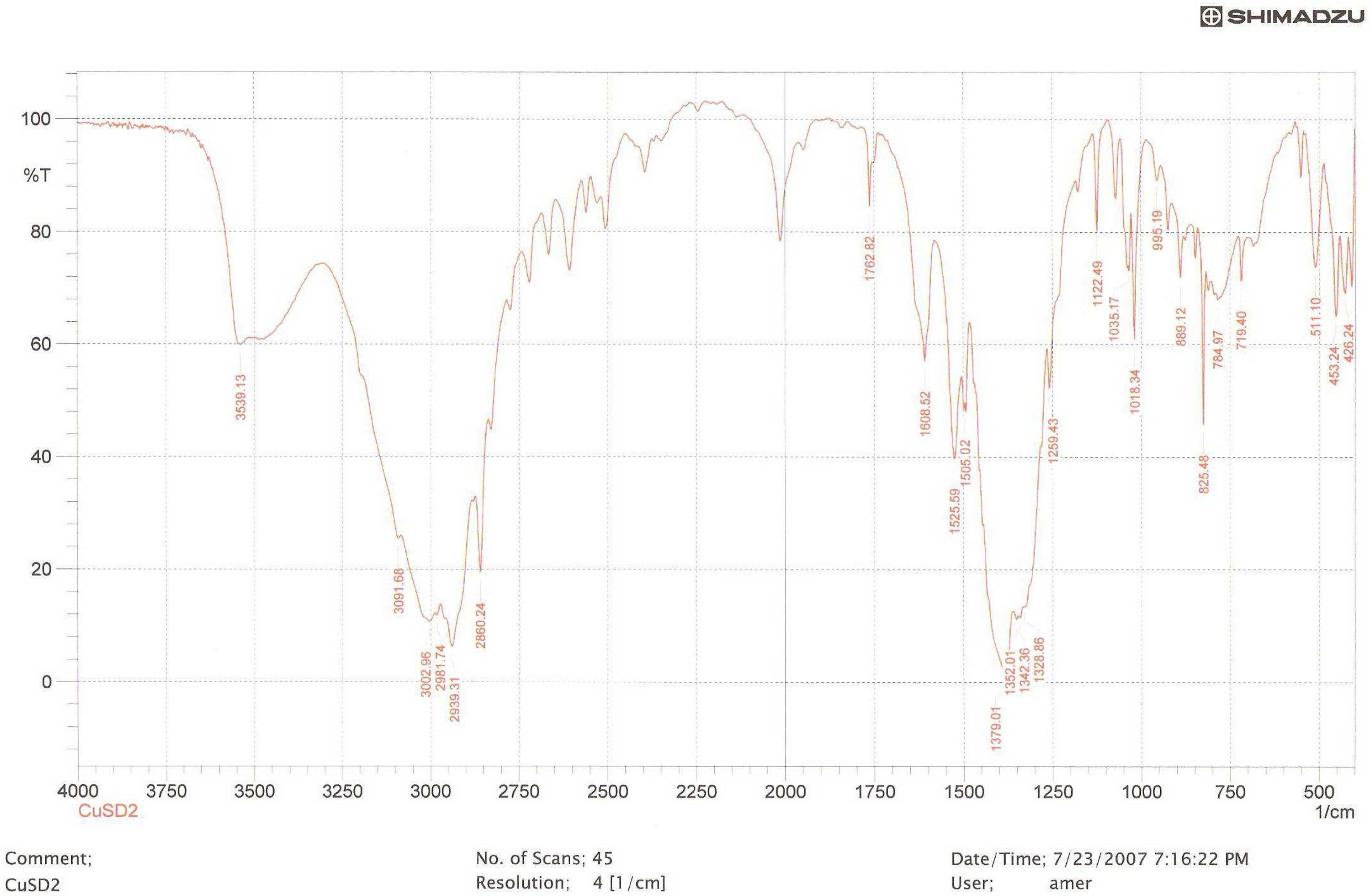


Figure (3-2): F.T.IR spectrum of [L_ACu(II)].

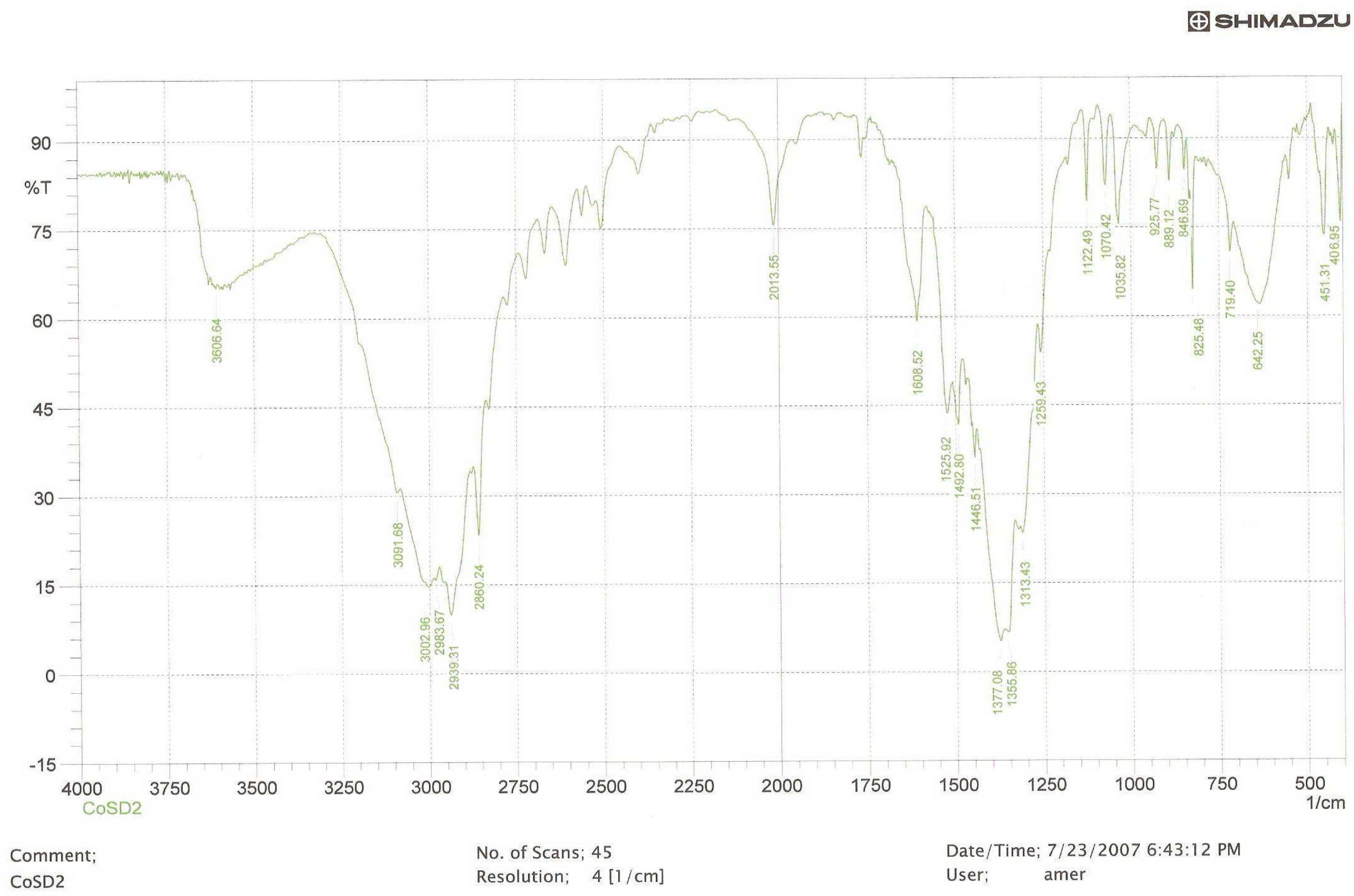


Figure (3-3): F.T.IR spectrum of [L_ACo(II)].

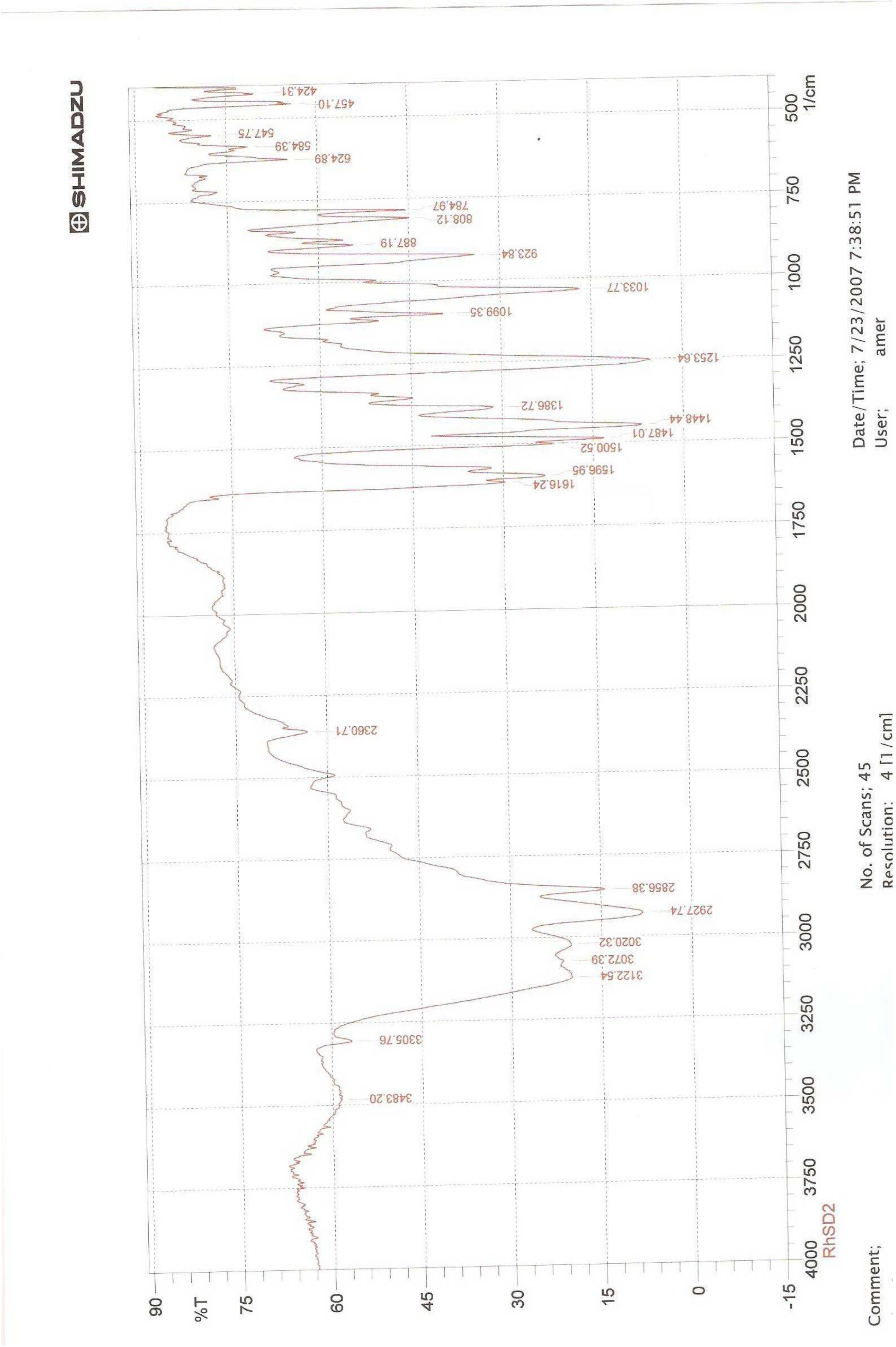


Figure (3-4): F.T.IR spectrum of [L_ARh(III)].

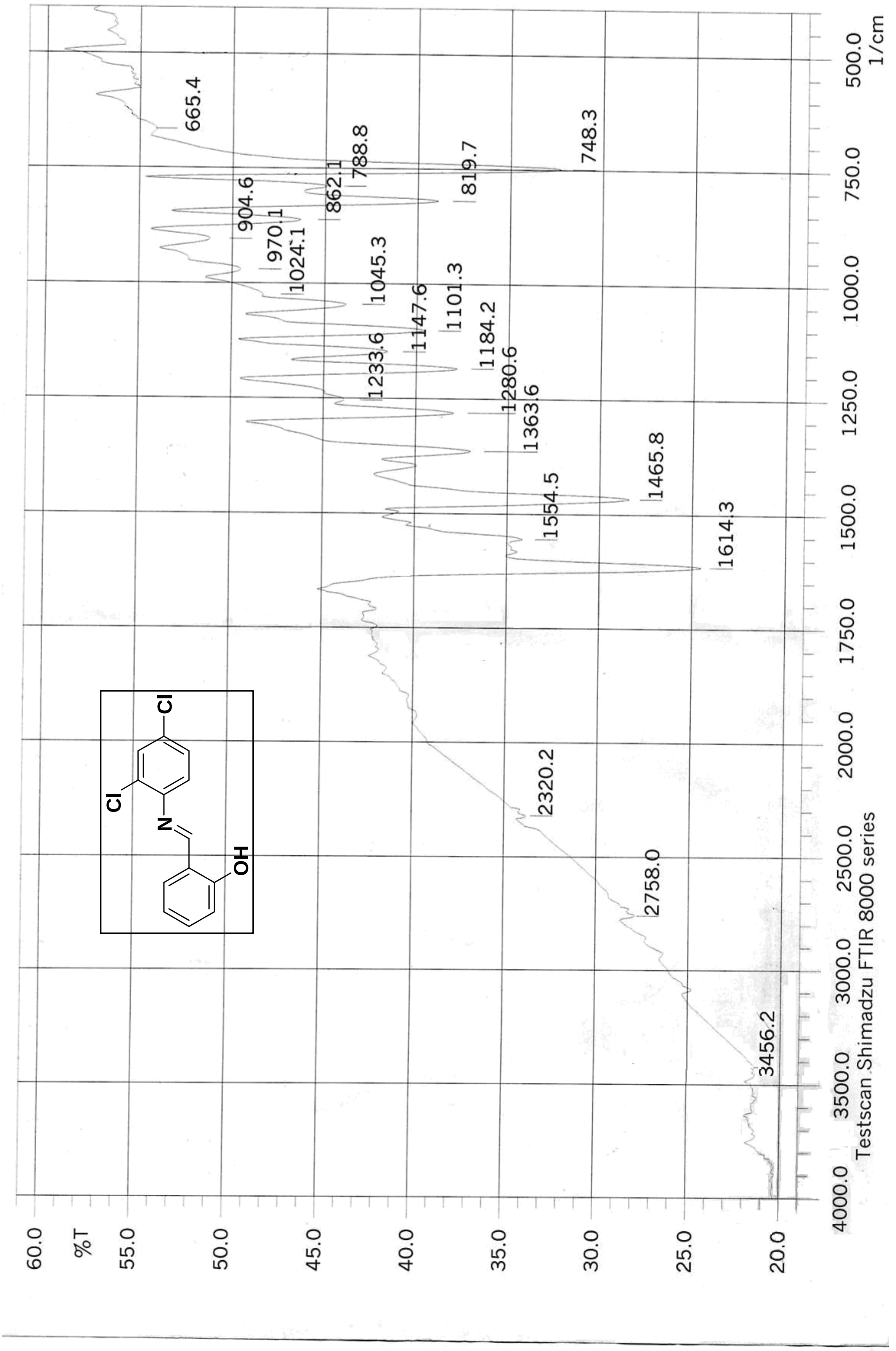


Figure (3-5): F.T.IR spectrum of[L_B].

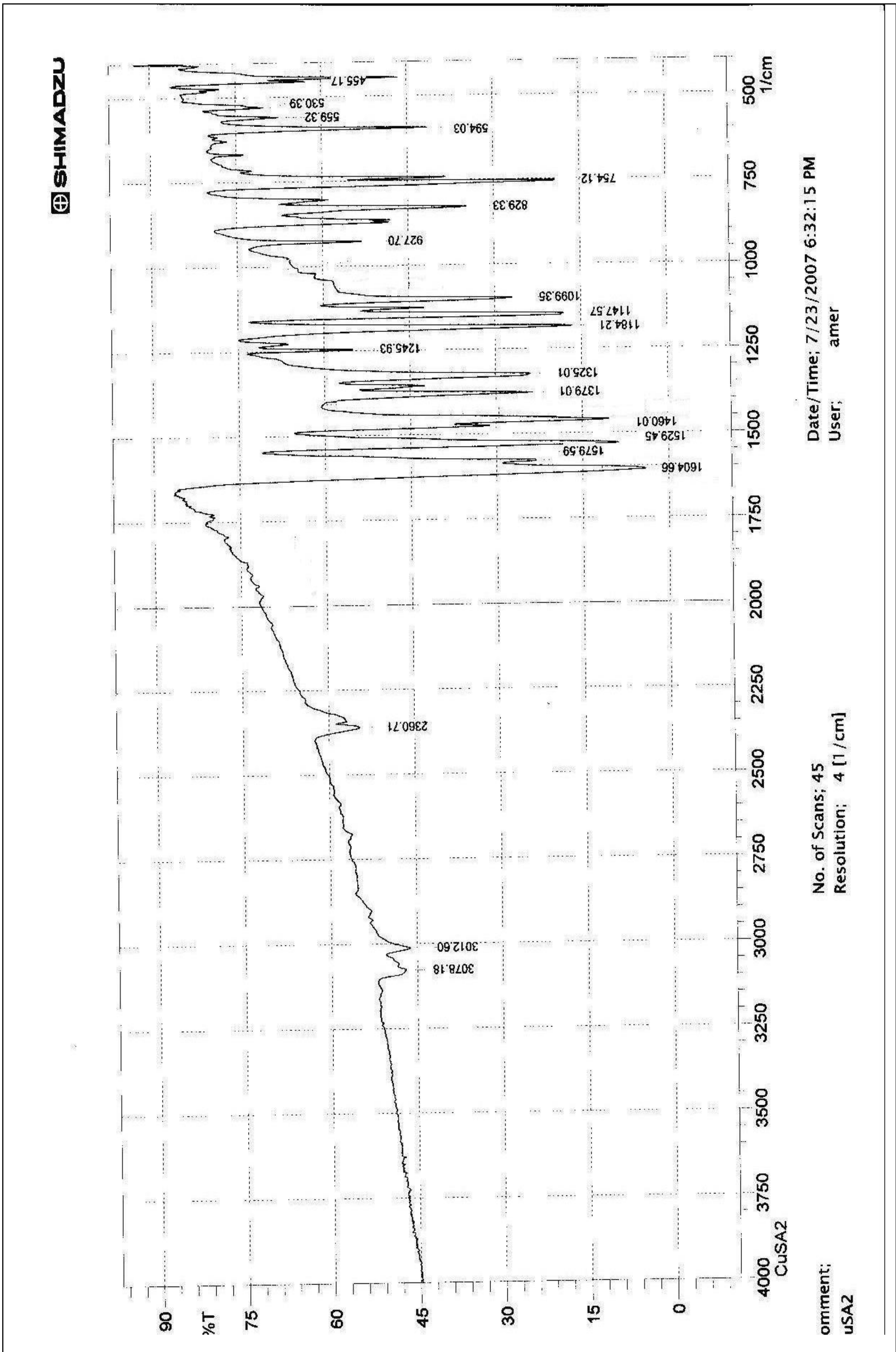


Figure (3-6): F.T.IR spectrum of [L_BCu(II)].

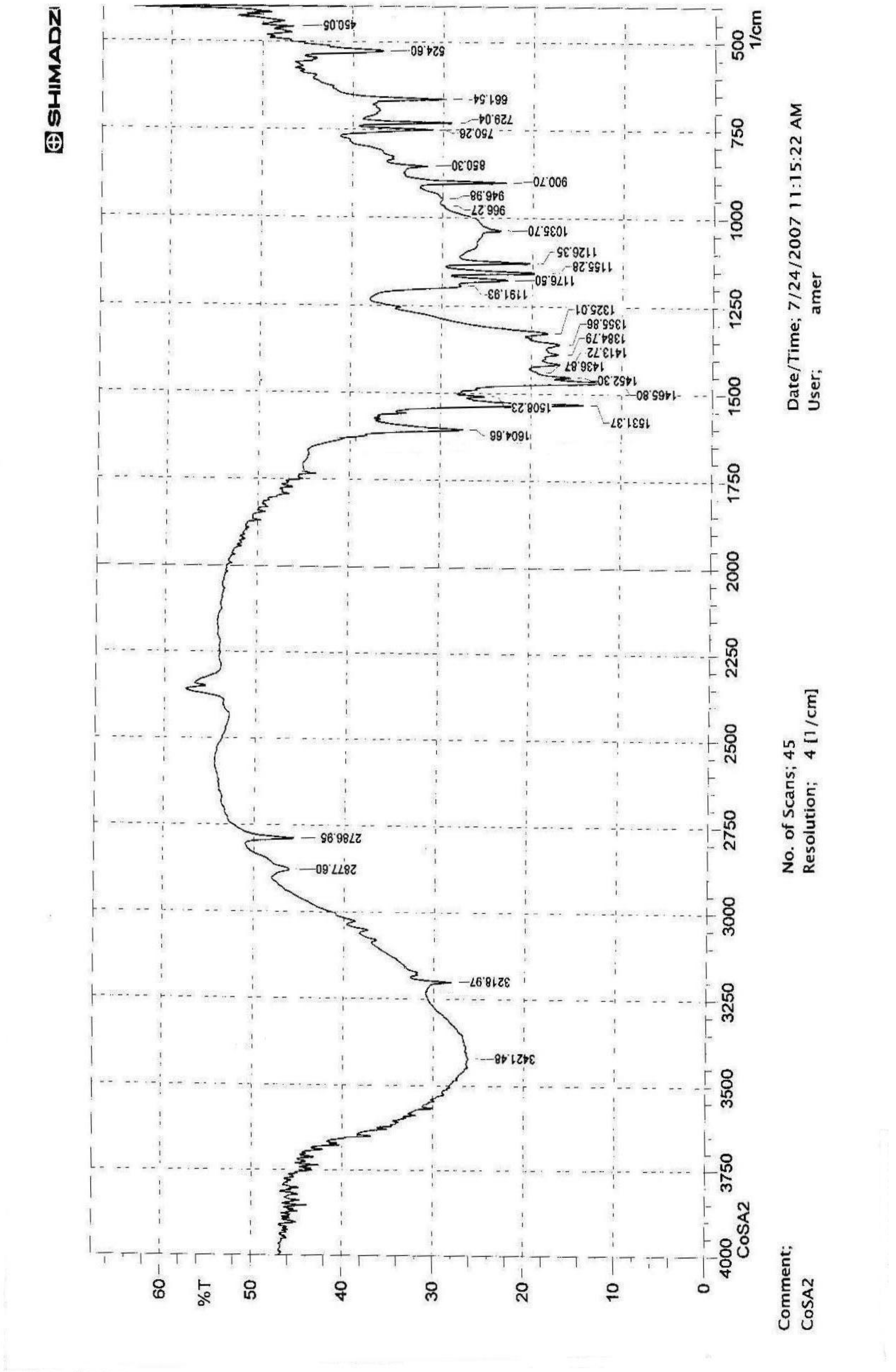


Figure (3-7): F.T.IR spectrum of [L_BCo(II)].

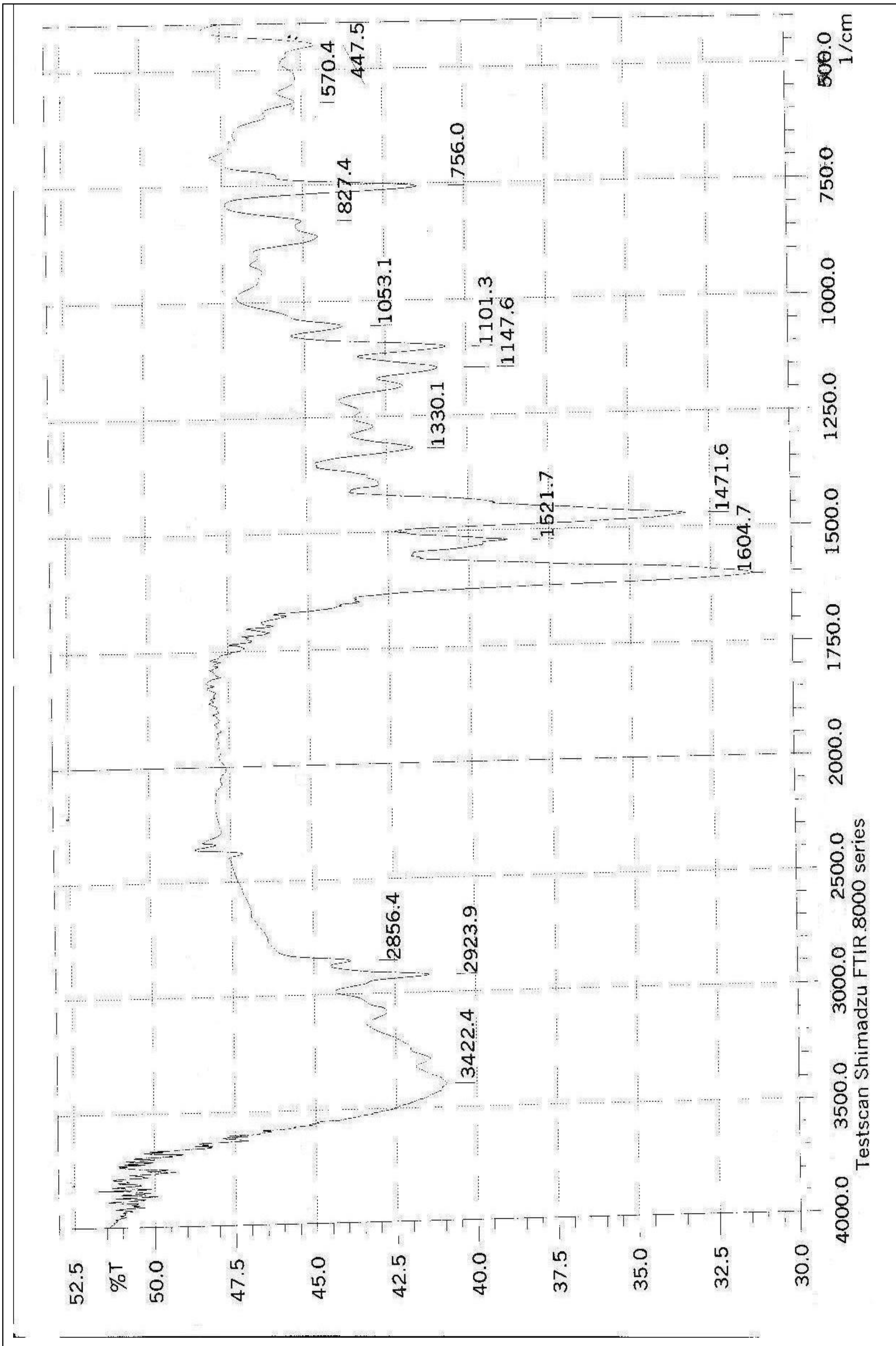


Figure (3-8): F.T.IR spectrum of [L_BRh(III)].

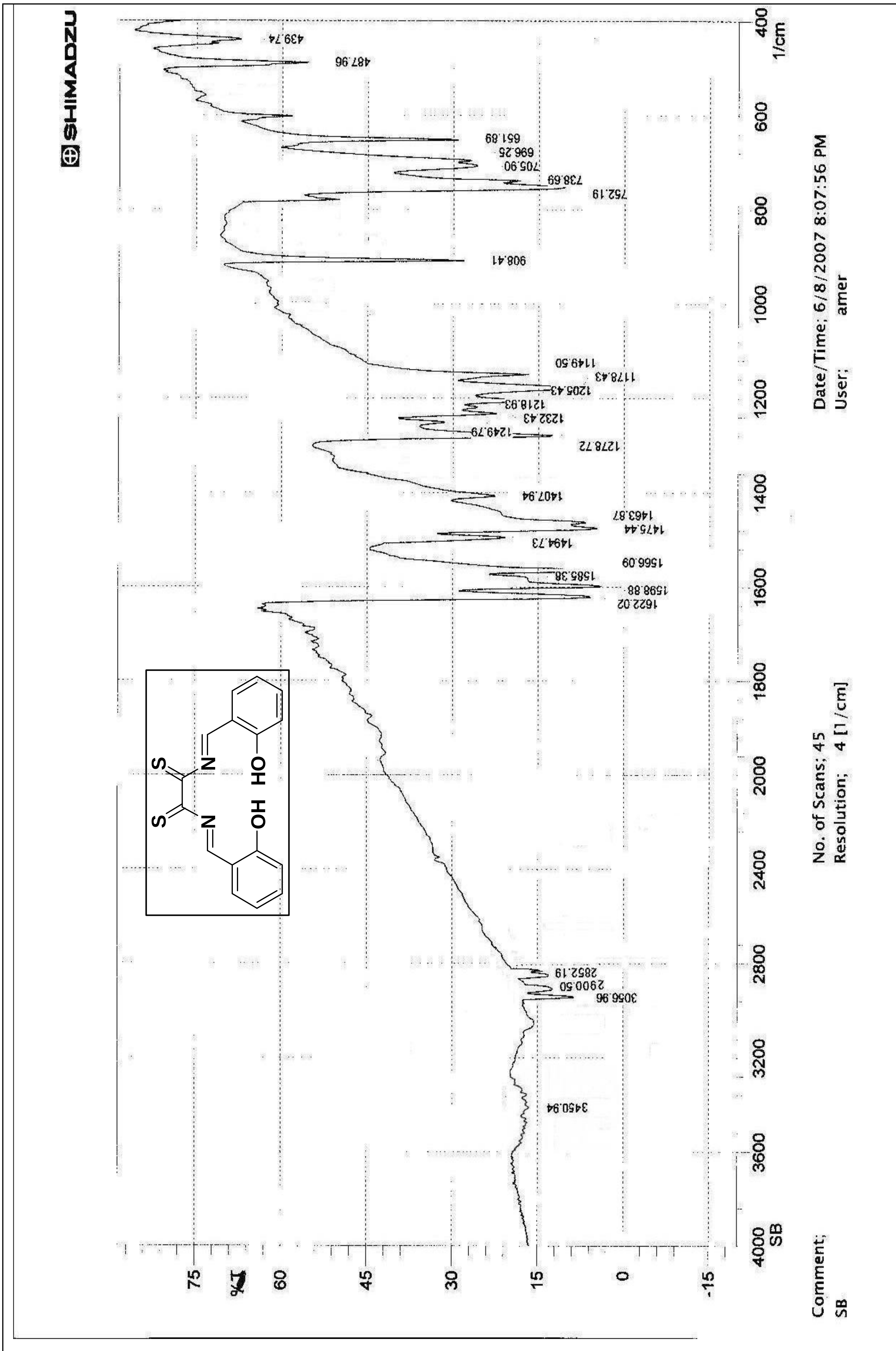


Figure (3-9): F.T.IR spectrum of [L_C].

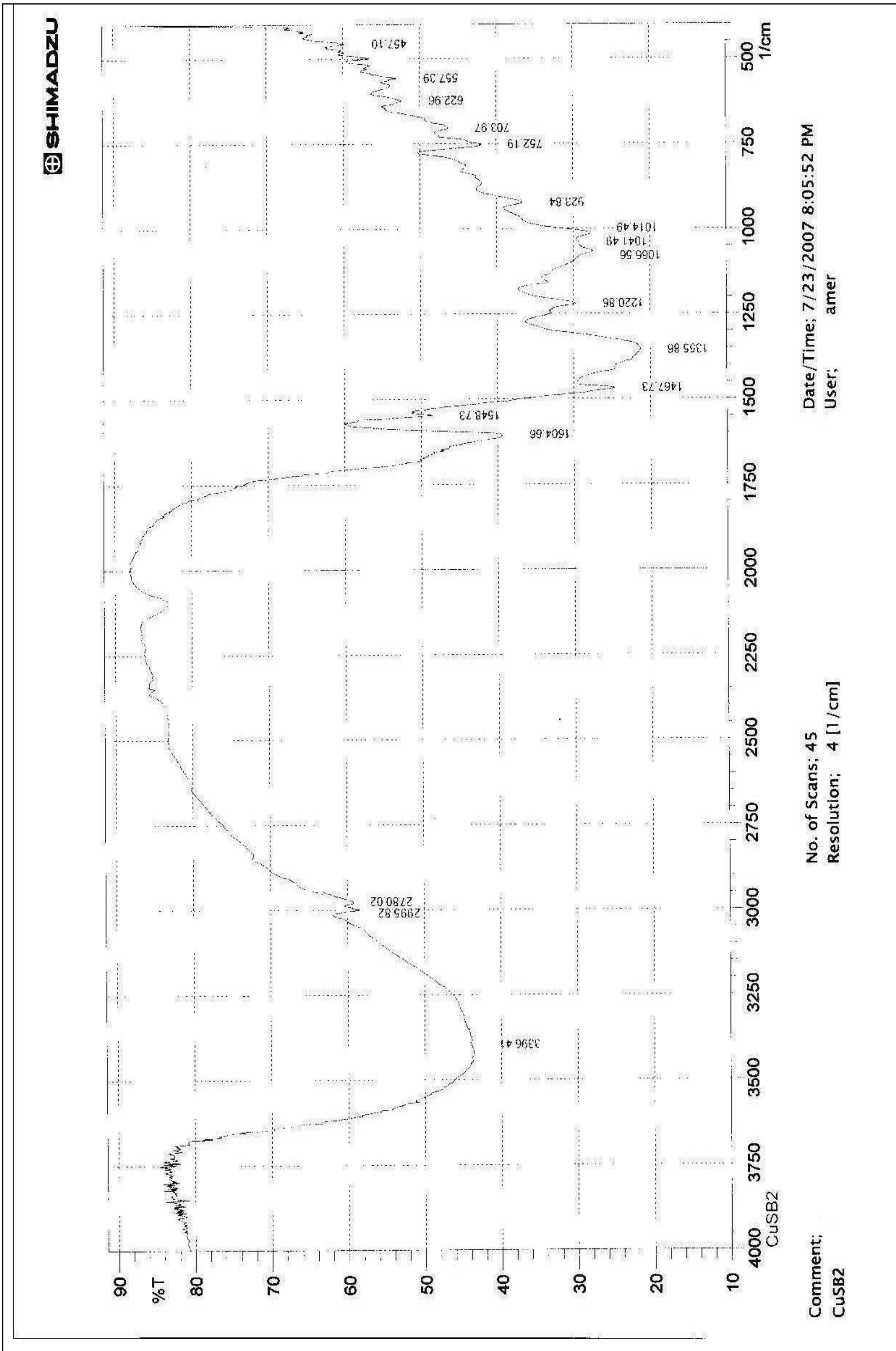


Figure (3-10): F.T.IR spectrum of $[L_C Cu(II)]$.

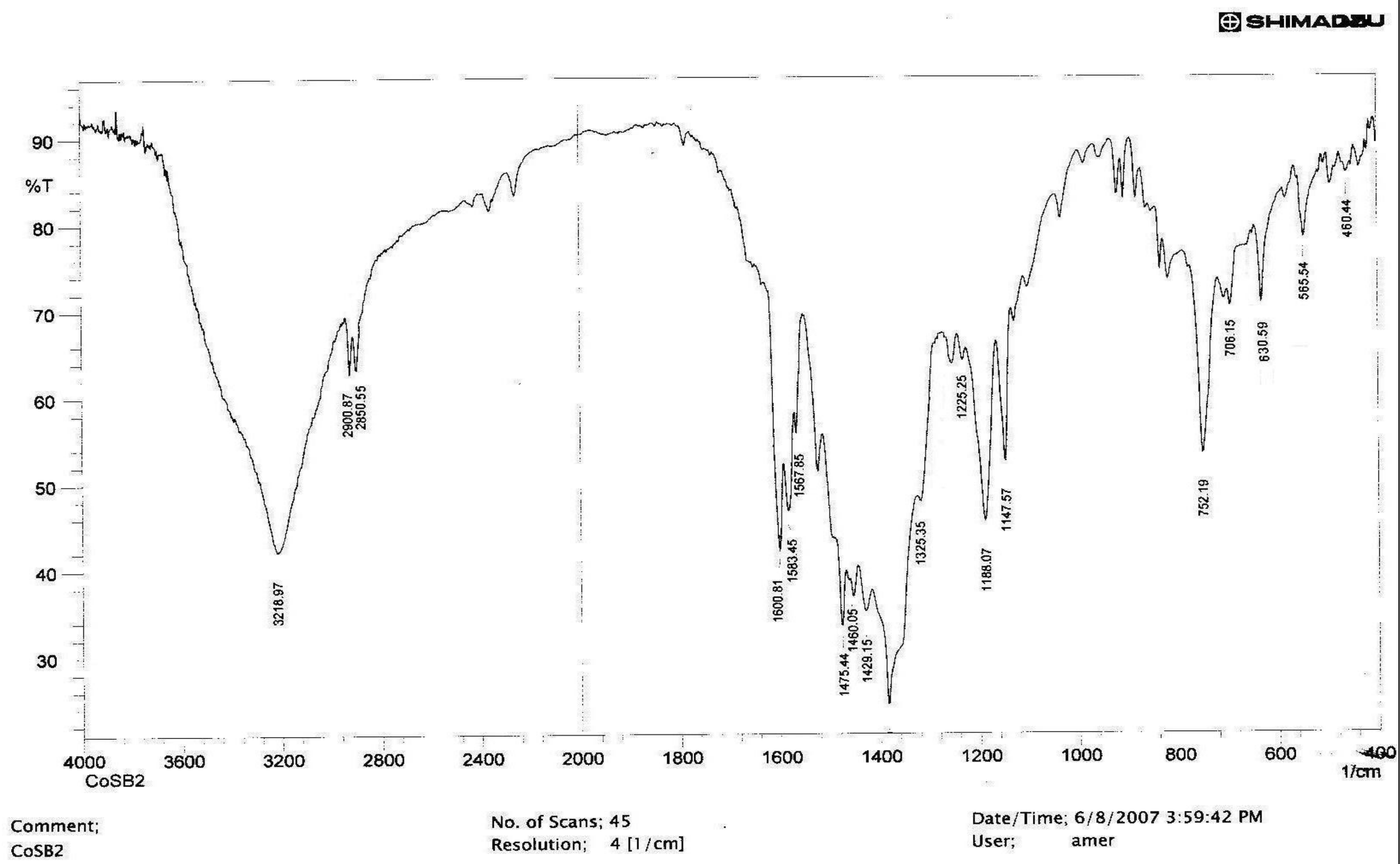


Figure (3-11): F.T.IR spectrum of [L_CCo(II)].

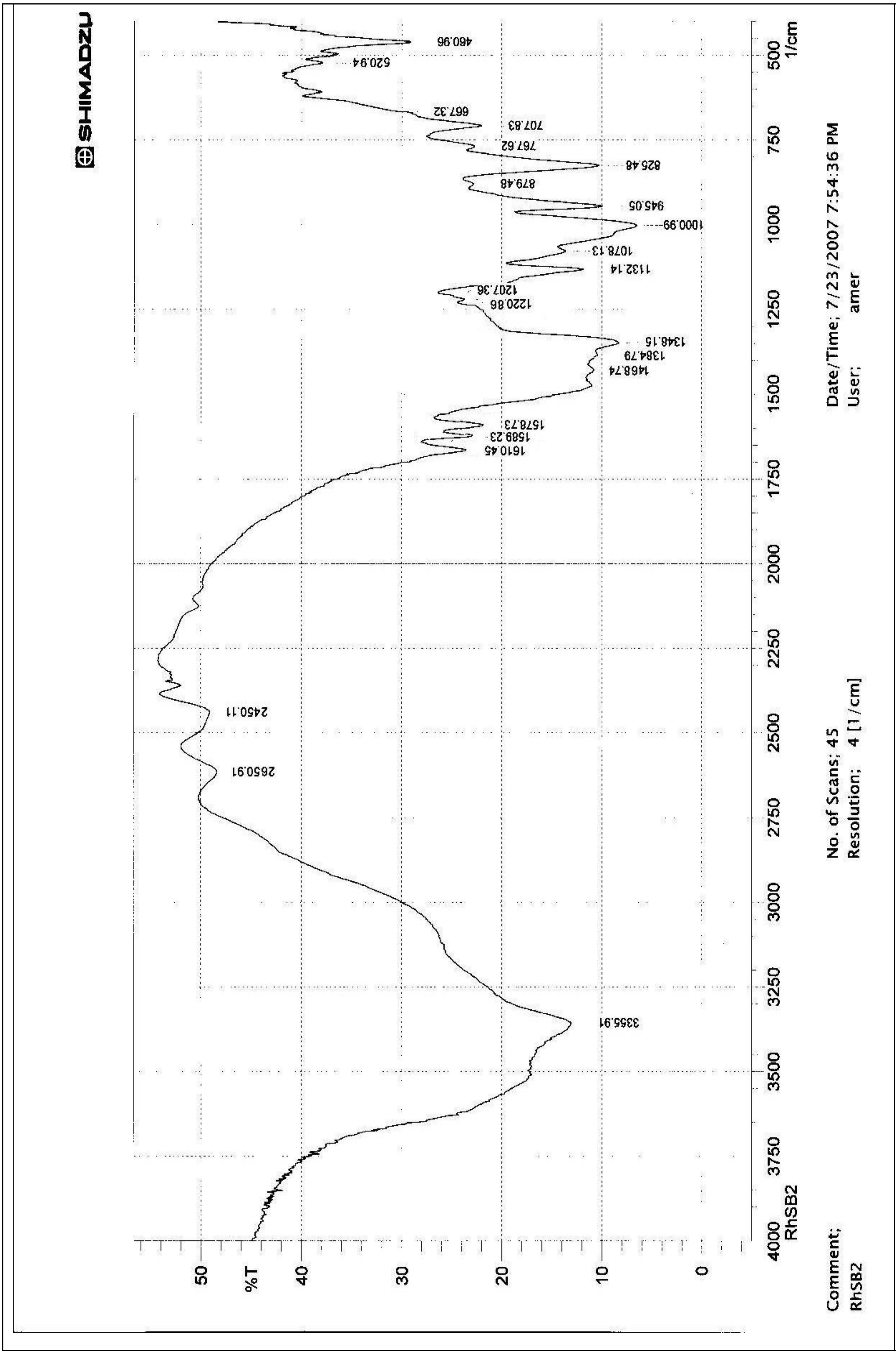


Figure (3-12): F.T.IR spectrum of [L_CRh(III)].

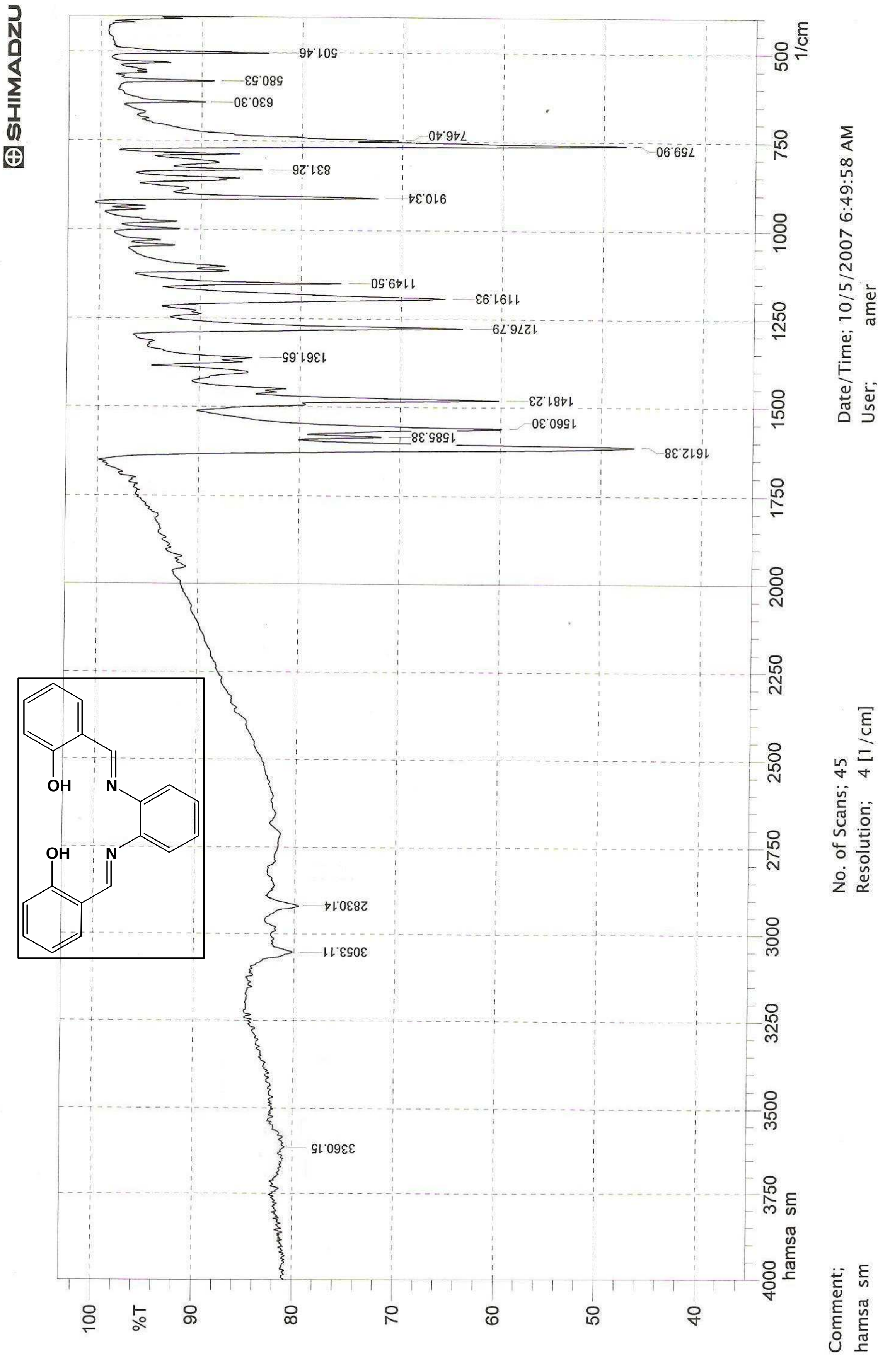


Figure (3-13): F.T.IR spectrum of [L_D].

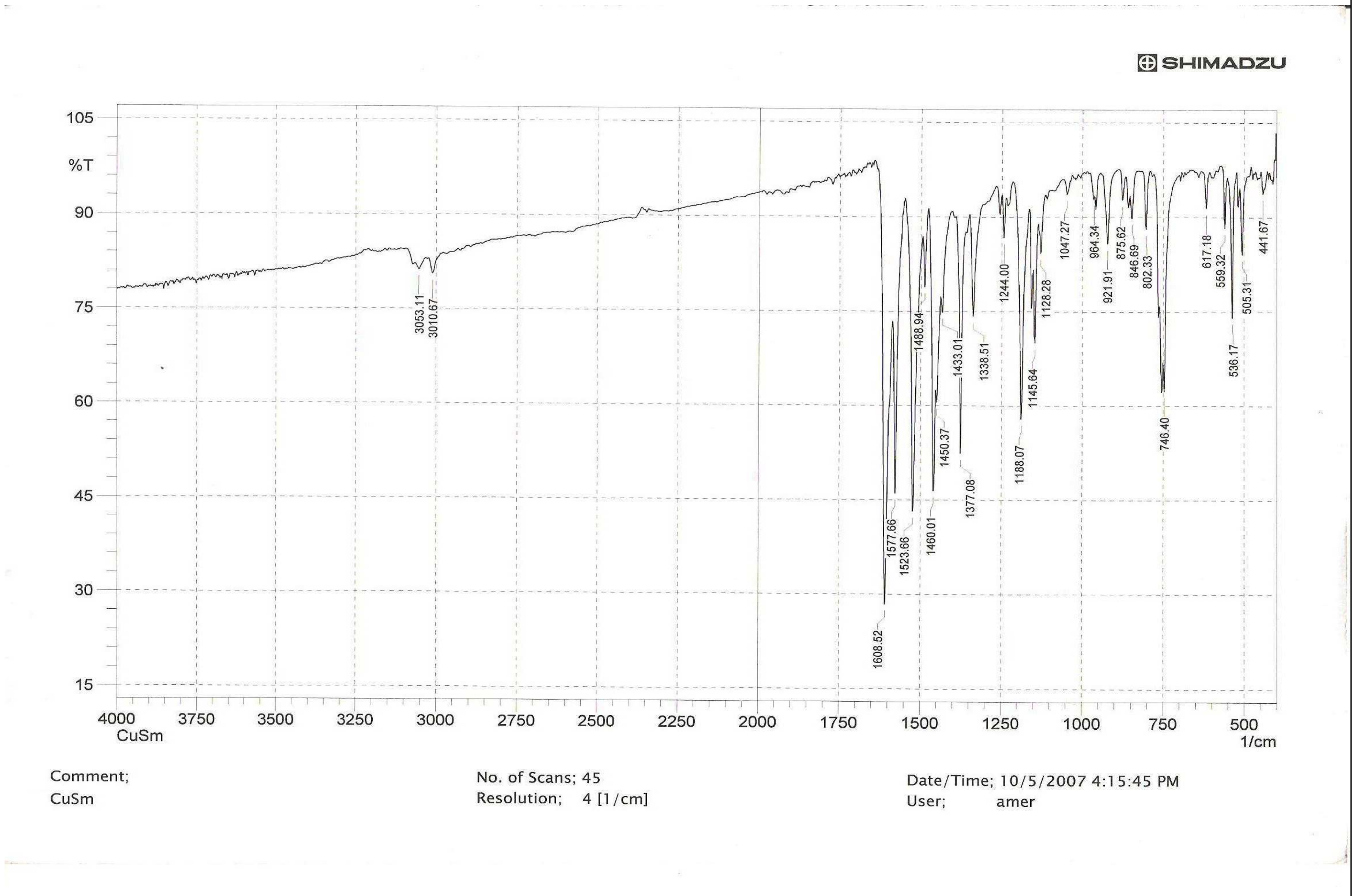


Figure (3-14): F.T.IR spectrum of [L_DCu(II)].

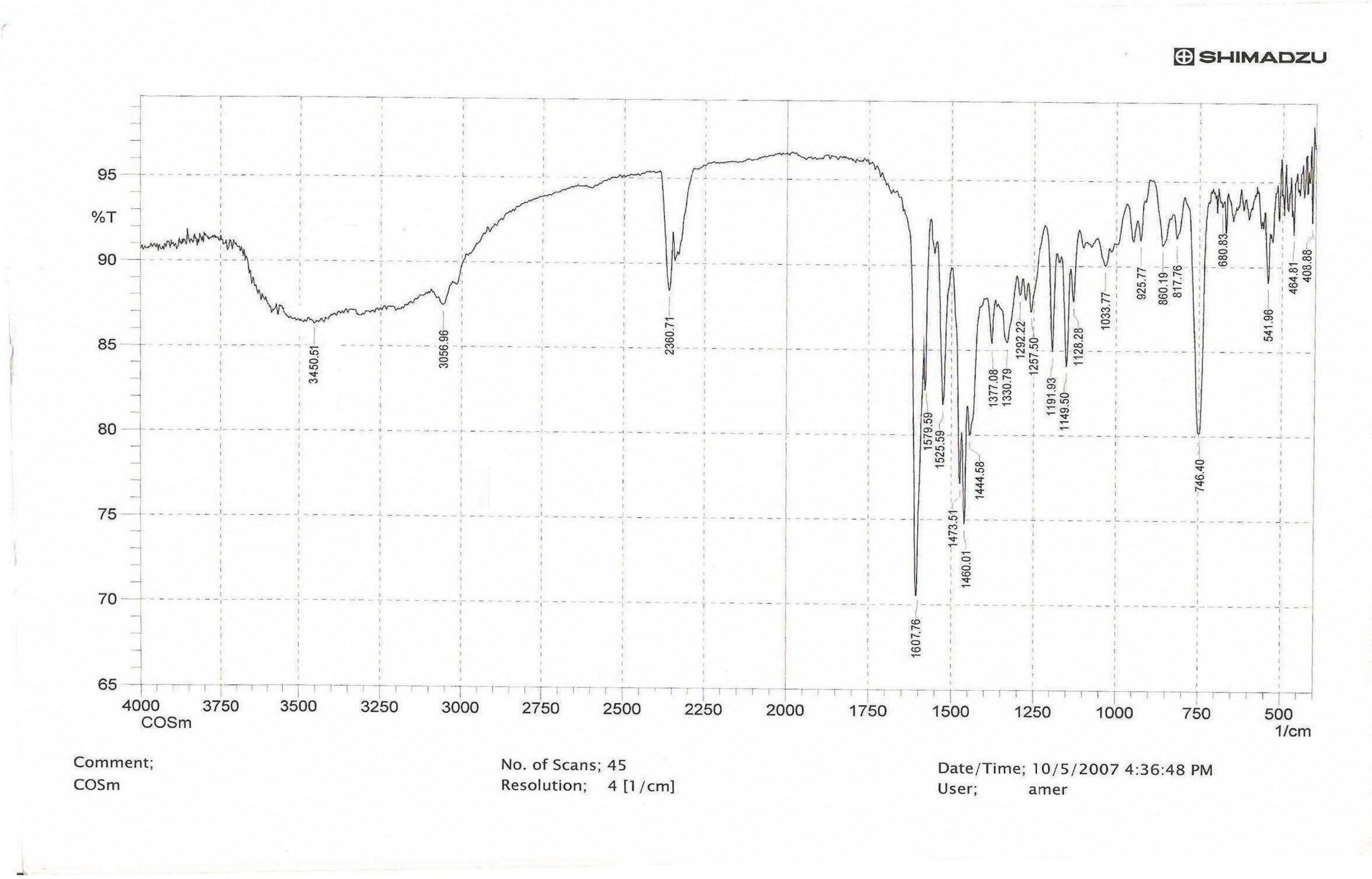


Figure (3-15): F.T.IR spectrum of $L_DCo(II)$.

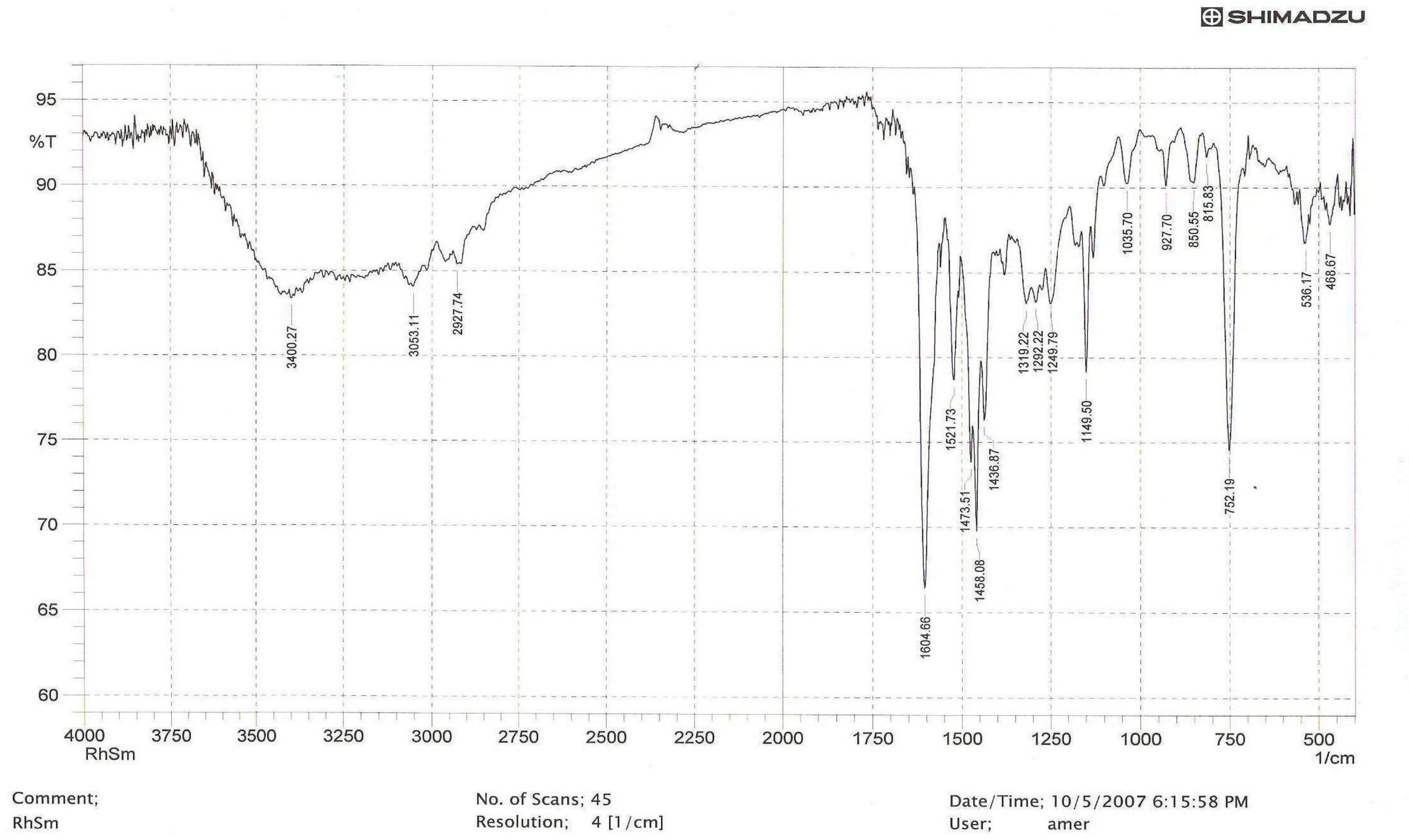


Figure (3-16): F.T.IR spectrum of [L_DRh(III)].

(3-3) Magnetic susceptibility measurements:-

Magnetic measurements are widely used in studying transition metal complexes. The magnetic properties are due to the presence of unpaired electrons in the partially filled d-orbital in the outer shell of these elements. These magnetic measurements give an idea about the electronic state of the metal ion in the complex. Also provide information about the type of bonding and strength of ligand field of complexes by giving information about the number of unpaired electrons (90).

The resultant magnetic moment of an ion is due to both orbital and spin motions (91). The magnetic moment is given by the following equation:

$$\mu_{s+L} = \sqrt{4s(s+1) + L(L+1)} \quad \text{B.M.}$$

μ = magnetic moment

S= spin quantum number

L= orbital quantum number

B.M = 9.27×10^{-24} J.T $^{-1}$

In the determination of the electronic structure requires consideration of the orbital moment, for most complexes of the first transition series the spin-only moment is sufficient, as any orbital contribution is small(92). So the effective magnetic spin of the complexes was measured using spin only magnetic moment according to the following equation:

$$\mu_{s.o} = \sqrt{4s(s+1)} \quad \text{B.M.}$$

or

$$\mu_{s.o} = \sqrt{n(n+2)} \quad \text{B.M.}$$

Where:

S= n $*$ (1/2), (n= number of unpaired electrons).

The value of magnetic susceptibility of the prepared complexes at room temperature is calculated using the following equation

$$\mu_{eff} = 2.828\sqrt{X_A * T} \quad \text{B.M.}$$

Where:

$X_A = X_M + D$

$X_M = X_g * M.wt$

Where:

X_A=atomic susceptibility.

X_M = molar susceptibility.

X_g =mass susceptibility.

D = Correction factor.

M.wt = Molecular weight of complex.

T = Temperature in Kelvin (ºC +273)

μeff =Effective magnetic moment.

Also the value of X_g can be calculated by the following relationships:

$$X_g = \frac{C * I * (R - R^0)}{(m_2 - m_1) * 10^9}$$

Where:

C= Calibration constant.

I= Length of the sample in the tube.

R= Reading of tube with sample.

R^0=Reading of tube empty.

m_2=Weight of tube with sample.

m_1=Weight of tube empty.

Table (3-14) shows the experimental values of magnetic moment which were usually greater than the calculated value of magnetic moment.

(3-4):Study of the electronic spectra and conductivity measurements of ligands and their metal complexes:-

Electronic absorption spectra of transition metal complexes are usually attributed to the partially filled d-orbital of the metal, the energy required for such transitions is that of the near UV and visible region.

Charge transfer spectra are due to transitions between metal and ligand. Study of electronic spectra of complexes help in the determination of structure of the complexes through the electronic interaction of the metal d-orbital and ligand orbital. In our case, the spectra were recorded in the range (200-1100) nm,

The molar conductance values of all the complexes have been measured in (DMSO) as a solvent at concentration of (10^{-3}M) and at room temperature (25°C), the molar conductivity was applied to help in the investigation of the geometrical structures of the complexes and determination electrolytic or non-electrolytic nature of the complexes (93, 94).

Table (3-13) show the positions of electronic absorption bands and their transitions and also include the calculated value of Racah parameter (B'), 10Dq and nephelauxetic factor (β), Table (3-14) show molar conductivity measurements for prepared complexes at room temperature and the suggested structure for each complex, the structures were suggested for the prepared complexes according to the position of the infra-red spectra, electronic absorption bands, atomic absorption, magnetic properties and electric conductivity measured for these complexes.

(3-4-1): Electronic Spectra of the Ligands L_A, L_B, L_C and L_D:-

The Electronic spectra of Schiff bases ligands in (UV-Vis) region in DMSO solvent at (10^{-3}M) have been generally exhibit in three main bands:

The first absorption band appeared at 249 nm (40,160cm^{-1}), 272 nm (36,764 cm^{-1}), 322 nm (31,055 cm^{-1}) and 302 nm (33,112 cm^{-1}) for L_A, L_B, L_C and L_D respectively which can be attributed to ($\pi \rightarrow \pi^*$) transition for the aromatic system.

The second absorption band are attributed to ($\pi \rightarrow \pi^*$) transition of imines group, which appeared at 322 nm (31,055 cm^{-1}), 327 nm (30,581 cm^{-1}), 359 nm (27,855 cm^{-1})and 339 nm (29,498 cm^{-1}) for L_A, L_B, L_C and $L_{D,}$ respectively(95). These bands were not significantly affected by chelating.

The third absorption band appeared at 348 nm (28,735 cm^{-1}), 405 nm (24,691 cm^{-1}), 415 nm (24,096 cm^{-1})and 392 nm (25,510 cm^{-1}) in the spectra of the ligands L_A, L_B, L_C and L_D respectively are assigned to ($n\rightarrow\pi^{*)}$ transition (96).Which are shifted to a longer wavelength (red shift) upon formation of the complexes. This shift may be attributed to the donation of the lone pairs of the nitrogen atoms of the Schiff base to the metal ion (N:→M) (97).

Figures (3-19), (3-23), (3-27) and (3-31) show the UV-Vis. Spectra of the new ligands L_A, L_B, L_C and L_D. Table (3-13) contains the position and assignment of the absorption bands.

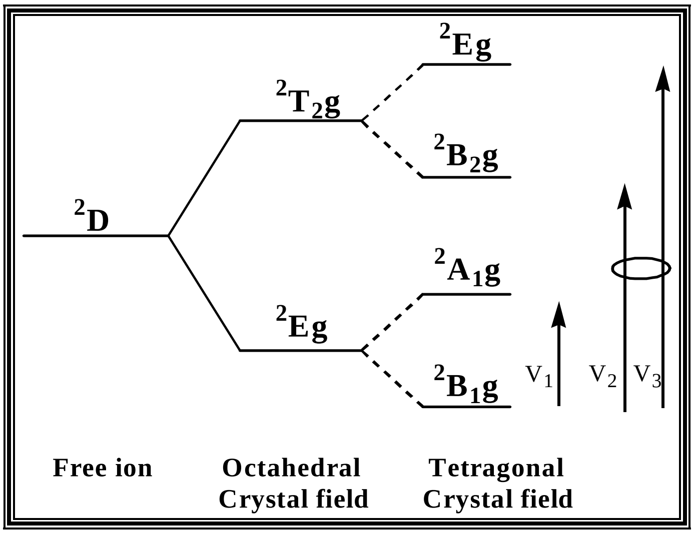
(3-4-2) Electronic Spectra of the L_A Complexes:-

A- UV-Visible Spectrum of the Cu (II) complex (L_ACu*(II)):-*

Electronic spectrum of complex (L_ACu(II)) is shown in Figure (3-20), Table (3-13). The brownish green color is attributed to the single broad absorption band in the region (11,000-16,000 cm^{-1})(1), the d^9 ion is characterized by large distortion from octahedral geometry. Octahedral complex for Cu (II) usually have three bands but unfortunately these bands can not be clearly assigned, this difficulty is due to the greater overlapping of the bands, which usually occurs in the case of Cu (II) complexes.

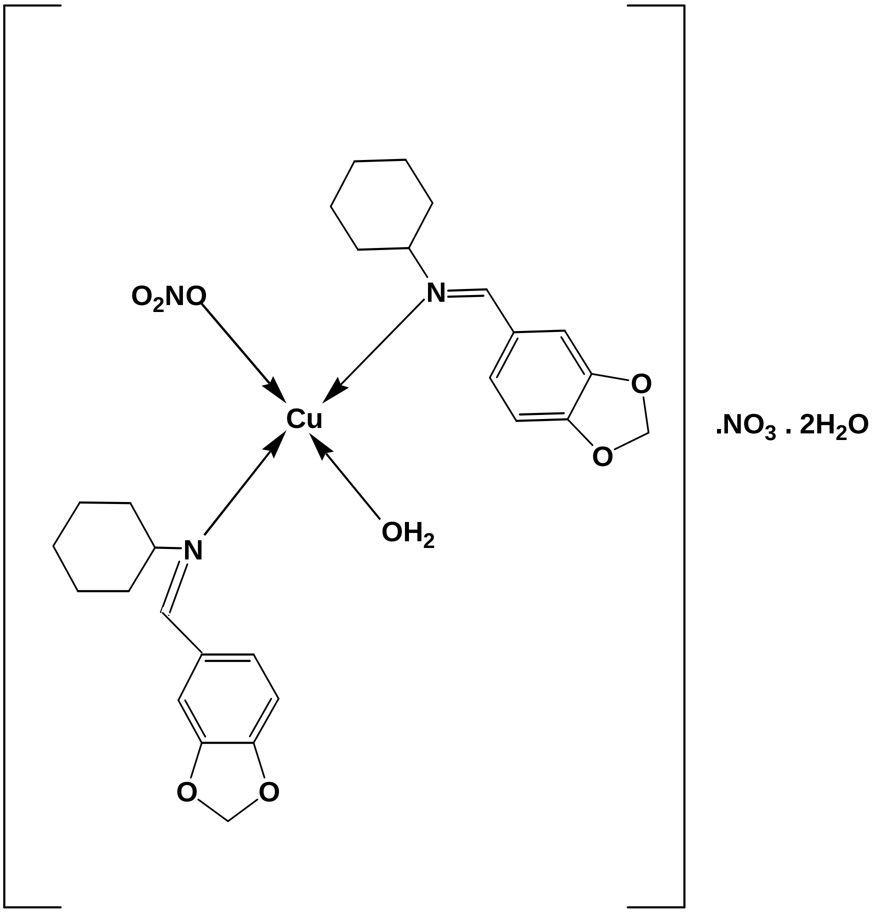
In the present work, the brownation green (L_ACu)complex show a broad band at (16077 cm^{-1}) which can be assigned to $^2B_{1g} \rightarrow$ ^2E_g transitions , this band refers to highly distorted octahedral geometry (Jahn-Teller distortion) (4, 98). Which strongly favor the square planar geometry.

The free ion ground ^2D term is expected to spilt in a crystal field in the same way as the ^5D term of the d^4 ion and a similar interpretation of the spectra is likewise expected , and according to the following (1, 98):



Scheme (3-5): Crystal field splitting of the ^2D term of a d^9 ion.

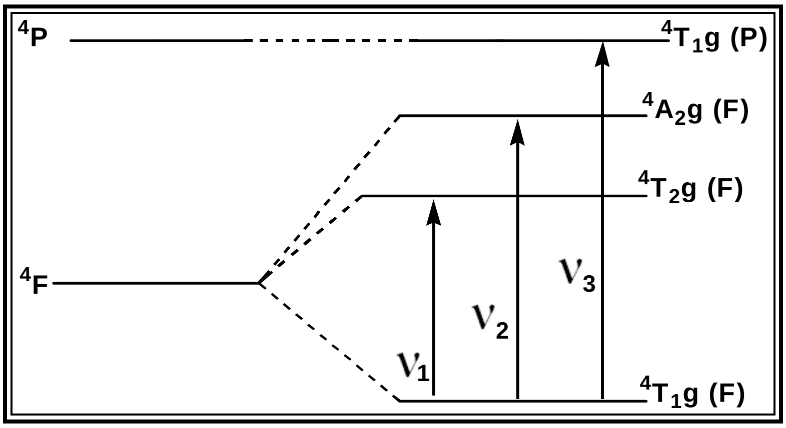
The magnetic moment value at room temperature of this complex is (1.21 B.M) lower than 1.73 B.M which is indicated the formation of square planar geometry(99). Conductivity measurements show that the complex is ionic Table (3-14), from these results and that of FT-IR study the suggested structure is as follows:



B- UV-Visible Spectrum of the Co(II) complex (L_ACo(II)):-

Electronic spectra of cobalt (II) complex Figure (3-21) show three transitions, but these transitions can not be assigned because of the greater overlapping of them(1, 4, 98).

The term symbol for the ground state of Co(II) ion ^4F which can split in octahedral crystal field as follows(4, 98):



Scheme (3-7): Crystal field splitting of the ^4F term of a d^7 ion.

So their are three allowed transitions could be noticed with octahedral geometry of Co (II) complexes (100).

^4T_1g (F) → ^4T_2g (F) ν_1 7500 – 12000 cm^{-1}
^4T_1g (F) → ^4A_2g (F) ν_2 14000 – 16000 cm^{-1}
^4T_1g (F) → ^4T_1g (P) ν_3 18000 – 21000 cm^{-1}

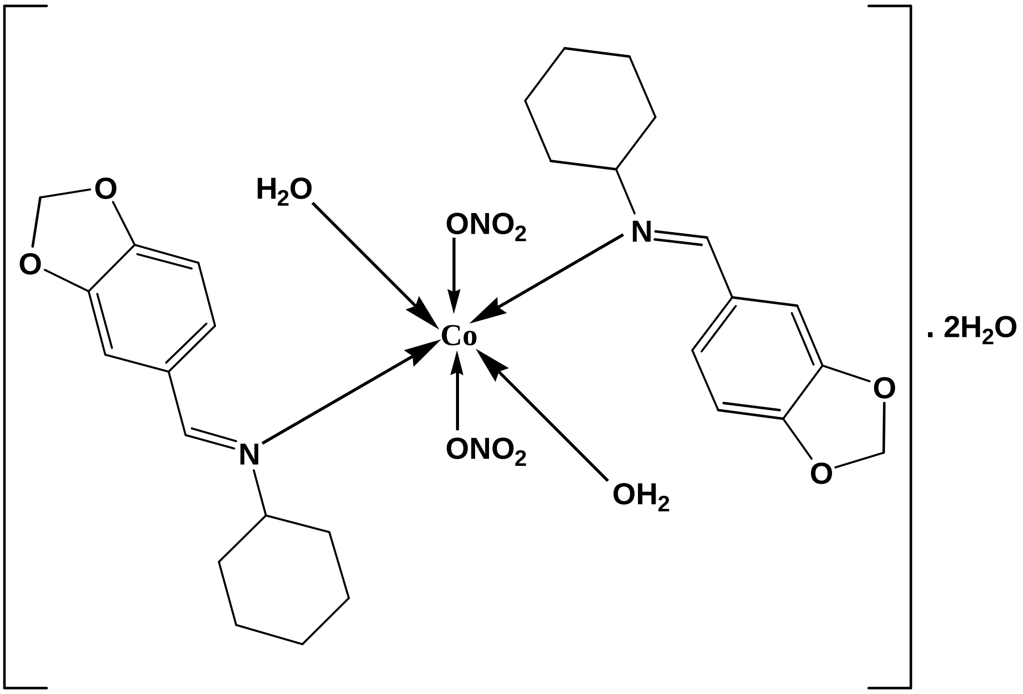
In the present work two bands appear; one at (13,792 cm^{-1}) and the other at (20,260 cm^{-1}) which were assigned to the transitions ν_2 and ν_3 respectively.

The value of ν_1 was calculated using Tanabe-Sugano diagram for d^7 system, figure (3-17) and found to be (6715 cm^{-1}) which refer to ^4T_1g (F) → ^4T_2g (F) transition. The different ligand field parameters have been calculated using the same diagram, the results are found in Table (3-13). The calculated neuphelauxetic factor (β) was of the value (0.95), this high value refer to the high ionic character of the bonding between the cobalt and the donor atom of the ligand, which reflect on the weakness of the ligand field (4).

Octahedral cobalt (II) complex however maintain a large contribution due to ^4F ground term and exhibit μeff in the range (4.8- 5.2 B.M) (1). The magnetic moment of the (L_ACo(II)) complex was (4.92 B.M), which show the complex to be paramagnetic and have three unpaired electrons indicating a high-spin octahedral configuration.

The formula was further confirmed to be non-ionic by conductivity measurement, Table (3-14).

From these results an octahedral geometry around Co (II) ion can be suggested as illustrated in the following structure



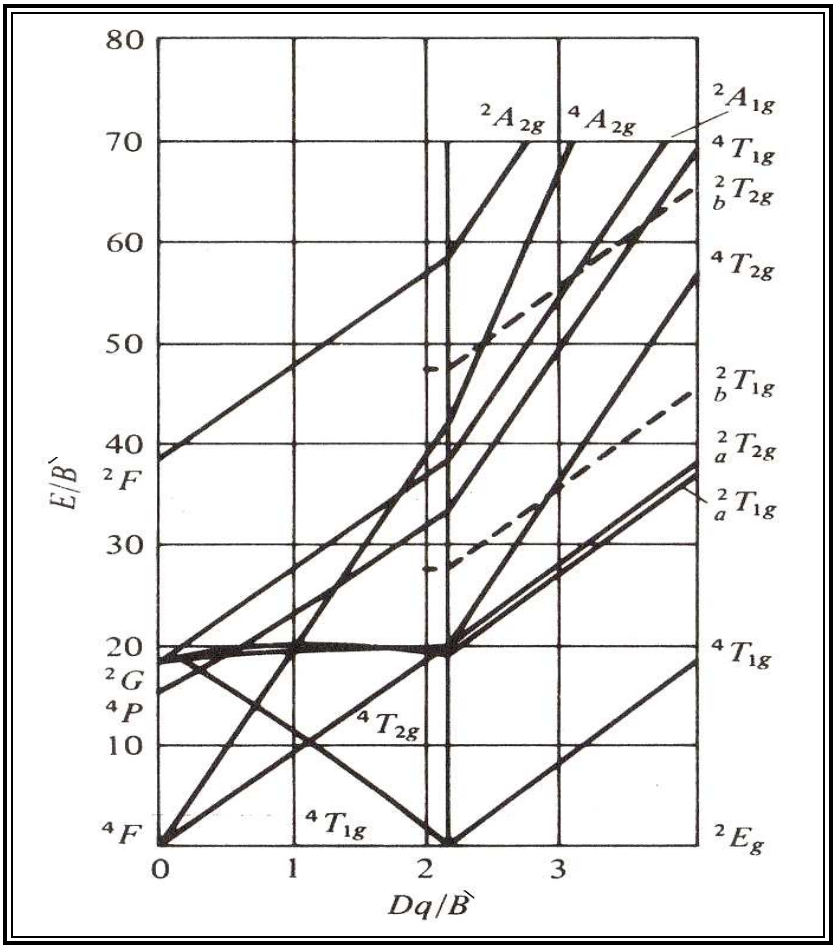


Figure (3-17): Tanabe-Sugano diagram for d^7 system.

C- UV-Visible Spectrum of the Rhodium(III)Complex(L_A Rh(III):-

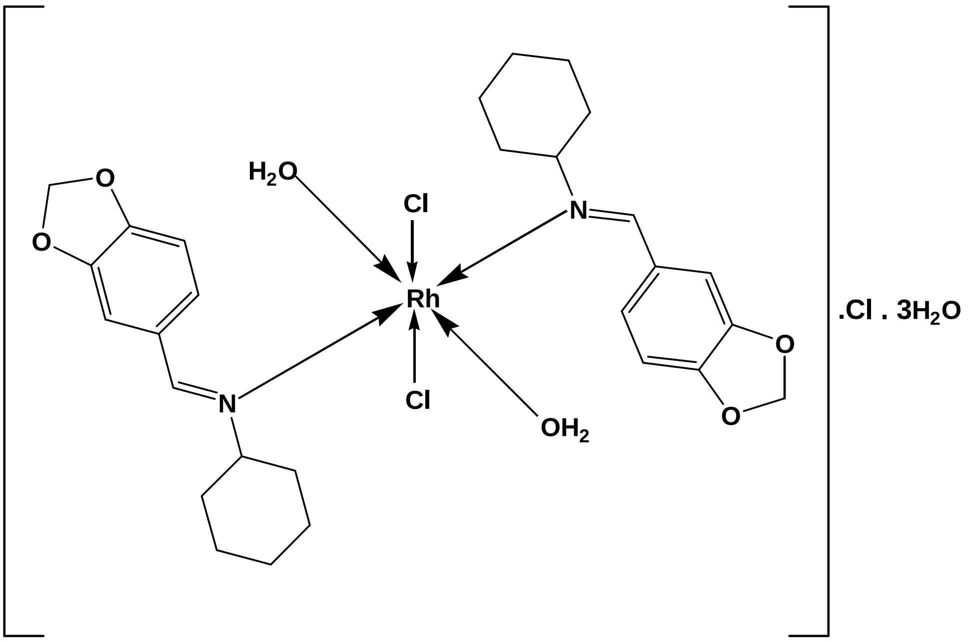
Rhodium (III) complexes exhibit two electronic spectra with spin allowed d-d transitions. These transitions correspond to the [ν_1 $^1A_{1g} \rightarrow {}^1T_{1g}$, and ν_2 $^1A_{1g} \rightarrow {}^1T_{2g}$], these bands resemble to those of reported transitions for other hex coordinated Rhodium complexes (101).

Although in many instances [$^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$] spin allowed ligand field transitions to be observed, also a weak band attributable to the spin-forbidden [$^1A_{1g} \rightarrow {}^3T_{1g}$] transition is indeed observed in some cases in the region of (11,000-14,000 cm^{-1}) (1, 102).

In the present work, the electronic spectra of reddish brown of complex, Figure (3-22) show a broad band at (20,530 cm^{-1}), a second band (27,660 cm^{-1}) which can be assigned to [ν_1 $^1A_{1g} \rightarrow {}^1T_{1g}$, and $\nu_2$$^1A_{1g} \rightarrow {}^1T_{2g}$] transitions, and also weak absorption band appear at (11,001 cm^{-1}) which can be assigned to transitions [$^1A_{1g} \rightarrow {}^3T_{1g}$]. These transitions which agree well with low spin and octahedral geometry for this complex (1, 102). The values of B^-, 10 Dq have been calculated using Tanabe-Sugano diagram for d^6 system, Figure (3-18).By fitting ratio of the frequencies (ν_2/ ν_1) of the observed spin-allowed bands to the Tanabe-Sugano diagram, which produce values of the interelectronic repulsion parameter B^- as well as of the crystal-field splitting 10 Dq.

The low value of neuphelauxetic factor (β) is (0.57) refer to considerable orbital overlap with strong covalence in the metal ligand σ bond(103). Rhodium(III) complex is diamagnetic which refer to strong field.

Conductivity measurements show that the complex is ionic Table (3-13), from these results and that of FT-IR study the suggested structure is as follows:



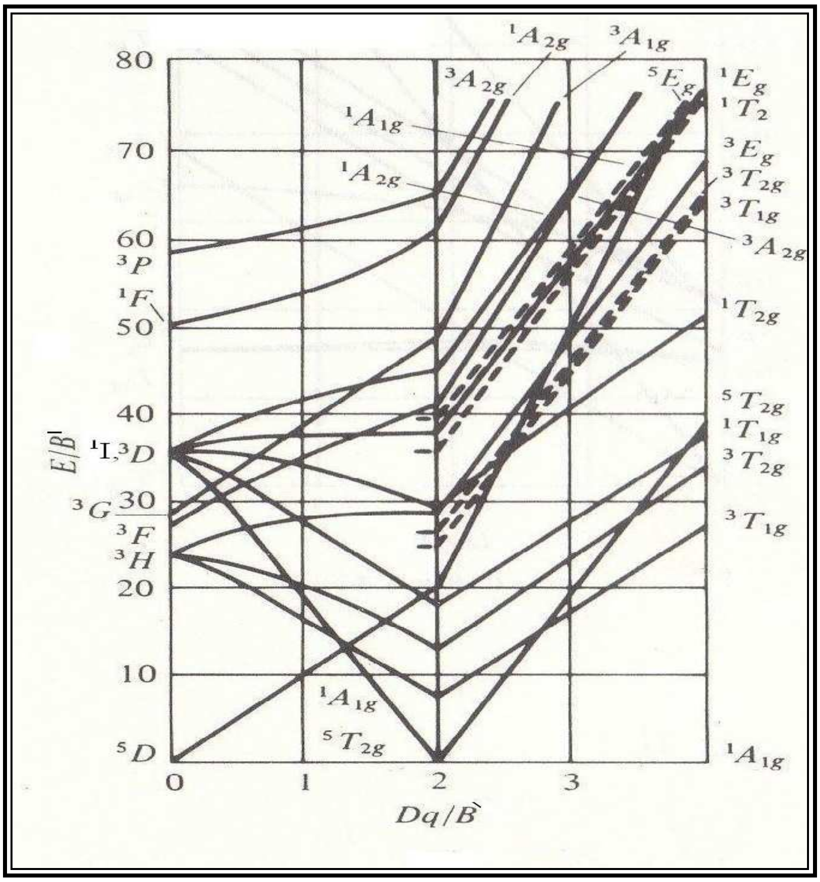


Figure (3-18): Tanabe-Sugano diagram for d^6 system

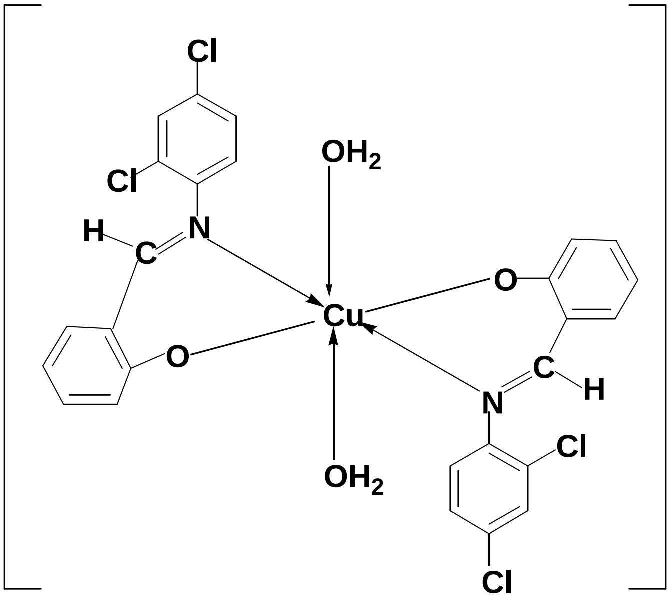
(3-4-3) Electronic Spectra of the L_B Complexes:-

A- UV-Visible Spectrum of the Cu(II) complex (L_BCu*(II)):-*

Electronic spectra of Cu(II) compounds show single broad absorption band in the region (11,000-16,000) cm^{-1}(1). The d^9 ion is characterized by large distortion from octahedral symmetry and the bond is unsymmetrical, being the result of a number of transitions, which are by no means easy to assign unambiguously. The free ion ground ^2D term is expected to split in a crystal field as shown in scheme (3-5)(1, 98).

In the present work, the brown color [L_BCu(II)] which suggest a strong field complex and show a broad band(1, 36) at (15,198 cm^{-1}) this band refer to distort octahedral geometry (Jahn-Teller distortion) (1, 98) which can be assigned to $^2Eg \rightarrow {}^2T_2g$ transitions, Figure (3-24), Table (3-13).

The value of ($\mu_{eff.}$) that have been measured for [L_BCu(II)] complex was (1.83 B.M.) this value is in the range of mononuclear octahedral geometry(104,105), Conductivity measurements show the complex to be non-ionic, Table (3-14).From these results and that of FT-IR study an octahedral geometry around Cu(II) ion can be suggested as illustrated in the following structure.



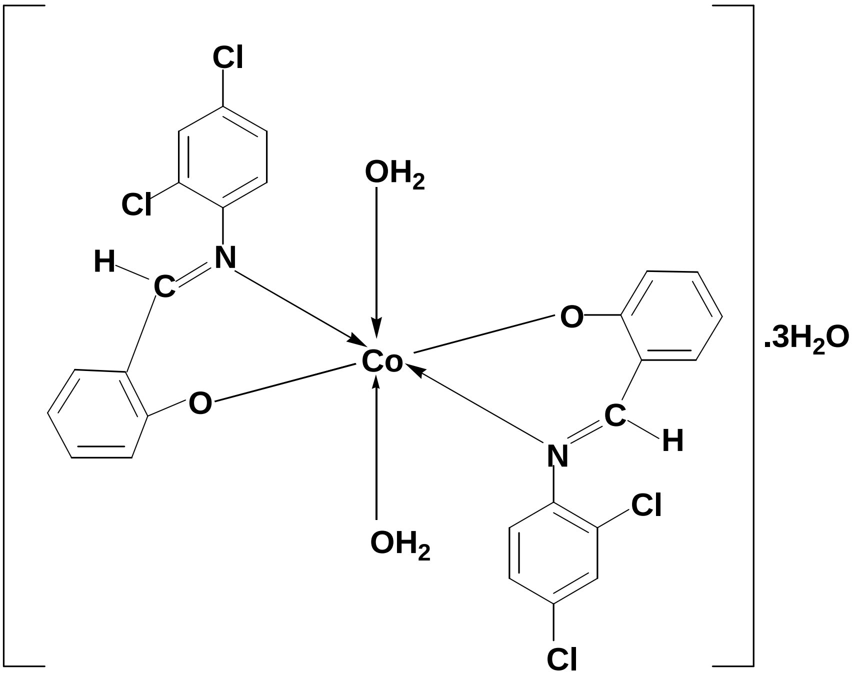
B- UV-Visible Spectrum of the Co(II) complex (L_BCo(II)):-

The spectral behavior of this complex, Figure (3-25), Table (3-13). was identical with that of [L_BCo(II)], which also shows two bands, one at 14,886 cm^{-1} and the other at (25,773 cm^{-1}) which was assigned to the transition [ν_2 ^4T_1g (F) → ^4A_2g (F)] and [$\nu_3$$^4T_1g$ (F) → ^4T_1g (P)] respectively, ν_1 was calculated using Tanabe-Sugano diagram for d^7 system and found to be (8975 cm^{-1}) which belong to the transition [^4T_1g (F) → ^4T_2g (F)].

The magnetic moment of [L_BCo(II)] complex was (4.85 B.M.), which show the complex to be paramagnetic.

The molar conductivity shows the complex to be octahedral and to be non-conducting, Table (3-14).

From these results and that of FT-IR study the suggested structure is follows:

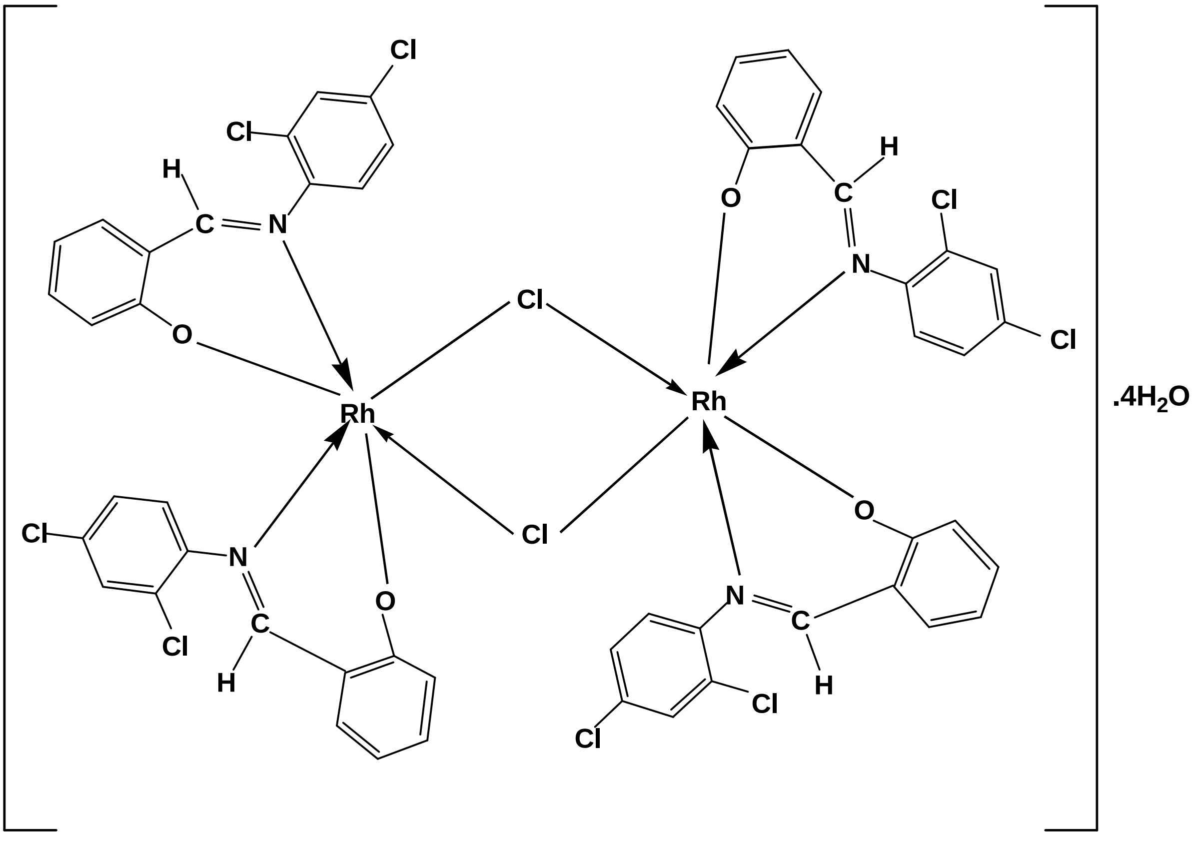


C- UV-Visible Spectrum of the Rhodium (III)Complex L_BRh(III):-

The electronic spectra of brown of [L_BRh(III)]complex, Figure (3-26), Table (3-13).show tow absorption band at (21,520 cm^{-1}), a second band (29,600 cm^{-1}) which can be assigned to [ν_1 $^1A_{1g} \rightarrow {}^1T_{1g}$, and $\nu_2$$^1A_{1g} \rightarrow {}^1T_{2g}$] transitions, and also weak absorption band appear at (13,869 cm^{-1}) which can be assigned to transitions [$^1A_{1g} \rightarrow {}^3T_{1g}$]. These transitions which agree well with low spin and octahedral geometry for this complex (1, 102). The values of B^-, 10 Dq have been calculated using Tanabe-Sugano diagram for d^6 system , Figure (3-18).By fitting ratio of the frequencies (ν_2/ ν_1) of the observed spin-allowed bands to the

Tanabe-Sugano diagram, which produce values of the interelectronic repulsion parameter B^- as well as of the crystal-field splitting 10 Dq.

The low value of neuphelauxetic factor (β) (0.53) refers to considerable orbital overlap with strong covalence in the metal ligand *σ* bond (103). Rhodium (III) complex is diamagnetic which refer to strong field. Conductivity measurements show that the complex is non-ionic Table (3-14), from these results and that of FT-IR study the suggested structure is as follows:



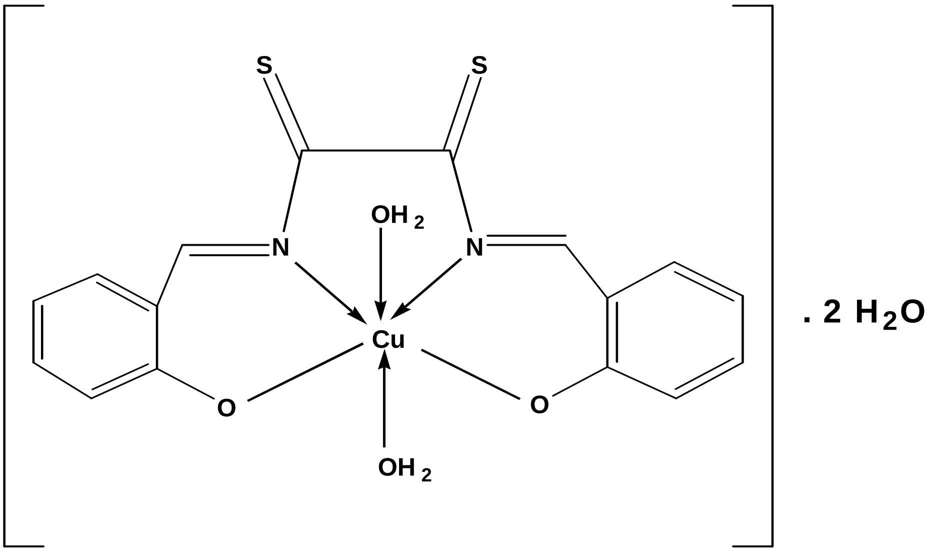
(3-4-4) Electronic Spectra of the L_C Complexes:-

A- UV-Visible Spectrum of the Cu(II) complex (L_CCu(II)):-

Electronic spectra of Cu(II) compounds show single broad absorption band in the region (11,000-16,000) $cm^{-1(1)}$. The free ion ground ^2D term is expected to split in a crystal field as shown in scheme (3-5) $^{(1, 98)}$.

In the present work, the deep brown color of [L_CCu(II)] complex which suggest a strong field complex and show a broad band at (13,123 cm^{-1}) this band refer to distort octahedral geometry (John-Teller distortion) $^{(1, 98)}$ which can be assigned to $^2Eg \rightarrow {}^2T_2g$ transitions$^{(1, 36)}$, Figure (3-28), Table (3-13).

The value of ($\mu_{eff.}$) that have been measured for [L_CCu(II)] complex was (1.92 B.M.) this value is in the range of mononuclear octahedral geometry$^{(104,105)}$, Conductivity measurements show the complex to be non-ionic, Table (3-14).From these results and that of FT-IR study an octahedral geometry around Cu (II) ion can be suggested as illustrated in the following structure .



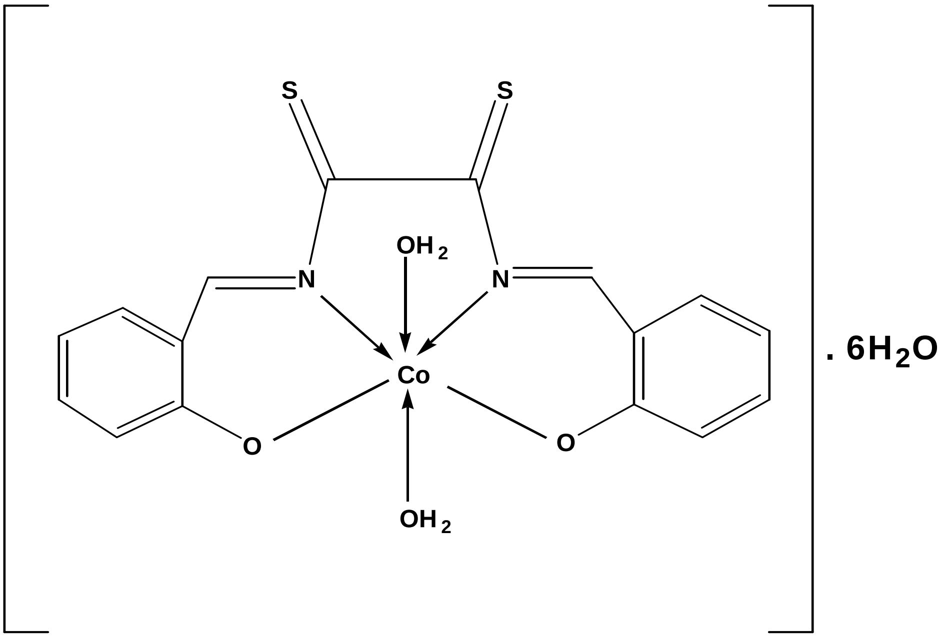
B- UV-Visible Spectrum of the Co (II) complex (L_CCo(II)):-

The spectral behavior of this complex, Figure (3-29), Table (3-13). Was identical with that of [L_CCo (II)], which also show two bands one at (14,500 cm^{-1}), and the other at (25,316 cm^{-1}) which was assigned to the transition [ν_2 ^4T_1g (F) → ^4A_2g (F)] and [$\nu_3$$^4T_1g$ (F) → ^4T_1g (P)] respectively.

The value of ν_1 was calculated using Tanabe-Sugano diagram for d^7 system, and found to be (8988 cm^{-1}) which refers to [^4T_1g (F) → ^4T_2g (F)] transition, 10Dq Value was also calculated from the diagram and found to be (10,930 cm^{-1}) referring to a weak field state.

The magnetic moment of the [L_CCo(II)] complex was (4.97 B.M.). That shows the complex is paramagnetic and has three unpaired electrons indicating a high spin octahedral configuration. The formula was further confirmed to be non-ionic by conductivity measurement, Table (3-14).

From these results an octahedral geometry around Co (II) ion can be suggested as illustrated in the following structure:

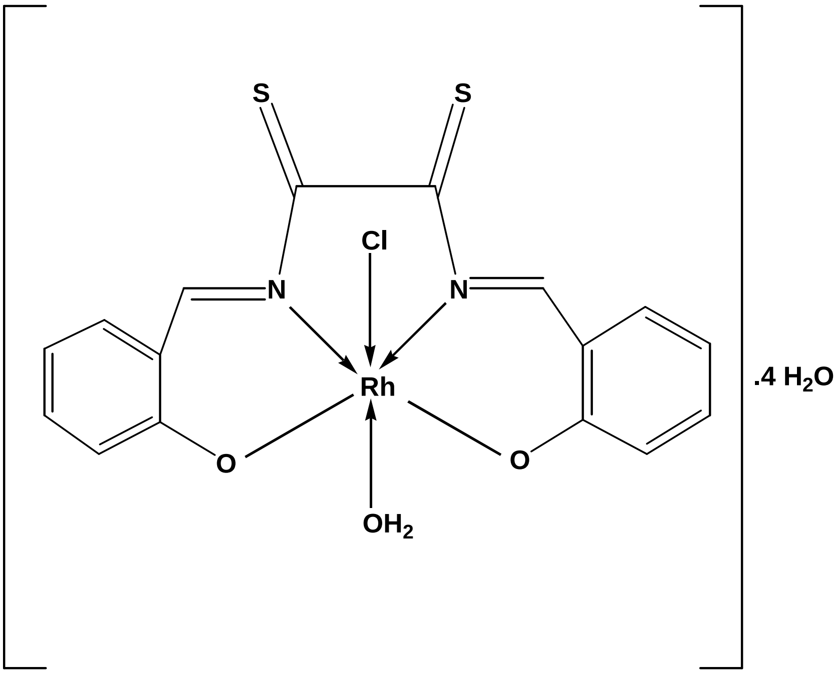


C- UV-Visible Spectrum of the Rhodium (III)Complex L_CRh(III):-

The electronic spectra of deep brown of [L_CRh (III)] complex, Figure (3-30), Table (3-13). Show tow absorption band at (22,272 cm^{-1}), a second band (29,980 cm^{-1}) which can be assigned to [ν_1 $^1A_{1g} \rightarrow {}^1T_{1g}$, and $\nu_2$$^1A_{1g} \rightarrow {}^1T_{2g}$] transitions, These transitions refer to low spin crystal-field and octahedral geometry for this complex (1, 102). The values of B^-, 10 Dq have been calculated using Tanabe-Sugano diagram for d^6 system Figure (3-18).By fitting ratio of the frequencies (ν_2/ ν_1) of the observed spin-allowed bands to the Tanabe-Sugano diagram, which produce values of the interelectronic repulsion parameter B^- as well as of the crystal-field splitting 10 Dq.

The low value of neuphelauxetic factor (β) (0.51) refer to considerable orbital overlap with strong covalent in the metal ligand σ bond (103). Rhodium (III) complex is diamagnetic which refer to strong field.

Conductivity measurements show that the complex is non-ionic; Table (3-14), from these results and that of FT-IR study the suggested structure is as follow.

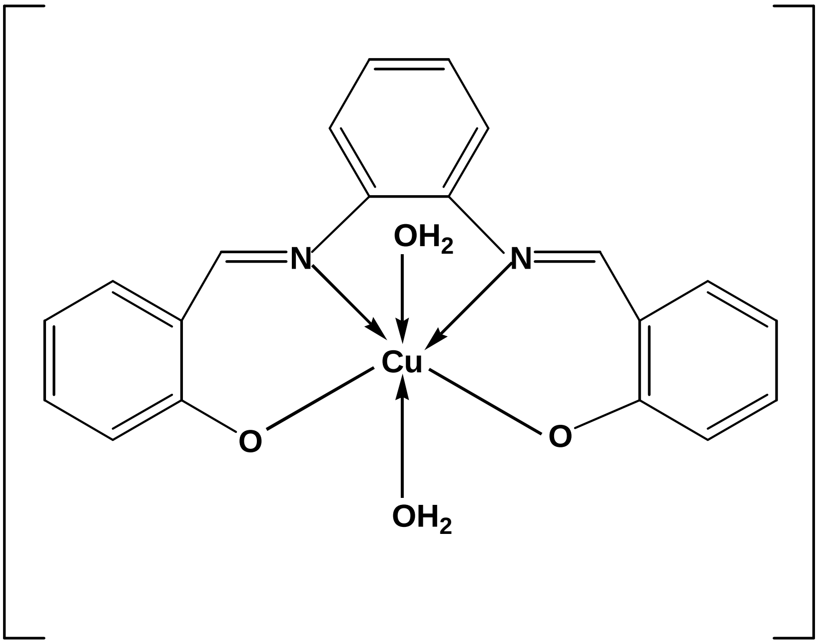


(3-4-5) Electronic Spectra of the L_D Complexes:-

A- UV-Visible Spectrum of the Cu(II) complex (L_DCu(II)):-

Electronic spectra of Cu (II) compounds show single broad absorption band in the region (11,000-16,000) cm^{-1} (1). The d^9 ion is characterized by large distortion from octahedral symmetry and the bond is unsymmetrical, being the result of a number of transitions, which are by no means easy to assign unambiguously. The free ion ground ^2D term is expected to split in a crystal field as shown in scheme (3-5) (1, 98).

In the present work, the brown color [L_DCu(II)] which suggest a strong field complex and show a broad band(1, 36) at (15,873 cm^{-1}) this band refer to distort octahedral geometry (Jahn-Teller distortion) (1, 98) which can be assigned to $^2Eg \rightarrow {}^2T_2g$ transitions, Figure (3-32), Table (3-13). The value of ($\mu_{eff.}$) that have been measured for [L_DCu(II)] complex was (1.95 B.M.) this value is in the range of mononuclear octahedral geometry(104, 105), Conductivity measurements show the complex to be non-ionic, Table (3-14).From these results and that of FT-IR study an octahedral geometry around Cu (II) ion can be suggested as illustrated in the following structure:



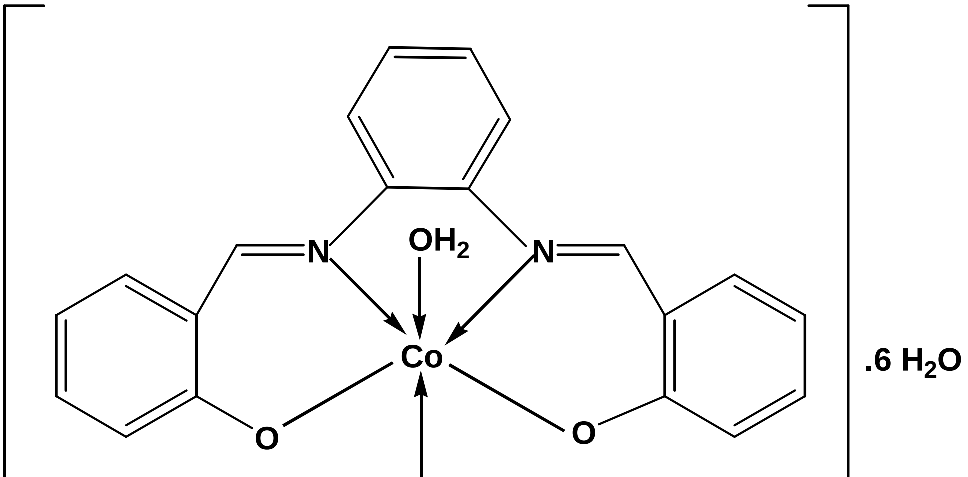
B- UV-Visible Spectrum of the Co(II) complex (L_DCo(II)):-

The spectral behavior of this complex, Figure (3-33), Table (3-13). Was identical with that of [L_CCo(II)], which also show two bands one at (14,284 cm^{-1}), and the other at (25,096 cm^{-1}) which was assigned to the transition [ν_2 ^4T_1g (F) → ^4A_2g (F)] and [$\nu_3$$^4T_1g$ (F) → ^4T_1g (P)] respectively.

The value of ν_1 was calculated using Tanabe-Sugano diagram for d^7 system, and found to be (8580 cm^{-1}) which refers to ^4T_1g (F) → ^4T_1g (P) transition, 10Dq Value was also calculated from the diagram and found to be (8,995cm^{-1}) referring to a weak field state.

The magnetic moment of the [L_DCo(II)] complex was (4.98 B.M.). That shows the complex is paramagnetic and has three unpaired electrons indicating a high spin octahedral configuration. The formula was further confirmed to be non-ionic by conductivity measurement, Table (3-14).

From these results an octahedral geometry around Co (II) ion can be suggested as illustrated in the following structure:



C- UV-Visible Spectrum of the Rhodium (III)Complex L_D Rh(III):-

The electronic spectra of red color of [L_DRh (III)] complex, Figure (3-34), Table (3-14). Show tow absorption band at (22,522 cm^{-1}), a second band (29,997 cm^{-1}) which can be assigned to [ν_1 $^1A_{1g} \rightarrow {}^1T_{1g}$, and $\nu_2$$^1A_{1g} \rightarrow {}^1T_{2g}$] transitions, these transitions refer to low spin crystal-field and octahedral geometry for this complex $^{(1, 102)}$. The values of B^-, 10 Dq have been calculated using Tanabe-Sugano diagram for d^6 system Figure (3-18).By fitting ratio of the frequencies (ν_2/ ν_1) of the observed spin-allowed bands to the Tanabe-Sugano diagram, which produce values of the interelectronic repulsion parameter B^- as well as of the crystal-field splitting 10 Dq. The low value of neuphelauxetic factor (β) (0.48) refer to considerable orbital overlap with strong covalent in the metal ligand σ bond $^{(103)}$. Rhodium (III) complex is diamagnetic which refer to strong field. Conductivity measurements show that the complex is non-ionic, Table (3-14). From these results and that of FT-IR study the suggested structure is as follow.

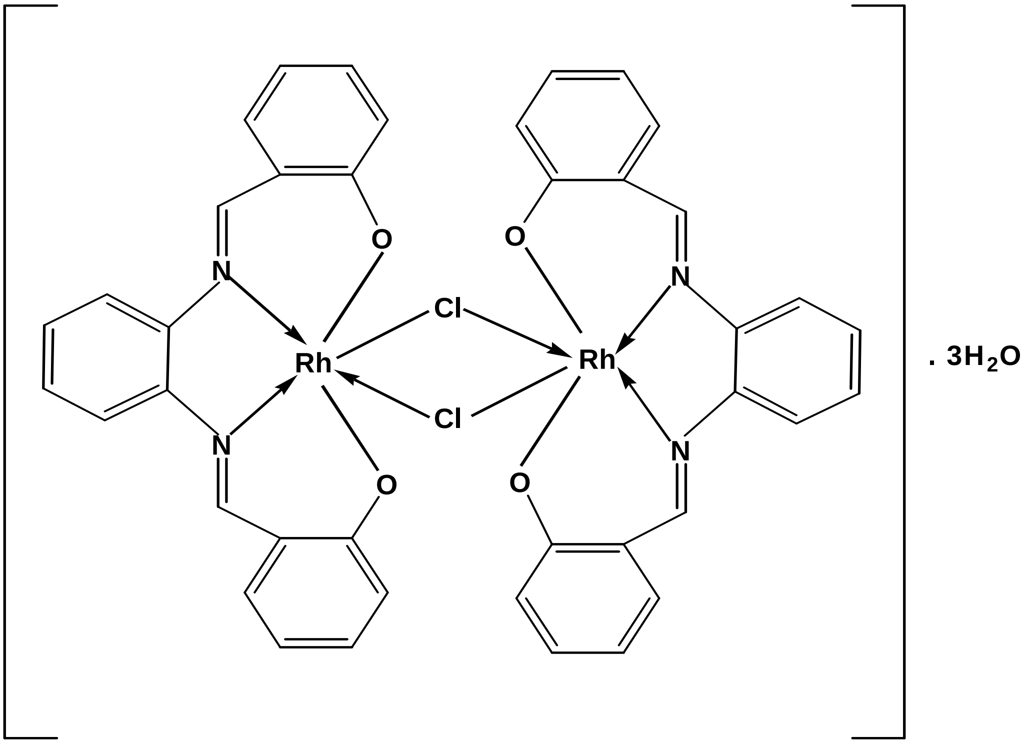


Table (3-13): The data of electronic spectra of the prepared compounds in DMSO solvent at (10^{-3} M) in (cm^{-1}).

Compound	Absorption bands(cm^{-1})	transition	B	B^-	β	10Dq	15 B^-
L_A	28,735 31,055 40,160	$n\rightarrow\pi^*$ $\pi\rightarrow\pi^*$ (imino) $\pi\rightarrow\pi^*$(aromatic)					
$L_ACu(II)$	16,077	$^{2}B_{1}g\rightarrow{}^{2}B_{2}g$ $^{2}B_{1}g\rightarrow{}^{2}Eg$					
$L_ACo(II)$	6715 13,792 20,260	$\nu_1{}^{4}T_{1}g(F)\rightarrow{}^{4}T_{2}g(F)$ $\nu_2{}^{4}T_{1}g(F)\rightarrow{}^{4}A_{2}g(F)$ $\nu_3{}^{4}T_{1}g(F)\rightarrow{}^{4}T_{2}g(P)$	971	927	0.95	8393	13,907
$L_ARh(III)$	11,001 20,530 27,660	$^{1}A_{1g}\rightarrow{}^{3}T_{1g}$ $\nu_1{}^{1}A_{1g}\rightarrow{}^{1}T_{1g}$ $\nu_2{}^{1}A_{1g}\rightarrow{}^{1}T_{2g}$	720	410	0.57	22,171	-
L_B	24,691 30,581 36,64	$n\rightarrow\pi^*$ $\pi\rightarrow\pi^*$ (imino) $\pi\rightarrow\pi^*$(aromatic)					
$L_BCu(II)$	15,198	$^{2}Eg\rightarrow{}^{2}T_{2}g$					
$L_BCo(II)$	8975 14,886 25,773	$\nu_1{}^{4}T_{1}g(F)\rightarrow{}^{4}T_{2}g(F)$ $\nu_2{}^{4}T_{1}g(F)\rightarrow{}^{4}A_{2}g(F)$ $\nu_3{}^{4}T_{1}g(F)\rightarrow{}^{4}T_{2}g(P)$	971	915.6	0.94	11,219	13,734
$L_BRh(III)$	13,869 21,520 29,600	$^{1}A_{1g}\rightarrow{}^{3}T_{1g}$ $\nu_1{}^{1}A_{1g}\rightarrow{}^{1}T_{1g}$ $\nu_2{}^{1}A_{1g}\rightarrow{}^{1}T_{2g}$	720	381.6	0.53	23,046	-

L_C	24,096 27,855 31,055	n→π* π→π* (imino) π→π*(aromatic)						
L_CCu(II)	13,123	$^2Eg\rightarrow{}^2T_2g$						
L_CCo(II)	8988 14,500 25,316	$\nu_1{}^4T_1g(F)\rightarrow{}^4T_2g(F)$ $\nu_2{}^4T_1g(F)\rightarrow{}^4A_2g(F)$ $\nu_3{}^4T_1g(F)\rightarrow{}^4T_2g(P)$	971	856.8	0.88	11,235	12,852
L_CRh(III)	22,272 29,980	$\nu_1{}^1A_{1g}\rightarrow{}^1T_{1g}$ $\nu_2{}^1A_{1g}\rightarrow{}^1T_{2g}$	720	367	0.51	23,740	-
L_D	25,510 29,498 33,112	n→π* π→π* (imino) π→π*(aromatic)						
L_DCu(II)	15,873	$^2Eg\rightarrow{}^2T_2g$						
L_DCo(II)	8995 14,284 25,096	$\nu_1{}^4T_1g(F)\rightarrow{}^4T_2g(F)$ $\nu_2{}^4T_1g(F)\rightarrow{}^4A_2g(F)$ $\nu_3{}^4T_1g(F)\rightarrow{}^4T_2g(P)$	971	826	0.85	11,244	13,640
L_DRh(III)	22,522 29,997	$\nu_1{}^1A_{1g}\rightarrow{}^1T_{1g}$ $\nu_2{}^1A_{1g}\rightarrow{}^1T_{2g}$	720	345	0.48	23,904	-

Table (3-14): Magnetic moments, Conductivity and Suggested Structures for Complexes of L_A, L_B L_C and L_D in (10^{-3} M) DMSO solvant.

Complex	Magnetic moment µeff. (B.M.)	Conductivity µS.cm^{-1}	Suggested structure
L_ACu(II)	1.21	48.5	Square planar
L_ACo(II)	4.92	20.0	Octahedral
L_ARh(III)	Diamagnetic	42.9	Octahedral
L_BCu(II)	1.83	15.3	Octahedral
L_BCo(II)	4.85	13.4	Octahedral
L_BRh(III)	Diamagnetic	18.2	Octahedral
L_CCu(II)	1.92	16.5	Octahedral
L_CCo(II)	4.97	19.7	Octahedral
L_CRh(III)	Diamagnetic	15.9	Octahedral
L_DCu(II)	1.95	20.5	Octahedral
L_DCo(II)	4.98	17.8	Octahedral
L_DRh(III)	Diamagnetic	21.6	Octahedral

Where the value of molar Conductive in DMSO solvent at (10^{-3}M) as follow (106).

DMSO	Non-electrolyte	Electrolyte type			
	0-20	1:1	1:2	1:3	1:4
		30-40	70-80	-	-

Table (3-15): Chemical formula and the name of L_A, L_B, $L_{C,}$ and L_D and their complexes:

Symbol	Chemical formula	Name
L_A	$C_{14}H_{17}NO_2$	piperonaldehyde cyclohexylimine
$L_ACu(II)$	$[Cu(L_A)_2(ONO_2)(H_2O)].NO_3.2H_2O$	aquonitrato bis [Piperonaldehyde cyclohexylimine] copper (II). nitrate. water (2)
$L_ACo(II)$	$[Co(L_A)_2(ONO_2)_2\ (H_2O)_2].\ 2H_2O$	diaquodinitrito bis [piperonaldehyde cyclohexylimine] cobalt (II). water (2)
$L_ARh(III)$	$[Rh(L_A)_2(Cl_2)(H_2O)_2].\ Cl.\ 3H_2O$	aquodichloro [bis (Piperonaldehyde cyclohexylimine)] rhodium (III). Chloride. Water (3).
L_B	$C_{13}H_9NOCl_2$	salicylidene-2,4-dichloroaniline
$L_BCu(II)$	$[Cu(L_B)_2(H_2O)_2]$	diaquo[bis(salicylidene-2,4-dichloroaniline)] copper (II)
$L_BCo(II)$	$[Co(L_B)_2(H_2O)_2].\ 3H_2O$	diaquo[bis(salicylidene-2,4-dichloroaniline)] cobalt(II). water (3)
$L_BRh(III)$	$[Rh_2(L_B)_4(Cl)_2].\ 4H_2O$	di-µ-chloro bis[bis(Salicylidene-2,4-dichloroaniline) rhodium(III)]. water (4)
L_C	$C_{16}H_{12}N_2O_2S_2$	bis salicylidene-dithiooxamide
$L_CCu(II)$	$[CuL_C(H_2O)_2].\ 2H_2O$	diaquo [bis salicylidene-dithiooxamide] copper (II) .water(2)
$L_CCo(II)$	$[CoL_C(H_2O)_2].\ 6H_2O$	Diaquo [bis salicylidene-dithiooxamide] cobalt (II). water(6)
$L_CRh(III)$	$[RhL_C\ H_2O\ Cl].\ 4H_2O$	aquo monochloro [bis salicylidene-dithiooxamide] rhodium (III). water(4)
L_D	$C_{20}H_{16}N_2O_2$	bis salicylidene -2-phenylenediamine
$L_DCu(II)$	$[CuL_D(H_2O)_2]$	diaquo [bis salicylidene -2-phenylenediamine] copper (II)
$L_DCo(II)$	$[CoL_D(H_2O)_2].\ 6H_2O$	diaquo [bis salicylidene -2-phenylenediamine] cobalt (II). water(6)
$L_DRh(III)$	$[Rh_2(L_D)_2(Cl)_2].\ 3H_2O$	di-µ-chloro bis[(bis salicylidene -2-phenylenediamine) rhodium(III)].water (3)

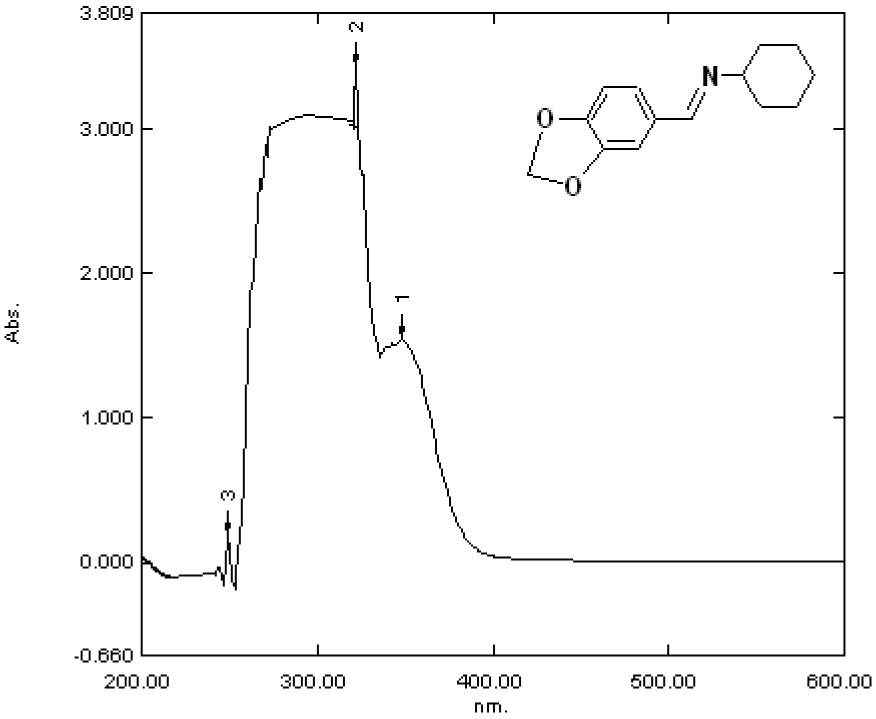


Figure (3-19): Electronic Spectrum of L_A

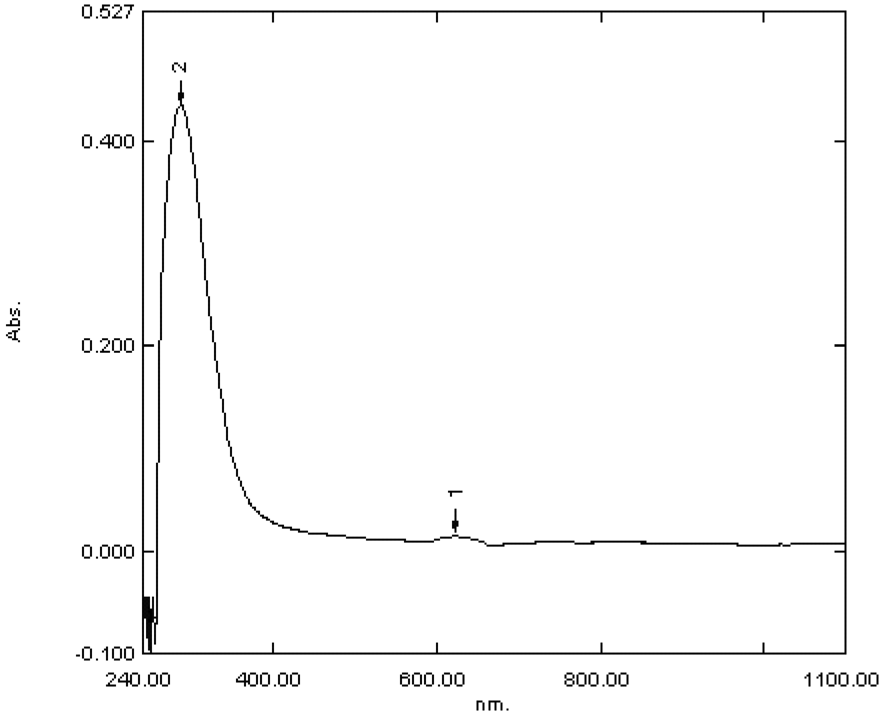


Figure (3-20): Electronic Spectrum of L_ACu(II)

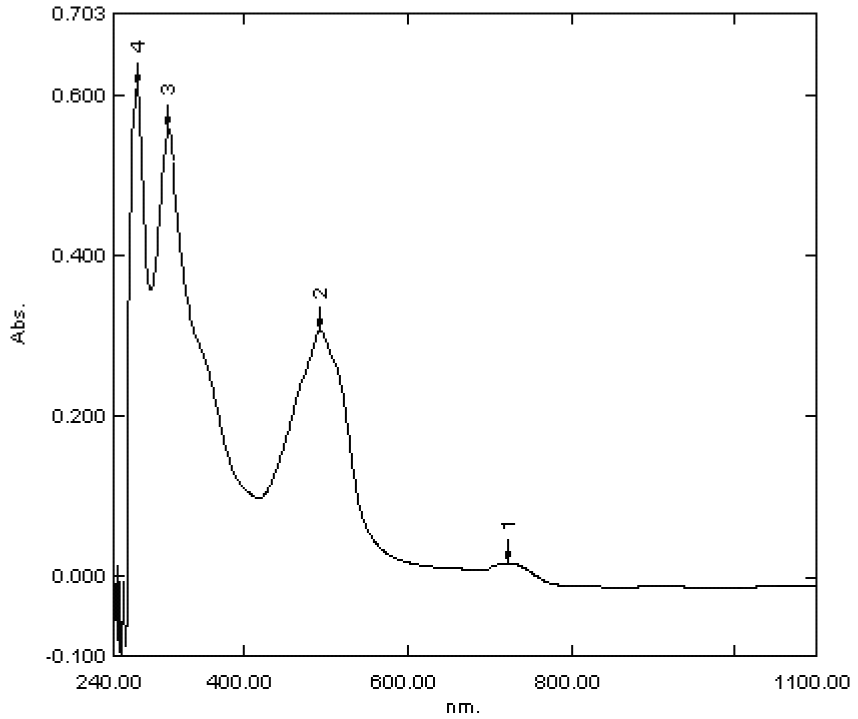


Figure (3-21): Electronic Spectrum of $L_ACo(II)$

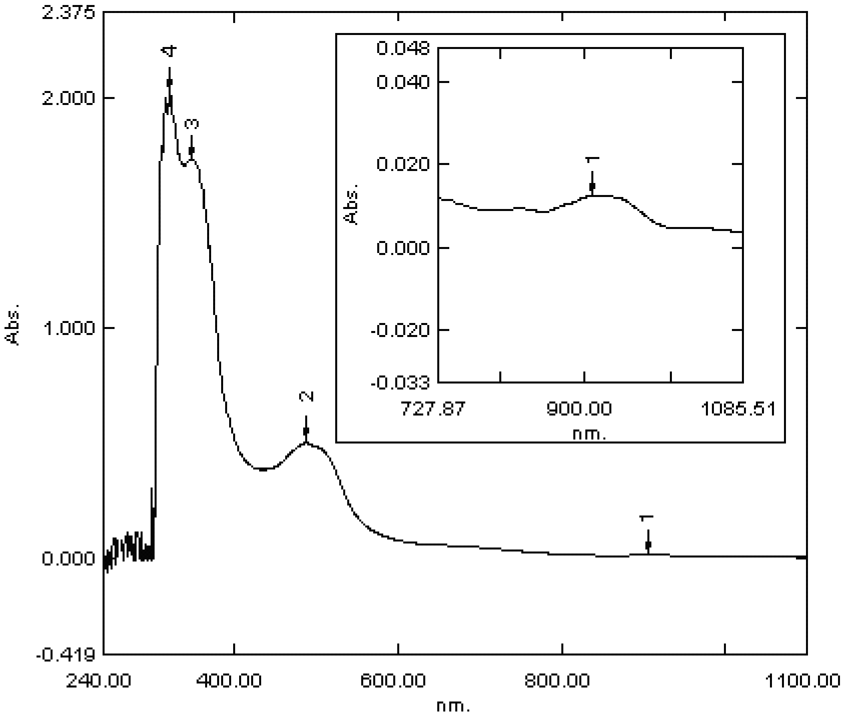


Figure (3-22): Electronic Spectrum of $L_ARh(III$***)***

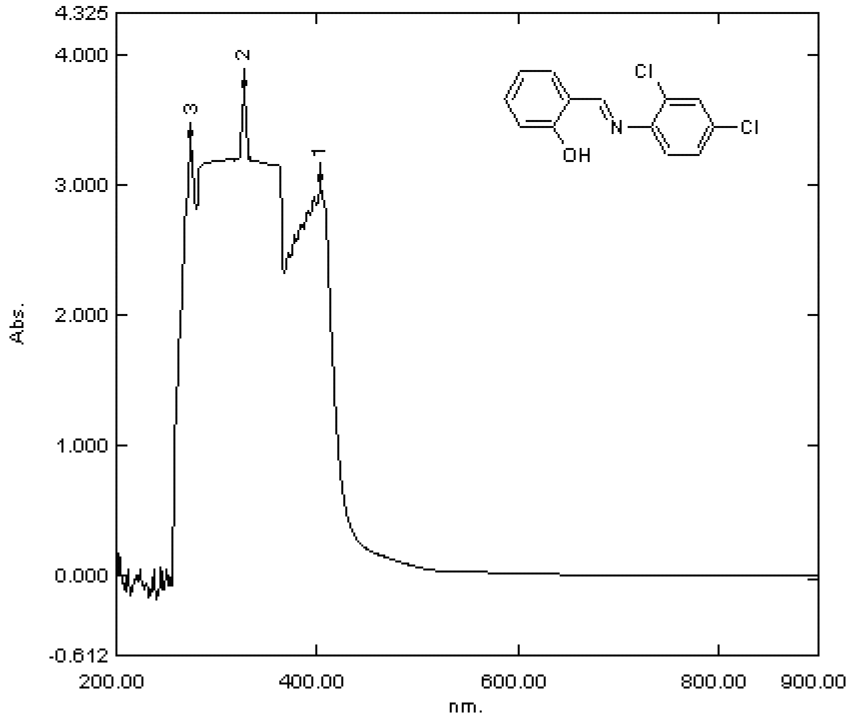


Figure (3-23): Electronic Spectrum of L_B

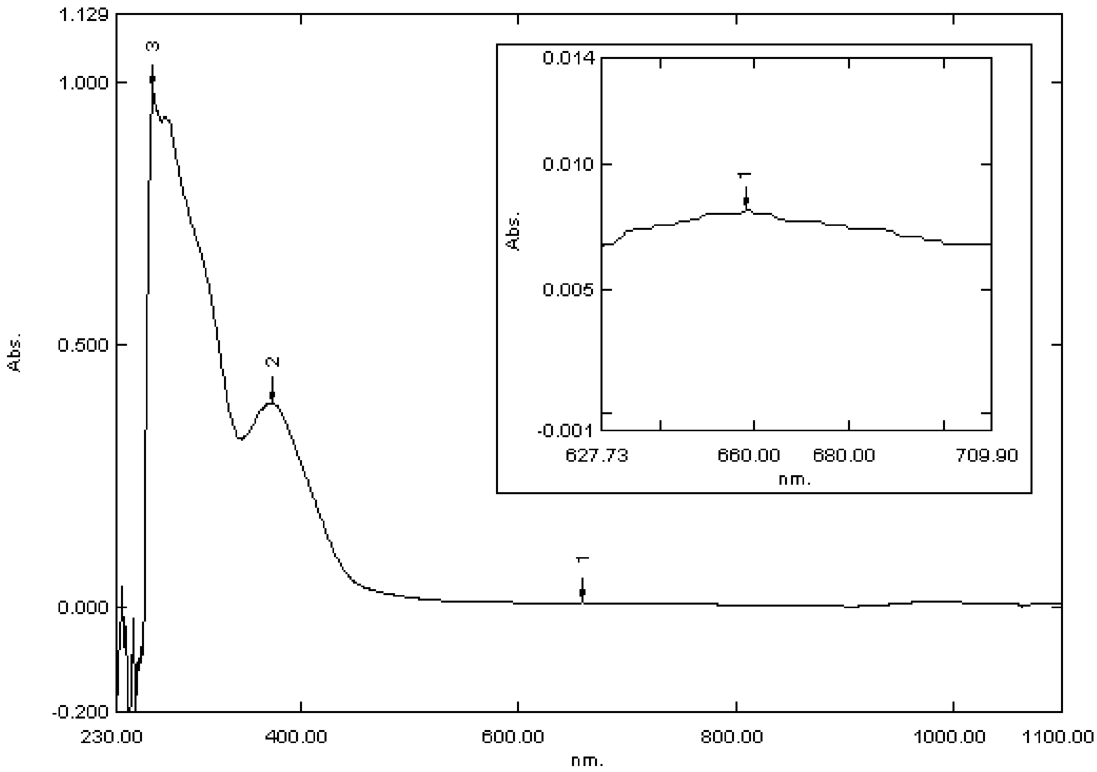


Figure (3-24): Electronic Spectrum of $L_BCu(II)$

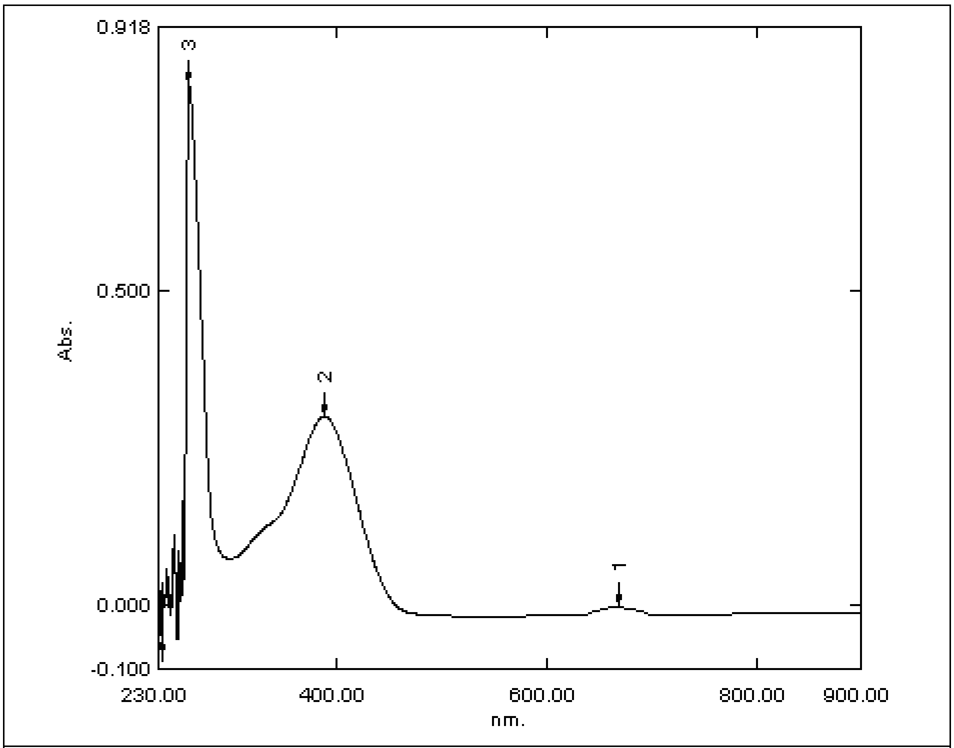


Figure (3-25): Electronic Spectrum of L_BCo(II)

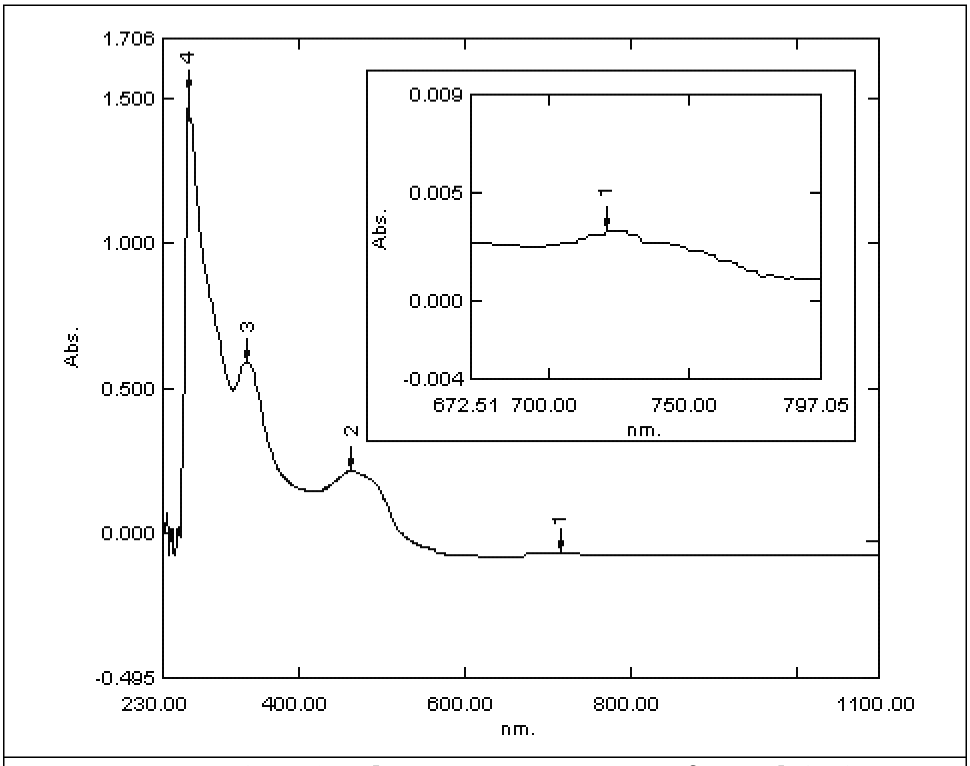


Figure (3-26): Electronic Spectrum of L_B Rh(III)

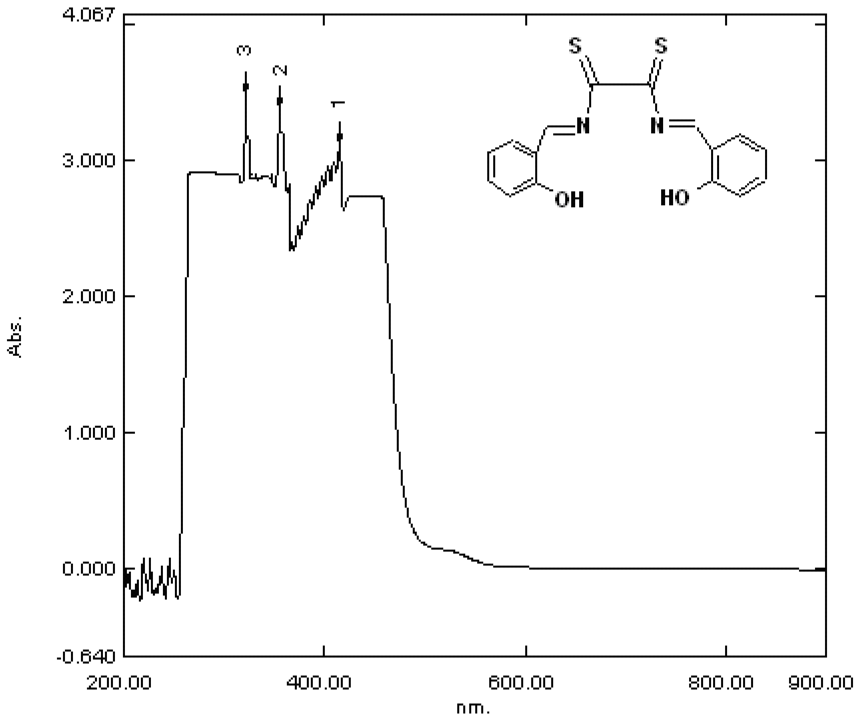


Figure (3-27): Electronic Spectrum of L_C

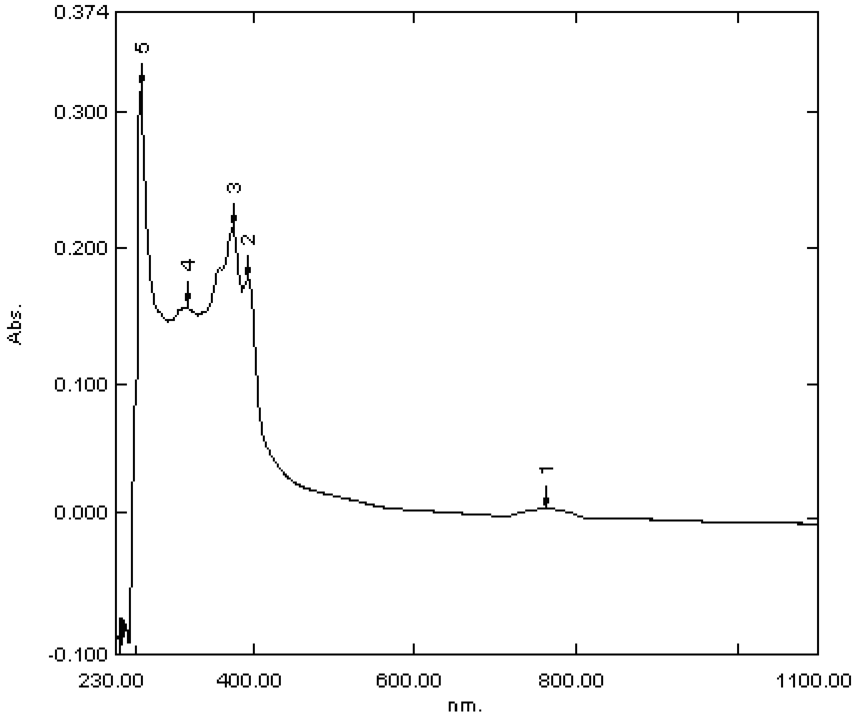


Figure (3-28): Electronic Spectrum of L_CCu(II)

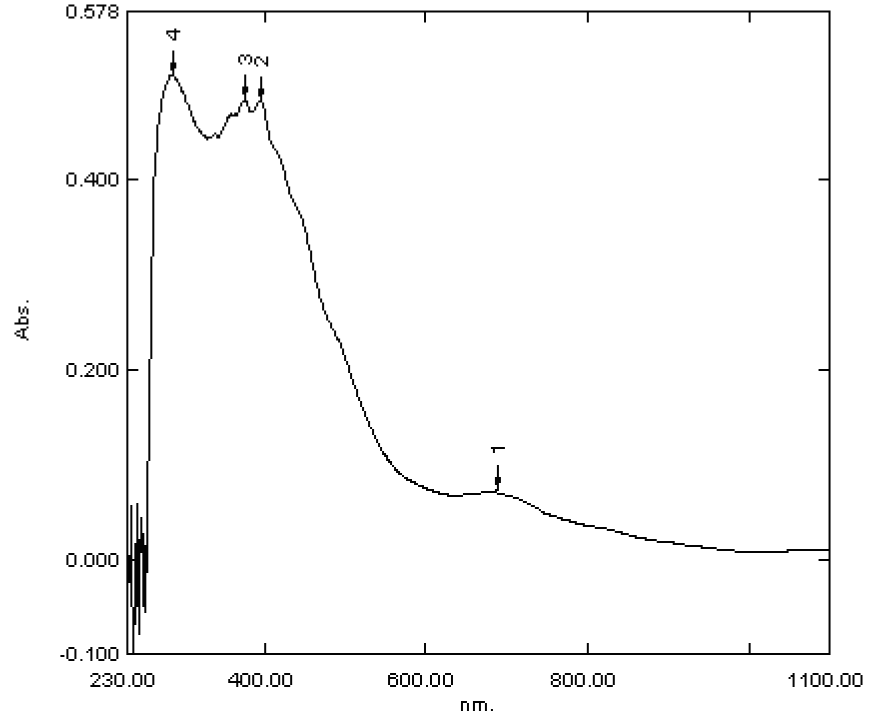


Figure (3-29): Electronic Spectrum of $L_CCo(II)$

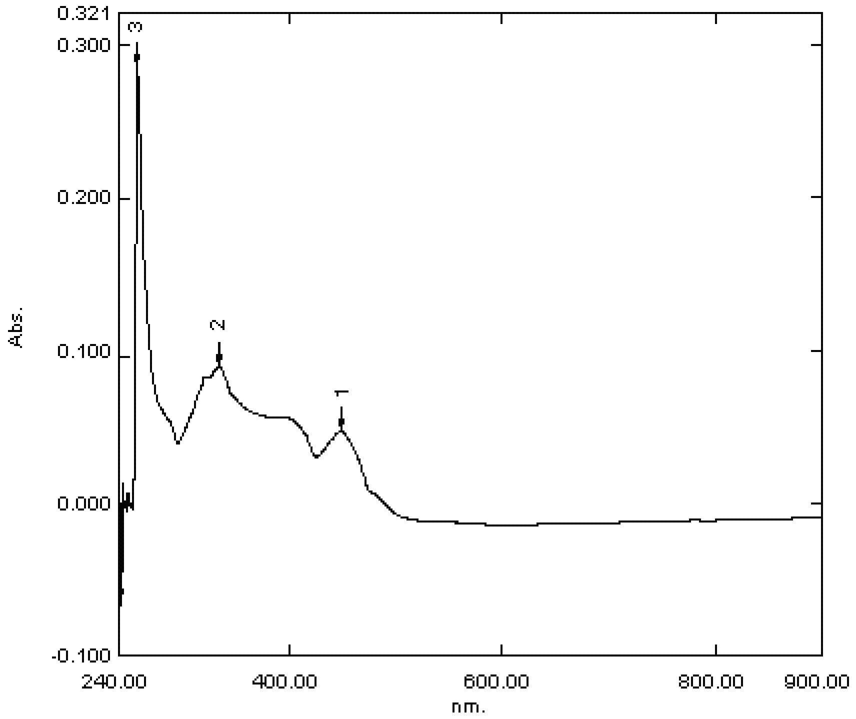


Figure (3-30): Electronic Spectrum of $L_CRh(III)$

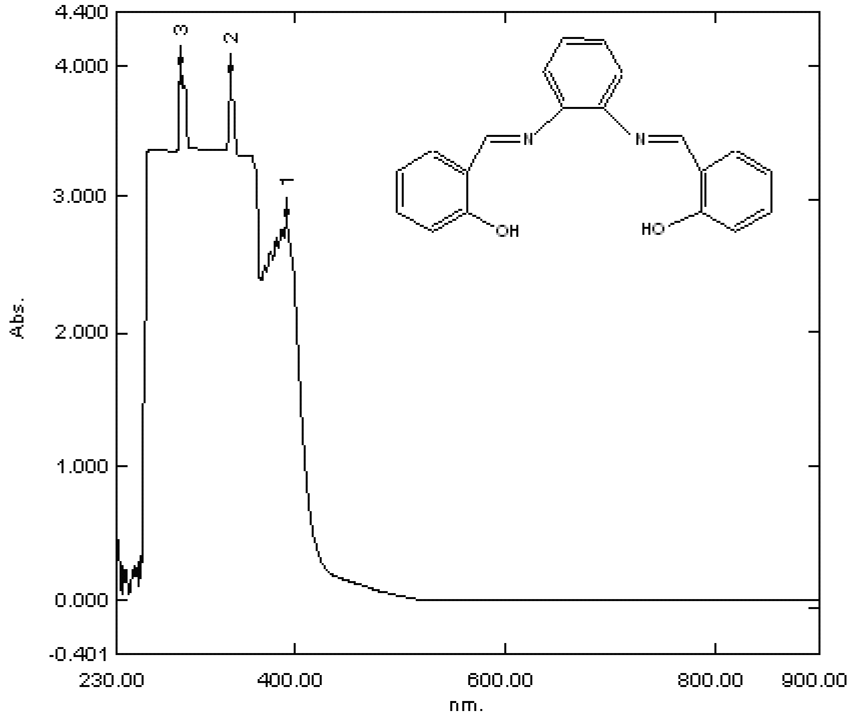


Figure (3-31): Electronic Spectrum of L_D

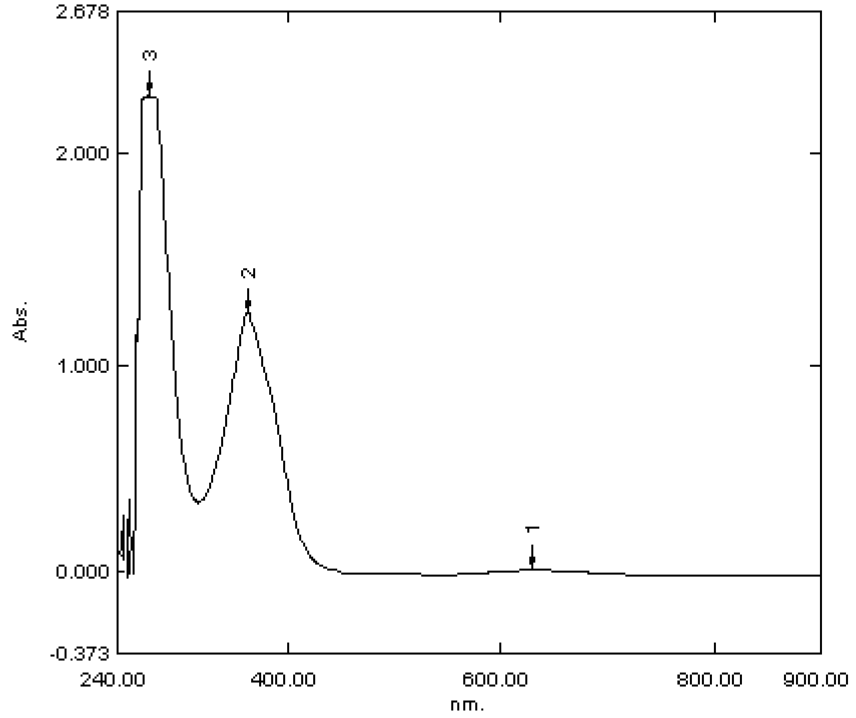


Figure (3-32): Electronic Spectrum of L_DCu(II)

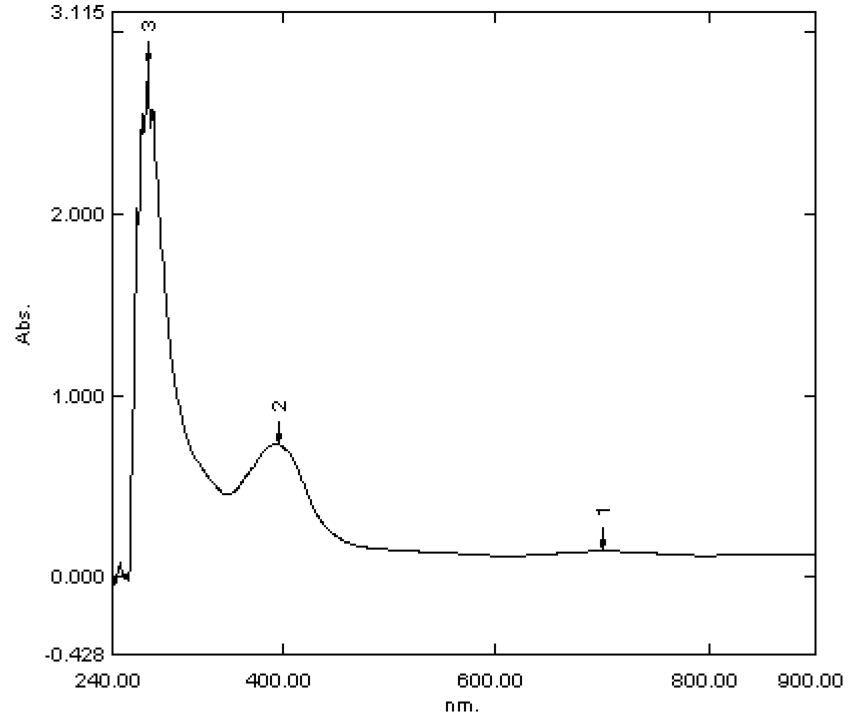


Figure (3-33): Electronic Spectrum of $L_DCo(II)$

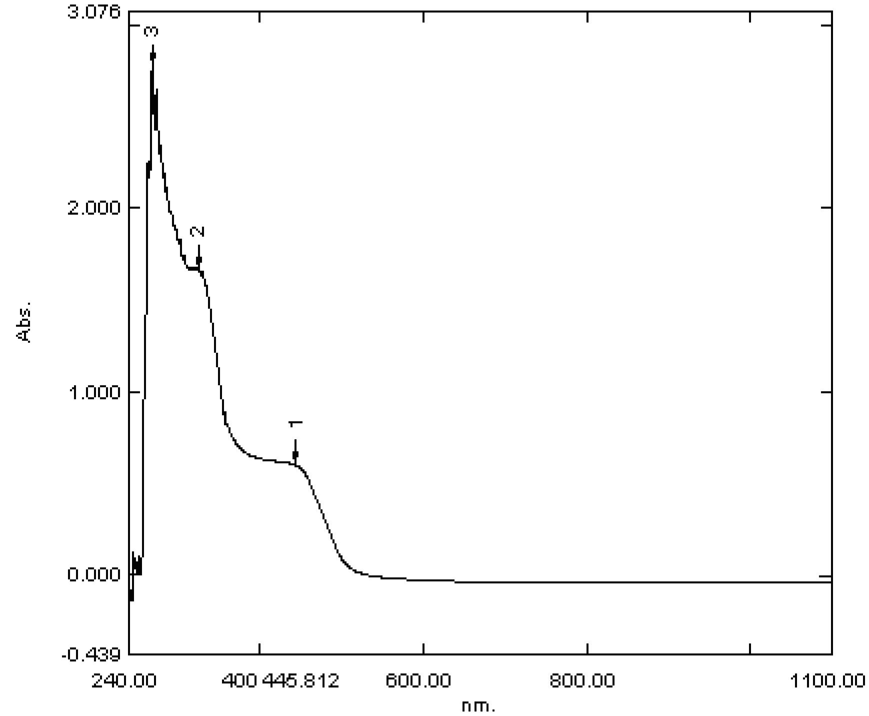


Figure (3-34): Electronic Spectrum of $L_DRh(III)$

(3-5) Conclusions:-

1- The different Schiff bases ligands which have been prepared showed different physical properties, the monodentate Schiff bases ligand show the lower melting point.

2- All the prepared ligands and its complexes were soluble in DMSO and DMF solvent.

3- The brown color of Cu (II) complexes of L_B, L_C and L_D ligands refer to these ligand behaves as ligands with strong field with Cu (II) ion.

4- The crystal-field splitting (10Dq) value which was calculated for Co (II) and Rh (III) complexes show that increases when increases number of donor atoms in the ligand (according to chelating effect on 10Dq).

5- All prepared schiff bases ligands behaves as ligands with strong filed when complexions with Rh(III) metal ion because the large size of this metal and have high oxidation state (according to effect of size and charge of the metal ion on 10Dq).

6- The value of neuphelauxetic factor (β) which have been calculated for Co (II) and Rh (III) complexes show that decreases its value when increase the covalent characterize between the metal and donor atoms of the ligand.

(3-6) Suggestion for future work:-

1- Synthesis of another set of transition metals complexes with the other transition metal ions.

2- Using C.H.N. microanalysis and NMR techniques to complete the identify of the structures of the Schiff base ligand and its metal complexes which were prepared.

3- Studying the effect of change solvent in the electronic spectrum of the Schiff base ligand and its metal complexes which were prepared.

4- More detailed investigation are required to reveal the biological activity of the prepared Schiff base and all the metal complexes against other micro-organisms to explore their activity and the synergic effect between the metal and the ligand.

Chapter two

Experimental part

(2-1) Chemicals:-

All the chemicals used in this work were of highest purity available and supplied without further purification as in Table (2-1).

Table (2-1): The Chemicals use their and purity manufacturers.

NO.	CHEMICALS	FORMULA	STATE	PURITY	SOURCE
1	Piperonaldehyde (Heliotropin)	$O.CH_2.O.C_6H_3.CHO$	Solid	99%	BDH
2	2-Hydroxybenzaldehyd (Salicyldehyde)	$C_7H_6O_2$	liquid	98%	Fluka
3	2,4-Dichloro aniline	$C_6H_8NCl_2$	Solid	99%	BDH
4	Dithiooxamide	$H_2NCSCSNH_2$	Solid	98%	BDH
5	Cyclohexylamine	$C_6H_{11}NH_2$	liquid	99%	BDH
6	Ortho-phenylene diamine	$C_6H_8N_2$	Solid	99%	BDH
7	Cupper(II) nitrate trihydrate	$Cu(NO_3)_2.3H_2O$	Solid	98%	BDH
8	Cobalt (III)nitrate hexahydrate	$Co(NO_3).6H2O$	Solid	99%	Fluka
9	Rhodium(III) trichloride hydrate	$RhCl_3.H_2O$	Solid	99%	BDH
10	Dimethyl Sulphoxide (DMSO)	CH_3SOCH_3	liquid	99%	BDH
11	Dimethyl Formamide (DMF)	$HCON(CH_3)_2$	liquid	99%	BDH
12	Ethanol(absolute)	CH_3CH_2OH	liquid	99.99%	BDH
13	Methanol	CH_3OH	liquid	99%	Merck
14	Dichloro Methane	CH_2Cl_2	liquid	99%	BDH
15	Acetone	$(CH_3)_2CO$	liquid	99%	Fluka
16	Chloroform	$CHCl_3$	liquid	98%	BDH
17	Carbon tetra chloride	CCl_4	liquid	98%	Merck
18	Diethyl ether	$(C_2H_5)_2O$	liquid	95%	Fluka
19	Benzene	C_6H_6	liquid	99%	BDH

(2-2) Techniques:-

1) Fourier Transform Infrared Spectrophotometer (FT-IR):

The infrared spectra of the prepared compounds were recoded using FT-IR-8300-***SHIMADZU,*** Single Beam Path Laser**.** Fourier transforms infrared spectrophotometer of Shimadzu Company as a potassium bromide (KBr) discs in the wave length range of (4000-400) cm^{-1}**.** The spectra **w**ere recorded in the laboratories of Chemistry Department**,** College of Science**,** AL-Nahrain University. Also another infrared spectrum of the prepared compounds were recoded using FT-IR-8400-***SHIMADZU,*** Single Beam Path Laser, thin film was performed by Central Organization of Standardization and Quality Control.

2) Electronic Absorption spectra:

The electronic spectra of the prepared compounds were obtained using ***SHIMADZU*** UV-Vis-160A Ultra-Violet Spectrophotometer, using (1.0 cm) quartz cell at room temperature in the range of wave-length (200-1100 nm).All the prepared ligands and complexes were dissolved in (DMSO) at (10^{-3} M). These were carried out in the laboratories of Chemistry Department, College of Science, AL-Nahrain University

3) Magnetic susceptibility measurements:-

The magnetic susceptibility values for the prepared complexes were obtained at room temperature using (Magnetic Susceptibility Balance), of Johnson mattey catalytic system division, England. These were carried out in the laboratories of Chemistry Department, College of Science, AL-Nahrain University.

4) Metal Analysis:-

The metals content of the complexes was measured using atomic absorption technique by ***PERKIN-ELMER-5000*** Flame Atomic Absorption Spectrophotometer for the determination of (Cu^{+2}, Co^{+2}) metal ions at (324.8 nm and 240.7 nm) respectively. The measurments were carried out in laboratories of Biology Department, College of Science, Baghdad University**,** and using ***GBC-933*** Flame plus Atomic Absorption Spectrophotometer for the determination of (Rh^{+3}) metal at (343.5 nm) and were carried out in laboratories of Chemistry Department, College of Science, Baghdad University**.**

5) Molar Conductivity:-

The molar conductivity measurements were carried out at (25 C^o) with concentration of (10^{-3} M) using Wissenschaftlich-Technische Werkstatten 8120 Weilheim I.O.B, Drucker-Printer instrument, W.Germany. All the complexes were dissolved in DMSO. The measurements were carried out in the laboratories of Chemistry Department, College of Science, AL-Nahrain University**.**

6) Melting point:-

Melting point apparatus of Gallen kamp M.F.B 600.01 was used to measure the melting points of all the prepared compounds. This was carried out in the laboratories of Chemistry Department, College of Science, AL-Nahrain University.

7) Solubility:-

The Solubility of the prepared compounds was tested by using different solvents (polar and non polar).

8- Vacuum Oven / GallenKamp / Germany.

9- Sensitive Electric Balance, Sartorius, Germany

(2-3) Preparation of the Schiff bases ligands:-(58, 59)

(2-3-1) Preparation of [L_A] ligand:-

This ligand was prepared by fusion of a mixture of (1.5 g, 10 mmole) of piperonaldehyde and (1.1 ml, 10 mmole) of cyclohexyalamine in crucible and heated on hot plate then three drops of glacial acetic acid were added as catalyst, A solid mass was formed which was washed with diethyl ether and recrystallized from ethanol then dried under vacuum oven at 30C^o for two days, melting point, colour and yield (%) are given in Table (3-1).

(2-3-2) Preparation of [L_B] ligand:-

A mixture of (1.0 ml, 10 mmole) of salicylaldehyde with (1.62 g, 10 mmole) of 2,4-dichloroaniline was dissolved in (25 ml) of absolute ethanol. Then to this mixture three drops of glacial acetic acid were added as catalyst, the resulting mixture was refluxed on hot plate with magnetic stirrer for two hours, A precipitate was formed, the precipitate was separated by filtration and washed with diethyl ether and recrystallized from ethanol, then dried under vacuum oven at 40C^o for two days, melting point, colour and yield (%) are given in Table (3-3).

(2-3-3) Preparation of [L_C] ligand:-

A mixture of (2.1 ml, 20 mmole) of salicylaldehyde and (1.202g, 10 mmole) of dithiooxamide was dissolved in (30 ml) of absolute ethanol. Then to this mixture three drops of glacial acetic acid were added as catalyst, the resulting mixture was heated with stirring under reflux for (48 hours), A precipitate was formed, the precipitate was separated by filtration and washed with diethyl ether and recrystallized from ethanol, then dried under vacuum oven at $40C^o$ for two days, melting point, colour and yield (%) are given in Table (3-5).

(2-3-4) Preparation of [L_D] ligand:-

A mixture of (1.68 mml, 16 mmole) of salicylaldehyde and (0.865 g, 8 mmole) of o-phenylenediamine was dissolved in (25 ml) of absolute ethanol. Then to this mixture added three drops of glacial acetic acid as catalyst, the resulting mixture was refluxed on hot plate with magnetic stirrer for (3 hours), A precipitate was formed, the precipitate was separated by filtration and washed with absolute ethanol then with diethyl ether and recrystallized from ethanol, then dried under vacuum oven at $40C^o$ for two days, melting point, colour and yield (%) are given in Table (3-7).

(2-4) Preparation of the metal complexes:- (60, 61)

(2-4-1) Preparation of the metal complexes of [L_A]:-

1) ***Copper (II) complex [L_ACu (II)]:-***

A Solution of (0.2089 g, 0.866 mmole) Copper nitrate trihydrate dissolved in (10 ml) of absolute ethanol was added to (0.4 g, 1.731 mmole) of [L_A] dissolved in (15 ml) of absolute ethanol. The mixture was refluxed with stirring for three hours, the resulting precipitate was filtered and washed with diethyl ether and recrystallized from hot ethanol then dried under vacuum at 40C^o for two days, the melting point, coulor and yield (%) are given in Table (3-1).

2) ***Cobalt (II) complex [L_A Co (II)]:-***

A Solution of (0.252g, 0.866 mmole) Cobalt nitrate hexahydrate dissolved in (10 ml)of absolute ethanol was added to (0.4 g, 1.731 mmole) of [L_A] dissolved in (15 ml) of absolute ethanol. The mixture was refluxed with stirring for three hours, the resulting precipitate was filtered and washed with diethyl ether and recrystallized from hot ethanol then dried under vacuum at 40C^o for tow day, the melting point, coulor and yield (%) are given in Table (3-1).

3) ***Rhodium (III) complex [L_ARh (III)]:-***

A Solution of (0.197 g, 8.66 mmole) Rhodium chloride monohydrate dissolved in (10 ml) of absolute ethanol was added to (0.4 g, 1.731 mmole) of [L_A] dissolved in (15 ml) of absolute ethanol. The mixture was refluxed with stirring for three hours, the resulting precipitate was filtered and washed with diethyl ether e and recrystallized from hot ethanol then dried under vacuum at 40C^o and under reduce pressure for two days, the melting point, coulor and yield (%) are given in Table (3-1).

(2-4-2) Preparation of the metal complexes of [L_B]:-

1*) Copper (II) complex [L_BCu (II)]:*-

A Solution of (0.227 g, 0.94 mmole) Cupper nitrate trihydrate dissolved in(10 ml) of absolute ethanol was added to(0.5 g, 1.88 mmole) of [L_B] dissolved in (15 ml) of hot absolute ethanol. The mixture was refluxed with stirring for three hours, when this mixture on hot plat with stirring added several drops of buffer pH (9). A crystalline precipitate was formed which was filtered and washed with diethyl ether and recrystallized from hot ethanol then dried under vacuum at 40C^o for two days, the melting point, coulor and yield (%) are given in Table (3-3).

2) Cobalt (II) complex [L_BCo (II)]:

A Solution of (0.273 g, 0.94 mmole) Cobalt nitrate hexahydrate dissolved in (10 ml) of absolute ethanol was added to (0.5 g, 1.88 mmole) of [L_B] dissolved in (15 ml) of hot absolute ethanol. The mixture was refluxed with stirring for three hours, when this mixture on hot plat with stirring added several drops of buffer pH (9). A crystalline precipitate was formed which was filtered and washed with diethyl ether and recrystallized from hot ethanol then dried under vacuum at 40C^o for tow days, the melting point, coulor and yield (%) are given in Table (3-3).

3) Rhodium (III) complex [L_BRh (III)]:-

A Solution of (0.214g, 0.94 mmole) Rhodium chloride dissolved in (10 ml) of absolute ethanol was added to (0.5 g, 1.88 mmole) of [L_B] dissolved in (15 ml) of hot absolute ethanol. The mixture was refluxed with stirring for three hours, when this mixture on hot plat with stirring added several drops of buffer pH (9). A fine crystalline precipitate was formed which was filtered and washed with diethyl ether and recrystallized from hot ethanol then dried under vacuum at 40C^o for two days, the melting point, coulor and yield (%) are given in Table (3-3).

(2-4-3) Preparation of the metal complexes of [L_C]:-

A general method was followed for the preparation of metal complexes of [L_C] which can be described below:

Ethanolic solution of each of the following metal salts of (0.301 mmole) of [(0.0728 g) $Cu(NO_3)_2.3H_2O$,(0.0877 g) $Co(NO_3)_2.6H_2O$ and (0.0685 g) $RhCl_3.H_2O$] was added to an ethanolic solution of (0.1g, 0.301 mmole) of [L_C]. The mixture was warmed for 5 min. then refluxed for 3 hours, when this mixture on hot plat with stirring added several drops of buffer pH (9) to complete the reaction. Fine crystalline powders were obtained with different coulors depending on the type of the metal salt, which were filtered and washed with diethyl ether and recrystallized from hot ethanol then dried under vacuum at 40C^o for two days, the melting point, coulor and yield (%) are given in Table (3-5).

(2-4-4) Preparation of the metal complexes of [L_D]:-

A general method was followed for the preparation of metal complexes of [L_D] which can be described below:

Ethanolic solution of each of the following metal salts of (1.266 mmole) of [(0.306 g) $Cu(NO_3)_2.3H_2O$, (0.368 g) $Co(NO_3)_2.6H_2O$ and (0.288 g) $RhCl_3.H_2O$] was added to an ethanolic solution of (0.4g, 1.266 mmole) of [L_D]. The mixture was warmed for 5 min. then refluxed for 3 hours, when this mixture on hot plat with stirring several drops of buffer pH (9) were added to complete the reaction. Fine crystalline powders were obtained with different coulors depending on the type of the metal salt, which were filtered and washed with diethyl ether and recrystallized from hot ethanol then dried under vacuum at 40C^o for two days, The melting point, coulor and yield (%) are given in Table (3-7).

Contents

Subject **Page**

Chapter three: Results and Discussion 34-109

References 110-118

Symbols and Abbreviations

Alde.	Aldehyed
B.M	Bohr Magneton
DMF	Dimethyl Formamide
DMSO	Dimethyl Sulfoxide
FT-IR	Fourier transform infrared
M.p.	Melting point
NMR	Nuclear Magnetic Resonance
UV-Vis	Ultraviolet –Visible
υ	Stretching
δ	Bending
σ	Sigma bond

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SYNTHESIS AND STUDY OF MIXED LIGAND COMLEXES OF COBALT (II), COPPER (II) AND RHODIUM (III) IONS

A Thesis
Submitted to the College of Science Al-Nahrain University in partial fulfillment of the requirements for the Degree of Master of Science in Chemistry

By
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(B.Sc. in chemistry 2005)
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June 2008 ***Jamadi Althani 1429***

جمهورية العراق
وزارة التعليم العالي والبحث العلمي
جامعة النهرين
كلية العلوم
قسم الكيمياء

تحضير ودراسة معقدات الكوبلت(II)، النحاس(II) والروديوم(III) مع مزيج من الليكندات

رسالة
مقدمة إلى كلية العلوم- جامعة النهرين
وهي جزء من متطلبات نيل درجة الماجستير في الكيمياء

من قبل

إيمان تُركي شمخي

بكالوريوس علوم كيمياء ٢٠٠٥
(جامعة النهرين)

باشراف

الأستاذ الدّكتورِ

أياد حمزة جاسم

جمادى الثاني ١٤٢٩ **حزيران ٢٠٠٨**

Supervisor certification

I certify that this thesis was prepared under my supervision at the Department of Chemistry, College of Science, Al-Nahrain University as a partial requirements for the Degree of Master of Science in Chemistry.

Signature:
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In view of the available recommendation, I forward this thesis for debate by the examining committee.

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Examining Committee's Certification

We, the Examining Committee, certify that we read this thesis and have examined the student ***Eman Turky Shamkhy***, in its contents and that, in our opinion; it is adequate as a thesis for the Degree of Master of Science, in Chemistry.

(Chairman).

Signature:

Name: Prof. Dr. MUSA F. H

Date: / /2008

(Member)	**(Member)**
Signature:	**Signature:**
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Date: / /2008	**Date: / /2008**

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Eman

2008

بِسْمِ اللهِ الرحْمن الرحِيم

﴿نَرْفَعُ دَرَجَاتٍ مَنْ نَشَاء وَفَوْقَ كُلِّ ذِي عِلْمٍ عَلِيمٌ﴾

﴿صَدَقَ اللهُ العَلِيُّ العَظِيمْ﴾

سورة يوسف الآية [٧٦]

الأهداء

الى من ثبت قدمي في طريق العلم .....

الى من اعطاني املاً كبيراً.....

الى شهيد جامعتي ومنبر العلم فيها.....

الى من ستبقى نتائجه العلميه سراجا وهاجا ينير لنا درب العلم.....

الى من يرقد بسلام في ارض السلام.....

الى ابي بعد ابي وفقيد رسالتي.....

اهدي ثمرة هذا الجهد المتواضع.....

الى روح الاستاذ الدكتور الطاهره

"أياد حمزة جاسم الخفاجي"

الخلاصة

تحضر قواعد شيف عادةً بطرائق متعددة ومن اكثرها شيوعاً التكاثف بين الأمينات والالديهايدات.

وقد حضرت بهذة الطريقة عدد من قواعد شيف من خلال التفاعل بين كل من cyclohexylamine مع piperonaldehyde وتفاعل 2,4-dichloroaniline مع salicylaldehyde وبنسبه موليه١:١ لتحضير

الليكند $[L_A]$ (Piperonaldehyde cyclohexylimine)

و اليكند$[L_B]$ (Salicylidene-2,4-dichloroaniline) على التوالي.

كذلك تفاعل (dithiooxamide مع salicylaldehyde) وتفاعل (o-phenylenediamine) مع (salicylaldehyde) وبنسبه مولية١:٢ لتحضير

الليكند $[L_C]$ (bis salicylidene-dithiooxamide)

و الليكند $[L_D]$ (bis salicylidene -o-phenylenediamine)) على التوالي.

شُخصت الليكندات المحضرة بوساطة تقنية TLC ، قياس درجات الأنصهار، أطياف الأشعة تحت الحمراء (F.T.IR)، والأشعة الفوق البنفسجية-المرئية (UV-Vis).

تم استخدام قواعد شيف المحضرة $[L_D, L_C, L_B, L_A]$ كليكندات لتحضير عدد من المعقدات الجديدة مع ايونات بعض العناصر الانتقالية التي تشمل

[Cu (II), Co (II), Rh (III)].

تم تحضير معقدات النحاس الثنائي والكوبلت الثنائي و الروديوم الثلاثي مع $[L_A]$ و معقدات النحاس الثنائي والكوبلت الثنائي و الروديوم الثلاثي مع $[L_B]$ بنسبة موليه١:٢ (فلز:ليكاند).

بينما تم تحضير معقدات النحاس الثنائي والكوبلت الثنائي و الروديوم الثلاثي مع [L_C] و معقدات النحاس الثنائي والكوبلت الثنائي و الروديوم الثلاثي مع [L_D] بنسبة موليه١:١ (فلز:ليكاند).

تم عزل المعقدات الفلزية المحضرة في الحالة الصلبة.وشُخصت المعقدات الجديدة بواسطة أطياف الأشعة تحت الحمراء (F.T.IR)، والأشعة الفوق البنفسجية-المرئية (UV-Vis)، وتقدير النسبة المئوية للفلزبتقنية الامتصاص الذري والقياسات المغناطيسية والتوصيلية الكهربائية.

أستناداً إلى نتائج القياسات أعلاه جرى أقتراح الصيغ التركيبية للمعقدات الجديدة و كالآتي:

١)الصيغ التركيبية لمعقدات الأيونات Rh(III), Co(II), Cu(II) مع الليكند [L_A] كالتالي:

$[Cu_2(L_A)_4(NO_3)_2]\ (NO_3)_2\ .6H_2O$

$[Co(L_A)_2(ONO_2)_2\ (H_2O)_2].2H_2O$

$[Rh(L_A)_2(Cl)_2(H_2O)_2]\ Cl.\ 3H_2O$

٢) الصيغ التركيبية لمعقدات الأيونات Rh(III), Co(II), Cu(II) مع الليكند[L_B] كالتالي:

$[Cu(L_B)_2(H_2O)_2]$

$[Co(L_B)_2(H_2O)_2].3H_2O$

$[Rh_2(L_B)_4(Cl)_2].4H_2O$

٣) الصيغ التركيبية لمعقدات الأيونات(Rh(III), Co(II), Cu(II مع الليكند[L_C] كالتالي:

$[CuL_C(H_2O)_2].2H_2O$

$[CoL_C(H_2O)_2].6H_2O$

$[RhL_C(H_2O)Cl].4H_2O$

٤) الصيغ التركيبية لمعقدات الأيونات $Cu(II)$, $Co(II)$, $Rh(III)$ مع الليكند $[L_D]$ كالتالي:

$[CuL_D(H_2O)_2]$
$[CoL_D(H_2O)_2].6H_2O$
$[Rh_2(L_D)_2(Cl)_2].3H_2O$

برزت الخصائص التركيبية والتآصرية المختلفة من خلال دراسة الكيمياء التناسقية لمعقدات الليكندات الجديدة.

فُسرتْ طبيعة التآصر بين أيون الفلز والذرات المانحة في الليكند بمعامل راكاح ومقاييس المجال الليكندي الأخرى والتي تم أحتسابها بوساطة مخطط (تنابا- سوكانو) لأيون الكوبلت الثنائي وايون الروديوم الثلاثي.