الخلاصة

تم في هذا البحث تحضير ثلاثة من الليكاندات الثلاثة التي تحتوي على حلقة البنزوثايازول المرتبطة بثلاث الديهايدات مختلفة عن طريق مجموعة الامين والتي اختيرت لتحضير سلسلة من معقدات بعض العناصر الانتقالية .

تم مفاعلة الليكاندات الثلاثة المحضرة

LI= ٢-(اسيتلدين) هايدرازين بنزوثايازول

LII=2-(*O*-ميثوكسي بنزلدين) هايدرازين بنزوثايازول

LIII=٢-(٢,4,6- تراي ميثوكسي بنزلدين) هايدرازين بنزوثايازول

مع ايونات العناصرالانتقالية (Cd(II), Cu(II), Co (II), Ni(II)) وتتم تحديدصيغ معقدات LI كالاتي:

$[Ni (LI)_2 (H_2O)_2]. (NO_3)_2$, $[Co (LI)_2 (H_2O)_2] Cl_2$

$[Cu (LI)_2 Cl_2]. 2C_2H_5OH$, $[Cd\ LI (H_2O)_2]. (NO_3)_2$

بينما كانت صيغ معقدات LII كالاتي:

$[Ni (LII)_2 (H_2O)_2. 2H_2O$, $[Co (LII)_2 (H_2O)_2] 2H_2O$

$[Cu_2 (LII)_2 Cl_2]. H_2O$, $[Cd (LII) (NO_3) H_2O] 2H_2O$

في حين كانت صيغ معقدات LIII كالاتي:

$[Ni (LIII)_2 (NO_3)_2]. 2H_2O$, $[Co (LIII)_2 Cl_2]. 6H_2O$

$[Cu (LIII)_2 .(H_2O)_2] Cl_2$, $[Cd\ LIII (H_2O)_2]. (NO_3)_2. C_2H_5OH$

تتم تشخيص جميع الليكاندات ومعقداتها الفلزية باستخدام التقنيات المناسبة والتي تضمنت درجات الانصهار واطياف الاشعة تحت الحمراء والمرئية- فوق البنفسجية وتحليل العناصر بطريقة الامتصاص الذري وقياسات الحساسية المغناطيسيه والتوصيلية الكهربائية.

وفقا للنتائج التي تم الحصول عليها وبخصوصا حسابات نظرية المجال البلوري تم اقتراح الصيغ التركيبية للمعقدات الجديدة والتي كانت ذات ثمانية السطوح عدا معقدات Cd(II) التي كانت رباعية السطوح وكذالك معقد AIICu الذي اظهر كونه مربع مستوي.

اظهر الليكندات سلوكا تناسقيا ثنائي الذرة مختلفا اعتمادا على الذرات المانحة في الليكاند المعني ونوع الايون الفلزي المرتبط به.

Abstract

The new ligands have been prepared in this work, which contain benzothiazole linked to three different aldehydes throw imine group. These three ligands include:

LI= 2- (Acetlidine) hydrazine benzothiazole.
LII= 2- (*O* -hedroxy benzylidine) hydrazine benzothiazole.
LIII=2-(2,4,6- trimethoxy benzylidine) hydrazine benzothiazole.

Which were reacted with the transition metal iones
(Ni(II) , Co(II) , Cu(II) , Cd(II)).

The molecular formulae for the new complexes were :
LI complexes:
$[Ni\ (LI)_2\ (H_2O)_2.\ (NO_3)_2$, $[Co\ (LI)_2\ (H_2O)_2]\ Cl_2$
$[Cu\ (LI)_2\ Cl_2].\ 2C_2H_5OH$ and $[Cd\ LI\ (H_2O)_2].\ (NO_3)_2$

LII complexes:
$[Ni\ (LII)_2\ (H_2O)_2].\ 2H_2O$, $[Co\ (LII)_2\ (H_2O)_2]\ 2H_2O$
$[Cu_2\ (LII)_2\ Cl_2].\ H_2O$ and $[Cd\ LII\ NO_3\ H_2O]\ 2H_2O$

LIII complexes:
$[Ni\ (LIII)_2\ (NO_3)_2].\ 2H_2O$, $[Co\ (LIII)_2\ Cl_2].\ 6H_2O$
$[Cu\ (LIII)_2\ .(H_2O)_2]\ Cl_2$ and $[Cd\ LIII\ (H_2O)_2].\ (NO_3)_2.\ C_2H_5OH$

All the three prepared ligands and their metal complexes were characterized using the appropriate techniques, i.e. melting point measurement, FTIR , UV-Vis spectroscopy, atomic absorption

spectroscopy, magnetic susceptibility and electrical conductivity measurement.

According to the data obtaeind, especially those from crystal field calculations, the structural formulae were suggested.

All complexes show to have octahedral shapes, except that of Cd (II) complex, which were of tetrahedral geometry and also that of AII Cu which was dimeric square planar.

The ligand, show different coordination behavior depending on the donor atoms and the type of the metal ion.

Chapter one

Introduction

Introduction:

Developments in inorganic and organometallic chemistry have resulted in a significantly increased understanding of the bonding, structure, and reactivity of coordination compounds.

These developments have been applied fruitfully to the design of model system that shed light on the behavior of metal ions in biological processes and ultimately to look more closely into these processes themselves(1).

On the other side, a large number of metal containing therapeutical agents and other biologically active complexes have been prepared and proven to be of great effectiveness in this respect(2).

1.1 Bioinorganic Chemistry:

The boundaries of inorganic chemistry extend from physical and organic chemistry to the boundaries of theoritical physics, this statement still valid even if we add boundaries of biological science.

Therefore inorganic chemistry can be considered as growing organism with respect to the increasing flow of data.

It is know that coordination chemistry refer to that part of inorganic chemistry which deals which studying the properties of both the central metal and the group of ligands surrounding it, in the first days of chemistry the coordination compounds were considered as a great chaleng for the inorganic chemist, now a days it forms a big part of the resent research in inorganic chemistry and about 70% of the issues published in inorganic chemistry are of coordination compound.

But even the classical coordination theories were extended and modified to include these complexes, it still suffering from series problems which are waiting to be resolved.

Inorganic biochemistry is the most growing filed which is based on the role of coordination compounds in the living system(3).

The importance of metal ions in the living system diver the interest of a large number of researchers in pure inorganic chemistry toward the filed of bioinorganic chemistry.

1.2 Interaction of Ligand with metal ion:

The study of the interaction of metal ions with different simple and complicated systems require, first of all, to be aware of the essential bases of coordination inorganic chemistry especially the structural and bonding aspects.

Of the most important theories in this respect is the hard and soft acids and bases theory (HSAB) of pearson, which show the tendency of metal ions to coordinate with certain groups in the structure of the ligand. depending on the nature of donating atom in this group(4), also to know the factors effecting the stability of the resulting complexes.

One of the earliest correlations was the Irving-Williams series of stability. For a given ligand, the stability of complexes with dipositive metal ions 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 a decrease in size a cross the series and in part from ligand filed effects. A second observation is that certain ligand form their most stable complexes with metal ions such as Ag^{+} , Hg^{+2} and Pt^{+2} , but other ligand seem to prefer ions such as Al^{+3} , Ti^{+4} and Co^{+3} .

Ligands and metal ions were classified as belonging to type (a) or (b) according to their preferential bonding. Class (a) metal ions include those of alkali metals, alkaline earth metals and lighter transition metals in higher oxidation states such as Ti^{+4} , Cr^{+3} , Fe^{+3} , Co^{+3} , and the hydrogen ion , H^{+} Class (b) metal ions include those of the heavier transition metals, and those in lower oxidation states such as Cu^{+} , Ag^{+} , Hg^{+2} , Pd^{+2} and Pt^{+2} . According to their prefences toward either class (a) or class (b) metal ions, ligands may be classified as type (a) or (b) respectively. Stability of these complexes may be summarized as follows:

Tendency to complex with class (a) metal ions	Tendency to complex with class (b) ions
N >> p > As > Sb	N << P >> As > Sb
O >> S > Se > Te	O << S < Se ~ Te
F > Cl > Br > I	F < Cl < Br < I

For example, phosphines (R_3P) and thioethers (R_2S) have s much greater tendency to coordinate with Hg^{+2} , Pd^{+2} , and Pt^{+2} , but ammonia, amines (R_3N), water, and fluoride ion prefer Be^{+2} , Ti^{+4} , and Co^{+3} . Such a classification has proved very useful in accounting for and predicting the stability of coordination compounds(5,6).

One of the most important phenomena that control the stability of the oxidation states of a certain element and the stabilization of one state among another states is known as (symbiosis)(7).

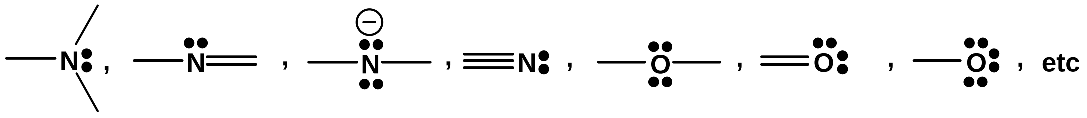
Often metal complexes expand their coordination number by interaction with a Lewis base. This may take place by interaction association or by adduct formation with solvent or other available

Ligands. The physical properties of the resulting complex often are significantly different from those of the complex not having the expanded coordination number(8).

1.3Metal Complexes of Polydentate Ligand:

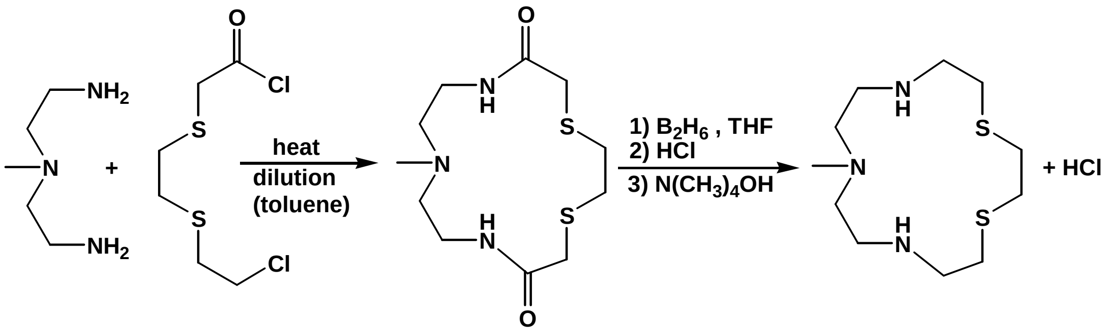
Since complex formation or Ligand substitution is stepwise even with polydentate Ligand, we may expect that polydentate Ligand, particularly those with nonequivalent coordination atoms, will exhibit varying dentate natures. Thus, the normally bidentate ethylenediamine can be monodentate(9) as $NH_2CH_2CH_2NH_3^+$ in the Cr (III) complex $[Cr(NH_2CH_2CH_2NH_3^+)(H_2O)_5]^+_4$, and ethylenediaminetetraaceticacid may coordinate as a bi-to hexa-dentate ligand.

It may be expected that this variation in the polydonation of a ligand will be especially marked for those ligands that contain donor atoms with quite varying affinities toward the metal ion. Such groups, with N and O as the coordinating atoms, may be

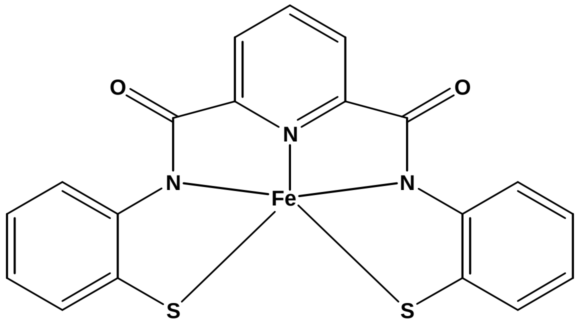


It may further be expected that the most important factors effecting the dentate nature of a polydentate ligand will be pH, solvent, the coordinated groups, the relative metal to ligand concentration and any factors that may effect the mechanism of ligand substitution. There have been a number of investigations(10) on the nature of the complexes formed with multidentate Ligands containing the N-hydroxyethyl group.

In 1972, (N_3S_2) macrocyclic(11) type Ligand was synthesizal according to the scheme shown in following equation.



In 2000 Maschark and Marlin(12) reported the synthesis of the Ligand [N,N◌̆◌̆-bis-(2-mercaptophenyl)pyridine-٢،6-dicarboxyimide]. It's complex with Fe(III) was also prepared, spectroscopic studies showed that the geometry around Fe(III) is a distorted trigonal bipyramidal, as shown in the following Figure:



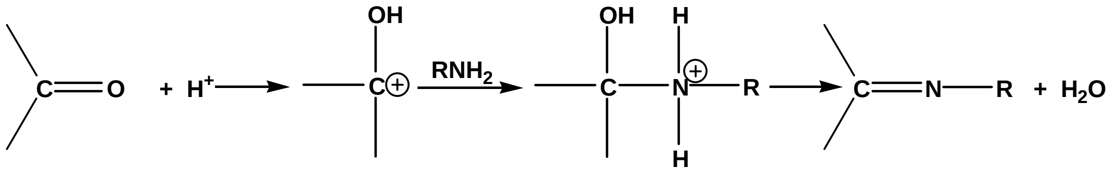
1.4 Schiff bases (SB):

The term Schiff base (SB) is used to define those organic compounds which contain the functional group (-C=N-) and can be designated structurally as R"R'C=NR).

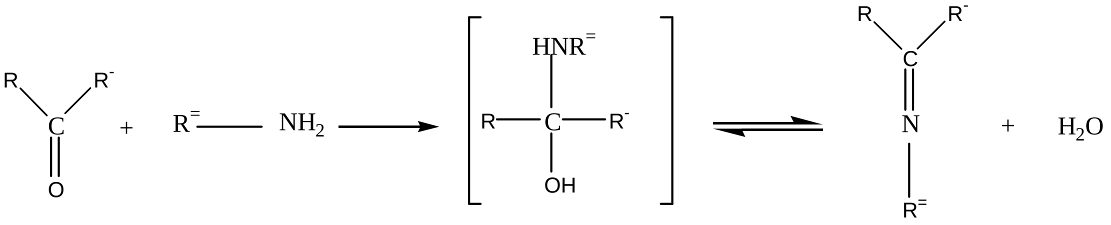
The nature of R group is limited to alkyl or aryl substituents or hydrogen at the point of attachment to the imino (C=N) carbon or nitrogen.

The Schiff bases (SB) were first prepared by (Schiff) in 1864(13,14) from the condensation reaction of aldehyde or Ketones with primary amines by refluxing the mixture in absolute ethanol, benzene, or any other suitable solvent for half or one hour some times, the reaction may be catalyzed by acid(15,16).

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 (SB).



The general mechanism of the Schiff base formation reaction can be depicted as follows:



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(17).

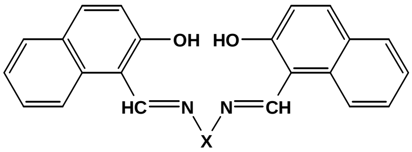
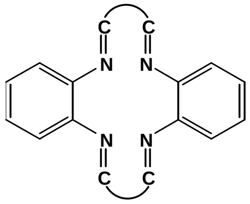
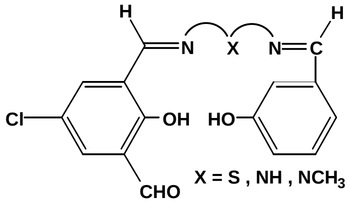
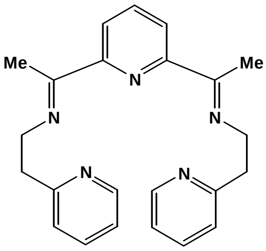
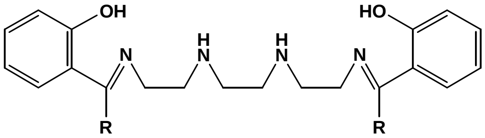
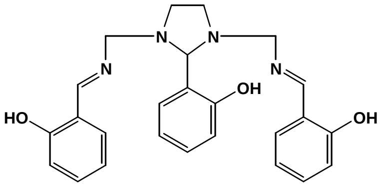
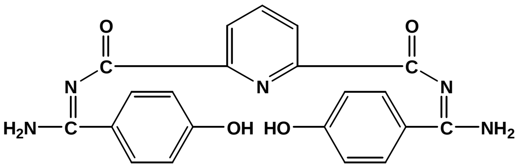
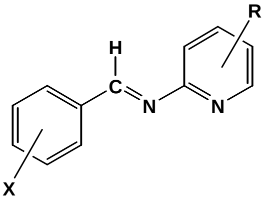
Staab(18) prepared Schiff bases (SB) by removing water which is formed by condensation of aldehyde with the amine by reflux in benzene, this done by mixing the anine and the aldehyde in benzene and then the residual solution is distilled under vacuum.

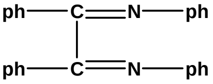
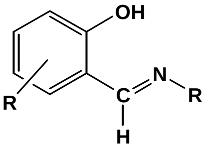
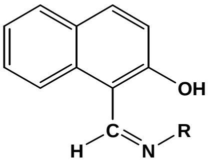
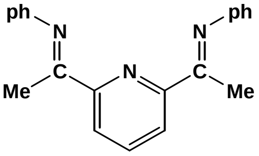
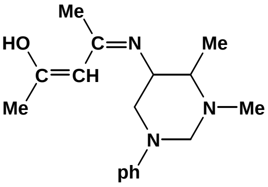
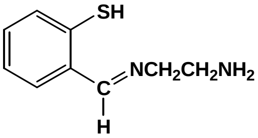
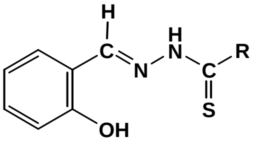
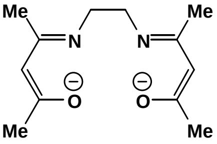
Imine (SB) and other C=N compound can be reduced by $LiAlH_4$, $NaBH_4$, Na-EtOH, hydrogen and catalyst, as well as with other reducing agents.

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 paries 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.

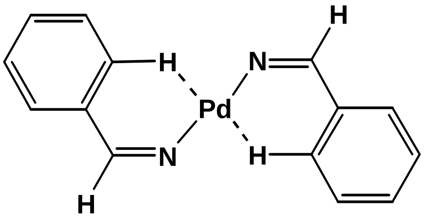
Table (1-1): Some Schiff bases with different donor atoms.

Complex	Donor atoms	Type of donor	Ref
	NNOO	Tetradentate	19
	NNNN	Tetradentate	20
	NNNOO, NNOOS	Pentadentate	21
	NNNNN	Pentadentate	22
	NNNNOO	Hexadentate	23
	NNNNOOO	Heptadentate	24
	NNNNNOOOO	Nanodentate	25
	N N	Bidentate	26- 27

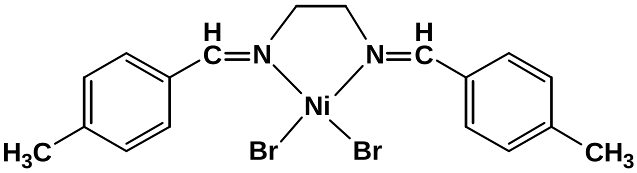
	N N	**Bidentate**	**28**
	N O	**Bidentate**	**29**
	N O	**Bidentate**	**30**
	**NNN**	**Tridentate**	**31**
	**NNO**	**Tridentate**	**32**
	**NNS**	**Tridentate**	**33**
	**NSO**	**Tridentate**	**34**
	**NNOO**	**Tetradentate**	**35**

The way the ligand coordinate to the metal ion is effected by the type and oxidation state of the metal ion in addition to the ligand structure. This can shown by the following examples.

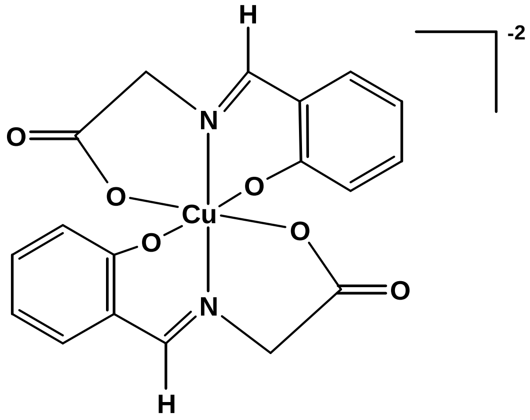
1) The monodentate (SB) phCH=NMe from the weak(29) M . . . H band which make extra stability for its complexes as in the following palladium complex.



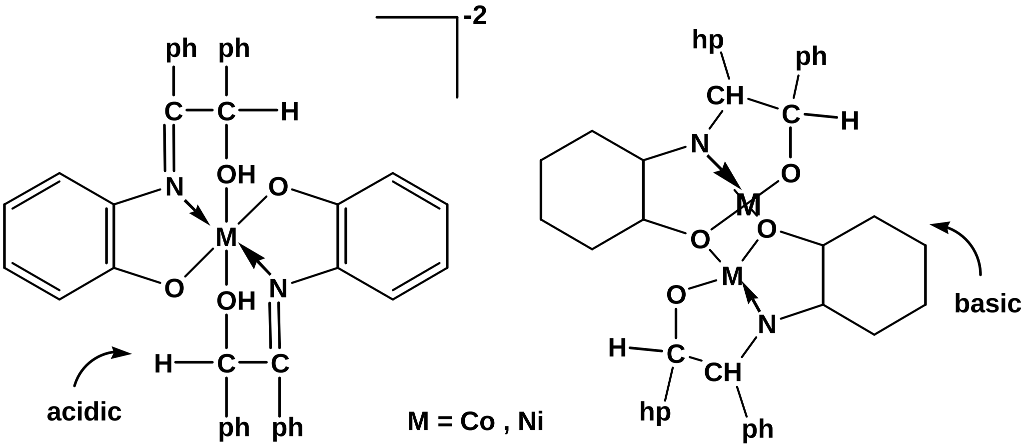
2) Bidentate (SB) containing tow nitrogen atoms from more stable chelating ring with the central metal ion as in the following nickel (II) complex(36).



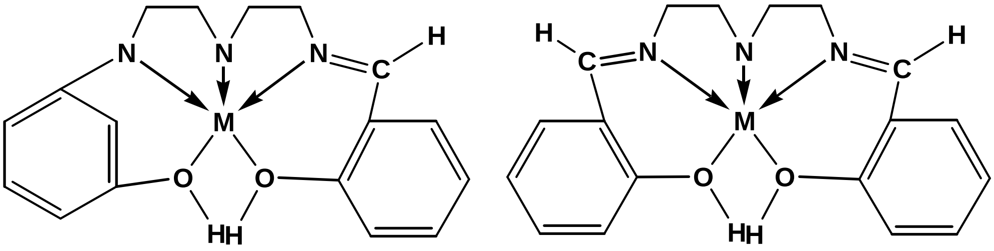
3) As an example of tridentate neutral Schiff base complexes is the following copper (II) complex(35).



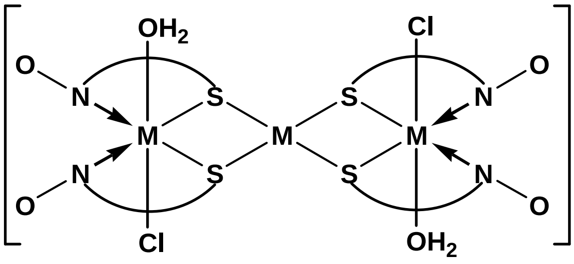
4) It was found that the ligands derived from benzoin and or the amino phenol(37) give mononuclear complex ions in neutral media, while binuclear brigded complexes were formed in basic media as in the following structures.



5) Some (SB) show high coordination number as that of bis (Salysilidin) diethylene triamine(38) which form complexes with cobalt(II) and nickel (II) having octahedral geometry in which the ligand behave as pentadentate in the neutral and basic media respectively.



6) There are some polynuclear complexes(39) of the (SB) which show different geometrical shapes around the metal ions as in the following complex, where the central metal has square planer geometry, which the other two metal atoms have octahedral geometry.



1.5 Infrared spectra of Schiff bases and their metal complexes:

The following are a review of the υC=N assignment, as recorded for Schiff bases and their metal complexes(3,14,40,41).

1) υ(C=N) appear around 1630 cm^{-1} in the free Schiff bases, the band around (1620-1610)cm^{-1} in manganese (III) complexes is observed indicating the coordination of imine nitrogen to the Mn(III) ion(42).

2) Coordination of chain polymers of Schiff bases derived from *o*-animobenzoic acid and terphthalaldehyde 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(43).

3) 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)(44).

4) The IR spectra of some Schiff bases derived from thiazoles and benzothiazoles. Showed a strong sharp band in the region (1630-1615) cm^{-1} for υ(C=N)(45).

5) Schiff bases, oximes, thiadiazoles, iminocarbonates, and guanidines show the C=N stretch(46) in the region (1689-1471) cm^{-1} .

6) the IR spectra of now series of Schiff bases derived from substituted, 4.5-disubstituted-2-amino-thiadzole, substituted-2-amino-benzothiazoles and *p*-hydroxy benzaldehyde show a strong sharp band in the region (1640-1625) cm^{-1} for υ(C=N)(47).

7) Strong band at 1600 cm^{-1} was corresponded to υ(C=N)⁽⁴⁸⁾ 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(49).

8) 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(50).

9) Patai suggest that υ(C=N) appear in the region (1680-1570) cm^{-1} the intensity of υ(C=N) is variable and it depend on the substituted group(51).

10) The IR spectra of Schiff bases derived from 4-phenyl-5-(*p*-aminophenyl)-3-mercapto-1,2,4-triadzole give string band in the region (1695-1650) cm^{-1} corresponding to υ(C=N)(52).

1.6 The Metal Complexes of Schiff Bases as Biologically Important Compounds:

Schiff bases and their metal complexes have a great deal of attention during the last decade from many workers to prepare new set of these bases and their transition metal complexes(53).

These complexes have proven to be antitumer and have carcinostatic activities(49,53). They show leukaemetic activity. Schiff bases, on the other side, have a great importance in the biological reactions like (visual process)(54) , and in the reaction that involve removing the amine group by enzymic effect (enzymatic transition reaction) and some B_6 -Catalysed reaction(55).

The biological activity of Schiff base is attributed to the formation of stable chelates with transition metal ions presents in cell(56).

Schiff base derived from sulfa drugs have been successfully used for the bacteriostatic activites and complexation(57).

A great deal of work concerning metal complexes of Schiff bases were concentrated on the cobalt (III) complexes, that are used reversible of oxygen carriers or a model for vitamin B_{12} Co-enzymes, the attention is also extended to Fe(II) complexes which are included in the hemoglobin found is some biological systems(58) .

It has been noticed the number of papers regarding the preparation of palladium and platinum complexes with Schiff bases increases rapidly.

The discovery of cis-platinum complex cis-$[pt(NH_3)_2Cl_2]$ as an antitumer agent by Rosenberg, led to development of platinum complexes chemistry designed for wide biological applications(59) Palladium and platinum are regarded as metal, so they react with soft legends that contain an electron-donating group like S and P, they also can form complexes with hard ligands(60), like oxygenating molecules or molecules which contain nitrogen.

Recently many research works (61) appeared deal with the study of palladium interaction with Schiff bases through cyclometylation reaction (this include metal containing cycle in which the metal is bonded to a carbon atom),

This reaction plays an important role in preparation of some organometallic compound in which these complexes are used as starting material to improve the stereochemistry of those compounds, these complexes are used in photochemical reactions.

Schiff bases and their analogues have great importance as catalysts in racemic reaction in peptide syntheses and in formation of amines that have biological origin (62).

Biological activity of complexes derived from hydrazones has been widely studied and contrasted, acting in processes such as antibacterial, antitumoral, antiviral, antimalarial and antituberculosis effect(63).

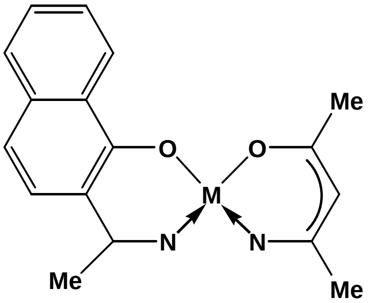
Organotin compound show a large spectrum of biological activities,In recent year, several investigators to test their antitumer activity(64,65), have been carried out.

These organotin complexes are effective antifouling antimicrobial and antiviral agents, therefore, much attention has been paid to their implication for antioncogenesis(66). They are also used as bactericides, fungicides and industrial and agriculture biocides (67).

The biological activity of the metal complexes of Schiff bases derived from sulpha drugs has led to considerable interest in their coordination chemistry, The condensation products of sulpha drugs with aldehydes and ketones are biologically active and also have good complexing ability, their activity increase on complexation with metal ion(52) .

Davar et.al(53).have prepared unsymmetrical Schiff base 1-hydroxy-2-acetonaphthoneacetyl acetone-ethylendiimine and its complexes with some transition metals [Ni(II), Cu(II) and pd(II)], These compounds were characterizes by elemental analysis, conductometric measurements, infrared and electronic spectra, NMR and mass spectroscopy square planar structure have been suggested for the complexes .

All the prepared complexes exhibit antibacterial activities because that complexes having hydroxyl naphthalene nucleus were more active than salicylaldehyde or hydroxylacetophenone Schiff bases, due to the naphthalene nucleus possessing-OH group increases the activity fig(1-8).



Recently anew set of Schiff bases have been prepared and these new compounds showed bactericidal activity.

Table (1-2) the molecular formule and biological activities of some metal complexes of a number of Schiff bases.

Molecular formula	Name	Metal ion	Biological activity	Ref
$C_{12}H_{15}N_5O_2S$	**4-phenyl-5-[*p*(*p*-nitrobenzylidene]phenyl)-3-mercapto-1,2,4-triazole**	Mn^{+2}, Co^{+2}, Cu^{+2}, Ni^{+2}, Pt^{+2}, Pd^{+2}	**Antibacterial activity**	**68**
$C_{25}H_{16}N_4S$	**4-phenyl-5-[*p*(α-naphthalidene)phenyl]-3-mercapto-1,2,4-triazole**	Co^{+2}, Cu^{+2}, Pd^{+2}	**Antibacterial activity**	**52**
$C_{18}H_{15}N_3OS$	**Thiocarboxy phenyl-4-allyl-5-phenyl-4H-1,2,4-triazole**	Hg^{+2}, Au^{+2}, Ca^{+2}, Cd^{+2}, Cu^{+2}, Fe^{+2}	**Antibacterial activity**	**69**
$C_{12}H_{11}N_3S_2$	**2-(benzylidene)-5-allylthio-1,3,4-thiadiazole**	Cu^{+2}, Fe^{+2}	-	**70**
$C_{17}H_{15}NO$	**B-naphthaldehyde-N-phenyl imine**	Cd^{+2}, Fe^{+3}, Co^{+2}, Cu^{+2}, Cr^{+3}, Hg^{+2}, V(IV)	-	**71**
$C_{12}H_{21}NO$	**B-naphthaldehyde-N-cyclohexyl imine**	Cd^{+2}, Fe^{+3}, Co^{+2}, Cu^{+2}, Hg^{+2},V(IV)	-	**72**
$C_{17}H_{14}N_2O_3S$	**2-hydroxy-1-naphthaldehyde salphanilamide**	Sn^{+4}	**Antimicrobial activity**	**72**
$C_{13}H_{12}N_2O_3S$	**Salicylaldehyde sulphanilamide**	Sn^{+4}	**Antimicrobial activity**	**72**

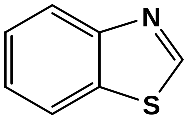
1.7 Benzothiazoles:

Benzothiazoles and its derivatives constitute an important class of compounds having a wide spectrum of biological activity, the early impetus to the study of benzothiazole chemistry come from the partial importance of benzothiazole ring.

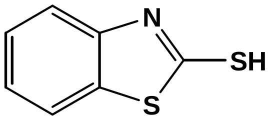
The biological importance of thiazole derivatives was further emphasized during the period 1940-1960 when work on the structure of antibiotic penicillin (73,74), showed the presences of thiazolidine ring in this important therapeutic agent.

During the last years, a large number of derivatives of sulfa thiazole has been prepared and studied chemically and biologically

Benzothiazoles are bicyclic systems (benzene ring fused with thiazole ring) with two heteroatoms, one sulfur atom and one nitrogen atom, where in the benzene ring is fused to the 4,5positions of thiazole ring like the structure (A).



(A)



(B)

2-mercaptobenzothiazoles are derivatives in which the 2-position is liked to the sulfur atom like the structure (B).

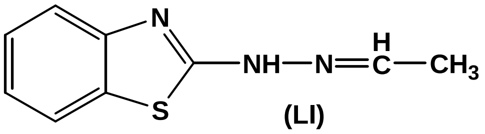
The benzothiazoles are aromatic because they are cyclic, planar molecules, and have five pairs of delocalized π-electrons; four of the pairs are shown as π-bonds, and one pair is shown as a pair of nonbonding electrons on the sulfur atom(75) Furthermore, the ease with which a large variety of such derivative can be prepared and the reactivity of the mercapto group make these compounds valuable starting materials for the preparation of many other benzothiazole.

1.8 Aim of the work:

The aim of the present work can be summarized as follow:

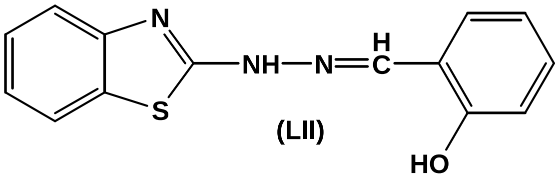
1) Three ligands have been chosen to be prepared starting form 2-mercapto benzothiazole; these ligands have the following structures.

(a)



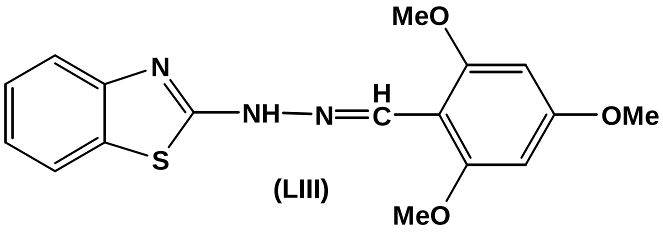
(LI)

(b)



(LII)

(c)



(LIII)

2) Complexes of these ligands with Ni(II), Co(II), Cu(II) and Cd(II) are to be prepared.

3) The study of the new prepared complexes using different method characterization is to be carried out.

Chapter three

Results and Discussion

3.1 physical properties of the prepared complexes:

The physical data for the prepared complexes in Tables (3-1) to (3-3) which show different melting points some of them were higher than the parent ligands; others were of lower melting points.

The colours of the complexes were useful in structural determination.

All the prepared compounds were stable towards air, moisture and light. All reactions were carried out under heating conditions and the solvent was absolute ethanol.

Identification and study of these complexes were carried out by metal analysis [the results are shown in Tables (3-1) to (3-3), infrared, ultra-violet visible spectrophotometery, magnetic susceptibility and electric conductivity measurements. According to these measurements the chemical formula of the prepared complexes have been suggested as given in Table (3-6).

Table (3-1): The physical properties of LI and its metal complexes.

Symbol	Colour	m.p. (^{o}C)	Yield (%)	Metal content	
				Clac.	Found
LI	Light gray	180	75	-	-
AINi	Light blue	250-253	72	9.8	10.1
AICo	Brick-red	242-246	69	10.7	10.4
AICu	Green	205-207	75	10.5	9.9
AICd	Deep blue	235-240	80	24.2	23.2

Table (3-2): The physical properties of LII and its metal complexes.

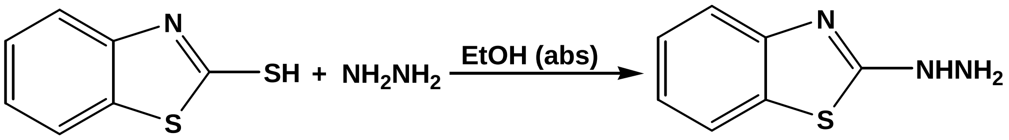
Symbol	Colour	m.p. (^{o}C)	Yield (%)	Metal content	
				Clac.	Found
LII	Off white	255	85	-	-
AIINi	Yellowish green	260-dec.	60	8.8	9.0
AIICo	Deep green	246-250	77	8.8	9.2
AIICu	Deep green	226-230	82	16.9	17.0
AIICd	Light brown	240-244	70	22.5	22.8

Table (3-3): The physical properties of LIII and its metal complexes.

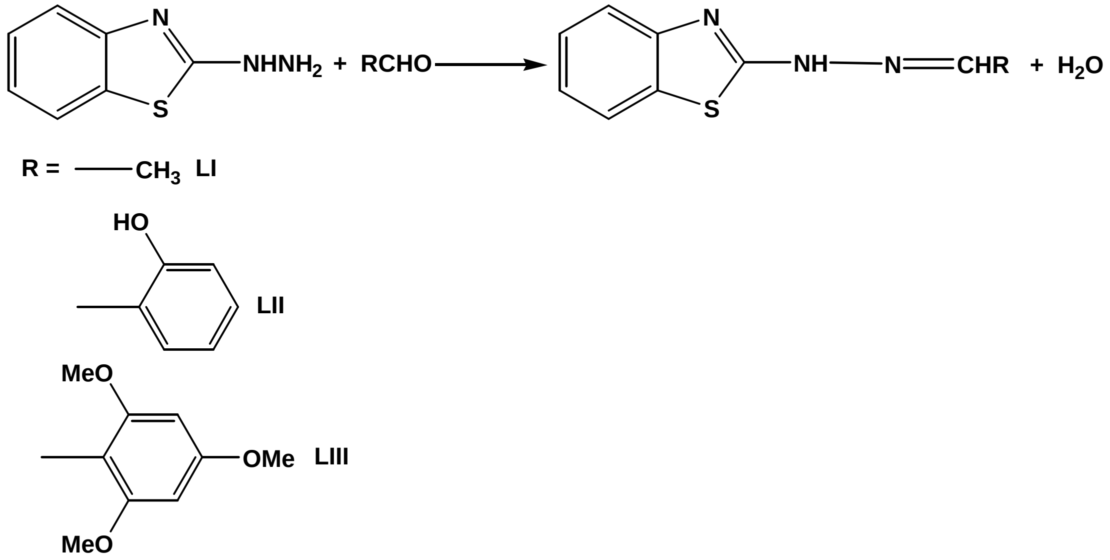
Symbol	Colour	m.p. (^{o}C)	Yield (%)	Metal content	
				Clac.	Found
LIII	Off white	210	70	-	-
AIIINi	Light green	220-dec.	85	6.6	7.0
AIIICo	Bright green	195-200	72	6.3	5.4
AIIICu	Olive green	165-170	70	7.6	7.9
AIIICd	Yellow	225-230	62	16.9	16.2

3.2 Preparation of the ligands:

The preparation of the ligands were performed through two steps, the first step include preparation of 2-hydrazino benzothiazole from reaction of 2-mercapto benzothiazole with hydrazine hydrate higher yield product with higher purity obtained in this method according to the following equation:



The second step was the formation of the Schiff base by using different aldehydes (mechanism mentioned in section 1.5).



3.3 Infra-Red spectra:

The FTIR 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}.

3.3.1 The FTIR spectrum of LI and its metal complexes:

The ligand LI containing the azomethine group. In general azomethine group (-C=N) absorption occurs in the region (1690-1470) cm^{-1} depending on the nature of groups linked to it(51,77).

The compound containing azomethine group shows basic coordination behavior toward metal ions coordinating via the nitrogen atoms, this coordination shifts the stretching frequency of azomethine group either toward higher frequency in some complexes(78,79,52) or toward lower frequency in others(80,81).

The increase in frequency may be due to the simultaneous strengthening of the (-C=N-) 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(78). The decrease in frequency indicates a decrease in the stretching force constant of (-C=N-) group as a consequence of the coordination through azomethine nitrogen. The double bond character between carbon and nitrogen is reduced(82,83).

The IR spectrum of the ligand LI, Figure (3-1), Table (3-4) showed the absence of the band at ~3303 cm^{-1} due to the (N-H) stretching vibration(46), and a strong new band appeared at 1614 cm^{-1} assigned to azomethine ν(HC=N) linkage, showing that amino and aldehyde moieties of the starting material were reacted and have been converted in to the azomethine group(84).

The bands appeared at 1589 and 1446 cm^{-1} refer to ν(C=C) of aromatic ring, and the band at 2923 cm^{-1} and 2858 cm^{-1} refer to ν(C-H) of aliphatic alkane, and the band at 3057 cm^{-1} refers to ν(C-H) of aromatic ring.

A) Nickel (II) complex (AINi):

The spectrum of (AINi) complex Figure (3-4), Table (3-4), shows the shifting of the azomethine band to lower frequency by (14 cm^{-1}) indicating the participation of azomethine nitrogen in the interaction with the Ni(II) ion.

The presence of new weak band observed at 576 cm^{-1} was assigned as ν(Ni-N) (85).

The appearance of a weak band at 682 cm^{-1} indicated the presence of coordinated water molecules in the structure(85,89).The bands related to the free nitrate(85) ion were found at 1419, 1272 and 1157 cm^{-1}.

B) Cobalt (II) complex (AICo):

The FTIR spectrum of (AICo) complex Figure (3-5), Table (3-4) the stretching frequency of azomethine group was shifted to a lower frequency by (12 cm^{-1}) and appeared at 1602 cm^{-1}.

Further condusive evidence of the coordination of the ligand with the studied metal ion was shown by the appearance of new weak low frequency band at 528 cm^{-1}, this was assigned to ν(M-N) vibration(85).

A broad band appeared at 3407 cm^{-1} indicating the presence of coordinated water in the molecule(85) structure of the complex.

C) Copper (II) complex (AICu)

The FTIR spectrum of (AICu) complex Figure (3-6), Table (3-4), show the shifting of azomethine band to a lower frequency and appear at 1602 cm^{-1} which indicate the participation of azomethine-nitrogen with Cu(II) atom.

A broad band appeared at 3685 cm^{-1} indicating the presence of ethanol molecule in the structure of the complex.

The presence of new weak band observed at 507 cm^{-1} was assigned as ν(Cu-N) (85).

D) Cadmium (II) complex (AICd):

The FTIR spectrum of (AICd) complex Figure (3-7), Table (3-4) showed similar behavior with no much difference compared to that of the ligand.

The FTIR spectrum shows the shifting of the azomethine band to lower frequency by (11 cm^{-1}) indicating the involvement nitrogen in coordination with metal ion Cd(II). The bands sat 1458, 1220 and 1035 cm^{-1} can be assigned as free nitrate ion(85).

The band at 501 cm^{-1} can be attributed to ν(Cd-N) (85), the weak band at 630 cm^{-1} indicated the presence of coordinated water molecules in the structure.

3.3.2 The FTIR spectra of LII and its metal complexes:

The comparison of FTIR spectra of the ligand (LII) and its metal complexes indicated that the ligand is principally coordinated to the metal ion in 2-ways (from azomethine-nitrogen and phenolic-oxygen), thus acting as a bidentate ligand.

Figure (3-2) shows azomethine band appeared at 1627 cm^{-1} and the band at 1269 cm^{-1} refers to the (C-O) stretching vibration(84,86).

The broad band at 3421 cm^{-1} assigned to the ν(O-H)(87) for the ligand, which was no longer found in the spectra of metal complexes indicating deprotonation and coordination of hydroxyl oxygen with the metal ion(88).

The band appear at 1558 cm^{-1} refers to ν(C=C) aromatic ring, and band at 3070 cm^{-1} refers to the ν(C-H) aliphatic, the band 3320 cm^{-1} refers to ν(N-H)(46).

A) Nickel (II) complexes (AIINi):

The FTIR spectrum of (AIINi) complex Figure (3-8), show the shifting of azomethine band to a lower frequency and appeared at 1612 cm^{-1} this indicate the participation of azomethine-nitrogen with Ni(II) atom.

Another difference appeared which was the red shifting of the phenolic (C-O) band by (37 cm^{-1}) in the spectrum of (AIINi) complex referring to chelation of the phenolic oxygen to the Ni(II) atom(84,86).

A broad band which appeared at 3407 cm^{-1} and another medium band at 754 cm^{-1} indicate the presence of both coordinating and lattice water molecules in the structure of (AIINi) complex.

The weak band at 529 and 440 cm^{-1} refer to ν(Ni-N) and ν(Ni-O) respectively(85).

B) Cobalt (II) complex (AIICo):

The FTIR spectrum of (AIICo) complex Figure (3-9), shows the shifting of azomethine band to a lower frequency by (11 cm^{-1}) and the shifting of ν(C-O) band to higher frequency by (39 cm^{-1}), this indicate the participation of both oxgen and nitrogen in the coordination of the (AIICo) complex.

A broad band appeared at 3405 cm^{-1} and another medium sharp band at 684 cm^{-1} indicates the presence of both coordinating and lattice water molecules in the structure of (AIICo) complex.

The presence of new weak band observedat 570 cm^{-1} and 472 cm^{-1} assigned to ν(Co-N) and ν(Co-O) respectively(85).

C) Copper (II) complex (AIICu):

On comparison of the copper (II) complex (AIICu) spectrum Figure (3-10), Table (3-4) with that of the free ligand, the following changes were observed. First, the ν(C=N) band was shifted to a lower frequency by (15 cm^{-1}), and the second was the shifting of ν(C-O) band to higher frequency by (28 cm^{-1}).

From the above information would indicate that the coordination of LII with copper (II) ion took place through nitrogen and oxygen atoms.

The presence of new weak band observed at 595 cm^{-1} and 474 cm^{-1} assigned to ν(Cu-N) and ν(Cu-O) respectively(85).

A broad band appeared at 3402 cm^{-1} indicates the presence of uncoordinated water molecule in the structure of the complex.

D) Cadmium (II) complex (AIICd):

The FTIR spectrum of (AIICd) complex Figure (3-11), Table (3-4) shows the shifting of ν(C=N) to a lower frequency by (11 cm^{-1}) and appear at 1616 cm^{-1}.

Also the band at 1272 cm^{-1} corresponding to ν(C-O) shift to higher frequency by (39 cm^{-1}). These observation indicated the participation of both oxygen and nitrogen in the complex.

A broad band appeared at 3438 cm^{-1} and another medium sharp band at 684 cm^{-1} indicates the presence of both coordinating and lattice water molecules in the structure of (AIICd) complex.

The bands at 578 and 470 cm^{-1} can be attributed to ν(Cd-N) and ν(Cd-O) respectively.

The band at 1471, 1272 and 1151 cm^{-1} referred to mono dentate nitrate group.

3.3.3 The FTIR spectra of LIII and its metal complexes:

The FTIR spectrum of LIII Figure (3-3) shows the same behavior of the LI, which contains the same group (azomethine group) which used to characterize the spectra of the complexes.

The comparison of the FTIR spectra of the ligand LIII and its metal complexes indicated that the ligand is principally coordinated to the metal ion in 2-ways (from azomethine-nitrogen), thus acting as a bidentate ligand.

The isomethine band appeared at 1620 cm^{-1} and the band at 1571 cm^{-1} refers to the ν(C=C) aromatic ring.

The band appeared at 3070 cm^{-1} refers to the ν(C-H) aromatic ring, the band 2941 and 2837 cm^{-1} refers to the ν(C-H) aliphatic, the band at 3300 cm^{-1} refers to the ν(N-H) stretching vibration.

A) Nickel (II) complex (AIIINi):

The FTIR spectrum of (AIIINi) complex Figure (3-12) show the shifting of azomethine band to a lower frequency and appeared at 1606 cm^{-1} indicates the participation of azomethine-nitrogen with Ni(II) atom.

A broad band appeared at 3448 cm^{-1} indicates the presence of uncoordinated water molecule in the structure of the complex.

The presence of new weak band at 560 cm^{-1} assigned to ν(Ni-N) (85), the bands at 1456 cm^{-1}, 1207 and 1078 cm^{-1} can be assigned as monodentate nitrate group(85).

B) Cobalt (II) complex (AIIICo):

The spectrum of (AIIICo) complex, Figure (3-13) show the similar behavior with no much difference compared to that of the ligand.

The FTIR spectrum show the shifting of the azomethine band by (10 cm^{-1}) this means the involvement of azomethine-nitrogen in coordination with metal ion Co(II)(84,86).

The presence of new weak band at 580 cm^{-1} assigned to ν(Co-N) (85), the broad band appear at 3446 cm^{-1} can be assigned to the presence of free water molecule in the structure.

C) Copper (II) complex (AIIICu):

The FTIR spectrum of (AIIICu) complex Figure (3-14) shows the shifting of azomethine band to a lower frequency and appeared at 1610 cm^{-1} which indicates the participation of azomethine-nitrogen with Cu(II) atom.

The appearance of a weak band at 682 cm^{-1} indicated the presence of coordinated water molecules in the structure(85,89). The band at 510 cm^{-1} can be attributed to ν(Cu-N)(85).

D) Cadmium (II) complex (AIIICd):

The FTIR spectrum of (AIIICd) complex, Figure (3-15), Table (3-4), shows the shifting of ν(C=N) to a lower frequency by (14 cm^{-1}) and appeared at 1606 cm^{-1}.

A broad band appeared at 3745 cm^{-1} indicating the presence of ethanol molecules in the structure, the appearance of a weak band at 756 cm^{-1} indicating the presence of coordinated water molecules in the structure.

The band found at 579 cm^{-1} can be attributed to ν(Cd-N)(85), the bands related to the uncoordinated(85) nitrate ion were found at 1458, 1217 and 1083 cm^{-1}.

Table (3-4): The most significant bands of (FTIR) spectra of LI, LII and LIII and their metal complexes.

Symbol	ν (C-H) aromatic	ν(C-H) aliphatic	ν(N-H)	ν(C=N)	ν(O-H)	ν(C-O)	ν(M-N)	ν(M-O)
LI	3057	2923 2858	3306	1614	-	-	-	-
AINi	3060	2920	3380	1600	-	-	576	-
AICo	3060	2900	3340	1602	-	-	528	-
AICu	3141	2931	3369	1602	-	-	507	-
AICd	3002	2920	3340	1603	-	-	501	-
LII	3070	-	3320	1627	3421	1233	-	-
AIINi	3039	-	3350	1612	3407	1270	529	440
AIICo	3043	-	3359	1616	3405	1272	570	472
AIICu	3080	-	3361	1612	3402	1261	595	474
AIICd	3040	-	3330	1616	3438	1272	578	470
LIII	3070	2941 2837	3300	1620	-	-	-	-
AIIINi	3065	2939 2840	3315	1606	-	-	560	-
AIIICo	3076	2941 2835	3305	1610	-	-	580	-
AIIICu	3132	2939	3320	1610	-	-	510	-
AIIICd	3066	2945 2837	3318	1606	-	-	579	-

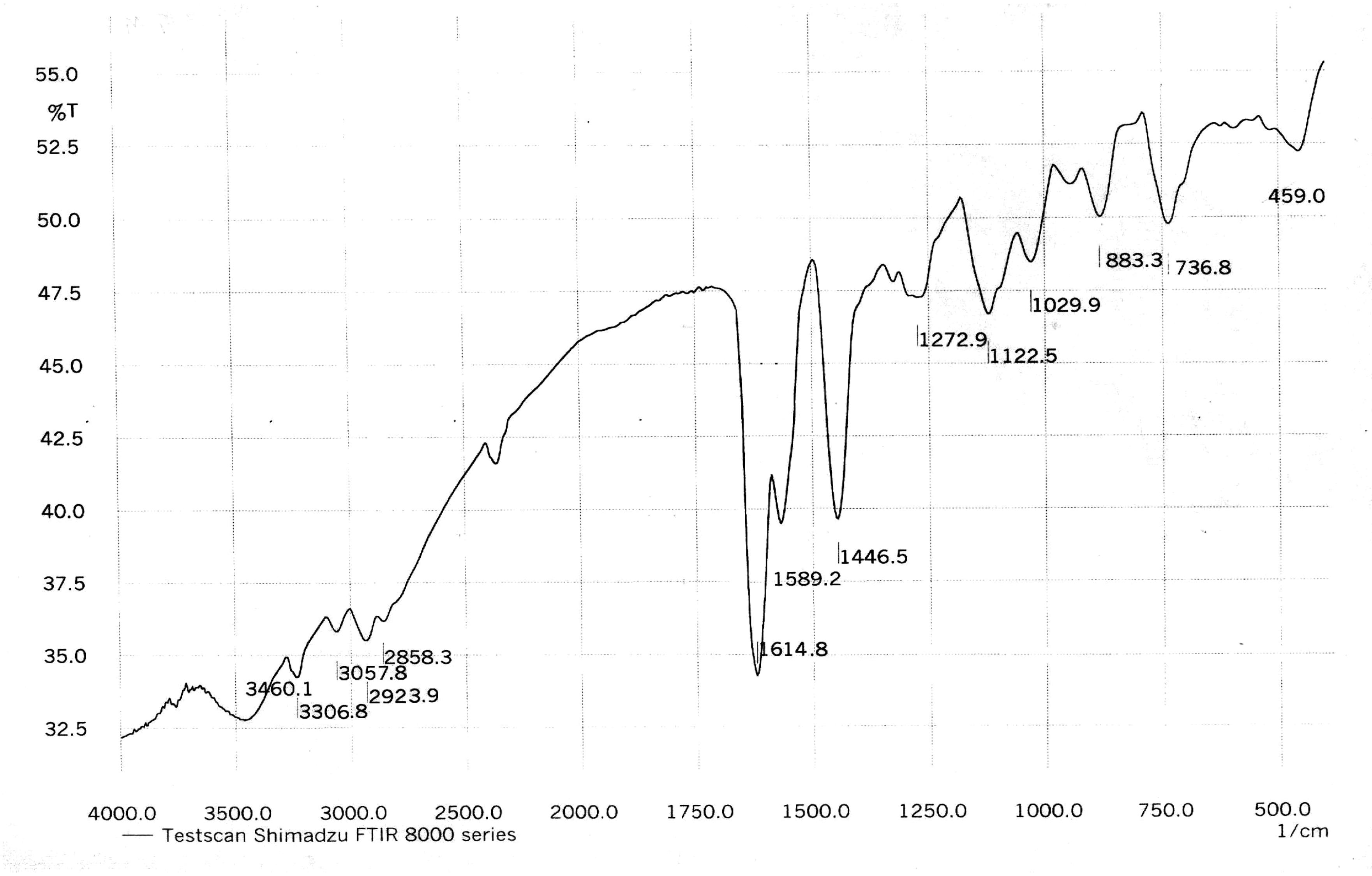


Figure (3-1): FTIR spectrum of LI

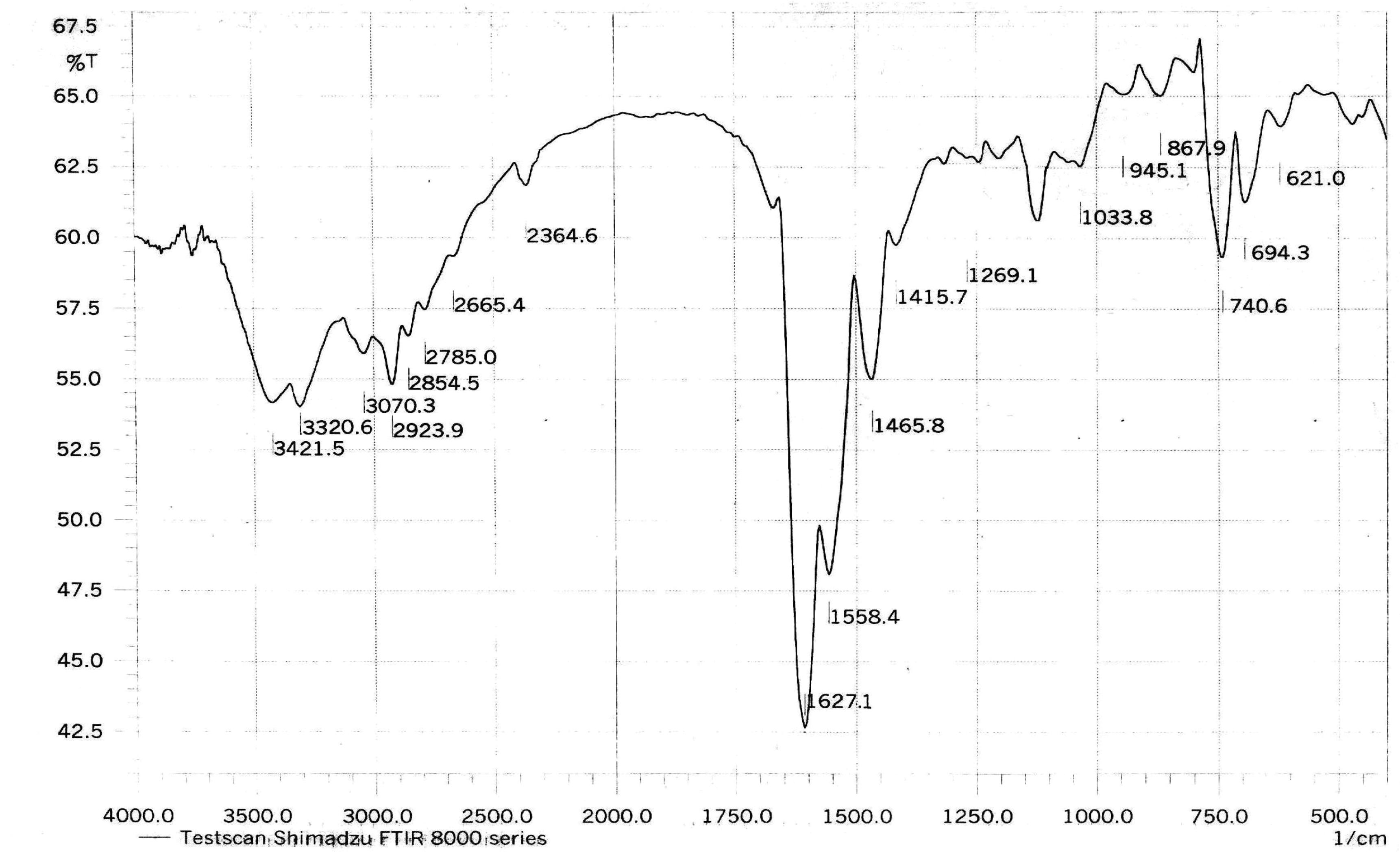


Figure (3-2): FTIR spectrum of LII

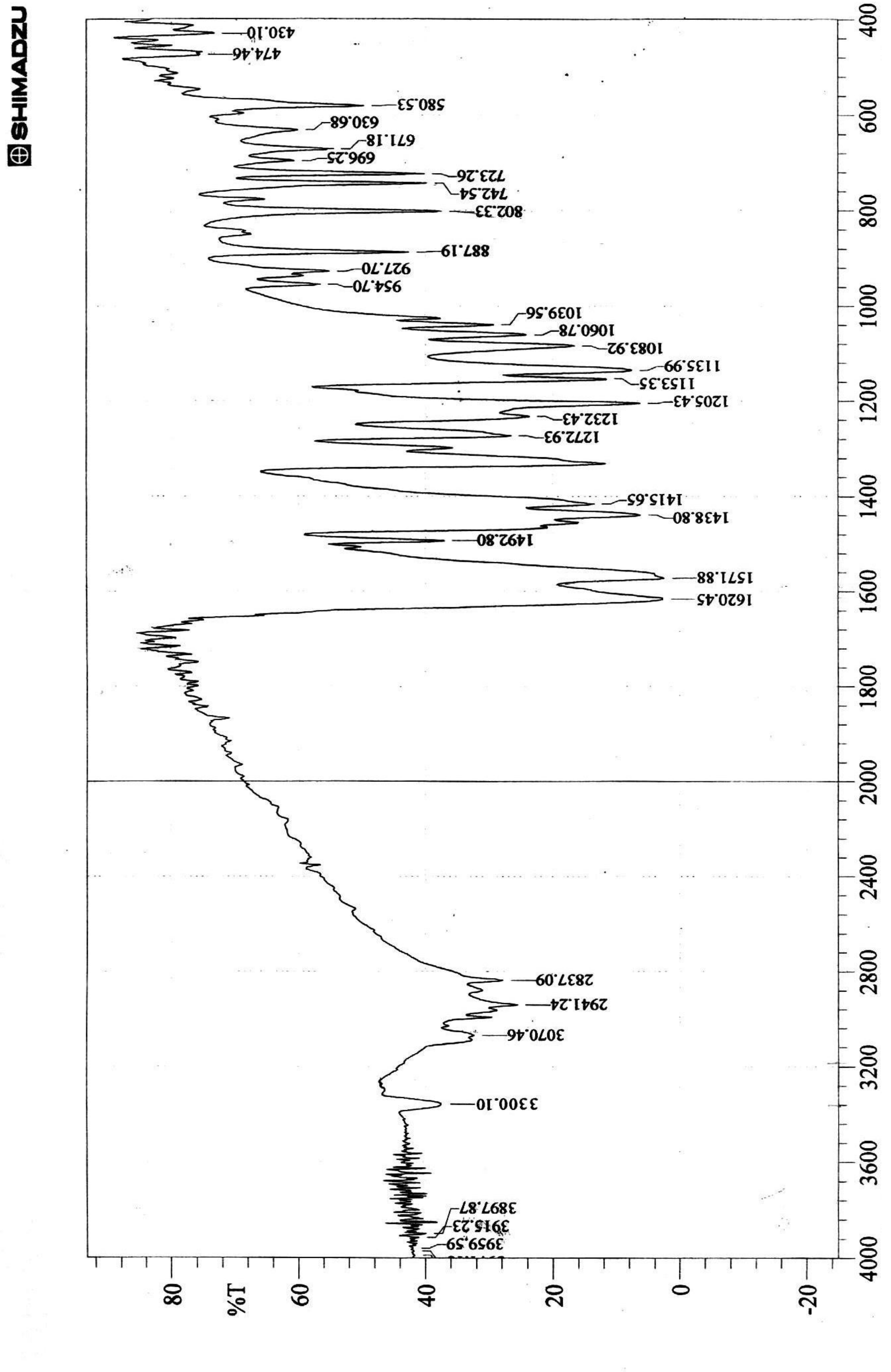


Figure (3-3): FTIR spectrum of LIII

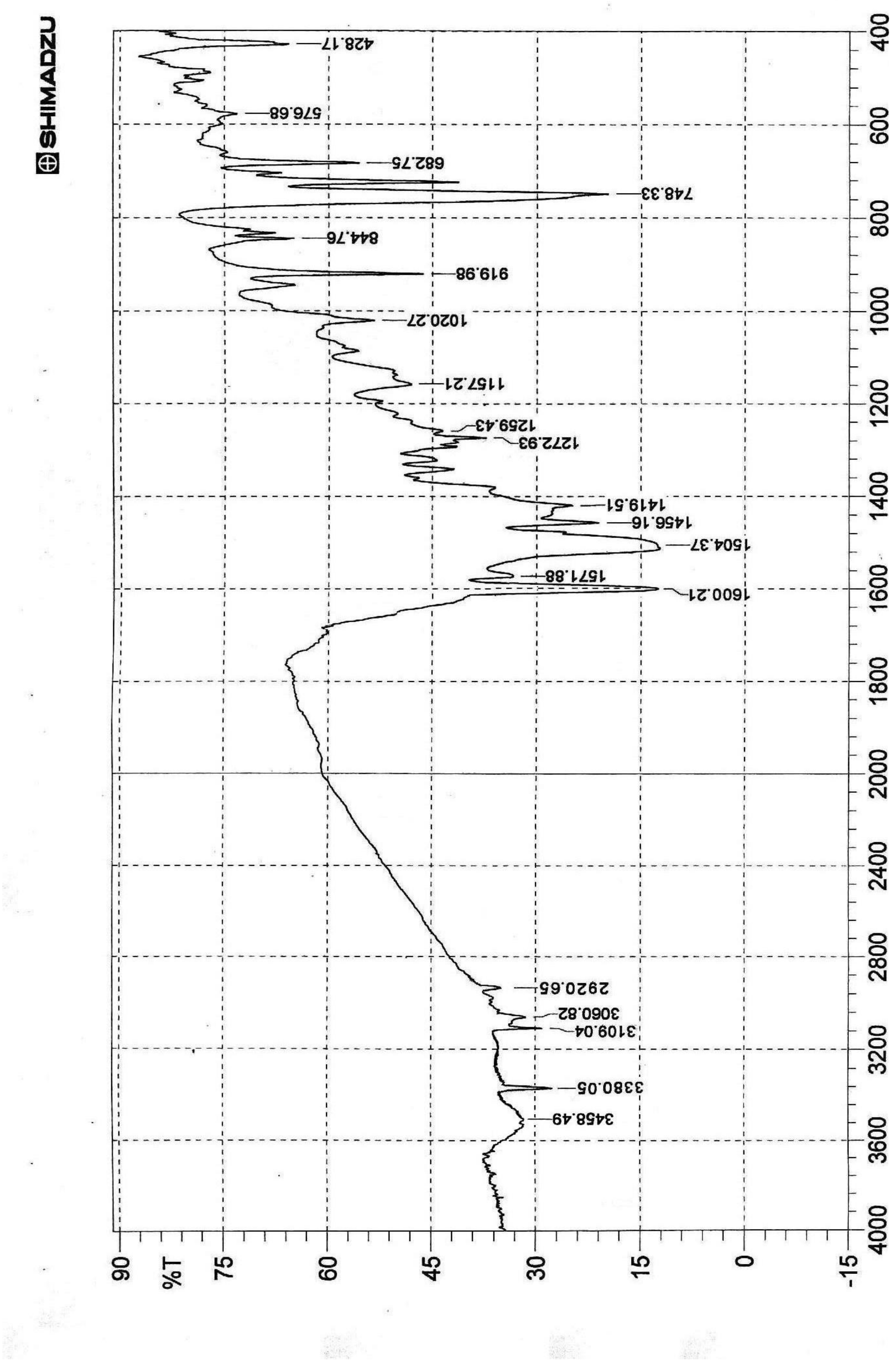


Figure (3-4): FTIR spectrum of AlNi

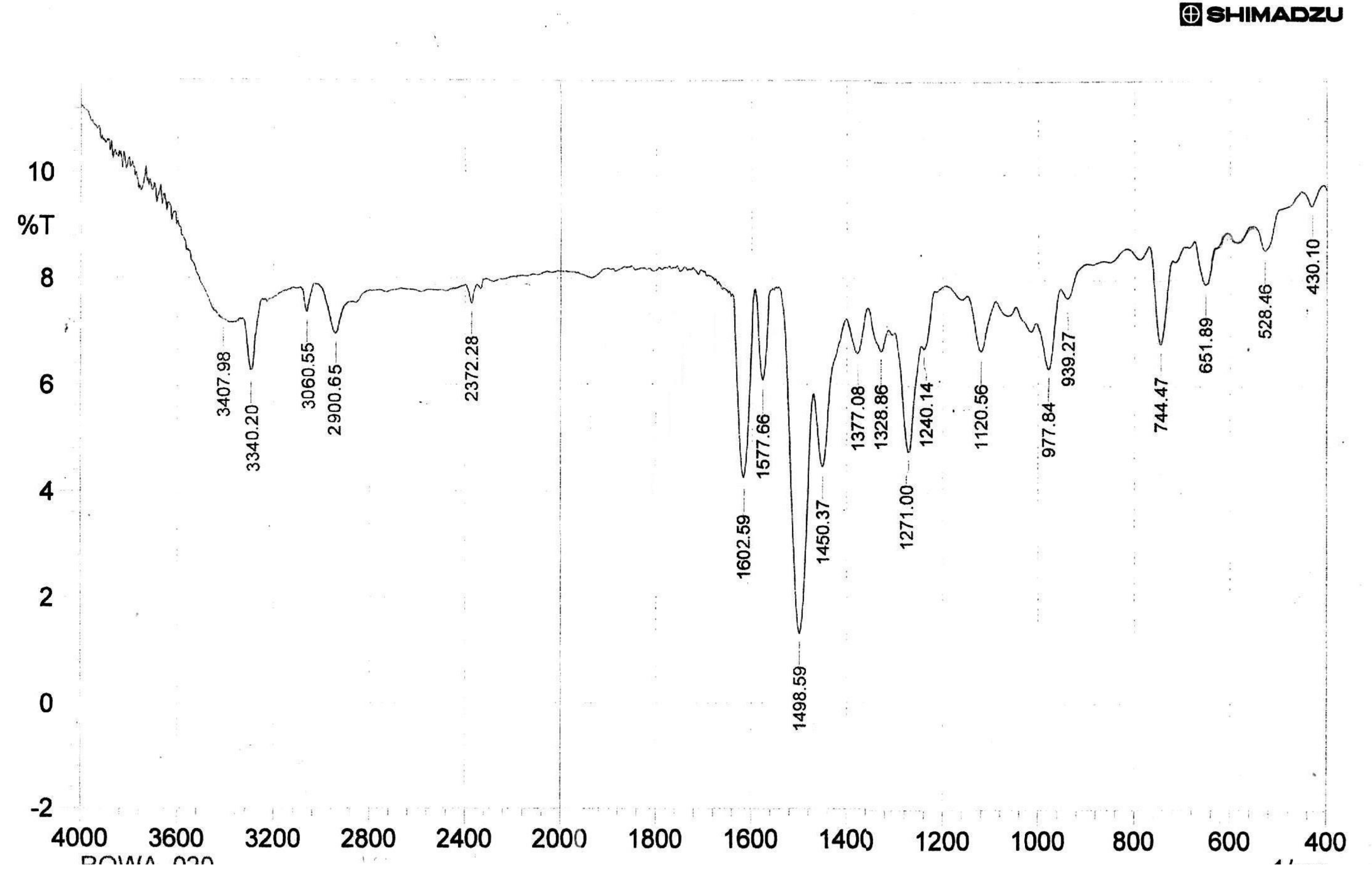


Figure (3-5): FTIR spectrum of AICo

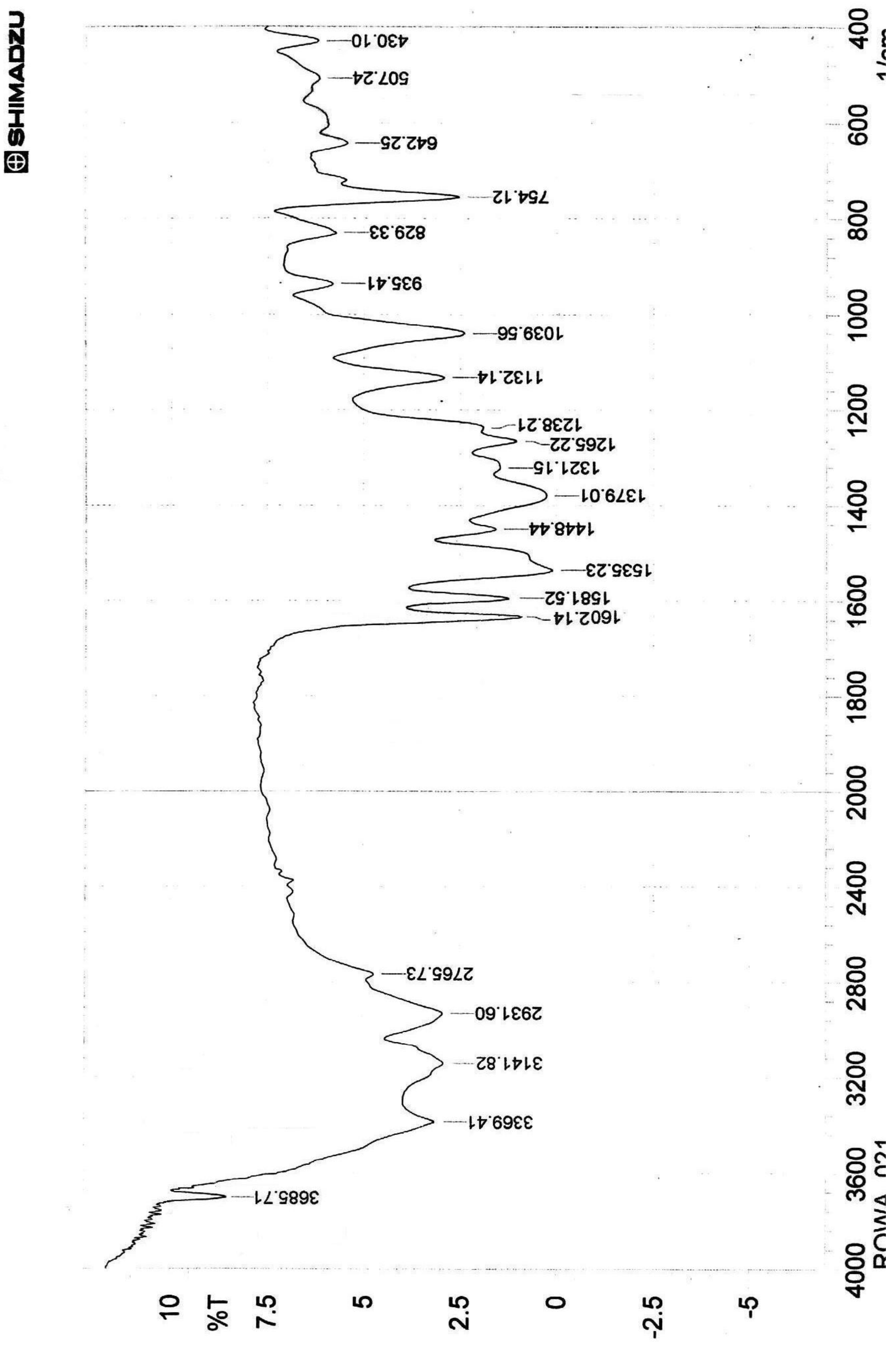


Figure (3-6): FTIR spectrum of AlCu

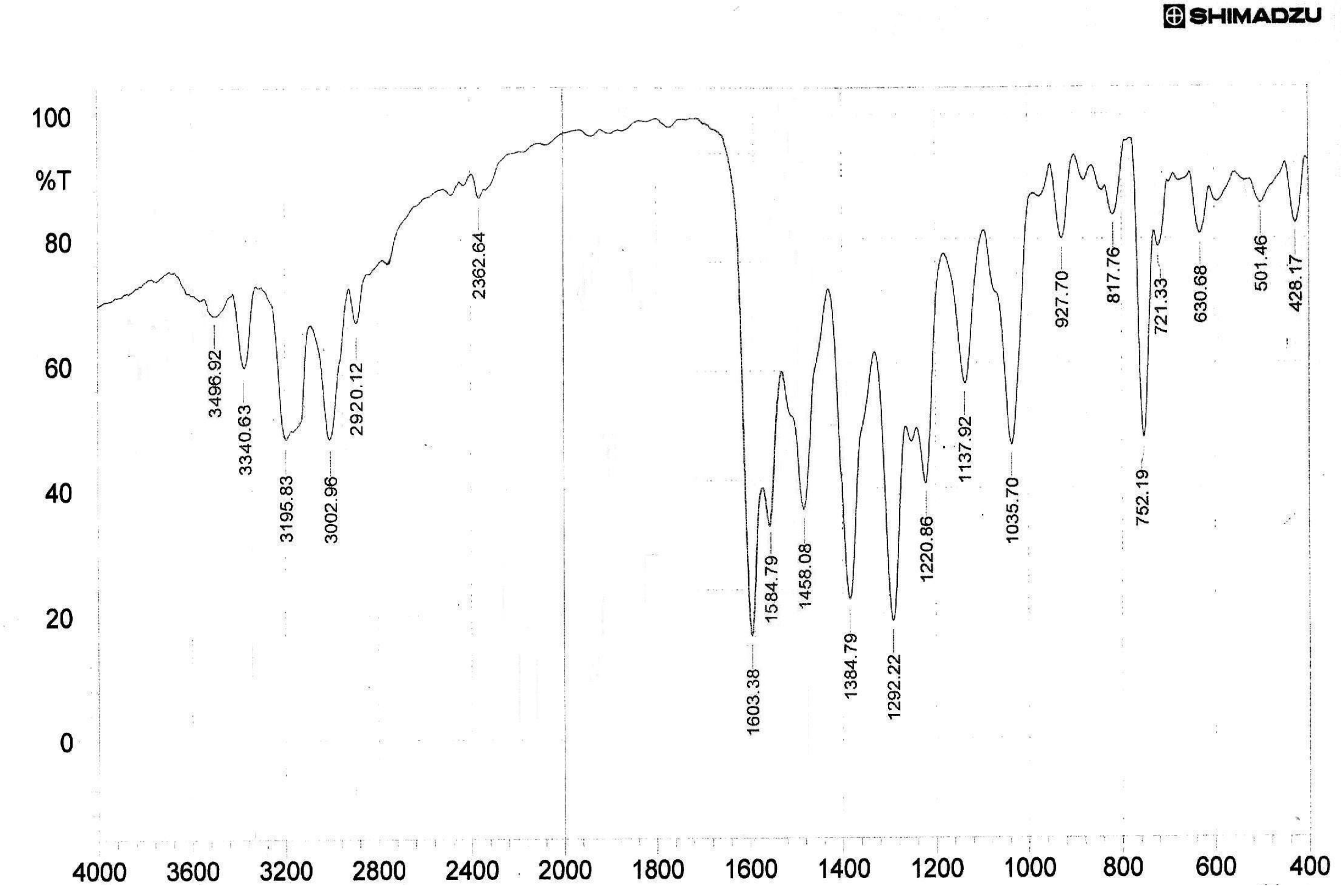


Figure (3-7): FTIR spectrum of AICd

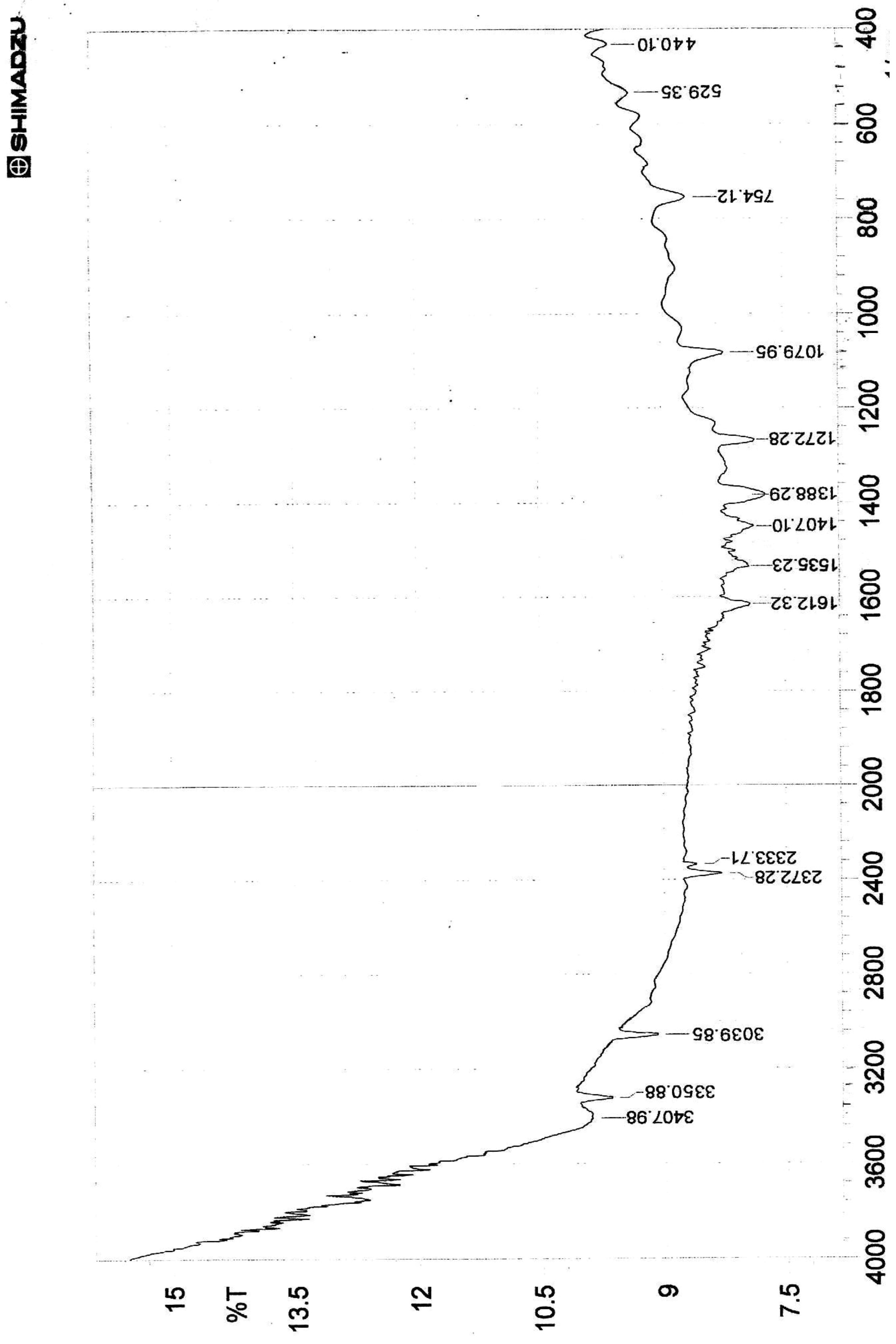


Figure (3-8): FTIR spectrum of AIINi

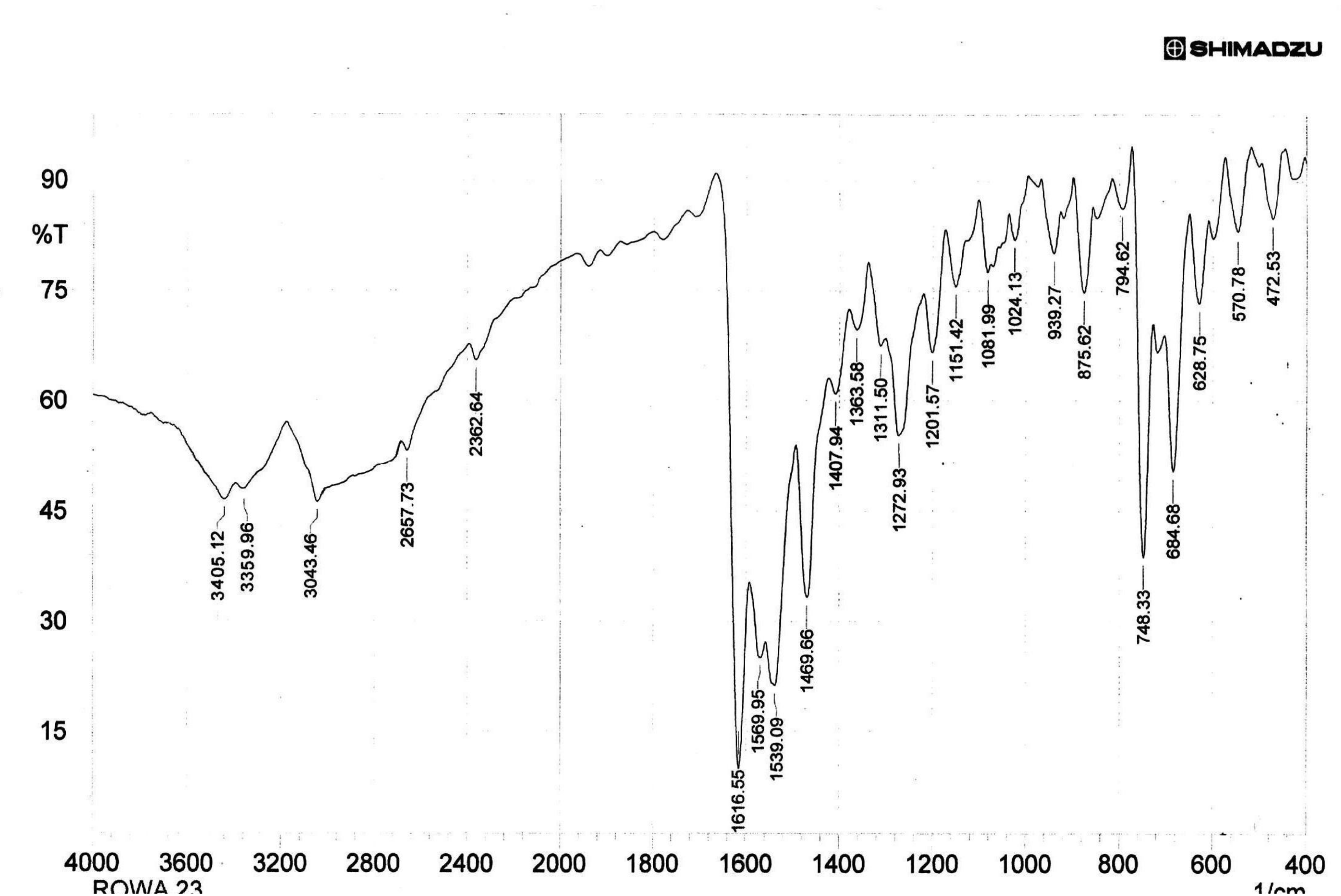


Figure (3-9): FTIR spectrum of AIICo

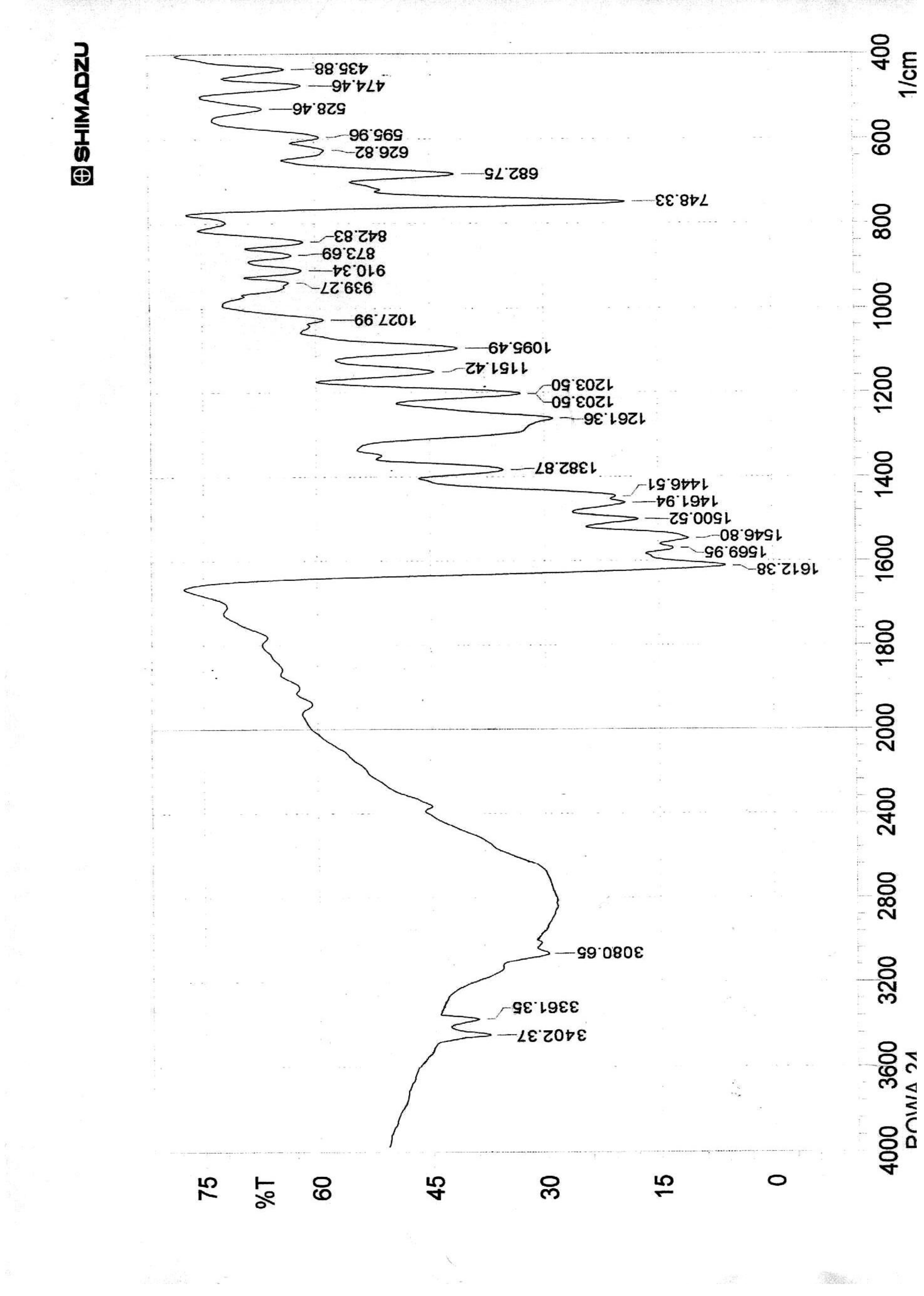


Figure (3-10): FTIR spectrum of AIIcu

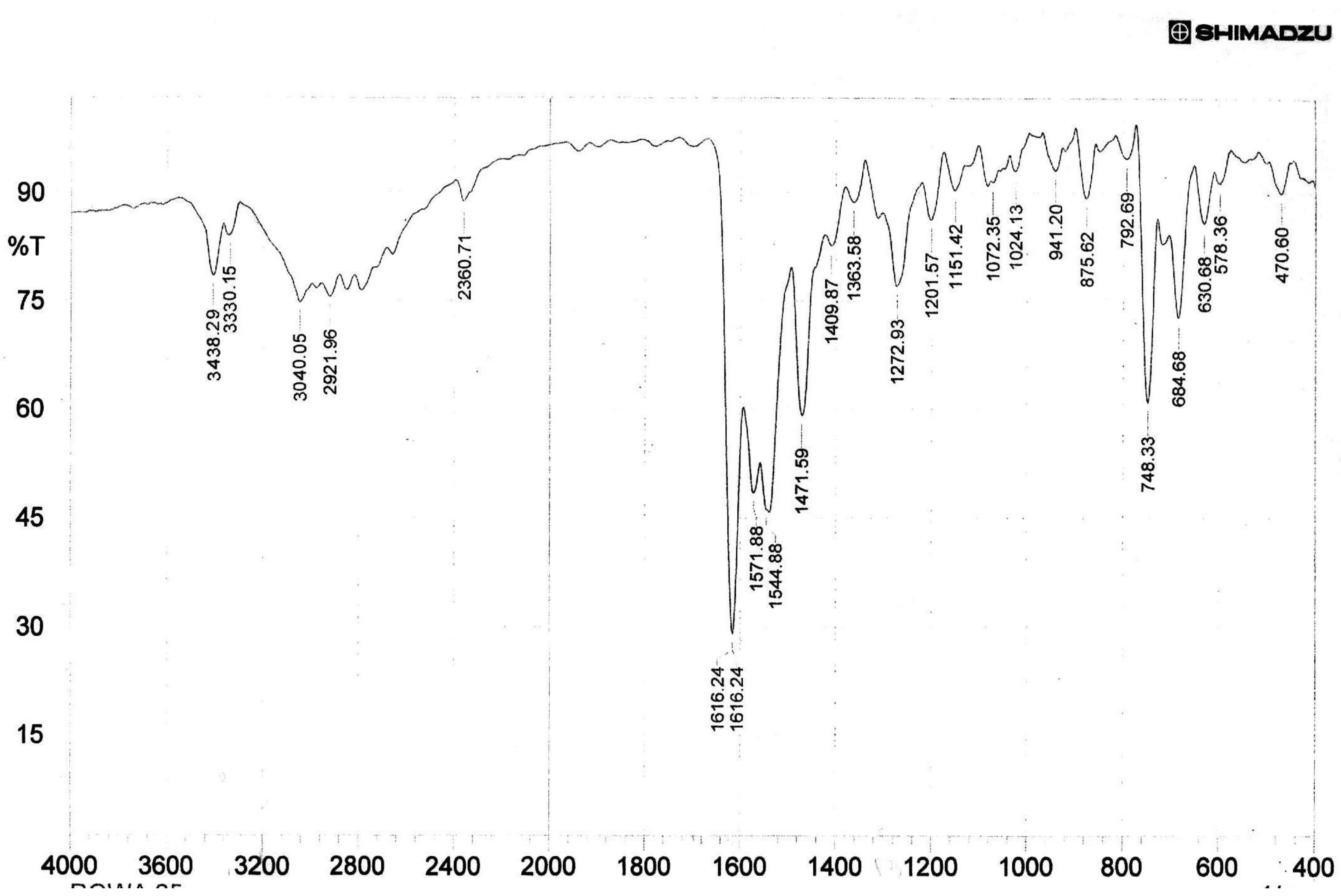


Figure (3-11): FTIR spectrum of AIICd

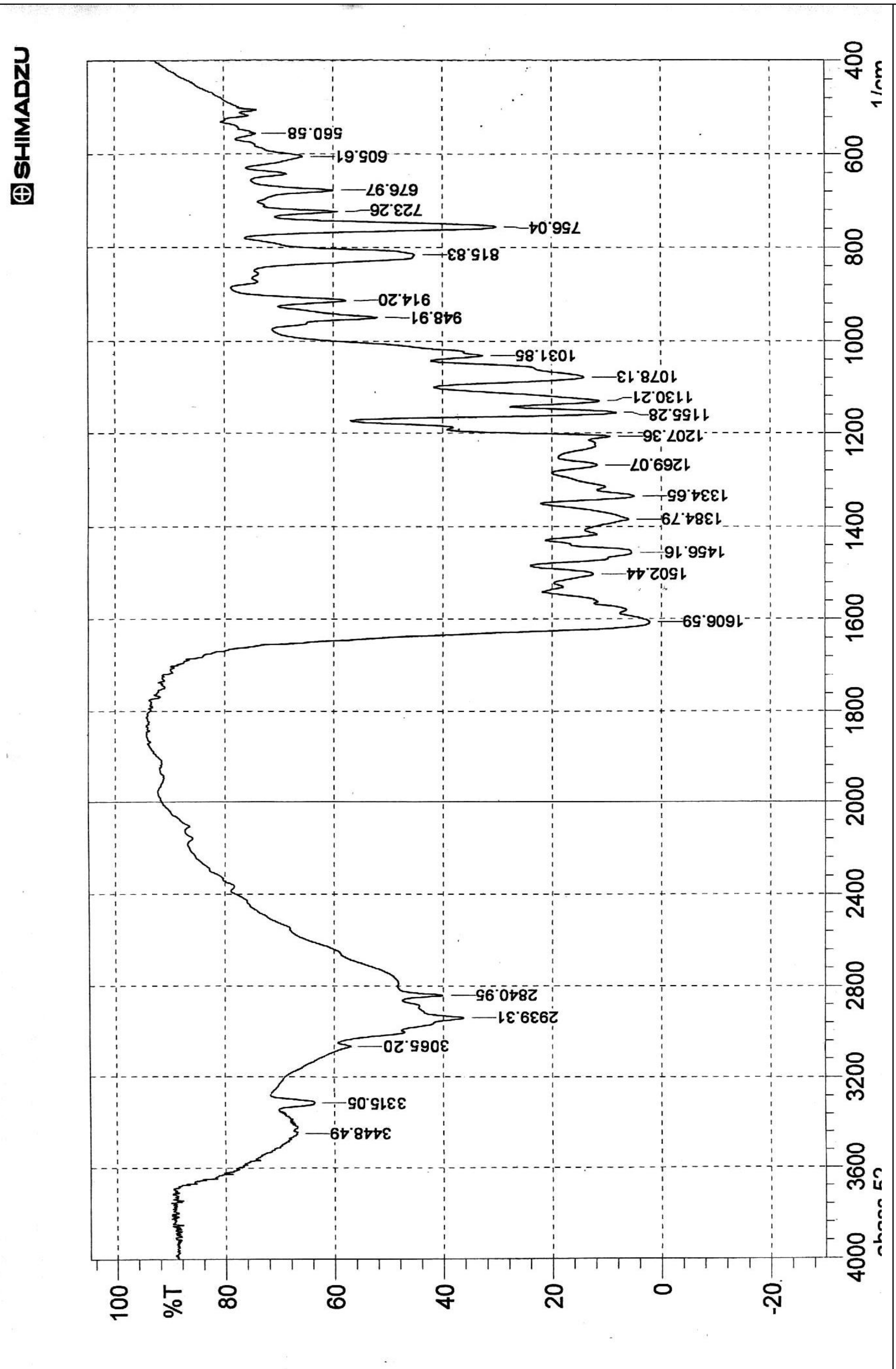


Figure (3-12): FTIR spectrum of AIIINi

)

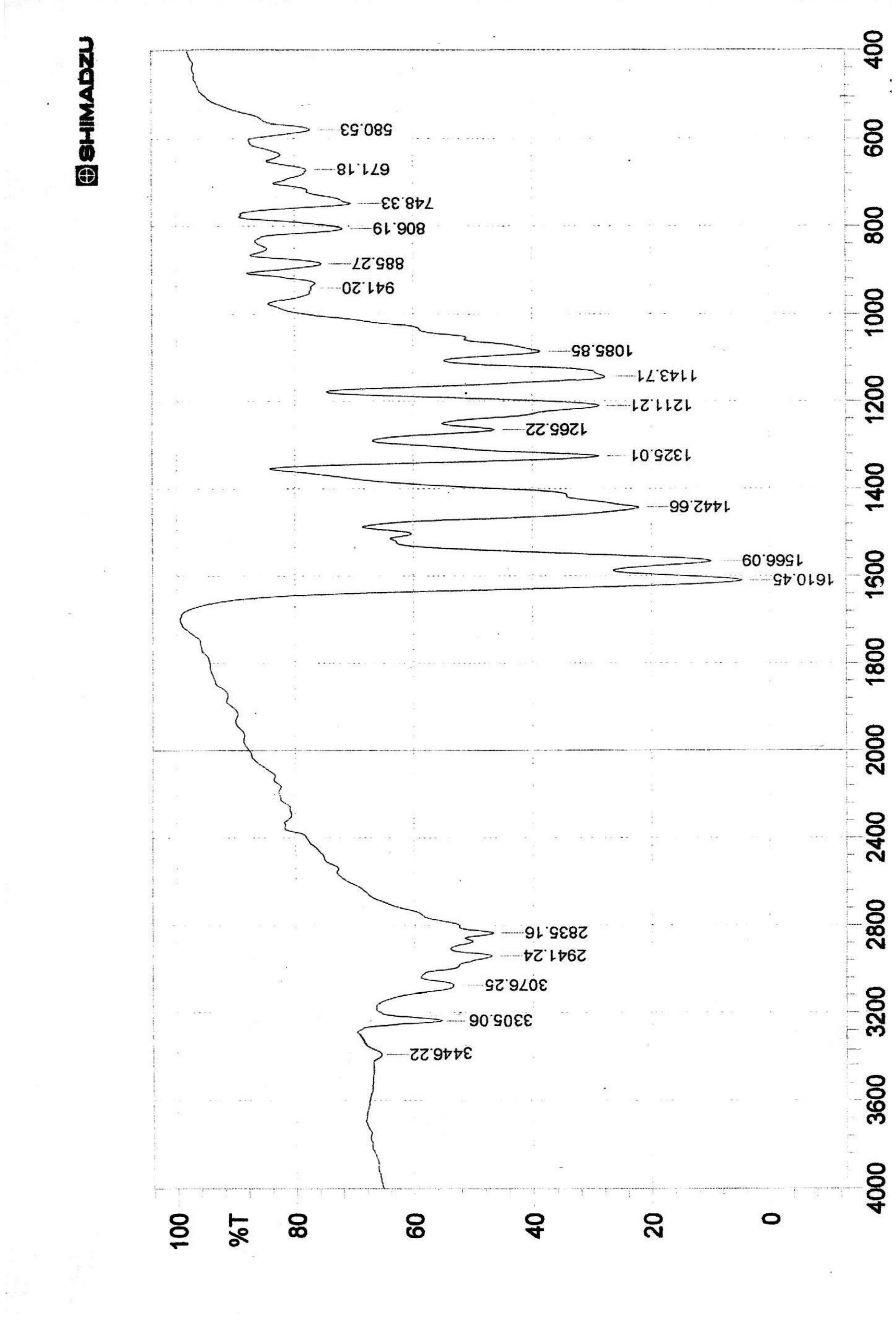


Figure (3-13): TIR spectrum of AIIICo

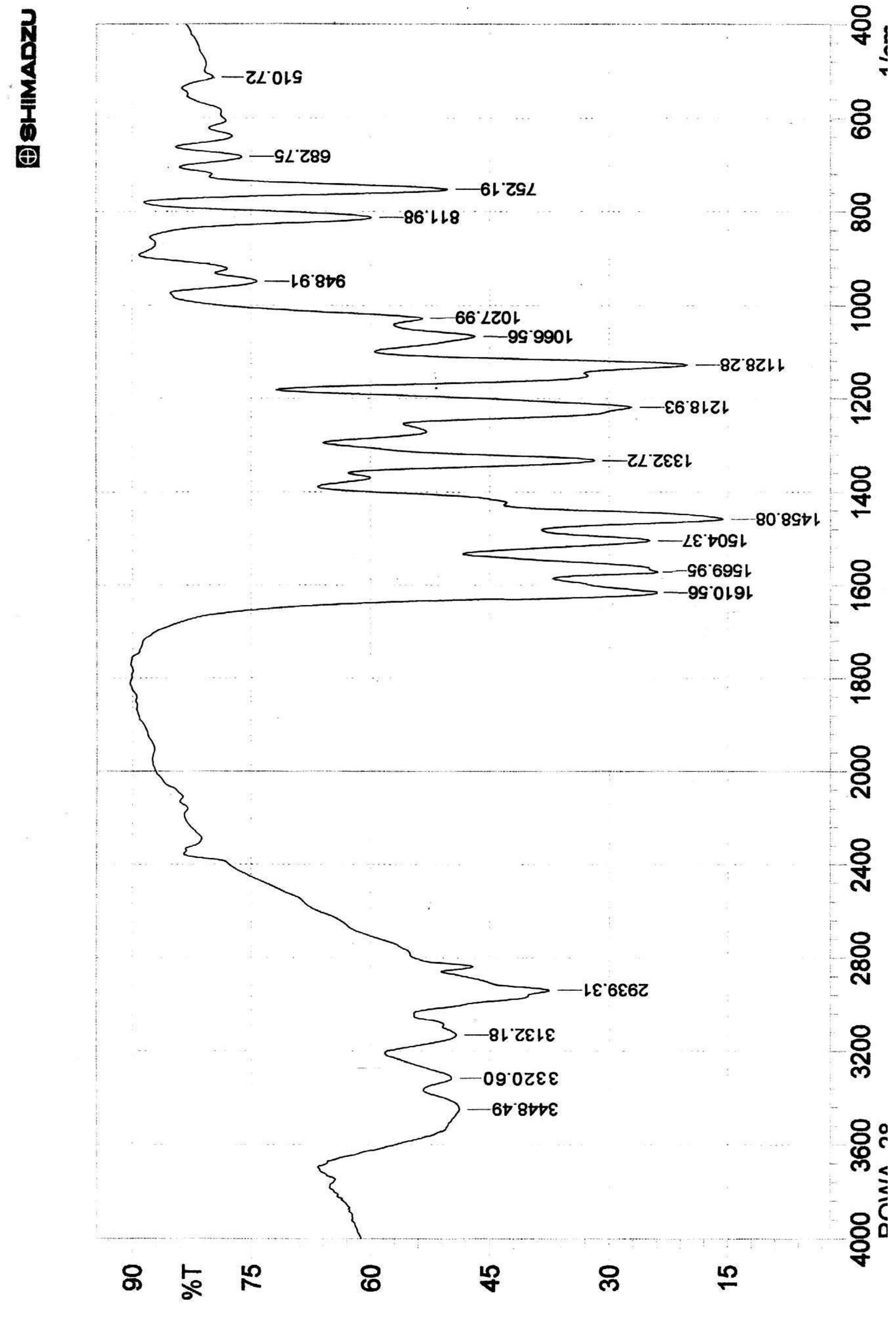


Figure (3-14): FTIR spectrum of AIIICu

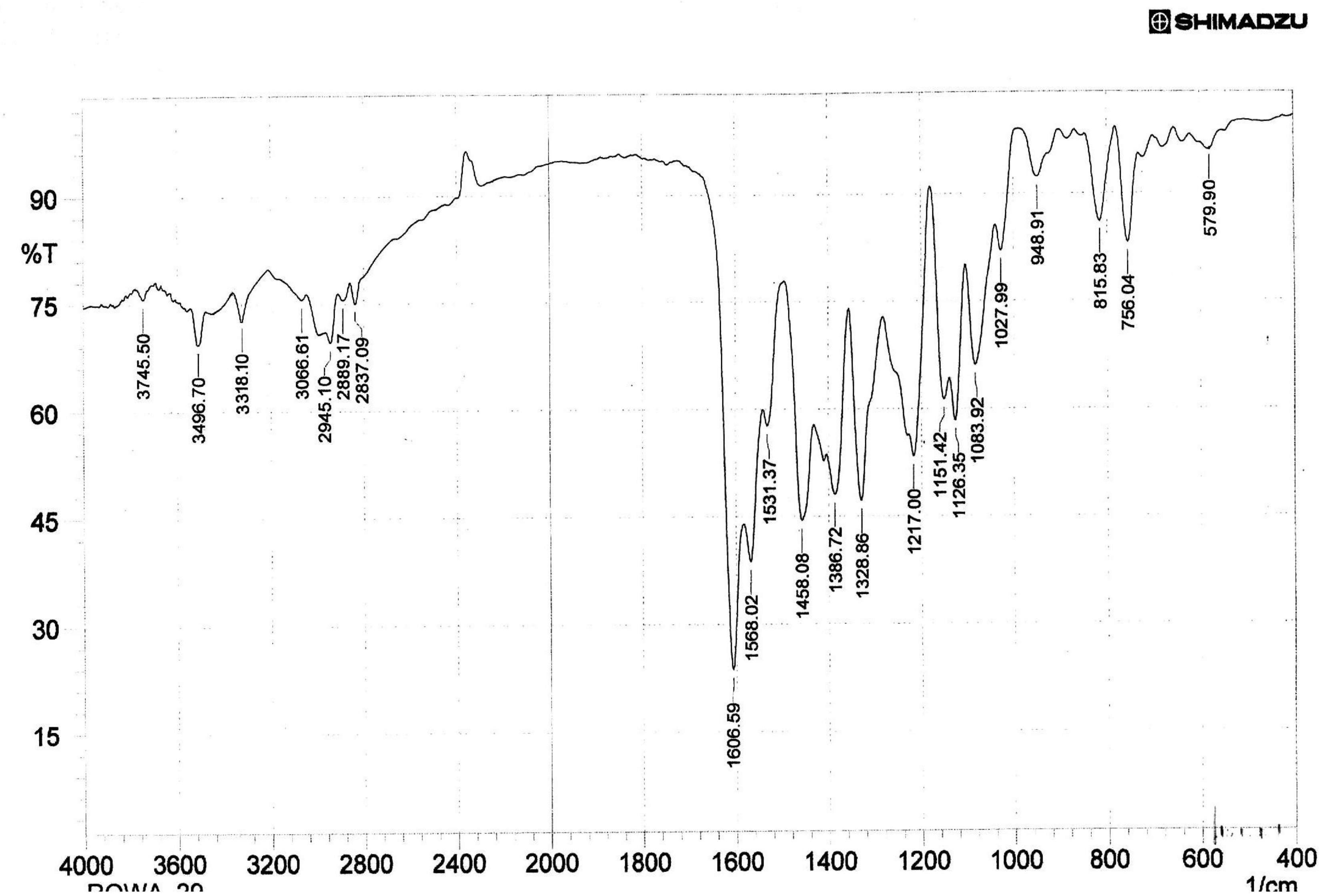


Figure (3-15): FTIR spectrum of AIIICd

3.4 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.

Measuring the magnetic susceptibility contributes to the determination of the structure of the complex, in furthermore, these measurements 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 effective magnetic spin of the complexes was measured using spin only magnetic moment according to the following equation:

$$\mu_{s.o} = 2\sqrt{S(S+1)} \quad \text{B.M.}$$

Where ***s*** = n/2 (n = no. of unpaired electrons).

In this work the results obtained from this equation were compared to the actual values obtained through magnetic measurements Table (3-6).

These values were corrected for diamagnetic effects using the following relationships:

$$\mu_{eff} = 2.828\sqrt{X_A.T}$$

$$X_A = X_M - D$$

$$X_M = X_g \times \text{M.wt}$$

Where:

T = absolute temperature 298K

X_A = Atomic susceptibility

X_M = molar susceptibility

X_g = Gram susceptibility

D = Correction factor.

The experimental value of magnetic moment is usually greater than the calculated value of magnetic moment; the magnetic moments for the prepared complexes are shown in the following table:

Table (3-5): The magnetic moments for complexes of LI, LII and LIII.

Complex	Magnetic moment (B.M)
AINi	**2.78**
AICo	**4.94**
AICu	**1.92**
AIINi	**2.79**
AIICo	**5.32**
AIICu	**1.11**
AIIINi	**2.82**
AIIICo	**5.06**
AIIICu	**1.80**

3.5 The electronic spectral study and conductivity measurements of the prepared compounds:

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 work, the spectra were recorded in the range (200-1100) nm, using dimethyl sulphoxide (DMSO) as a solvent.

Conductivity measurements of the prepared complexes in the appropriate solvent are used to decide whether a complex is electrolyte or neutral(91,92). Table (3-6) shows the positions of the electronic absorption bands and their transitions and also include the calculated values of Racah parameter (B'), 10 Dq and nephelauxetic factor (B), Table (3-7) showed the conductivity data for the prepared complexes at room temperature and the suggested structure for each complex, the structures were suggested for the prepared complexes according to the band positions of the infra-red spectra, electronic absorption bands, atomic absorption, magnetic properties and electronic conductivity measured for these complexes.

3.5.1 Complexes of LI:

A) Ni(II) complex (AINi):

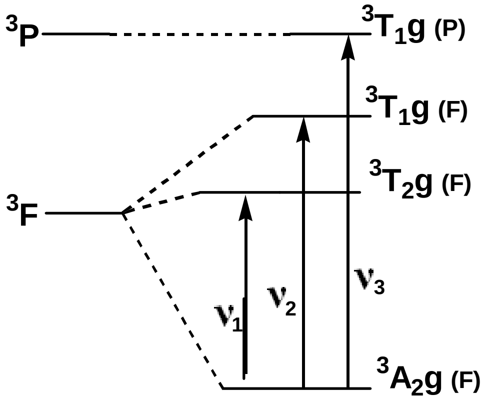
Ni(II) complex spectrum in DMSO, Figure (3-16) show three bands, the first two bands at 15,503 cm^{-1} and 24,69 cm^{-1} were assigned as belonging to transitions:

^3A_2g (F) → ^3T_1g (F) (ν_2)

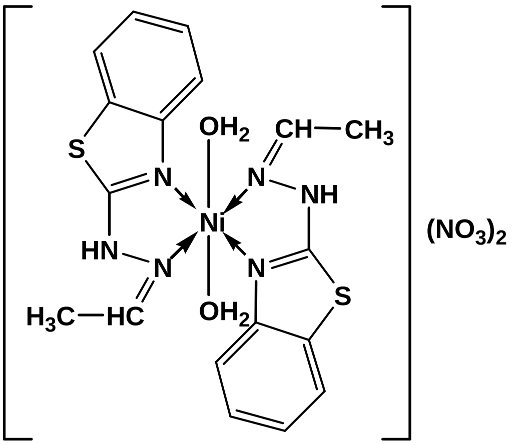
^3A_2g (F) → ^3T_1g (P) (ν_3)

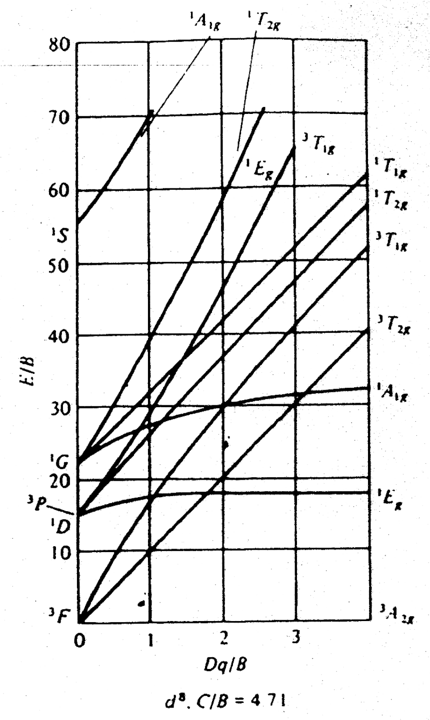
The value of ν_1 was calculated using Tanabe-Sugano digram for d^8 system, scheme (3-1), and found to be 8,443 cm^{-1} which refer to ^3A_2g (F) → ^3T_2g (F) transition , this value represent the crystal field splitting value (10 Dq) indicating weak field effect, the different ligand field parameters have been calculated using same diagram, the results are found in Table (3-6).

The term symbol for the ground state of Ni(II) ion ^3F can split in octahedral crystal field as follows



The magnetic susceptibilty and molar conductivity indicate the complex to be (Oh), and to be conducting from these results and that of FTIR study the suggested structure is as follows:



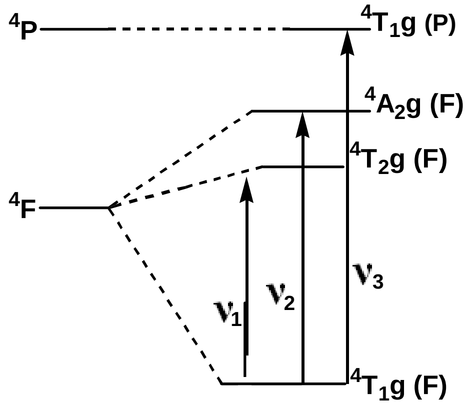


Scheme (3-1): Tanabe-Sugano diagram for d^8 system.

B) Co(II) complex (AICo):

Electronic spectrum of cobalt (II) complex usually show three transitions, but these transitions can not be assigned easily because of the greater overlapping of them(93,101,102). Octahedral complexes of Co(II) are reported to consist of two bands one in the 15,400-15,500 cm^{-1} and the other in the 20,000-20,800 cm^{-1} regions(103).

The term symbol for the ground state of Co(II) ion is ^4F which can split in octahedral crystal field as follow(102).

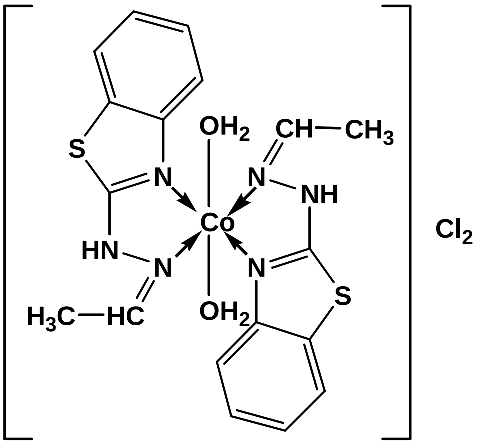


In the present work the two bands; complex show one at 15,479 cm^{-1} and the other at 20,202 cm^{-1} Figure (3-17) which is assigned to the transition ν_2 and ν_3 respectively.

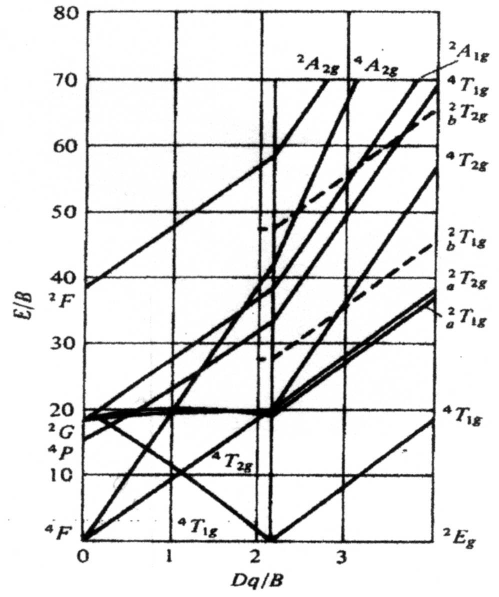
The value of ν_1 was calculated using Tanabe-Sugano diagram for d^7 system, scheme (3-2), and found to be 7,870 cm^{-1} which refers to ^4T_1g (F) → ^4T_2g (F) transition, 10 Dq value was also calculated from diagram and found to be 9,837 cm referring to a weak field state. The different ligand filed parameters have been calculated using the same diagram, the results found in Table (3-6).

Octahedral cobalt (II) complex however, maintain a large contribution due to ^4Tg ground term and exhibits µeff. in the range (4.8-5.6 B.M.) (104), the magnetic measurement of the (AICo) complex is 4.94 B.M. shows the complex is paramagnetic and have three unpaired electrons indicating a high-spin octahedral configuration.

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



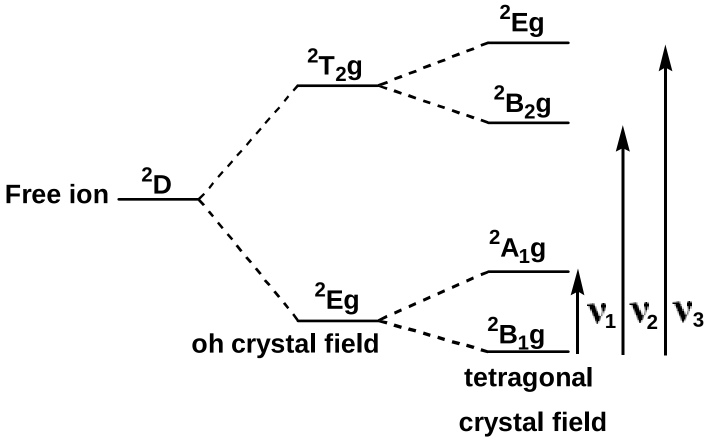
The formula was further confirmed to be ionic by conductivity measurements.



Scheme (3-2): Tanabe-Sugano diagram of d^7 system.

C) Cu(II) complex (AICu):

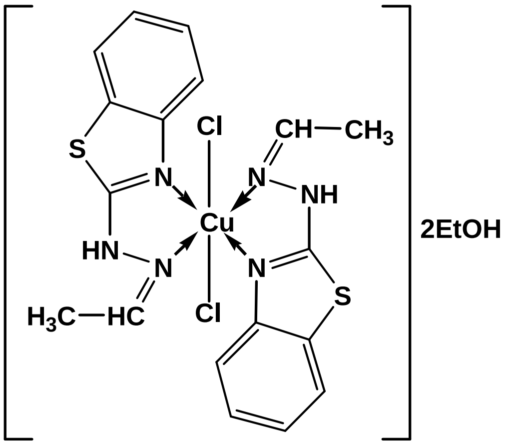
Cu(II) compound are blue or green because of single broad absorption band in the region (11,000-16,000 cm^{-1})$^{(94)}$. The d^9 ion is characterized by large distortion from octahedral symmetry and the bond is unsymmetrical, being the result of a number of transitions, which are by no means easy to assign unambiguously. The free ion ground ^2D term is expected to split in a crystal field in the same way as the ^5D term of the d^4 ion and a similar interpretation of the spectrum is likewise expected, and according to the following diagram(6,93,94).



Unfortunately, this is more difficult because of the greater over lapping of bands, which occurs in the case of Cu(II).

In the present work, the green (AICu) complex shows a broad band(94) at 15,576 cm^{-1} can be assigned to $^2Eg \rightarrow {}^2T_2g$ transitions, Figure (3-18).

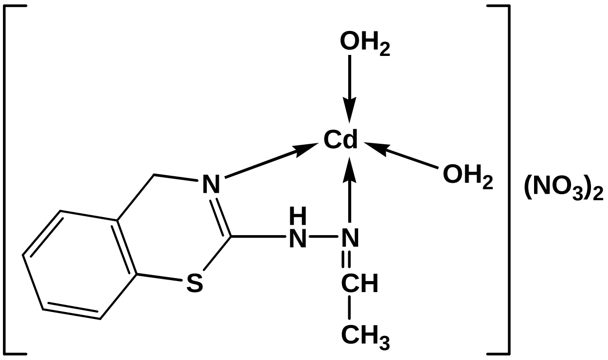
The magnetic susceptibility and molar conductivity indicate the complex to be octahedral, and to be non-conductive, Table (3-7). From these results and that of FTIR study the suggested structure is as follows:



D) Cd(II) complex (AICd):

Since the UV-Visible spectrum of d^{10} ion do not furnish a lot of information, so some shifting and change in the shape of the bands were compared with these of the ligand, therefore possible geometry around these ions can be suggested considering the metal analysis, FTIR spectra and taking in account the available structures found in the literature(6,93,94).

These observations led us to suppose tetrahedral geometry for (AICd) complex:



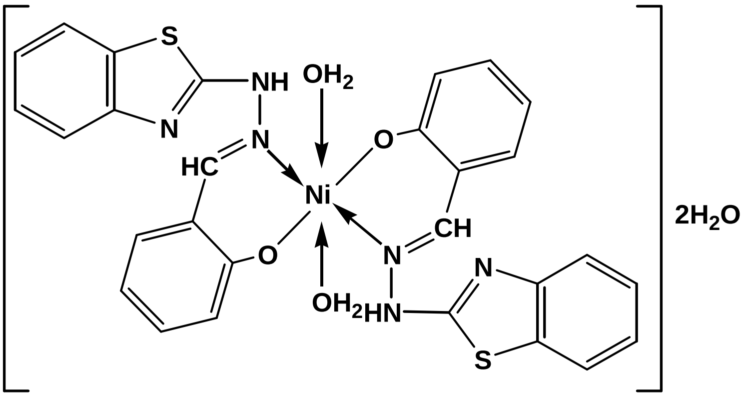
Conductivity measurements showed that the AICd complex is ionic; Table (3-7).

3.5.2 Complexes of LII:

A) Ni(II) complex (AIINi):

The spectral behavior of this complex, Figure (3-19) was identical with that of (AINi), which also shows two bands, one at 15,625 cm^{-1} and the other at 25,773 cm^{-1} which was assigned to the transitions ν_2 and ν_3 respectively, ν_1 was calculated using Tanabe-Sugano diagram for d^8 system and found to be 8,715 cm^{-1} belong to the transition ^3A_2g (F) → ^3T_1g (F).

The magnetic susceptibility and molar conductivity indicate the complex to be octahedral, and to be non-conducting, Table (3-6). From these results and that of FTIR study the suggested structure is as follows:

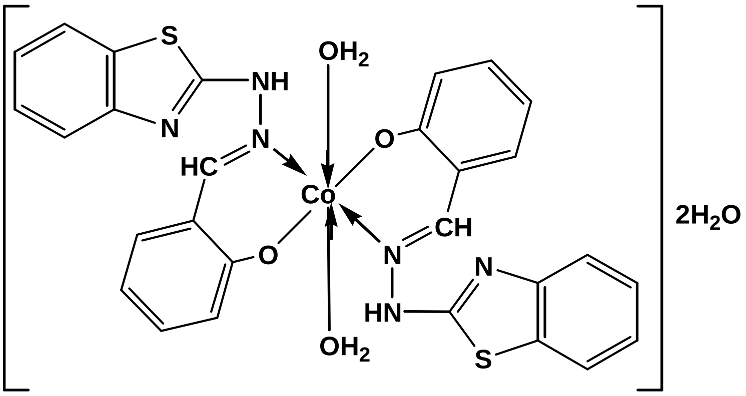


B) Co(II) complex (AIICo):

The spectral behavior of this complex, Figure (3-20) was identical with that of (AICo), which also shows two bands, one at 15,384 cm^{-1} and the other at 20,492 cm^{-1} which was assigned to the transition ν_2 and ν_3 respectively, ν_1 was calculated using Tanabe-Sugano diagram for d^7 system and found to be 7,185 cm which belong to the transition ^4T_1g (F) → ^4T_2g (F).

The magnetic susceptibility and molar conductivity show the complex to be octahedral and to be non-conducting, Table (3-7).

From these results and that of FTIR study the suggested structure is follows:



C) Cu(II) complex (AIICu):

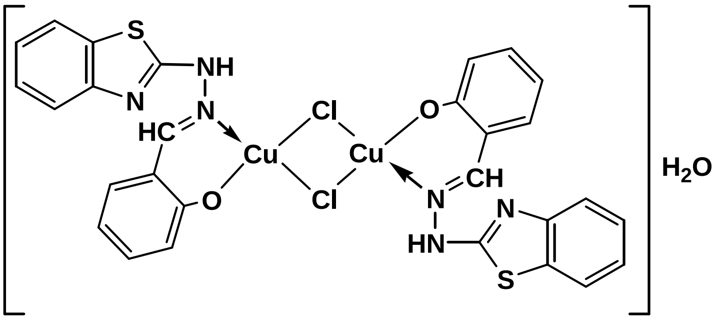
Electronic spectrum of the dark green complex (AIICu) is shown in Figure (3-21), Table (3-6). The dark green color is attributed to the single broad absorption band in the region (16000-2000 cm^{-1})(85), the d^9 ion is characterized by large distortion from octahedral geometry. Octahedral complex for 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.

The center of the broad band has been assigned at 16,129 cm^{-1}; this band refers to distorted octahedral geometry (Jahn-Teller distortion)(95,43).

The term symbol for the ground state of Cu(II) ion ^2D which can split in crystal field like (AICu).

The low value of magnetic moment (1.11 B.M.) Table (3-6) can be attributed to the high spin-spin coupling(6,96-99) of two adjacent copper atoms (dimeric structures).

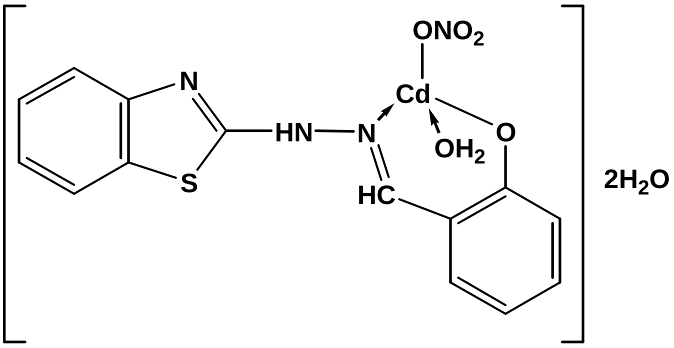
Therefore the expected geometry of the complex is as follows:



Conductivity measurements show that the complex is non-ionic.

D) Cd(II) complex (AIICd):

Conductivity measurements showed that the complex was non-conductive, and from the FTIR study the structure of this complex can be regarded as of tetrahedral geometry:

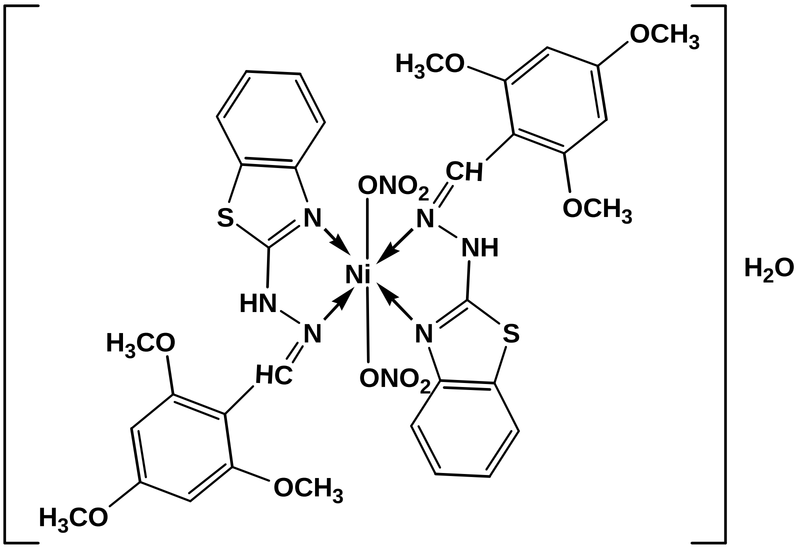


3.5.3 Complexes of LIII:

A) Ni(II) complex (AIIINi):

Electronic spectrum of (AIIINi) Figure (3-22), show two bands on at 15,797 cm^{-1} and the other at 25,125 cm^{-1} which refer to the transitions ^3A_2g (F) → ^3T_1g (F) and ^3A_2g (F) → ^3T_1g (P) respectively.The value of ν_1 was calculated using Tanabe-Sugano diagram for d^8 system, and found to be 8,351 cm^{-1} refering to ^3A_2g (F) → ^3T_2g (F) transition, which is also equal to 10 Dq value indicating a high spin complex.

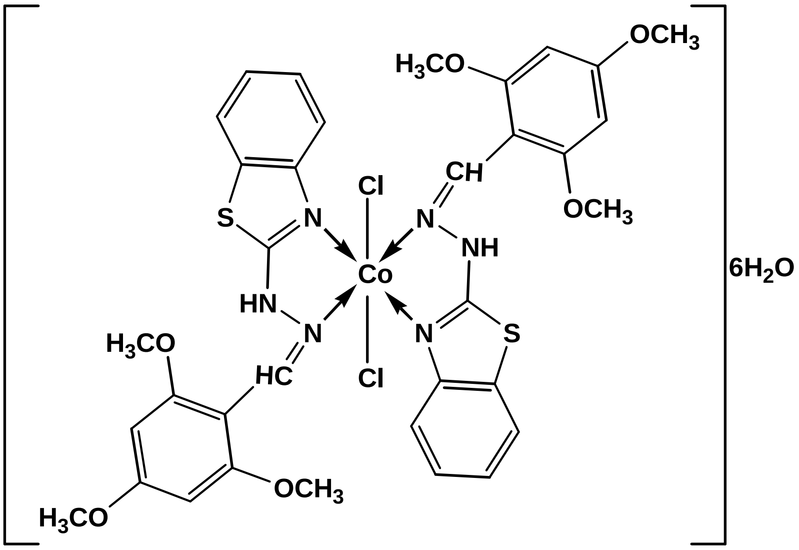
The magnetic susceptibility and molar conductivity show the complex to be octahedral and to be non-conducting, from these results and that of FTIR study the suggested structure is as follows:



B) Co(II) complex (AIIICo):

Electronic spectrum of (AIICo), Figure (3-23), show two bands on at 15,408 cm^{-1} and the other 20,000 cm^{-1} which are assigned to the transitions $^{4}T_{1}g$ (F) → $^{4}A_{2}g$ (F) and $^{4}T_{1}g$ (P) → $^{4}A_{2}g$ (F) respectively. The value of ν_3 was calculated using Tanabe-Sugano diagram for d^7 system, and found to be 7,573 cm^{-1} which refers to $^{4}T_{1}g$ (F) → $^{4}T_{2}g$ (F) transition.

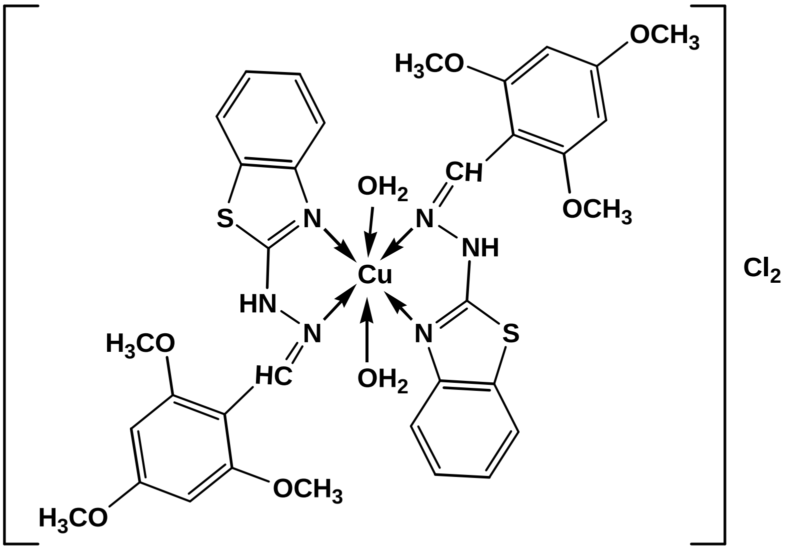
The magnetic susceptibility and molar conductivity indicate the complex to be octahedral and to be non-conductive, from these results and that of FTIR study the suggested structure is as follows:



C) Cu(II) complex (AIIICu):

The spectral behavior of this complex, Figure (3-24) was identical with that of (AICu)(100), which also show a broad band at 15,267 cm^{-1} that refers to ^{2}Eg→ $^{2}T_{2}g$ transitions.

The magnetic susceptibility and molar conductivity show the complex to be octahedral and to be conductive, from these results and that of FTIR study the suggested structure is as follows:



D) Cd(II) complex (AIIICd):

Conductivity measurements showed that the complex is ionic, and from FTIR study the structure of this complex can be regarded as tetrahedral geometry as follows

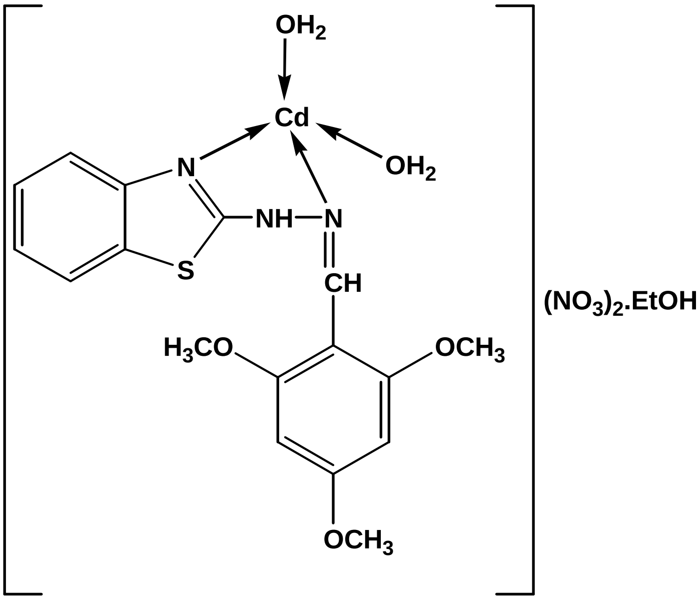


Table (3-6): Electronic spectral data for complexes of LI, LII and LIII in DMSO solvent (cm^{-1}).

Symbol	Absorption Bands cm^{-1}	Transitions	B	B'	*β*	10Dq	15B'
AINi	8,443 15,503 24,691	$^3A_2g(F)\rightarrow{}^3T_2g$ (F) $^3A_2g(F)\rightarrow{}^3T_1g$ (F) $^3A_2g(F)\rightarrow{}^3T_1g$ (P)	1030	991	0.96	8,443	14,865
AICo	7,870 15,479 20,202	$^4T_1g(F)\rightarrow{}^4T_2g$ (F) $^4T_1g(F)\rightarrow{}^4A_2g$ (F) $^4T_1g(F)\rightarrow{}^4T_1g$ (P)	971	804	0.82	9,837	12,071
AICu	15,576	$^2Eg\rightarrow{}^2T_2g$	-	-	-	-	-
AIINi	8,715 15,625 25,773	$^3A_2g(F)\rightarrow{}^3T_2g$ (F) $^3A_2g(F)\rightarrow{}^3T_1g$ (F) $^3A_2g(F)\rightarrow{}^3T_1g$ (P)	1030	1016	0.98	8,715	14,049
AIICo	7,185 15,384 20,492	$^4T_1g(F)\rightarrow{}^4T_2g$ (F) $^4T_1g(F)\rightarrow{}^4A_2g$ (F) $^4T_1g(F)\rightarrow{}^4T_1g$ (P)	971	955	0.98	7,670	14,325
AIICu	16,129	$^2B_1g\rightarrow{}^2A_1g$ $^2B_1g\rightarrow{}^2B_2g$	-	-	-	-	-
AIIINi	8,351 15,797 25,125	$^3A_2g(F)\rightarrow{}^3T_2g$ (F) $^3A_2g(F)\rightarrow{}^3T_1g$ (F) $^3A_2g(F)\rightarrow{}^3T_1g$ (P)	1030	10,57	0.98	8,351	15,141
AIIICo	7,573 15,408 20,000	$^4T_1g(F)\rightarrow{}^4T_2g$ (F) $^4T_1g(F)\rightarrow{}^4A_2g$ (F) $^4T_1g(F)\rightarrow{}^4T_1g$ (P)	971	845	0.87	7,962	12,687
AIIICu	15,267	$^2Eg\rightarrow{}^2T_2g$	-	-	-	-	-

Table (3-7): Magnetic moment, Conductivity and suggested structure for complexes of LI, LII and LIII.

Complex	Magnetic moment Meff (B.M.)	Conductivity Ms.cm^{-1}	Suggested structure
AINi	2.78	72	Octahedral
AICo	4.94	80	Octahedral
AICu	1.92	20	Octahedral
AICd	Diamagnetic	75	Tetrahedral
AIINi	2.79	10	Octahedral
AIICo	5.32	12	Octahedral
AIICu	1.11	20	Square planar
AIICd	Diamagnetic	15	Tetrahedral
AIIINi	2.82	19	Octahedral
AIIICo	5.06	20	Octahedral
AIIICu	1.80	77	Octahedral
AIIICd	Diamagnetic	75	Tetrahedral

Table (3-8): The Chemical Formula and the name of the LI and their complexes

Symbol	Chemical Formula	Name of the Compound
LI	$C_9H_9N_3S$	2-(Acetlidin)hydrazino benzothiazole
AINi	$[Ni\ (LI)_2\ (H_2O)_2\ ].(NO_3)_2$	Diaquo bis [2-(Acetlidin)hydrazino benzothiazole] Nickel(II).nitrate
AICo	$[Co\ (LI)_2\ (H_2O)_2].Cl_2$	Diaquo bis [2-(Acetlidin)hydrazino benzothiazole] Cobalt(II).Chloride
AICu	$[Cu(LI)_2\ CL_2].2C_2H_5OH$	Dichloro bis [2-(Acetlidin)hydrazino benzothiazole]Copper(II).Ethanol(2)
AICd	$[\ Cd\ LI\ (H_2O)_2].(NO_3)_2$	Diaquo[2-(Acetlidin)hydrazino benzothiazole]Cadmium(II).nitrate .

Table (3-9): The Chemical Formula and the name of the LII and their complexes.

Symbol	Chemical Formula	Name of the Compound
LII	**$C_{14}H_{12}N_3OS$**	**2-(O-hydroxy benzylidine) hydrazino benzothiozole.**
AIINi	**$[Ni\ (LII)_2\ (H_2O)_2].2H_2O$**	**Diaquo bis [2-(O-hydroxy benzylidine) hydrazino benzothiozole] Nickel(II). Water(2).**
AIICo	**$[Co\ (LII)_2\ (H_2O)_2].2H_2O$**	**Diaquo bis [2-(O-hydroxybenzylidine) hydrazino benzothiozole] Cobalt(II). Water(2).**
AIICu	**$[Cu_2\ (LII)_2\ Cl_2].H_2O$**	**Di-µ-Chloro-bis [2-(O-hydroxy benzylidine) hydrazino benzothiozole] Copper(II).Water(1).**
AIICd	**$[Cd\ LII\ (H_2O)\ (NO_3)].2H_2O$**	**Aquo nitrato [2-(O-hydroxy benzylidine) hydrazino benzothiozole] Cadmium(II).Water(2).**

Table (3-10): The Chemical Formula and the name of the LIII and their complexes.

Symbol	Chemical Formula	Name of the Compound
LIII	$C_{17}H_{17}N_3O_3S$	2-(2,4,6-trimethoxy benzylidine) hydrazine benzothiozole.
AIIINi	$[Ni\ (LIII)_2\ (NO_3)_2].H_2O$	Dinitrato bis [2-(2,4,6-trimethoxy benzylidine) hydrazino benzothiozole] Nickel(II). Water(1).
AIIICo	$[Co\ (LIII)_2\ Cl_2].6H_2O$	Dichloro bis [2-(2,4,6-trimethoxy benzylidine) hydrazino benzothiozole] Cobalt(II). Water(6).
AIIICu	$[Cu(LIII)_2(H_2O)_2].Cl_2$	Diaquo bis [2-(2,4,6-trimethoxy benzylidine) hydrazino benzothiozole] Copper(II).Chloride
AIIICd	$[Cd\ LIII\ (H_2O)_2].(NO_3)_2.\ C_2H_5OH$	Diaquo [2-(2,4,6-trimethoxy benzylidine) hydrazino benzothiozole] Cadmium(II). Ethanol(1). nitrate.

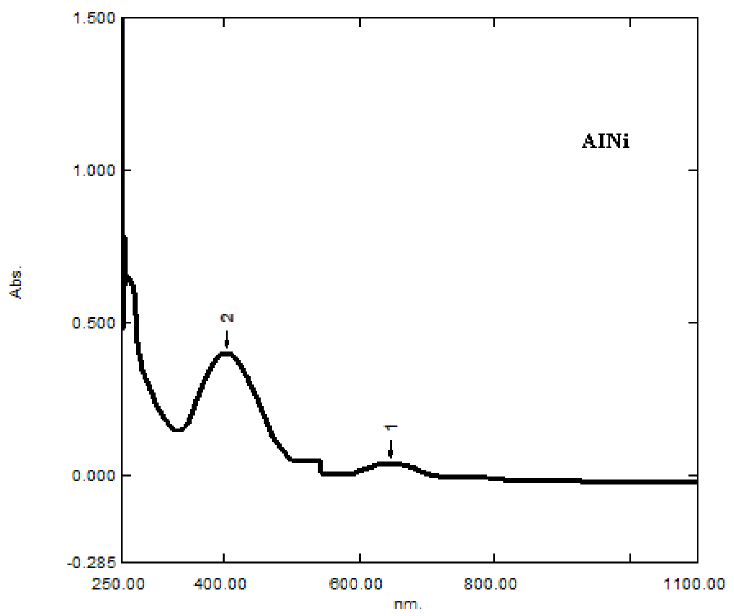


Figure (3-16): Electronic Spectrum of LINi

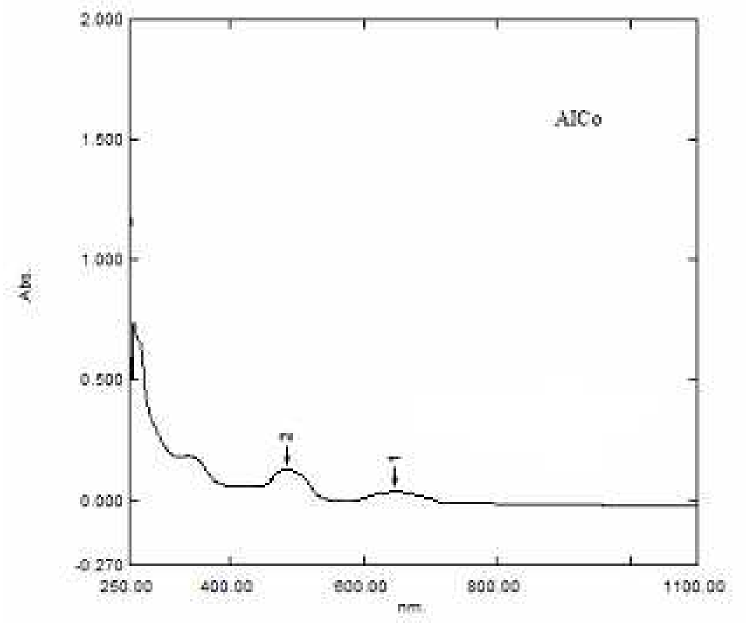


Figure (3-17): Electronic Spectrum of LICo

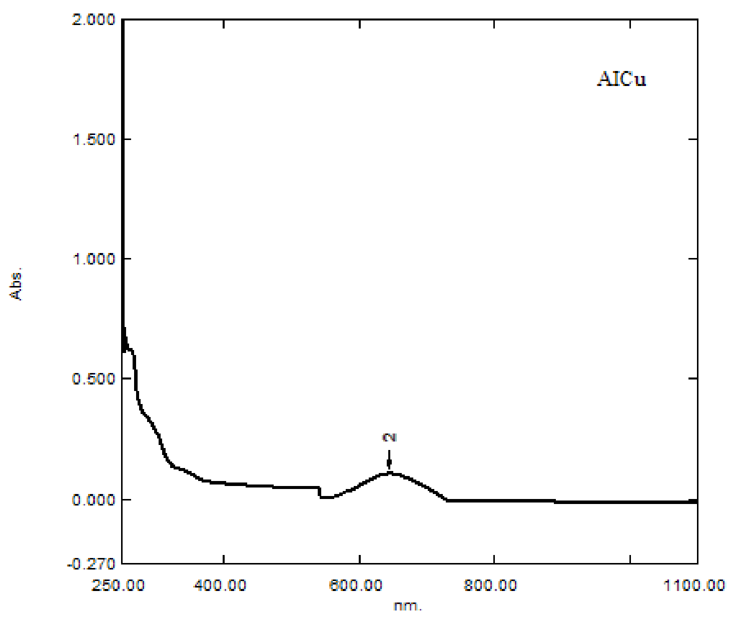


Figure (3-18): Electronic Spectrum of LICu

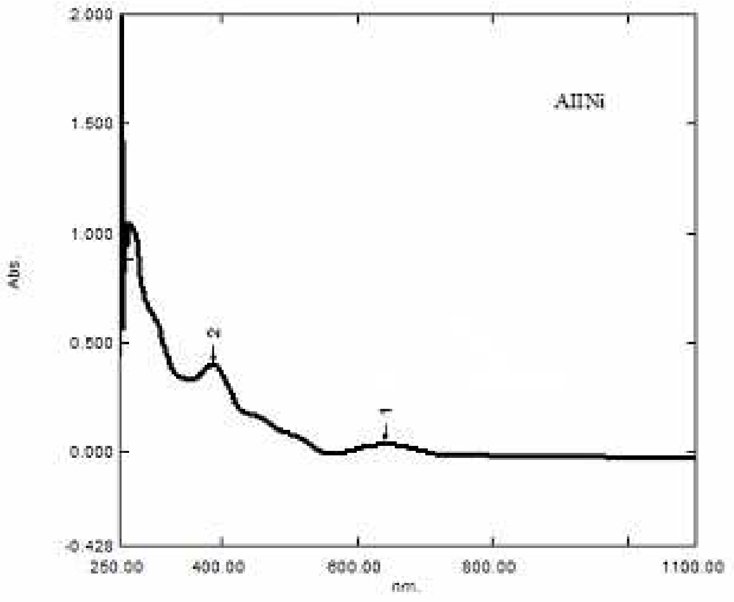


Figure (3-19): Electronic Spectrum of LIINi

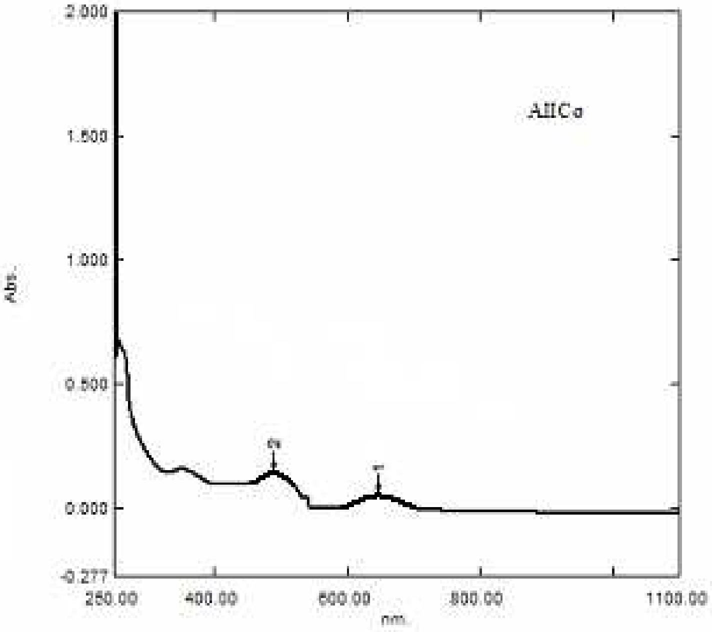


Figure (3-20): Electronic Spectrum of LIICo

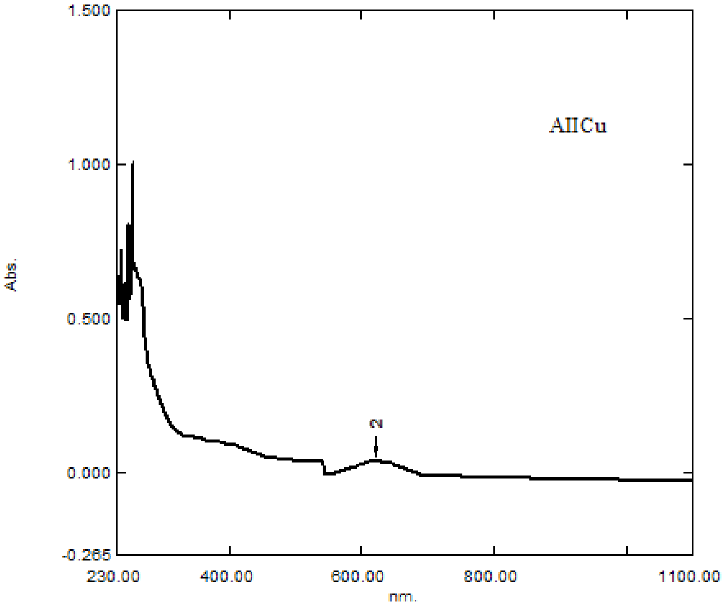


Figure (3-21): Electronic Spectrum of LIICu

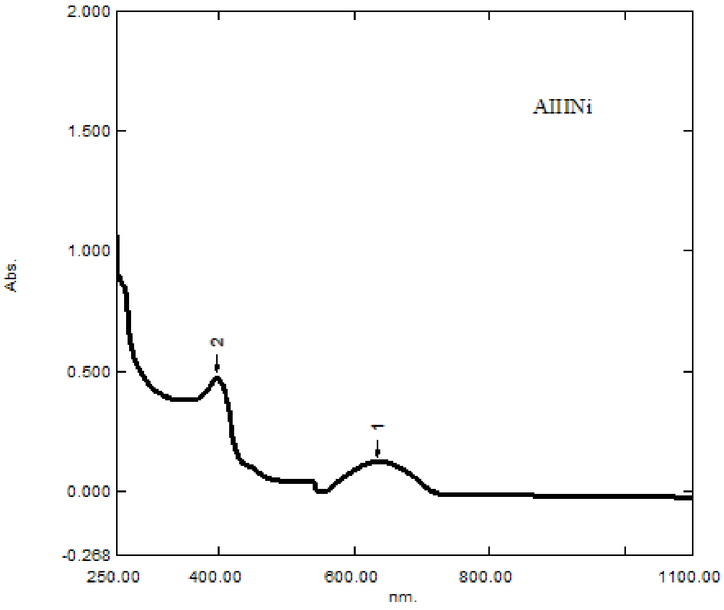


Figure (3-22): Electronic Spectrum of LIIINi

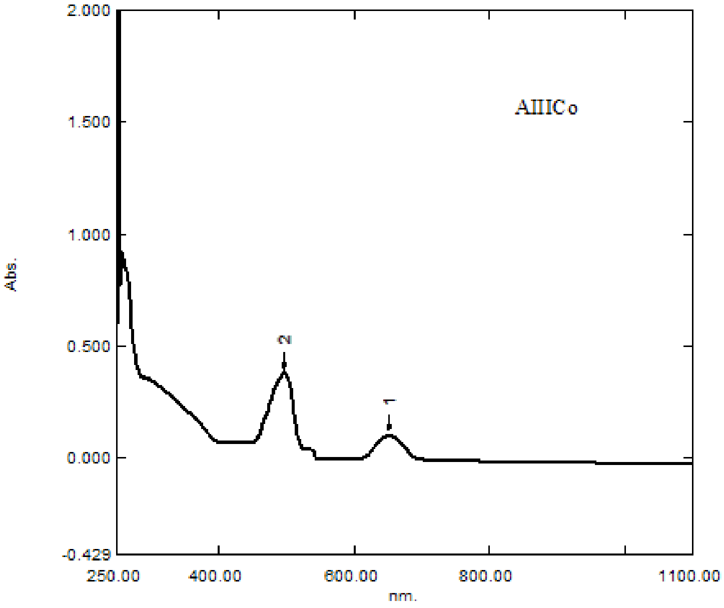


Figure (3-23): Electronic Spectrum of LIIICo

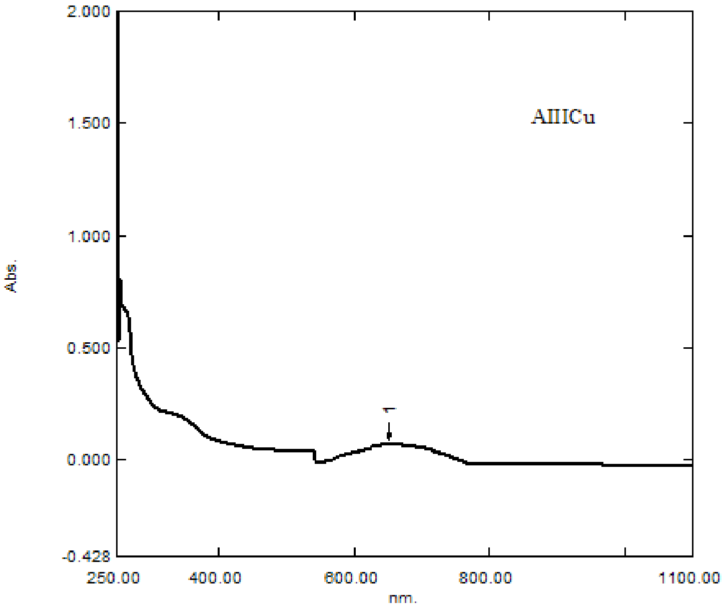


Figure (3-24): Electronic Spectrum of LIIICu

Suggestion for future work:

The following suggestion can be postulated to ensure completion of the work:

1) Using C.H.N. microanalysis and NMR techniques to complete the identify of the structures of the Schiff base and its metal complexes prepared.

2) Preparation of another set of transition metal complexes with the other transition metal ions.

3) Making a screening antibacterial and antifungal activity of the Schiff base and all the metal complexes, to explore their activity and the synergic effect between the metal and the ligand.

Chapter two

Experimental part

2.1 Instrumentation:

A) Fourier Trans form infrared spectrophotometer (FTIR):

The infrared spectra of the prepared compound were recoded using FTIR 8300 Fourier transform infrared spectrophotometer of ***SHIMADZU*** company as a potassium bromide (KBr) discs in the ware number range of (4000-400) cm^{-1}.

B) Electronic Absorption spectra:

The electronic spectra of the prepared complexes 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).

C) Magnetic susceptibility measurements:

The magnetic susceptibility values for the prepared complexes were obtained at room temperature using (Magnetic Susceptibility Balance) of Johnson mettey catalytic system division, England.

D) Metal Analysis.

The metal content of the complexes was measured using atomic absorption technique by Berkin-Elmer 5000 Atomic Absorption Spectrophotometer for the determination of (Co^{+2}, Cu^{+2}, Ni^{+2}, Cd^{+2})

E) Conductivity measurement:

The molar conductivity measurements were obtained using corning conductivity 220.

F) Melting point:

Gallen Kamp M.F.B, 600.01Melting point apparatus was used it measure the melting point of all the prepared compounds.

2.2 Chemicals:

All the chemicals used in this work were of highest purity available and the supplied without further purification.

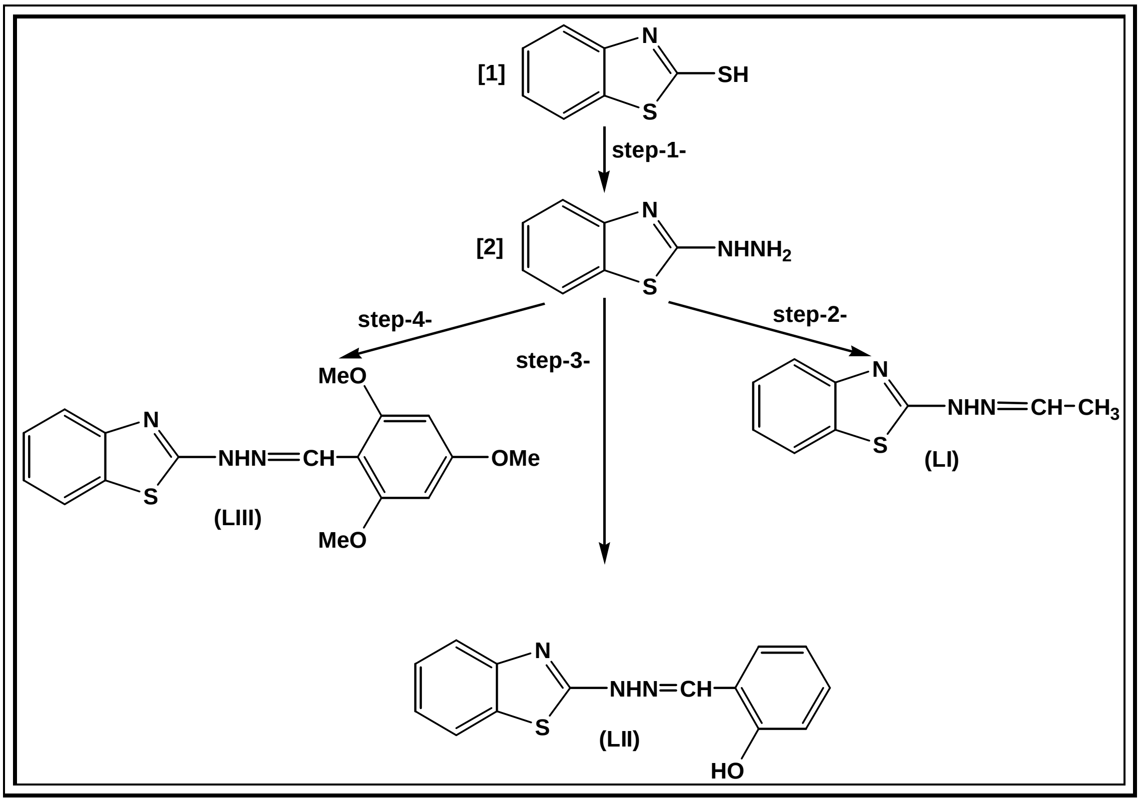
The following Table (2-1) shows the purity the reagents and the companies which supply themes.

Table (2-1): Chemicals and Their Manufacturers.

Compound	Purity %	company
2-Mercapto benzothiazole	97	BDH
Hydrazine hydrate	85	Merck
Absolute ethanol	99.99	BDH
Acetaldehyde	97	Fluka
Salicylaldehyde	97	Merck
2,4,6-Trimethoxy benzaldehyde	98	BDH
Nickel nitrate hexahydrate	96	BDH
Cobalt chloride dihydrate	99	Fluka
Copperic chloride dihydrate	95	Fluka
Cadmium nitrate hexahydrate	98	BDH
Dimethyl sulphoxide (DMSO)	99.9	BDH

2.3 Procedures of the step wise synthesis:

The step wise synthesis of the three ligands (LI, LII, LIII) were preformed as follows starting form 2-mercapto benzothiazole.



Scheme(2-1) Reagents and Conditions; step-1- hydrazine hydrate, EtOH (abs.), reflux (6h); step-2- acetaldehyde, EtOH (abs.), reflux (5h); step-3- salicylaldehyde,EtOH(abs.), reflux (2h); step-4- 2,4,6-Trirmethoxy benzaldehyde, EtOH (abs.), reflux(2h).

2.4 Methods of preparation:

2.4.1 Synthesis of 2-hydrazino benzothiazole:

2-mercapto benzothiazole (2-MPT) (1.67 g, 0.01 mole) dissolved in absolute ethanol, was added hydrazine hydrate (85%) (0.5 g, 0.317ml 0.01mole) and the mixture was then refluxed for 6 hours, excess solvent was distilled off, The resulting solid then was separated out on cooling and filtered, dried and recrystallized form ethanol(76), yield 84 %, m. p. (203-205°C) and light Brown needle-like.

2.4.2 Preparation of the Schiff bases ligands LI, LII, and LIII:

A) 2-(acetlidine) hydrazine benzothiazole (LI):

A mixture of (0.5 g), ($3x10^{-3}$ mole) of 2-hydrazino thiazole with (0.133g, $3x10^{-3}$ mole) of acetaldehyde was dissolved in (20ml) of absolute ethanol, the resulting mixture was heated with stirring under reflux for 5 hours, alight gray precipitate was formed then filtered and dried, yield (75%), m. p. (180 °C).

B) 2-(*O*-hedroxy benzylidine) hydrazine benzothiazole (LII):

A mixture of (0.5 g, $3x10^{-3}$ mole) of 2-hydrazino benzothiazole with (0.369 g, $3x10^{-3}$ mole)of salicylaldehyde was dissolved in (30 ml) of absolute ethanol, the resulting mixture heated with stirring under reflux for two hours, a off white precipitate was formed, and then filtered and dried, yield (85%), m. p. (255 °C).

C) 2-(2,4,6-tri methoxy benzylidine) hydrazine benzothiazole (LIII):

A mixture of (0.5g, 3X10^{-3} mole) of 2-hydrazino benzothiazole with (0.593 g, 3.5X10^{-3} mole) of 2,4,6-trimethoxy benzaldehyde was dissolved in (20 ml) of absolute ethanol, the resulting mixture heated with stirring under reflux for two hours, an off white precipitate was formed, and then filtered and dried, yield (70%), m. p.(210 °C).

2.5 Preparation of the new complexes:

2.5.1 Complexes of LI:

A) Ni(II) complex (AINi):

(0.5g, 2.6X10^{-3} mole) of (LI) was dissolved in (10 ml) absolute ethanol and mixed with (0.38 g, 1.3X10^{-3}mole) of the Nickel nitrate hexahydrate that dissolved in (5 ml) absolute ethanol, the mixture then was refluxed for (1 hour), the resulting precipitate was filtered and washed with absolute ethanol and dried under reduced pressure, the prepared complex was soluble in (DMSO) and partially soluble in warm absolute ethanol, melting point, colour and yield (%) are given in Table (3-1).

B) Co(II) complex (AICo):

(0.5 g, 2.6X10^{-3} mole) of (LI) was dissolved in (10 ml) absolute ethanol and mixed with (0.2 g, 1.3X10^{-3} mole) of the Cobalt chloride dihydrate that dissolved in (5 ml) absolute ethanol, the mixture then was refluxed for (1 hour), the resulting precipitate was filtered and washed with absolute ethanol and dried under reduced pressure, the prepared complex was soluble in (DMSO) and partially soluble in warm absolute ethanol, melting point, colour and yield (%) are given in Table (3-1).

C) Cu(II) complex (AICu):

The same procedure as in (2.5.1)-B- was followed for the preparation of Cu (II) complex, melting point; colour and yield (%) are given in Table (3-1).

D) Cd(II) complex (AICd):

(0.25 g, 1.3X10^{-3} mole) of (LI) was dissolved in (10 ml) absolute ethanol and mixed with (0.45 g, 1.3X10^{-3} mole) of the Cadmium nitrate hexahydrate that dissolved in (5 ml) absolute ethanol, the mixture then was refluxed for (1 hour), the resulting precipitate was filtered and washed with absolute ethanol and dried under reduced pressure, the prepared complex was soluble in (DMSO) and partially soluble in warm absolute ethanol, melting point, colour and yield (%) are given in Table (3-1).

2.5.2Complexes of LII:

A) Ni(II) complex (AIINi):

(0.5 g, 1.8X10^{-3} mole) of (LII) was dissolved in (10 ml) absolute ethanol and mixed with (0.27 g, 9.2X10^{-4} mole) of the Nickel nitrate hexahydrate that dissolved in (5 ml) absolute ethanol, the mixture heated with stirring under refluxed for (1 hour), the resulting precipitate was filtered and washed with absolute ethanol and dried under reduced pressure, the prepared complex was soluble in (DMSO) and partially soluble in warm absolute ethanol, melting point, colour and yield (%) are given in Table (3-1).

B) Co(II) complex (AIICo):

(0.5 g, $1.8X10^{-3}$ mole) of (LII) was dissolved in (10 ml) absolute ethanol and mixed with (0.15 g, $9.2X10^{-4}$ mole) of the Cobalt chloride dihydrate that dissolved in(5 ml) absolute ethanol, the mixture then was refluxed for (1 hour), the resulting precipitate was filtered and washed with absolute ethanol and dried under reduced pressure, the prepared complex was soluble in (DMSO) and partially soluble in warm absolute ethanol, melting point, colour, and yield (%) are given in Table (3-1).

C) Cu(II) complex (AIICu):

(0.5 g, $1.8X10^{-3}$ mole) of (LII) was dissolved in (10 ml) absolute ethanol and mixed with (0.32 g, $1.8X10^{-3}$ mole)of the Copperic chloride dihydrate that dissolved in (5 ml) absolute ethanol, the mixture then was refluxed for (1 hour), the resulting precipitate was filtered and washed with absolute ethanol and dried under reduced pressure, the prepared complex was soluble in (DMSO) and partially soluble in warm absolute ethanol, melting point, colour, and yield (%) are given in Table (3-1).

D) Cd(II) complex (AIICd):

(0.5 g, $1.8X10^{-3}$ mole) of (LII) was dissolved in (10ml) absolute ethanol and mixed with (0.64 g, $1.8X10^{-3}$ mole) of the Cadmium nitrate hexahydrate that dissolved in (5 ml) absolute ethanol, the mixture heated with stirring under refluxed for (1 hour), the resulting precipitate was filtered and washed with absolute ethanol and dried under reduced pressure, the prepared complex was soluble in (DMSO) and partially soluble in warm absolute ethanol, melting point, colour, and yield (%) are given in Table (3-1).

2.5.3 Complexes of (LIII):

A) Ni(II) complex (AIIINi):

(0.5 g, $1.4X10^{-3}$ mole) of (LIII) was dissolved in (10 ml) absolute ethanol and mixed with (0.2 g, $7.2X10^{-4}$ mole) of the Nickel nitrate hexahydrate that dissolved in (5 ml) absolute ethanol, the mixture heated with stirring under refluxed for (1 hour), the resulting precipitate was filtered and washed with absolute ethanol and dried under reduced pressure, the prepared complex was soluble in (DMSO) and partially soluble in warm absolute ethanol, melting point, colour, and yield (%) are given in Table (3-1).

B) Co (II) complex (AIIICo):

(0.5 g, $1.4X10^{-3}$ mole) of (LIII) was dissolved in (10 ml) absolute ethanol and mixed with (0.12 g, $7.2X10^{-4}$ mole) of the Cobalt chloride dihydrate that dissolved in (5 ml) absolute ethanol, the mixture heated with stirring under refluxed for (1 hour), the resulting precipitate was filtered and washed with absolute ethanol and dried under reduced pressure, the prepared complex was soluble in (DMSO) and partially soluble in warm absolute ethanol, melting point, colour and yield (%) are given in Table (3-1).

C) Cu(II) complex (AIICu):

The same procedure as in (2.5.٣)-B- was followed for the preparation of Cu (II) complex, melting point, colour and yield (%) are in Table (3-1).

D) Cd(II) complex (AIIICd):

(0.5 g, 1.4X10^{-3} mole) of (LIII) was dissolved in (10 ml) absolute ethanol and mixed with(0.5 g, 1.4X10^{-3}mole) of the Cadmium nitrate hexahydrate that dissolved in (5 ml) absolute ethanol, the mixture heated with stirring under refluxed for (1 hour), the resulting precipitate was filtered and washed with absolute ethanol and dried under reduced pressure, the prepared complex was soluble in (DMSO) and partially soluble in warm absolute ethanol, melting point, colour, and yield (%) are given in Table (3-1).

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الأسم: سما محمد علي العزاوي .

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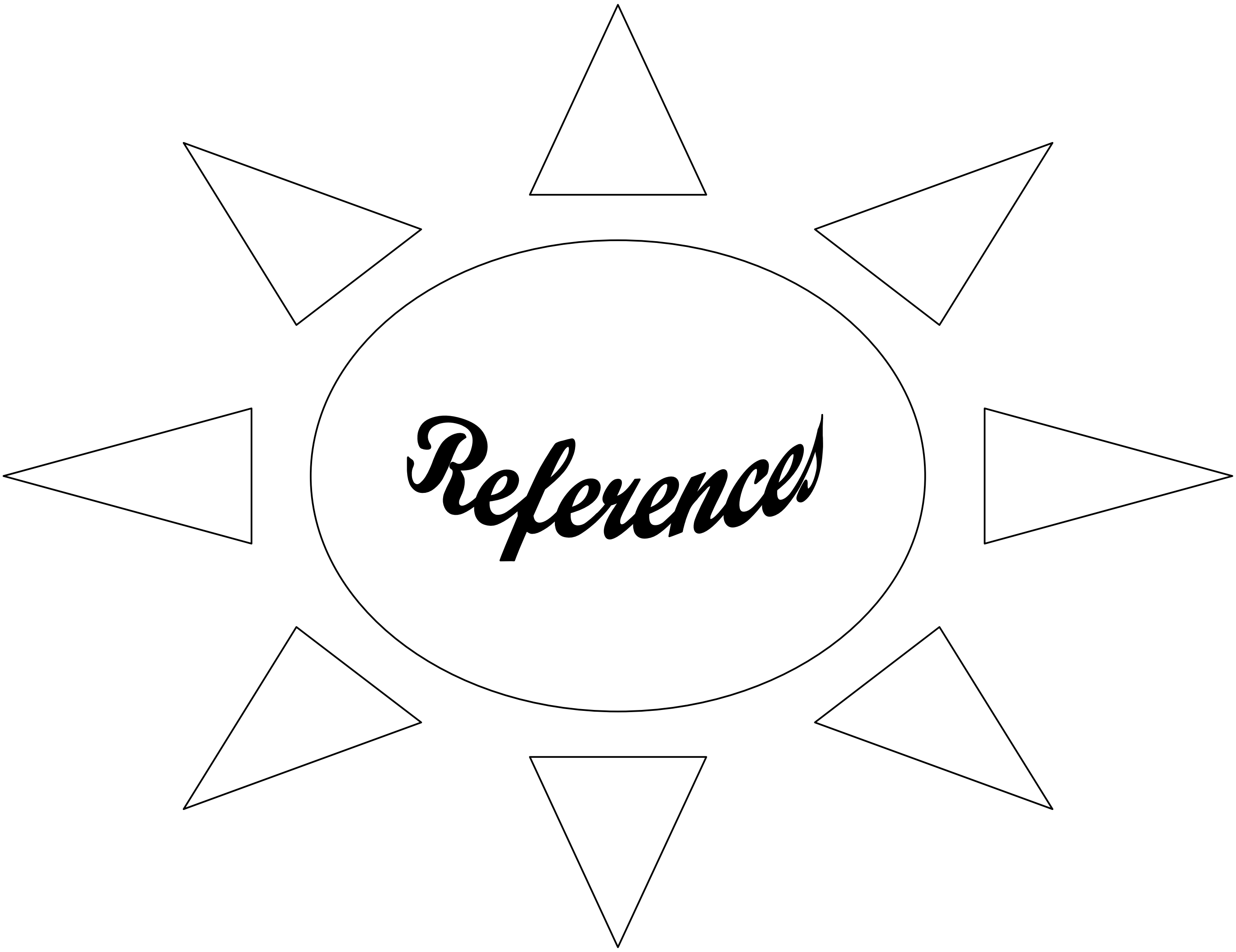
عنوان الاطروحه: تحضير وتشخيص بعض معقدات العناصر الأنتقالية مع قواعد شف المشتقة من ٢- هيدرازينو بنزوثايازول



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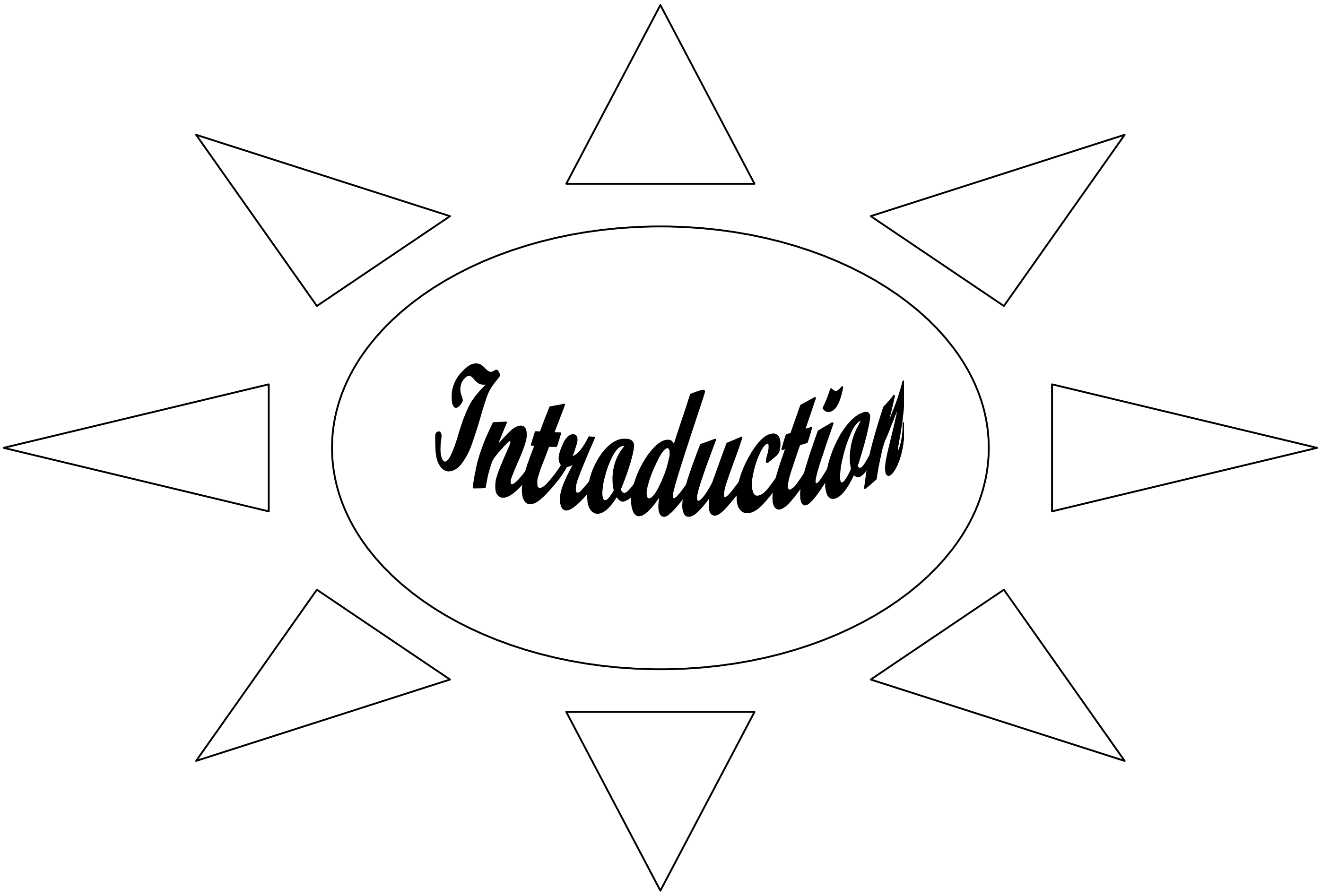
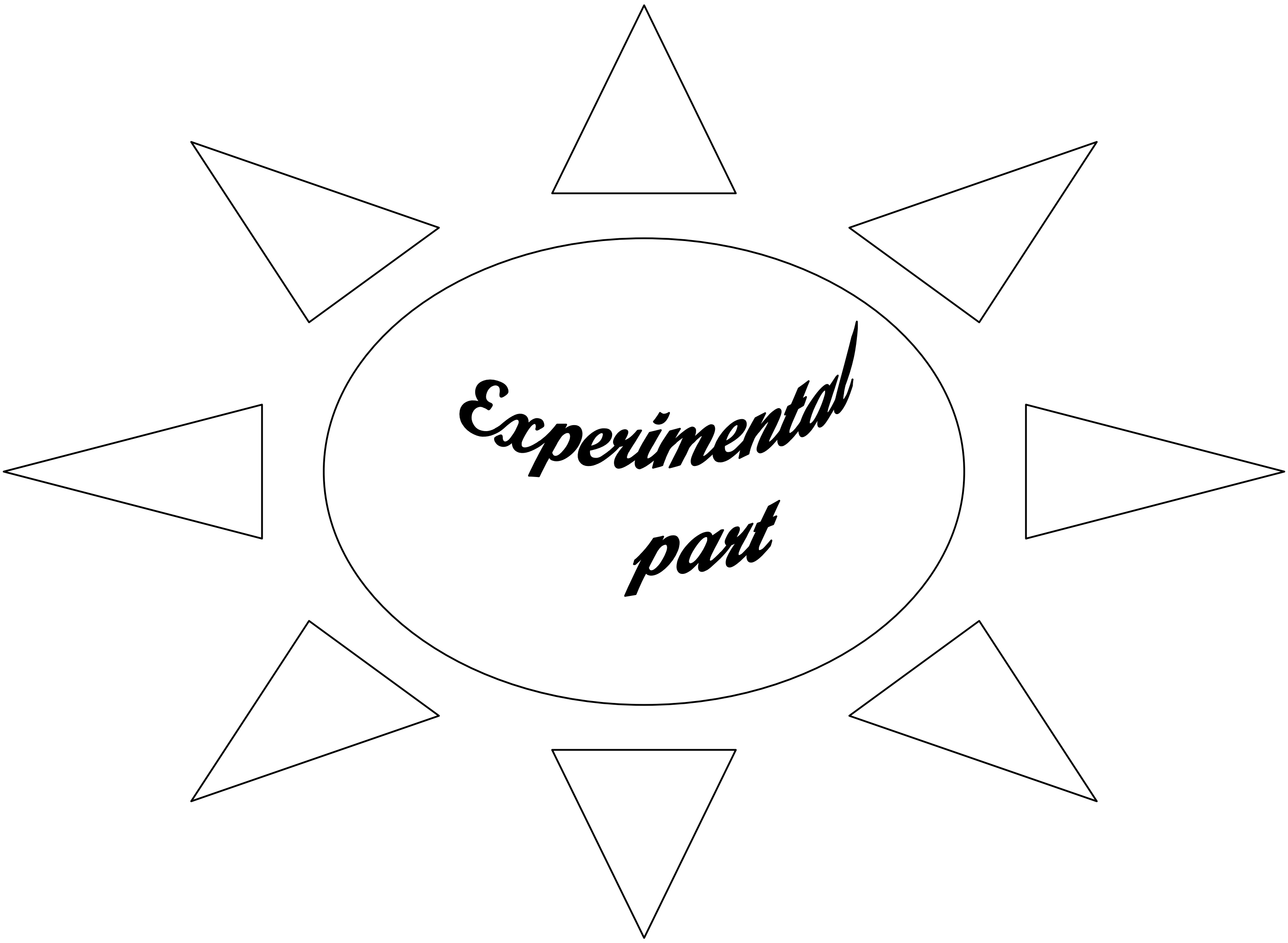
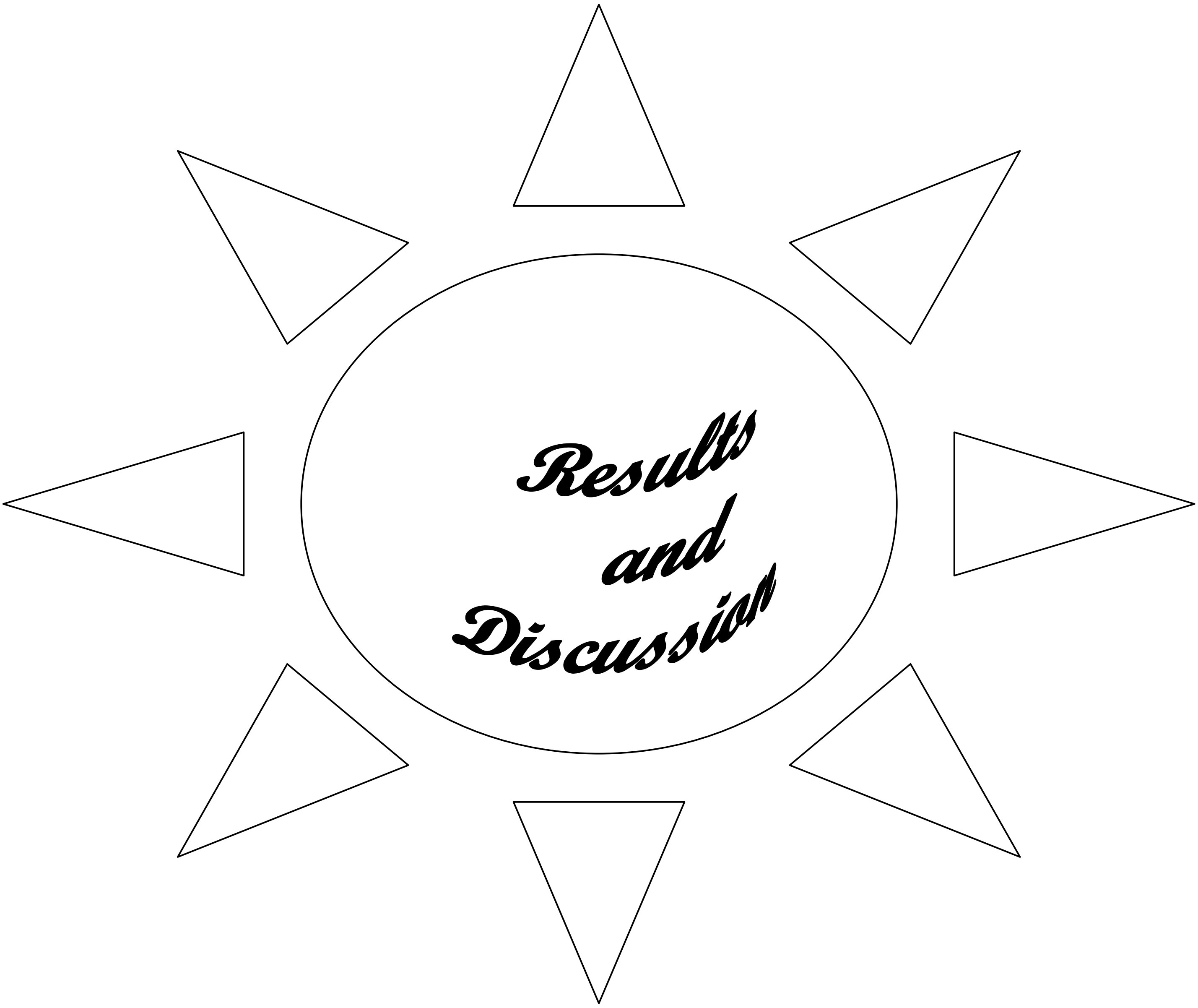


Introduction



Experimental part



Results and Discussion

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Sama
2007

Symbols and Abbreviations

FT-TR	*Fourier transform infrared*
Uv-Vis	*Ultraviolet-Visible*
DMSO	*Dimethyl Sulfoxide*
ETOH	*Ethanol*
Oh.	*Octahedral*
B.M.	*Bohr magneton*
ν	*Stretching*
nm	*Nanometer*
λ	*Wave length*
M.P.	*Melting point*

Republic of Iraq
Ministry of Higher Education
and Scientific Research
Al-Nahrain University
College of Science
Department of Chemistry

SYNTHYESIS AND CHARACTERIZATION OF SOME TRANSITION METAL COMPLEXES WITH SCHIFF BASES DERIVED FROM 2-HYDRAZINO BENZOTHIAZOLE

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
Sama Mohammed Ali Al-Azawi
(B.Sc. 2004)

April 2007 *RabeeaAlthani1428*

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

تحضير وتشخيص بعض معقدات العناصر الأنتقالية مع قواعد شف المشتقة من ٢-هيدرازينو بنزوثيازول

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

من قبل
سما محمد علي العزاوي
بكالوريوس ٢٠٠٤ (جامعة النهرين)

ربيع الثاني ١٤٢٨
نيسان٢٠٠٧

بسم الله الرحمن الرحيم

الرحمن ، علم القران ، خلق الانسان ،
علمه البيان

صدق الله العلي العظيم

سورة الرحمن

الاية(١-٤)

الاهداء

الى وطني الحبيب مهد الحضارات الأنسانية وأول معلم للبشرية..........العراق

الى من ارضعتني لبان الحنان والايمان التي كانت في حياتي اروع ماخلق الرحمن ....امي

الى من توج اسمي باسمه واسكنني شغاف قلبه الذي انار لي دربي ....ابي

الى رفيقة حياتي وصديقة عمري وقدوة دربي ....اختي

الى محيط امالي وعنوان عزتي وسؤددي ....اخي

الى باعث بهجتي وزينة حياتي.........ابن اختي

الى من ساندتني وسكنت شغاف قلبي..........صديقتي همسة الحبوبي

الى كل من له معزة في قلبي

اهدي ما وفقني اليه ربي ثمرة جهدي

سما

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