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

PREPARATION AND CHARACTERIZATION OF OXADIAZOLE DERIVATIVES AND HYDRAZINO BENZOTHIAZOLE AND THEIR TRANSITION METAL COMPLEXES

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

تحضير ودراسة مشتقات الأوكسادايازول والهيدرازينو بينزوثايازول ومعقداتها الفلزية

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

من قبل
همسة أحمد الحبوبي
بكالوريوس ٢٠٠٤ (جامعة النهرين)

ربيع الثاني١٤٢٨
نيسان٢٠٠٧

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.**

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Examining Committee's Certification

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

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Dean of the college of Science
Date:

الإهداء

إلى من جعل الجنة تحت أقدامها وتآنس روحي بقربها ويستنير دربي بدعائها وتخفو أحزاني بإبتسامة عيناها .....

أمي حنان الدنيا كلها ورمز التضحية

إلى من شجعني على خوض التجربة وجعلني أمسك بدفة المركب وبموج هذه الحياة ......

أبي العزيز

إلى خير من كانت في قدرتي التي شدت من أزري وهونت على أمري والتي جاوز حبها عدد ما في القلب من نبضات .....

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إلى رفيقة دربي والتي أحسها أقرب من شغاف قلبي إلي .....

صديقتي سمـــا

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الخلاصة

تم في هذا البحث تحضير ثلاث من الليكاندات الجديدة والتي أختيرت لتحضير سلسلة من معقدات بعض العناصر الأنتقالية (Ni^{+2}, $Co^{+٢}$, Cd^{+2}, Hg^{+2}, Cu^{+2})
يحتوي اليكاند الأول (LI) على مجموعة (NSC) ويتضمن مشتق الأوكسادايزول، أما (LIII),(LII) فقد تم تحضيرها عن طريق تفاعل شف بين ٢- كلوريد نيزوثايزول مع ٢- كلوروبنزالديهايد وبارا- هيدروكسي- بنزلديهايد على التوالي .

شخصت الليكاندات المحضرة بواسطة طيف الأشعة تحت الحمراء (FT.IR)، ودرجات الأنصهار. تم تحضير وعزل المعقدات الفلزية لليكندات في الحالة الصلبة وكانت مستقرة تجاه الضوء والحرارة والرطوبة. شخصت المعقدات الجديدة بواسطة أطياف الأشعة تحت الحمراء (FT.IR)، والأشعة الفوق البنفسجية-المرئية (UV-Vis)، والقياسات المغناطيسية والتوصلية الكهربائية، اضافة الى تحديد نسبة الفلز بطريقة الأمتصاص الذري اللهبي .
أستنادا الى نتائج القياسات أعلاه تم أقتراح الصيغ التركيبية وكالاتي:

١) معقدات الايونات Cd (II), Co (II), Hg(II), Ni (II), Cu (II) مع الليكند الأول (LI):
أعطى معقد النحاس الصيغة الجزيئية $[Cu(LI)_2Cl_2]\,H_2O$ ذات شكل ثماني السطوح
وأظهر معقد النيكل الصيغة الجزيئية $[Ni(LI)_2(H_2O)_2](NO_3)_2.H_2O$ ذات شكل ثماني السطوح
بينما يملك معقد الزئبق الصيغة الجزيئية $[Hg(LI)_2Cl_2]\,C_2H_5OH$ ذات شكل ثماني السطوح
ومعقد الكوبلت يمتلك الصيغة الجزيئية $[Co(LI)_2Cl_2]\,2C_2H_5OH$ ذات شكل ثماني السطوح .
و معقد الكادميوم يمتلك الصيغة الجزيئية $[Cd(LI)_2]\,(NO_3)_2.H_2O$ ذات شكل رباعي السطوح.

٢) اظهرت الايونات Ni(II), Cd(II), Co(II), Cu(II) مع الليكند الثاني (LII) الصيغ والأشكال التالية:
شكل ثماني السطوح $[Cu(LII)_2Cl_2].\,H_2O$

شكل ثماني السطوح	$[Co (LII)_2(EtOH)_2]\ Cl_3$
شكل رباعي السطوح	$[Cd (LII) (NO_3)_2]\ H_2O$
شكل ثماني السطوح	$[Ni (LII)_2 (NO_3)_2].\ 2H_2O$

٣) اظهرت الايونات Ni(II), Cd(II), Co(II), Cu(II) مع الليكندالثالث (LIII) الصيغ الجزيئية التالية:

شكل ثماني السطوح	$[Cu (LIII)_2\ H_2O]\ Cl_2$
شكل ثماني السطوح	$[Co (LIII)_2\ Cl_2].\ 2\ H_2O$
شكل رباعي السطوح	$[Cd\ LIII\ (H_2O)_2].\ (NO_3)_2.\ H_2O$
شكل ثماني السطوح	$[Ni (LIII)_2 (H_2O)_2].\ (NO_3)_2.\ H_2O$

برزت الخصائص التركيبية والتأصرية المختلفة من خلال دراسة الكيمياء التناسقية بمعقدات الليكندات الجديدة.

فسرت طبيعة التأصر بين أيونات الفلز والذرات المانحة في الليكند بمعامل راكاح ومقياس قوة المجال الليكاندي الأخرى والتي تم احتسابها بواسطة مخطط (تنابا- سوكانو).

Abstract

Three new ligands have been prepared in this work, which were chosen to synthesis a new set of transition metal complexes [Cu (II), Ni (II), Hg (II), Cd (II) and Co (II)].

LI=(2-[5-phenyl-2-methylthio-1,3,4-oxadizole]-5-phenyl-1,3,4-oxadiazole), LII=2-(***O***-chloro benzylidine) hydrazine benzothiazole and LIII=2-(p-hydroxy benzylidine) hydrazine benzothiazole were prepared by Schiff reaction between 2-mercaptobenzothiazole and 2-chlorobenzaldehyde and p-hydroxy benzaldehyde.

The new ligands were characterized by the Infra-red spectroscopy and melting points.

The metal complexes, were prepared and isolated in pure solid state, and found to be stable toward light, heat and moisture. These new complexes were characterized via FT.IR , UV-Vis Spectroscopy, magnetic and conductivity measurements. In addition the metal contain were determind by atomic absorption measurement.

According to the result of the above measurements, the following formula were suggested by atomic absorption measurement.

LI complexes:
$[Cu (LI)_2 Cl_2]. H_2O$ which was of Oh geometry
$[Ni (LI)_2 (H_2O)_2] (NO_3)_2. H_2O$ which was of Oh shape
$[Hg (LI)_2 Cl_2]. C_2H_5OH$ which was of Oh geometry
$[Co (LI)_2 Cl_2]. 2C_2H_5OH$ which was of Oh geometry
$[Cd (LI)_2] (NO_3)_2. H_2O$ which was of Th geometry

LII complexes:

$[Cu (LII)_2 Cl_2].2 H_2O$ which was of Oh geometry
$[Ni (LII)_2 (NO_3)_2]. 2H_2O$ which was of Oh shape
$[Co (LII)_2 (EtOH)_2] Cl_3$ which was of Oh geometry
$[Cd LII (NO_3)_2. H_2O$ which was of Td geometry

LIII complexes:

$[Cu (LIII)_2 (H_2O)_2] Cl_2$ which was of Oh geometry
$[Ni (LIII)_2 (H_2O)_2]. (NO_3)_2 H_2O$ which was of Oh shape
$[Co (LIII)_2 CL_2]. 2H_2O$ which was of Oh geometry
$[Cd LIII (H_2O)_2]. (NO_3)_2$. H2O which was of Td geometry

Different bonding and structural behavior were revealed through the study of the coordination chemistry of the metal complexes of the new ligands.

The nature of bonding between the metal ion and the donor atoms of the ligands were demonstrated through the calculaion of Racah parameter and the other ligand field parameters, which were calculated by using the suitable Tanabe-Sugano diagrams.

Symbols and Abbreviations

FT-IR	Fourier transform Infrared
UV-Vis	Ultraviole-Visible
DMSO	Dimethyl Sulfoxide
ETOH	Ethanol
Oh	Octahedral
Th	Tetrahedral
B.M	Bohr magneton
γ	Stretching
nm	Nanometer
λ	Wave length
m.p	Melting point
B	Racah parameter
β	Nephelauxetic factor
ph	Phenyl
ph C-N	Phenyl Carbon-Nitrogen
dec.	decomposition

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بسم الله الرحمن الرحيم

و انزل الله عليك الكتب و الحكمة و علمك

مالم تكن تعلم وكان فضل الله عليك عظيما

صدق الله العلي العظيم

سورة النساء

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Chapter two

Experimental part

2.1 Chemicals and Techniques

1-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 reagents and the companies which supply them.

Table (2-1): Chemicals and their manufacturers

compounds	Purity %	Company
Cadmium nitrate trihydrate	98	BDH
Carbon disulfide	99	Merck
Chloroacetic acid	97	BDH
2-Chloro benzaldehyde	95	BDH
Cobalt chloride dihydrate	99	Fluka
Copper chloride dihydrate	95	Fluka
Dimethyl sulphoxide	99.9	BDH
Ethanol (absolute)	99.99	BDH
Hydrazine hydrate	85	Merck
Hydrochloric acid	87.8	BDH
4-Hydroxy benzaldehyde	97	Merck
2-Mercapto benzothiazole	95	BDH
Mercury chloride	98	Fluka
Nickel nitrate hexahydrate	96	BDH
Phosphorus oxychloride	99	Fluka
Potassium hydroxide	85	BDH
Sodium bicarbonate	99.7	BDH

2- Techniques:

A) Infrared spectrophotometer:

Infrared spectra were recorded on F.T.IR-8300 Fourier Transforms Infrared Spectrophotometer (***SHIMADZU***) as potassium bromide disc in the (4000-400) cm^{-1} spectral range.

B) Electronic absorption spectra:

The electronic spectra of the complexes were obtained using ***SHIMADZU*** UV-Vis 160A Ultra-Violet Spectrophotometer at room temperature using quartz cells of 1.0 cm length and using ethanol or DMSO as solvent, in the range of wave length (200-1100) nm.

C) Magnetic susceptibility measurement:

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

D) Metal analysis:

The metals content of the complexes was measured using atomic absorption technique by PERKIN-ELMER-5000 Atomic Absorption Spectrophotometer for the determination of (Co^{+2},Cu^{+2}, Cd^{+2}, Ni^{+2}, Hg^{+2}).

E) Conductivity measurements:

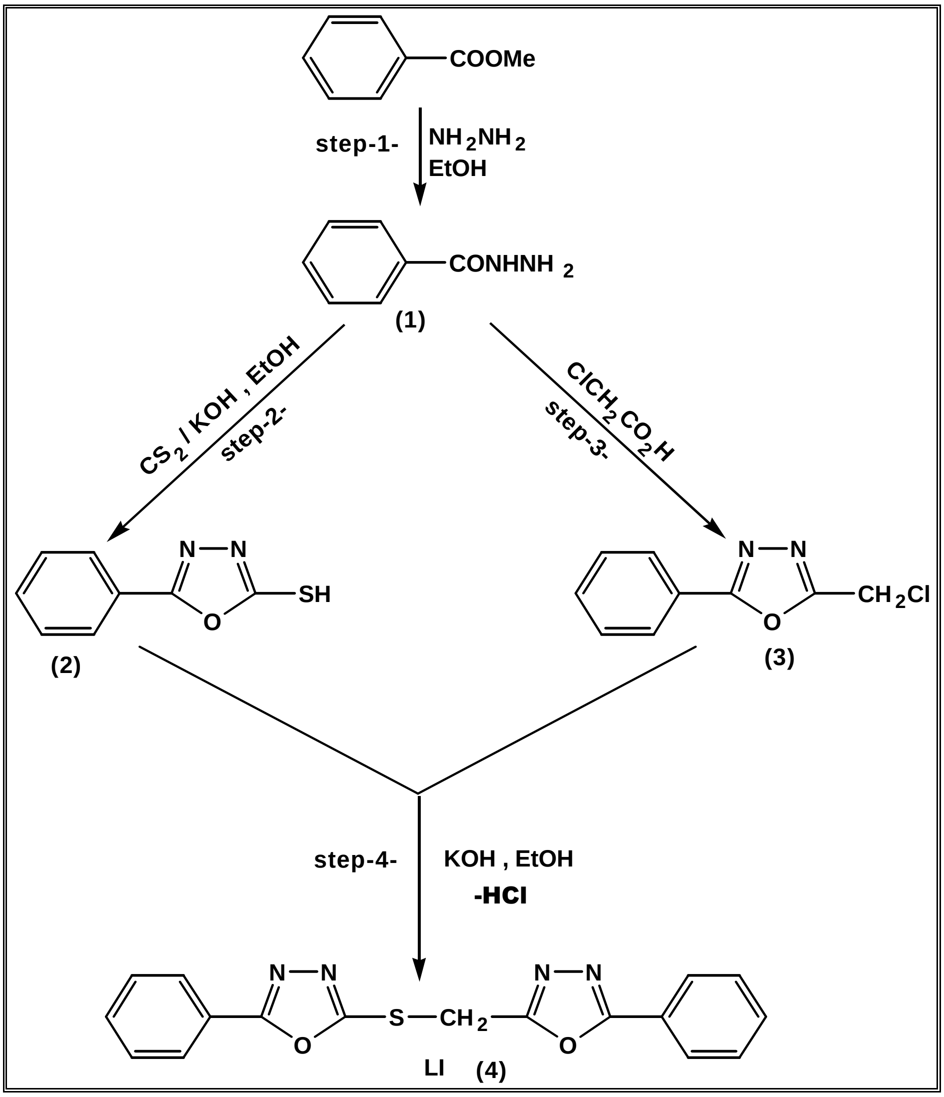
The molar conductivity measurements were obtained using corning conductivity 220.

F*) Melting point instrument:*

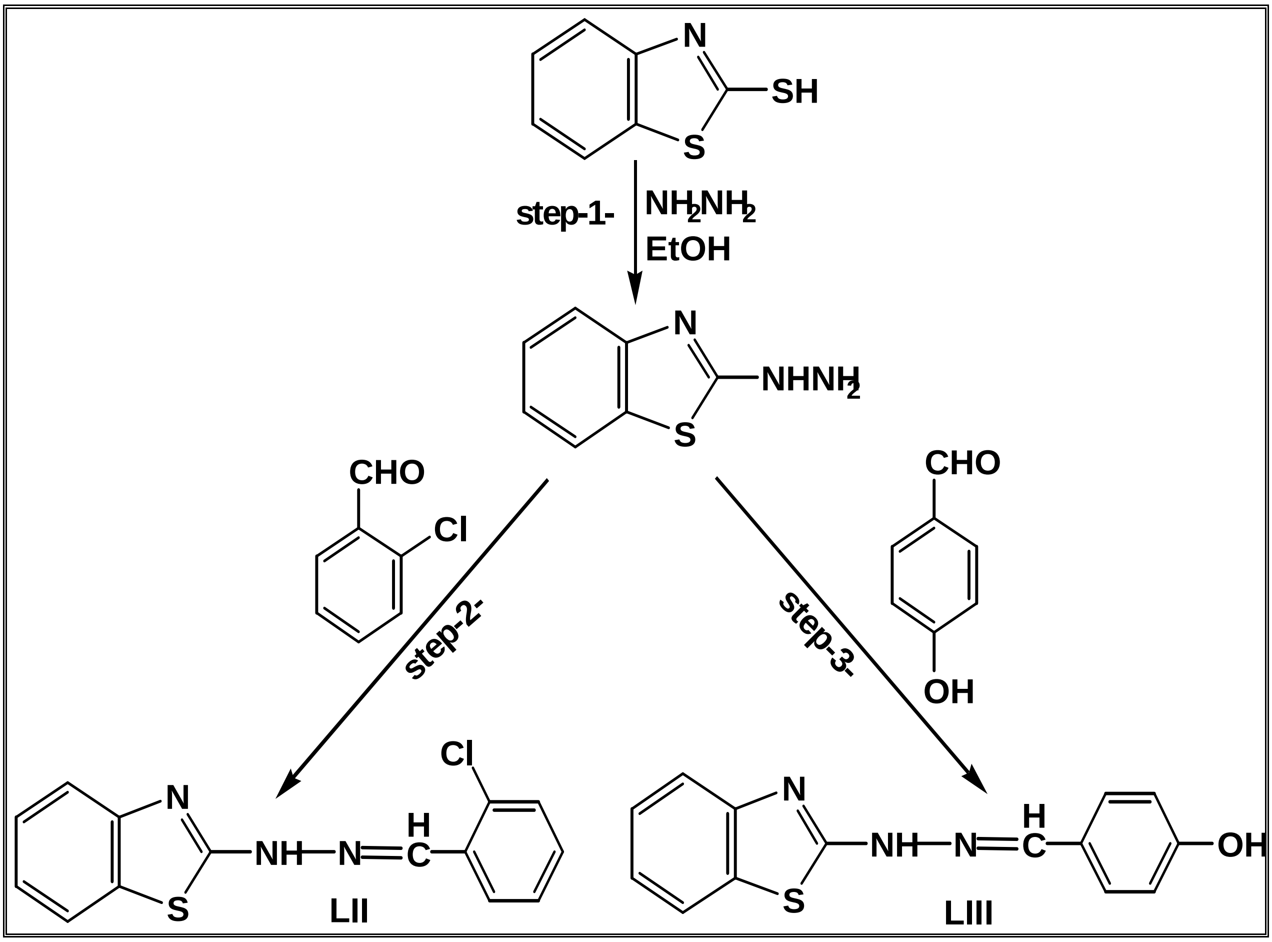
Gallenkamp M.F.B 600.01 of melting point apparatus was used to measure the melting points of all the prepared compounds.

2.2 Procedures of the stepwise synthesis:

The stepwise synthesis of 1,3,4-oxadiazoles, and 2-mercapto-benzothiazole are outlined in schemes (2-1), (2-2) respectively.



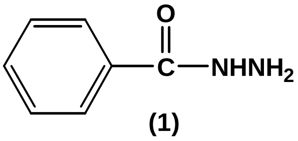
Scheme (2-1) Reagents and Conditions; step1: hydrazine hydrate ,EtoH, reflux (2hrs); step2: CS_2, KOH, EtOH, dil.HCl, reflux (7hrs); step3: chloro acetic acid, $POCl_3$, EtOH, $NaHCO_3$, reflux (9hrs) ; step4: KOH, EtOH, reflux (5hrs).



Scheme (2-2) Ragent and Condition; step1: hydrazine hydrate, EtOH (abs), reflux (6hrs); step2: 2-Chloro benzaldehyde, EtOH (abs), reflux (1hr); step3: P-hydroxy benzaldehyde, EtOH (abs), reflux (6hrs) .

2.3 Methods of preparation:

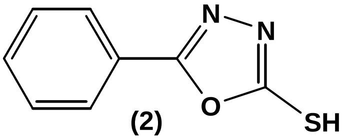
2.3.1 Preparation of Acid hydrazides:



(1)

A mixture of methyl benzoate (0.16 mole, 27g, 25 ml) and excess of hydrazine hydrate (15 ml) were refluxed for (2 hrs). The precipitate which separated on cooling was filtered and washed with cold water (64), m.p. (113-117°C), yield (71%), white precipitate.

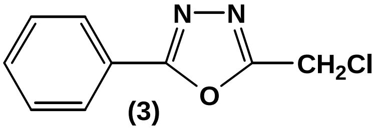
2.3.2 Preparation of 5-(phenyl)-1,3,4 -oxadiazol-2-thiol:



(2)

To a solution of the corresponding acid hydrazide (0.02 mole,2.72g) in ethanol (25 ml) at (0°C) was added carbon disulfide (0.04 mole, 3.04g, 2.5ml) and potassium hydroxide (0.02 mole, 1.12g) the mixture was refluxed for (7hrs). The solvent was evaporated and the residue dissolved in water and acidified with (5ml) dilute hydrochloric acid. The precipitate was filtered and recrystallized from (ethanol-water), Scheme (2-1) , m.p. (214-216 °C), Yield (84%), off white precipitate.

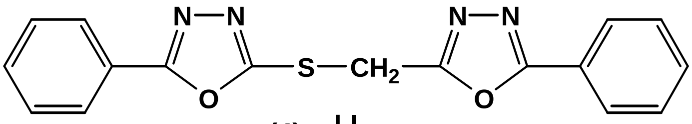
2.3.3 Preparation of 5-phenyl-2-chloro methyl-1,3,4-oxadiazole:



(3)

A mixture of acid hydrazides (1) (1.36 g,0.01 mole), Chloroacetic acid (0.92 g, 0.01 mole) and add phosphorous oxytrichloride (5 ml) was refluxed for (9 hrs), the mixture was then cooled, poured into ice-water and made alkaline by adding sodium bicarbonate solution. The resulting solid was filtered, dried and recrystallized (from a mixture of acetone and ethanol) to give the titled compound, Scheme (2-1), m.p. (107-109 °C), yield (70%)(65).

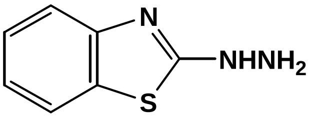
2.3.4 Preparation of 2-[5-phenyl-2-methylthio-1,3,4-oxadiazole]-5-phenyl-1,3,4-oxadiazole (LI):



(4) LI

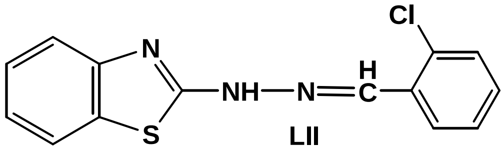
To 5-(phenyl)-1,3,4-oxadizole-2-thiol (0.4 g, 2.8x10^{-3} mole) [3] and 5-phenyl-2-chloromethyl-1,3,4-oxadiazole (0.44 g, 2.2x10^{-3} mole) [4] dissolved in (30 ml) of 99.9 % ethanol, a solution of (0.14 g, 3.5x10^{-3} mole) of potassium hydroxide was added. The mixture was then refluxed for (5 hrs). The solution was then concentrated to a small volume; A precipitate was obtained by adding ice-water. The solid was filtered off dried and recrystallized from ethanol, Scheme (2-1) , m. p. (138-140 °C), Yield 89 % , off white precipitate.

2.3.5 Preparation of 2-hydrazino benzothiazole:



To a solution of 2-mercapto benzothiazole (1.67 g, 0.01 mole) dissolved in (15 ml) ethanol. hydrazine hydrate (85%) (0.32 g, 0.317 ml, 0.01 mole) was added and the mixture was then refluxed for (6 hrs), excess solvent was distilled off, the resulting solid separated out on cooling, filtered, dried and recrystallized to obtain off white crystals precipitate, scheme (2-2), m. p. (203-205°C) , yield (80%)(66).

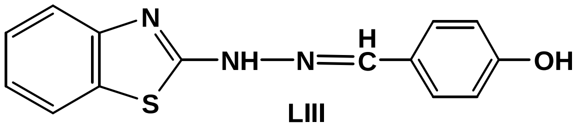
2.3.6 Preparation of the Schiff bases ligand 2-(O-chloro benzylidin) hydrazino benzothiazole (LII):



LII

A Solution of (0.5 g, 3X10^{-3} mole) 2-hydrazino benzothiazole and (0.426 g, 3X10^{-3} mole) 2-chloro benzaldehyde was dissolved in (20 ml) of a absolute ethanol. The resulting mixture was heated with stirring under reflex for one hour. The result was filtered and recrystallized to obtain light green precipitate, scheme (2-2), m.p. (233-235 °C), yield (89 %).

2.3.7 Preparation of the Schiff bases ligand 2-(p-hydroxy benzylidine) hydrazino benzothiazol(LIII):



LIII

A Solution of (0.5 g, 3X10^{-3} mole) 2-hydrazion benzothiazole and (0.38 g, 3X10^{-3} mole) of P-hydroxy benzaldehyde in (20 ml) of absolute ethanol was heated with stirring under reflex for (6 hrs), the result was filtered and recrystallized to obtain off-white precipitate, scheme (2-2), m. p. (249 °C) ,yield (70 %).

2.4. Preparation of the metal complexes:

2.4.1 Preparation the metal complexes of the LI:

1) Copper (II) complex (LICu):

A Solution of (0.1 g, 5.9X10^{-4} mole) $CuCl_2.2H_2O$ dissolved in (5 ml) ethanol was added to (0.4 g, 1X10^{-3} mole) of LI dissolved in (10 ml) ethanol. The mixture was refluxed with stirring under-reflux for one hour, The resulting bright green precipitate was filtered , washed with hot ethanol and dried under vacuum. Melting point, color and yield (%) are given in Table (3-1)

2) Nickel (II) complex (LINi):

A Solution of (0.17 g, 5.9X10^{-4} mole) $Ni(NO_3)_2.6H2O$ dissolved in (5 ml) of ethanol was added to (0.4 g, 1X10^{-3} mole) of LI dissolved in (10 ml) ethanol. The mixture was refluxed with stirring for one hour; The resulting precipitate was filtered and washed with hot ethanol then dried under vacuum. The melting point, color and yield (%) are given in Table (3-1)

3) Cobalt (II) complex (LICo):

A Solution of (0.098 g, 5.9X10^{-4} mole) $CoCl_2.2H_2O$ dissolved in (5 ml) ethanol was added to (o.4 g, 1X10^{-3} mole) of LI dissolved in (10 ml) ethanol. The mixture was refluxed with stirring for one hour; The resulting precipitate was filtered and washed with hot ethanol then dried under-vacuum. Melting point, color and yield (%) are given in Table (3-1).

4) Cadmium (II) complex(LICd):

A Solution of (0.2 g, 5.9X19^{-4} mole) $Cd(NO_3)_2.3H_2O$ dissolved in (5 ml) of absolute ethanol was added to (0.4g, 1X10^{-3} mole) of LI dissolved in (10 ml) ethanol. The mixture was refluxed with stirring for one hour; The precipitate was filtered and washed with hot ethanol. Melting point, color, and yield (%) are given in Table (3-1)

5) Mercury (II) complex (LIHg):

A Solution of (0.16 g, 5.9X10^{-4} mole) $HgCl_2$ dissolved in (5 ml) ethanol was added to (0.4 g, 1X10^{-3} mole) of LI dissolved in (10 ml) ethanol. The mixture was refluxed with stirring for one hour, the resulting precipitate was filtered and washed with hot ethanol them dried under-vacuum. Melting point, color and yield (%) are given in Table (3-1).

2.4.2 Preparation the metal complexes of the ligand (LII):

1) Cobalt (II) complex (LIICo):

A Solution of (0.14 g, 8X10^{-4} mole) $CoCl_2.2H_2O$ dissolved in (5 ml) ethanol was added to (0.5 g, 2X10^{-3} mole) of LII dissolved in (10 ml) ethanol. The mixture was refluxed with stirring for 30 min, then the precipitate was filtered and washed with hot ethanol then dried under-vacuum, melting point, color and yield (%) are given in Table (3-2).

2) Copper (II) complex (LIICu):

The same procedure as in (2.4.1-1) was followed for the preparation of Co(II) complex. The yield (%) and melting point given in Table (3-2).

3) Nickel (II) complex (LIINi):

A Solution of (0.25 g, 8X10^{-4} mole) $Ni(NO_3)_2.6H_2O$ dissolved in (5 ml) ethanol was added to (0.5 g, 2X10^{-3} mole) of LII dissolved in (10 ml) ethanol. The mixture was refluxed with stirring for one hour, then the precipitate was filtered and washed with hot ethanol then dried under-vacuum, melting point, color and yield (%) are given in Table (3-2).

4) Cadmium (II) complex (LIICd):

A Solution of (0.29 g, 9x10^{-4} mole) $Cd(NO_3)_2.3H_2O$ dissolved in (5 ml) ethanol was added to(0.5 g, 2x10^{-3} mole) of LII dissolved in (10 ml) ethanol. The mixture was refluxed with stirring for one hour, then the precipitate was filtered and washed with hot ethanol then dried then under-vacuum, melting point, color and yield (%) are given in Table (3-2).

2.4.3 Preparation the metal complexes of the ligand (LIII):

1) Copper (II) complex (LIIICu):

A Solution of (0.16 g, 9x10^{-4} mole) $CuCl_2.2H_2O$ dissolved in (5 ml) ethanol was added to (0.5 g, 2x10^{-3} mole) of LIII dissolved in (10 ml) ethanol. The mixture was refluxed with stirring for one hour, the resulting precipitate was filtered and washed with hot ethanol then dried under-vacuum, melting point, color and yield (%) are given in Table (3-3).

2) Nickel (II) complex (LIIINi):

A Solution of (0.27 g, 9x10^{-4} mole) $Ni(NO_3)_2.6H_2O$ dissolved in (5 ml) ethanol was added to (0.5 g, 2x10^{-3} mole) of LIII dissolved in (10 ml) ethanol. The mixture was refluxed with stirring for one hour, then the precipitate was filtered and washed with hot ethanol then dried under-vacuum, melting point, color and yield (%) are given in Table (3-3).

3) Cobalt (II) complex (LIICo):

A Solution of (0.15 g, 9x10^{-4} mole) $CoCl_2.2H_2O$ dissolved in (5 ml) ethanol was added to (0.5 g, 2x10^{-3} mole) of LIII dissolved in (10 ml) ethanol. The mixture was refluxed with stirring for one hour, then the precipitate was filtered and washed with hot ethanol then dried under-vacuum, melting point, color and yield (%) are given in Table (3-3).

4) Cadmium (II) complex (LIIICd):

A Solution of (0.32 g, 8X10^{-4} mole) $Cd(NO_3)_2.3H_2O$ dissolved in (5 ml) ethanol was added to(0.5 g, 2X10^{-3} mole) of LIII dissolved in (10 ml) ethanol. The mixture was refluxed with stirring for one hour, then the precipitate was filtered and washed with hot ethanol then dried then under-vacuum, melting point, color and yield (%) are given in Table (3-3).

Chapter three

Results and Discussion

3.1 Physical properties of the prepared complexes:

Tables (3-1), (3-2) and (3-3) show the physical data for the prepared complexes. The new complexes showed different melting points, some of them were higher than the parent ligand; others were of lower melting points. The colors 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 absolute ethanol as solvent

Identification and study of these complexes were carried out by metal analysis [the result are shown in tables (3-1), (3-2) and (3-3)], infra-red, Ultra-visible spectrophotometer, magnetic susceptibility and electronic conductivity measurements. According to these measurements the chemical formulae of the prepared complexes have been suggested as given in table (3-6).

Table (3-1): Physical properties for LI and its metal complexes.

Complexes	Color	m.p.(C^{o})	Yield (%)	Metal content (%)	
				Calc.	Found
LI	Off white	138-140	89	-	-
LICu(II)	Bright green	129-131	71	8.0	7.7
LINi(II)	Brown	158	66	6.2	6.3
LICo(II)	Greenish-blue	160-162	75	6.4	6.6
LICd(II)	White	150-151	70	12.5	12.0
LIHg(II)	Light gray	190-192	65	20.27	-

Table (3-2): Physical properties for LII and its metal complexes.

Complexes	Color	m.p. (C^{o})	Yield (%)	Metal content (%)	
				Calc.	Found
LII	Light green	233-235	89	-	-
LIICo(II)	Reddish brown	225-227	79	7.3	8.1
LIICu(II)	Green	203-204	60	8.6	7.9
LIINi(II)	Yellowish-green	245	80	7.4	7.8
LIICd(II)	Brown	249-251	72	20.8	21.1

Table (3-3): Physical properties for LIII and its metal complexes.

Complexes	Color	m.p. (C^{o})	Yield (%)	Metal content (%)	
				Calc.	Found
LIII	Off-white	248-250	70	-	-
LIIICu(II)	Dark green	162-163	70	9.0	9.5
LIIINi(II)	Deep green	230(dec)	65	7.6	7.4
LIIICo(II)	Yellow	240-242	81	8.4	9.0
LIIICd(II)	Light brown	234-235	75	20.0	19.6

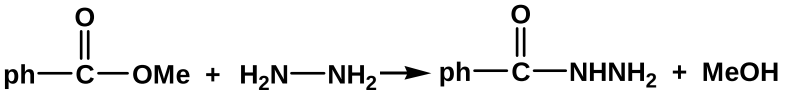
3.2 Infra-Red Spectral study:

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

3.2.1 The F.T.IR spectra of LI and its metal complexes:

3.2.1.A The infrared spectra of Acid hydrazides:

Benzoyl hydrazine was prepared by the reaction of appropriate ester with hydrazine hydrate as shown in equation (3-1).



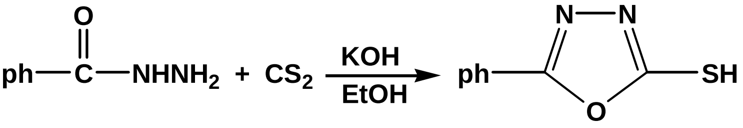
$$ph-\overset{\overset{O}{\|}}{C}-OMe + H_2N-NH_2 \longrightarrow ph-\overset{\overset{O}{\|}}{C}-NHNH_2 + MeOH$$

.....equation (3-1)

The IR spectrum of this compound Figure (3-1) show the amide bands at (3298 and 3203cm^{-1}) of asymmetric and symmetric N-H stretching of (NH_2) group .There is another stretching band around (1661 cm^{-1}) assigned to the amide carbonyl group. Also, the sharp band appeared around (1450cm^{-1}) is due to the combination band of (C-N) stretching and (C-H) bending .The band at (3018cm^{-1}) is due to the aromatic ν(C-H) and the other stretching band around (1566cm^{-1}) can be assigned to the ring ν(C=C). The mono substituted benzene absorption appeared at (682cm^{-1})(68).

3.2.1.B The infrared spectrum of 5-phenyl -1, 3, 4 -oxadiazole-2-thiol:

The titled compound way prepared through the reaction of benzoyl hydrazide with carbon disulfide in the presence of potassium hydroxide in absolute ethanol, equation (3-2).

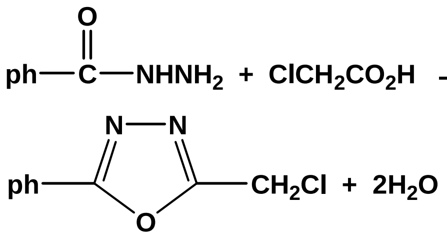


.....equation (3-2)

The I.R spectrum of this compound, Figure (3-2), displayed an absorption band at (1604 cm^{-1}) assigned to (C=N) stretching, a band in the range (1292-1069 cm^{-1}) assigned for (C-O-C) asymmetric and symmetric cyclic grouping in oxadiazole are a good evidence for the presence of 1, 3, 4-oxadiazole ring , and a nother bands at (1350 cm^{-1}) and (3143 cm^{-1}) due to (C=S) and (N-H) stretching vibrations respectively .The presence of peak at (2580 cm^{-1}) established the existance of the thiol form in the solid state.

3.2.1.C The infrared spectrum of 5-phenyl-2-chloro methyl-1, 3, 4-oxadiazole:

The titled compound was prepared through the reaction of benzoyl hydrazide with chloroaceticacid in the presence of phosphorous oxychloride, equation (3-3).



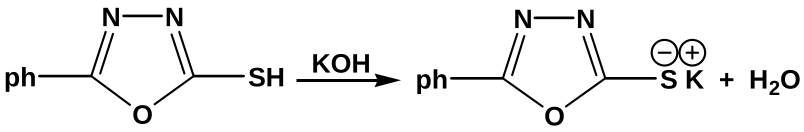
.....equation (3-3)

The IR spectrum of this compound, Figure (3-3), shows absorption band at (1680 cm^{-1}) assigned to (C=N) stretching a band in the range (1244- 1016 cm^{-1}) was observed, which is due to (C-O-C) cyclic grouping in oxadiazole ring.

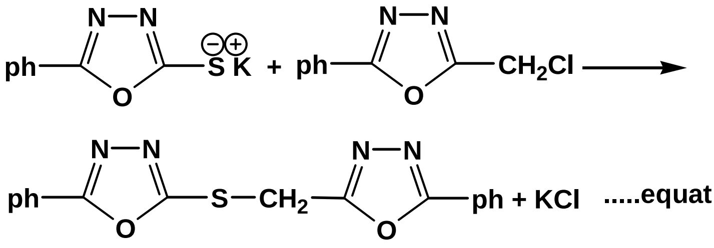
The I.R spectrum also displayed a band at (2856 cm^{-1}) due the aliphatic (C-H) stretching and also showed the band in the region (1548 cm^{-1}) due to (C=C) stretching.

3.2.1.D The infrared spectrum of 2-[5-phenyl-2-methylthio-1,3,4-oxadaizole]-5-phenyl-1,3,4- oxadiazole (LI):

LI was prepared via the reaction of potassium salt of 5-phenyl-2-mercapto-1,3,4-oxadiazole with 5-phehyl-2-chloro methyl-1,3,4-oxadiazole as seen in equations (3-4) and (3-5).



.....equation (3-4)



.....equation (3-5)

The I.R spectrum, Figure (3-4), table (3-4) show the appearance of (C-H) absorption band at (2927 cm^{-1}) which was utilized to confirm the formation of alkylthio derivative. The spectrum showed the disappearance of the band at (2580 cm^{-1}) assigned to (S-H) stretching and appearance of a band at (1353 cm^{-1}) due to (C=S) stretching, and a bands at (1076 cm^{-1}) due to (C-S) stretching also the spectrum showed at typical absorptions of oxadiazole ring endo cyclic (C-O-C) at (1280 cm^{-1}) and absorption band of ν(C=N) near (1617 cm^{-1}).

3.2.2 The infrared spectra of LI complexes:

A) Cadmium (II) complex (LI Cd):

The spectrum of (LI Cd) complex, Figure (3-5), Table (3-4), show the shifiting of ν(C=N) band to lower frequency by (14) cm^{-1}) and appeared at (1603 cm^{-1}) indicating the participation of nitrogen in the coordinate with cadmium (II) ion.

The broad band found in the region (3000-3600 cm^{-1}) refers to the presence of water molecules out of the coordination sphere. The band at (559 cm^{-1}) can be attributed to ν (Cd-N)$^{(68)}$.

The bands related to the uncoordinated nitrate ion were found at (1448, 1247 and 1097 cm $^{-1)}$ $^{(68)}$

B) Cobalt (II) complex (LI Co):

The Figure (3-6), Table (3-4), show the FT. I.R spectrum of cobalt (II) complex. The appearance of a band near (1610 cm^{-1}) assigned to ν(C=N) band of oxadiazole moiety. The presence of new weak band observed at (563 cm^{-1}) have been assigned to ν (Co-N) (68).

C) Mercury (II) complex (LI Hg):

Mercury (II) ion is known to have different geometrical shapes ranging from linear to tetrahedral or octahedral(69).

For octahedral complexes the shape is distorted with two bonds much shorter than the otherfor, which can some times regarded as linear complex(70).

In this work a mercury (II) complex (LI Hg), Figure (3-7) ,Table (3-4), was prepared and characterized by the shift of ν(C=N) bond to a lower frequency by (17 cm^{-1}) and appeared at (1600 cm^{-1}) . The coordination took place through nitrogen atom present in ligand LI with mercury (II) ion, the band at (550 cm^{-1}) can be attributed to ν(Hg-N)(68). The band appeared at (3650 cm^{-1}) refer to the presence of uncoordinated ethanol molecule in the structure.

D) Nickel (II) complex (LI Ni):

The I.R spectrum of (LI Ni) complex ,figure (3-8), Table (3-4), shows the shifting of ν(C=N) to lower frequency by (13) cm^{-1} and appeared at (1604 cm^{-1}). The observation at (545 cm^{-1}) indicated the participation of nitrogen in the complex (Ni-N)(68). A broad band found in the region (3200-3600 cm^{-1}) and another medium sharp band at (736 cm^{-1}) indicate the presence of both coordinating and lattice H_2O molecules in the structure of (LI Ni) complex.

The bands related to the free nitrate ion were found at 1014, 1267, 1450 cm^{-1},and the observation at (470 cm^{-1}) indicated the participation of oxygen in the complex (Ni-OH_2) (68) .

F) Copper (II) complex (LI Cu):

The most significant difference in the I.R spectra of the ligand and its copper complex, Figure (3-9), Table (3-4), show the shifting of C=N stretching frequency of the oxadiazole ring of LI to lower frequency due to coordinating of the metal to the nitrogen of oxadiazole ring and appeared at (1611cm^{-1}). The band at (599 cm^{-1}) can by assigning to ν(Cu-N)(68).

The band found in the region (3440 cm^{-1}) refers to the presence water molecules out of the coordination sphere (71).

3.3 The FT. I.R spectra of LII and it's metal complexes:

The ligand (LII) containing the azomethine group. In general azomethine group (-C=N-) absorption occurs in the region (1690-1470)cm^{-1} depending on the nature of group linked to it(24,42) the compound containing azomethine group shows basic coordinating behavior toward metal ions coordinating via the nitrogen atoms. This coordination shifts the stretching frequency of (-C=N-) group either toward higher frequency in some complexes (54,72,73), or toward lower frequency in other(74, 75).

The increase in frequency may be due to the simultaneous strengthening of the (-C=N-) band 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 (72). 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 (76, 77).

The IR spectrum of the ligand LII, Fig (3-10), Table (3-4) showed appeared of the band at 3326 cm^{-1} due to the (N-H) stretching vibration (78), and a strong new band appeared at 1630cm^{-1} assigned to azomethine ν(HC=N) linkage, showing that amino and aldehydes moieties of the starting material were reacted and have been converted into the azomethine group(79). The bands appeared at 1574 and 1475 cm^{-1} refer to ν(C=C) of aromatic ring, and the band at 3063 cm^{-1}refer to ν(C-H) of aromatic ring.

A) Cadmium (II) complex (LII Cd):

The spectrum of (LIICd) complex, Figure (3-11), Table (3-4), show the shifting of the azomethine band to a lower frequency by (12) cm^{-1} indicating the participation of azomethine nitrogen in the interaction with the cadmium (II) ion. The presence of new weak band observed at (588) cm^{-1} was assigned as ν(Cd-N) (68). The broad band appeared at (3449) cm^{-1} in the spectra of Cd (II) complex indicated the presence of lattice water molecule in (LII Cd) complex. The bands appeared at (1444, 1371, and 1224) cm^{-1} refered to monodentate nitrate group (68). The presence of weak band observed at (428) cm^{-1} was assigned as ν(Cd-ONO_2) (68) .

B) Cobalt (II) complex (LII Co):

The spectrum of Co(II) complex (LII Co), Figure (3-12), Table (3-4), show the azomethine band shifted to lower frequency and appeared at (1616)cm^{-1}.This indicated the participation of azomethine in complexation. The weak band at (594) cm^{-1} refers to the ν (Co-N) band (68).

C) Nickel (II) complex (LII Ni):

The IR spectrum of (LII Ni) complex, Figure (3-13), Table (3-4), show the shifting of azomethine band to lower frequency and appeared at (1620) cm^{-1}.This indicated the participation of azomethine-nitrogen, with Ni (II) ion. The band at (550) cm^{-1} can be attributed to ν(Ni-N) (68).

A broad band appeared at (3448) cm^{-1} indicating the presence of uncoordinated water molecule in the structure, and the observation at (428cm^{-1}) indicated the participation of oxygen in the complex (Ni-ONO_2)(68) .

The new bands appeared at (1452, 1363 and 1274) cm^{-1} refer to a monodentate nitrate group(68).

D) Copper (II) complex (LII Cu):

The spectrum of copper (II) complex, Figure (3-14), Table (3-4) show the azomethine band stretching at (1610 cm^{-1}) with highly reduced intensity, this indicates the involvement of azomethine nitrogen in coordination.

The band at (574 cm^{-1}) can be assigned as ν(Cu-N)(68). A broad band appeared at (3473 cm^{-1}) indicating the presence of lattice water molecule in the structure.

3.4. The FT-IR spectra of LIII and it`s metal complexes:

The IR spectrum of LIII, Figure (3-15), Table (3-4), show the same behavior of LII which contain the same group (azomethine) which is used to characterize the spectra of the complexes. The azomethine band appeared at (1626 cm^{-1}) and the band at (3341 cm^{-1}) refers to the (N-H) stretching vibration.

The band appear at (1571cm^{-1}) refers to ν (C=C) of aromatic ring, and the band appeared at (3099 cm^{-1}) refers to the ν (C-H) aromatic ring.

The broad band at (3463 cm^{-1}) assigned to the ν (O-H) in para position of aromatic ring. Medium to strong intensity band appear at (1261 cm^{-1}) which may be assigned to the phenolic (C-O) stretching mode.

A) Cadmium (II) complex (LIII Cd):

The I.R spectrum of (LIII Cd) complex, Figure (3-16), Table (3-4), shows the shifting of ν(C=N) to lower frequency by (14cm^{-1}) and appeared at (1612 cm^{-1}). The presence of new weak band observed at (545 cm^{-1}) can be assigned to ν (Cd-N) (68), and another weak band observed at (491 cm^{-1}) indicated the participation of oxygen in the complex (Cd-ONO$_2$) (68).

A broad band which appeared at (3446 cm^{-1}) and another medium sharp band at (703 cm^{-1-}) indicate the presence of both coordinating and lattice water molecules in the structure of (LIII Cd) complex. The bands appeared at (1473, 1287 and 1081 cm^{-1}) refer to the presence of uncoordinate nitrate group.

B) Cobalt (II) complex (LIII Co):

The spectrum of (LIII Co) complex, Figure (3-17), Table (3-4), show the shifting of the azomethine stretching band to a lower frequency by (20 cm^{-1}) indicating the participation of azomethine nitrogen in the coordination with the cobalt (II) ion.

The appearance of new weak band at (526 cm^{-1}) can be assigned to ν (Co-N) (68).

A broad band which appeared at (3490 cm^{-1}) indicates the presence of uncoordinated water molecule in the structure of the complex.

C) The spectrum of (LIII Ni):

The spectrum of (LIII Ni) complex, Figure (3-18), Table (3-4), show the shifting of the azomethine stretching to a lower frequency by (10 cm^{-1}) indicating the participation of azomethine nitrogen in the interaction with the nickel (II) ion. The presence of new weak band observed at (597 cm^{-1}) was assigned to ν (Cd-N), and appearance of new weak band at (~430 cm^{-1}) can be assigned to ν ($Ni-OH_2$) (68).

The bands related to the free nitrate ion were found at (1448, 1247 and 1018 cm^{-1})(68).

The bands at (3452 and 639 cm^{-1}) refer to the presence of both coordinated and lattice water molecules.

D) Copper (II) complex (LIII Cu):

The I.R spectrum of (LIII Cu) complex, Figure (3-19), Table (3-4), shows the shifting of ν (C=N) to a lower frequency by (22 cm^{-1}) and appeared at (1608 cm^{-1}). The appearance of weak band (628 cm^{-1}) indicating the presence of coordinated water molecules in the structure.

The presence of new weak band observed at (558 cm^{-1}) was assigned to ν (Cu-N)(68), and appearance of new weak band at (~410 cm^{-1}) can be assigned to ν ($Cu-OH_2$) (68).

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

Complexes	**ν(C-H) aromatic**	**ν(C-H) aliphatic**	**ν (C=N)**	**ν(M-N)**	**ν(M-O)**
LI	**3010**	**2927**	**1617**	**-**	**-**
LI Cd	**3058**	**2851** **2934**	**1603**	**559**	**-**
LI Co	**3030**	**2858** **2937**	**1610**	**563**	**-**
LI Hg	**3020**	**2885**	**1600**	**550**	**-**
LI Ni	**3062**	**2850** **2937**	**1604**	**545**	**470**
LI Cu	**3078**	**2921**	**1611**	**599**	**-**
LII	**3062**	**-**	**1630**	**-**	**-**
LII Cd	**3033**	**-**	**1618**	**588**	**428**
LII Co	**3058**	**-**	**1616**	**594**	**-**
LII Ni	**3031**	**-**	**1620**	**550**	**428**
LII Cu	**3064**	**-**	**1610**	**574**	**-**
LIII	**3099**	**-**	**1626**	**-**	**-**
LIII Cd	**3033**	**-**	**1612**	**545**	**491**
LIII Co	**3075**	**-**	**1606**	**526**	**-**
LIII Ni	**3066**	**-**	**1610**	**597**	**~430**
LIII Cu	**3044**	**-**	**1608**	**558**	**~410**

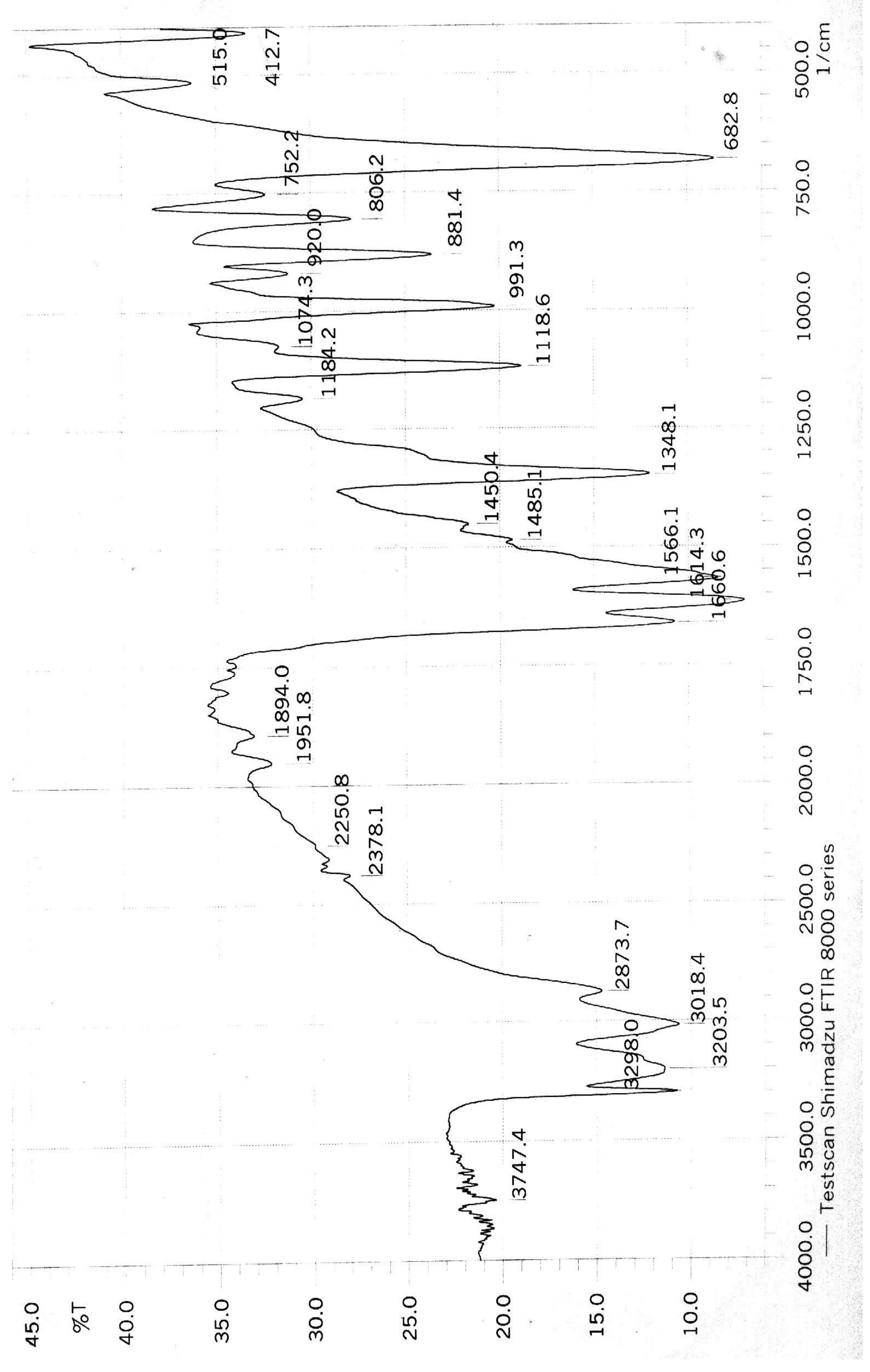


Figure (3-1): F.T.IR spectrum of acid hydrazide.

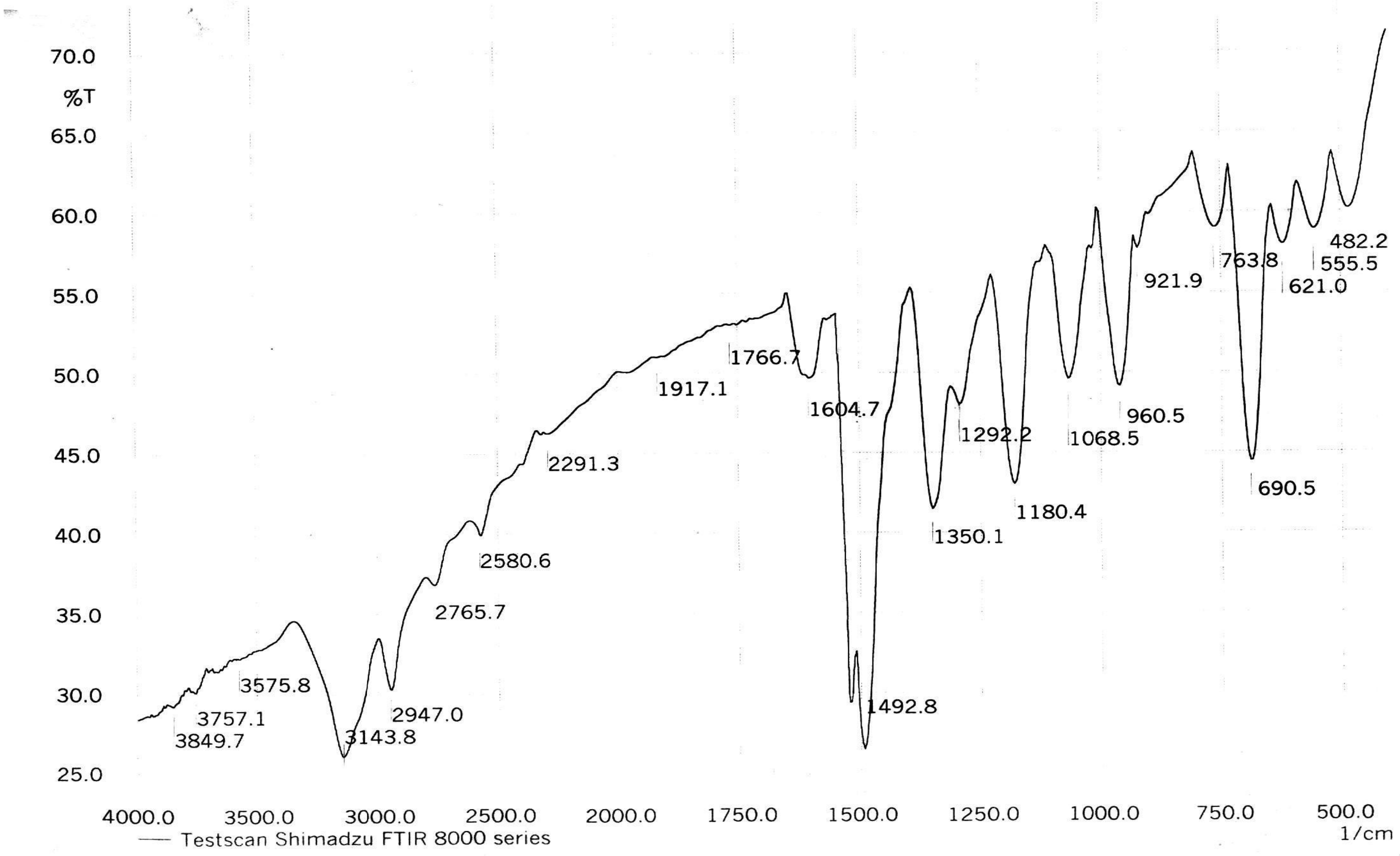


Figure (3-2): F.T.IR spectrum of 5-phenyl-1,3,4-oxadiazole-2-thiol [2].

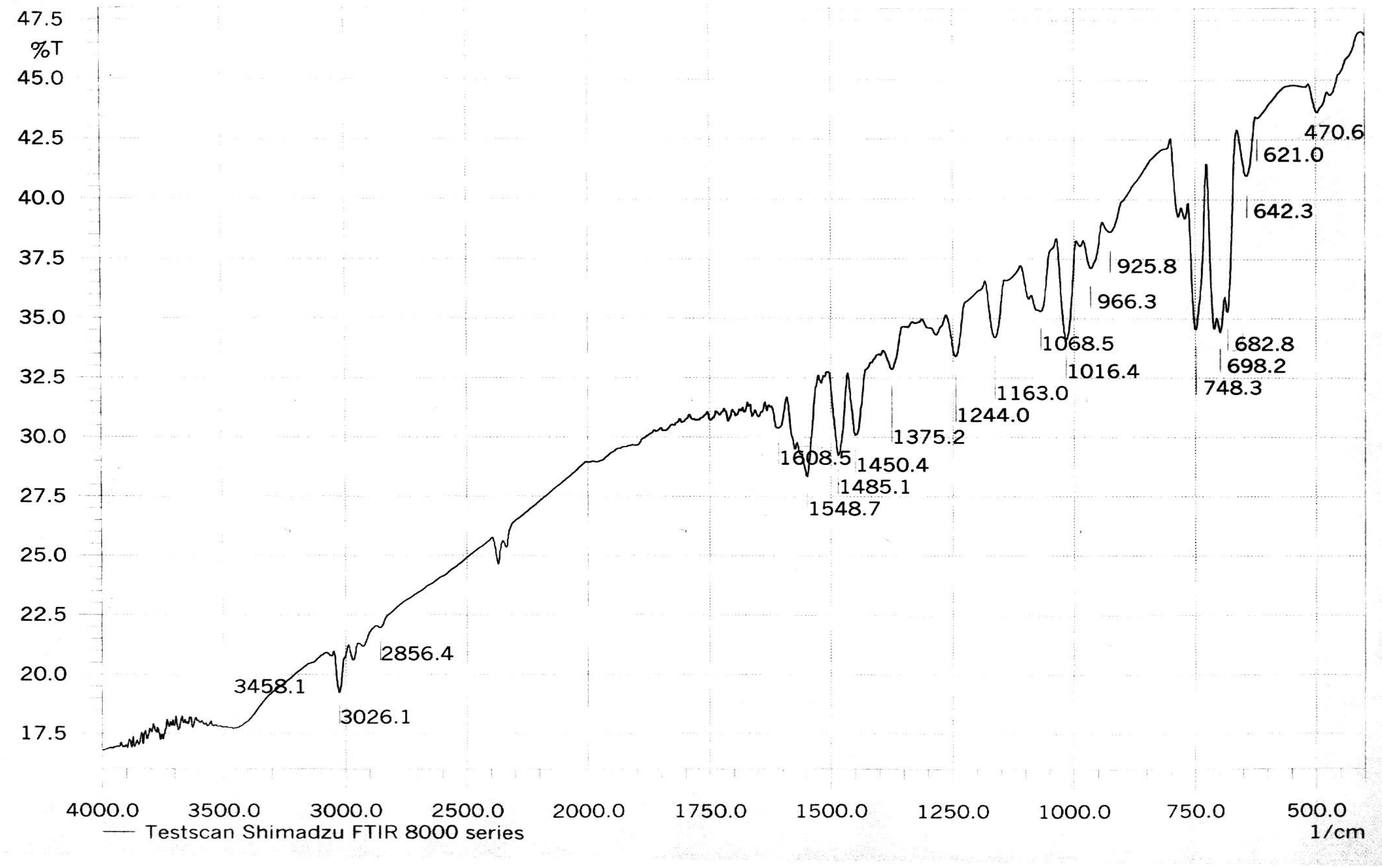


Figure (3-3): F.T.IR spectrum of 5-(phenyl)-2-chloromethyl-1,3,4-oxadiazole [3].

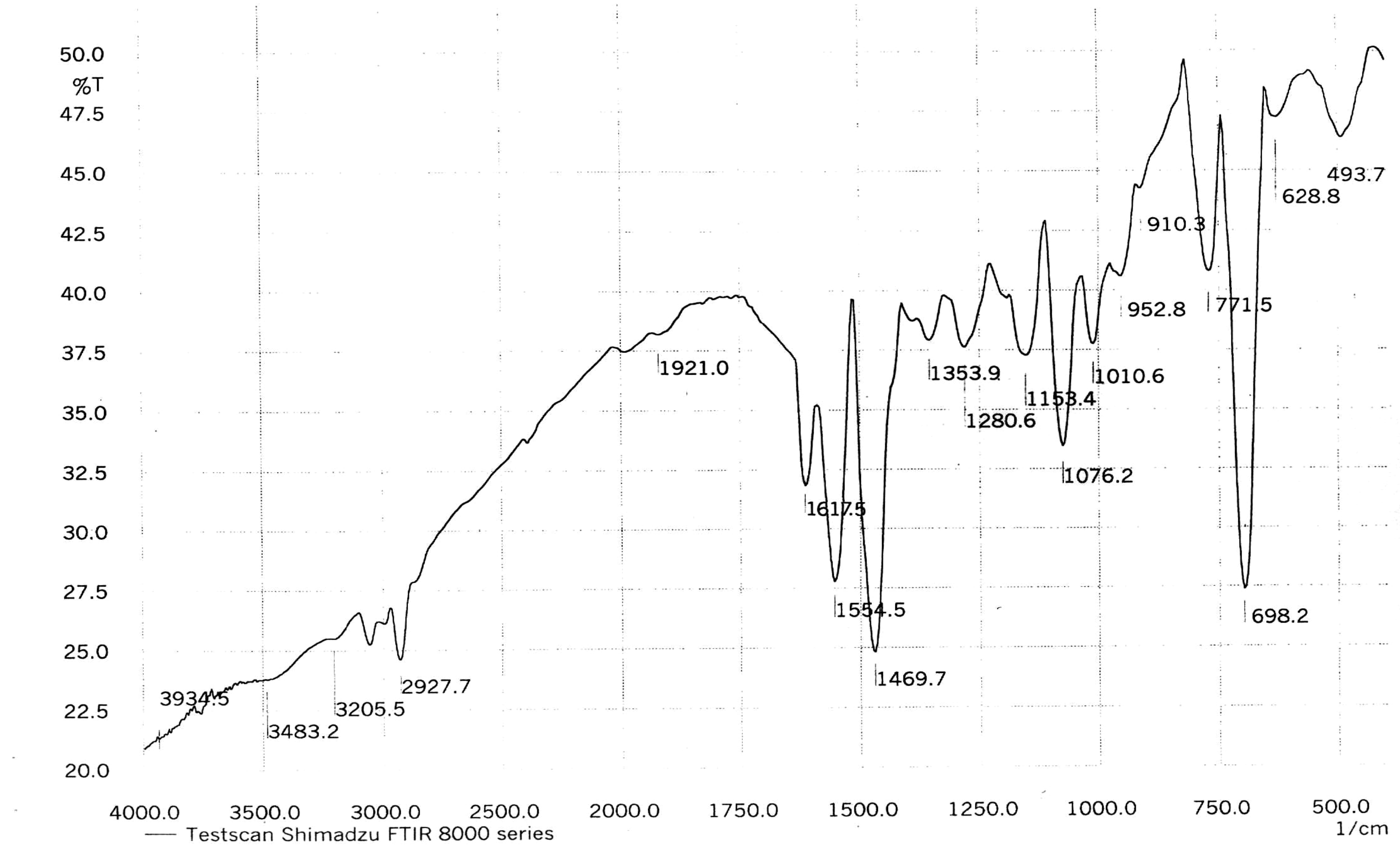


Figure (3-4): F.T.IR spectrum of LI.

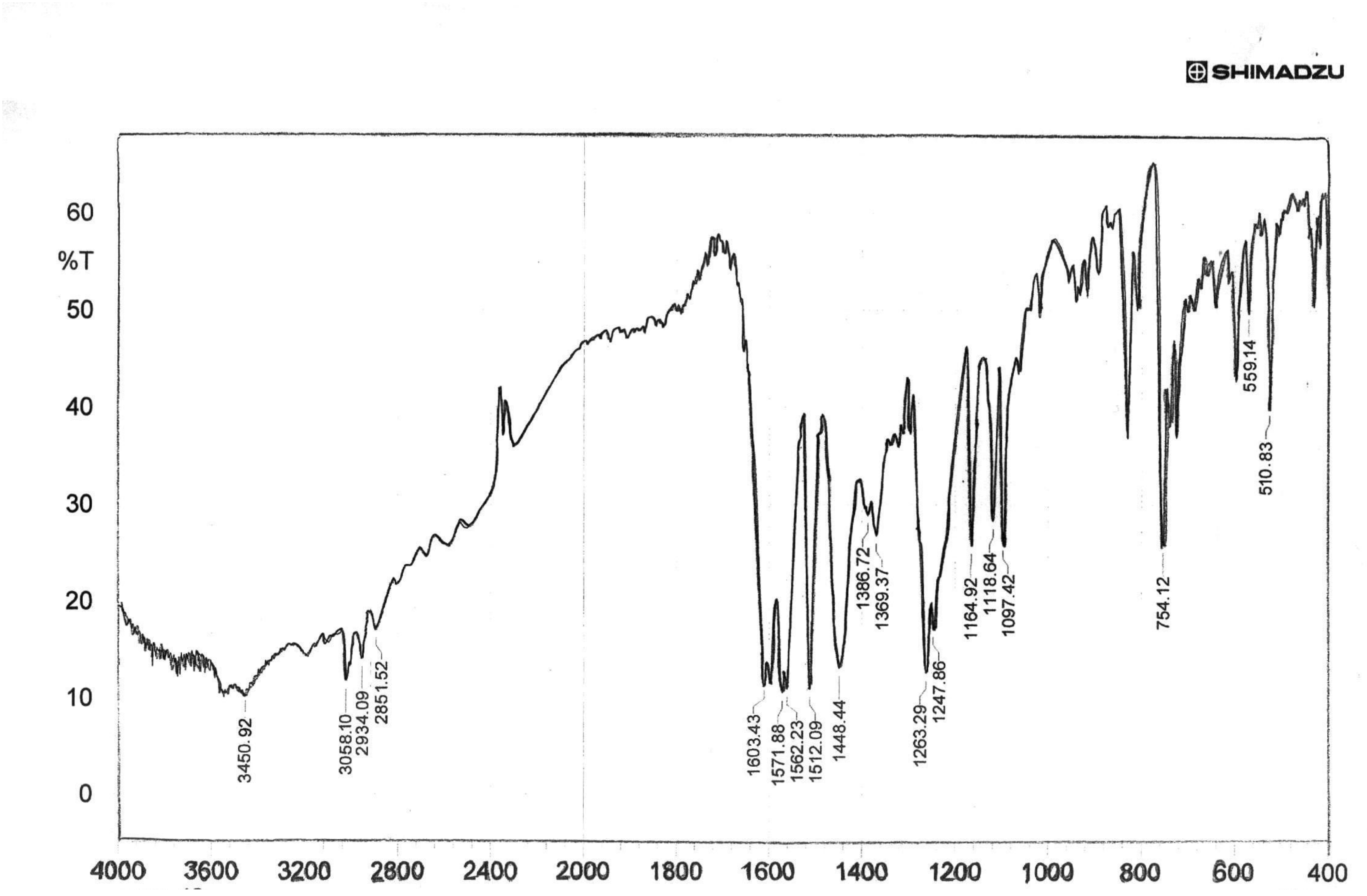


Figure (3-5): F.T.IR spectrum of LICd.

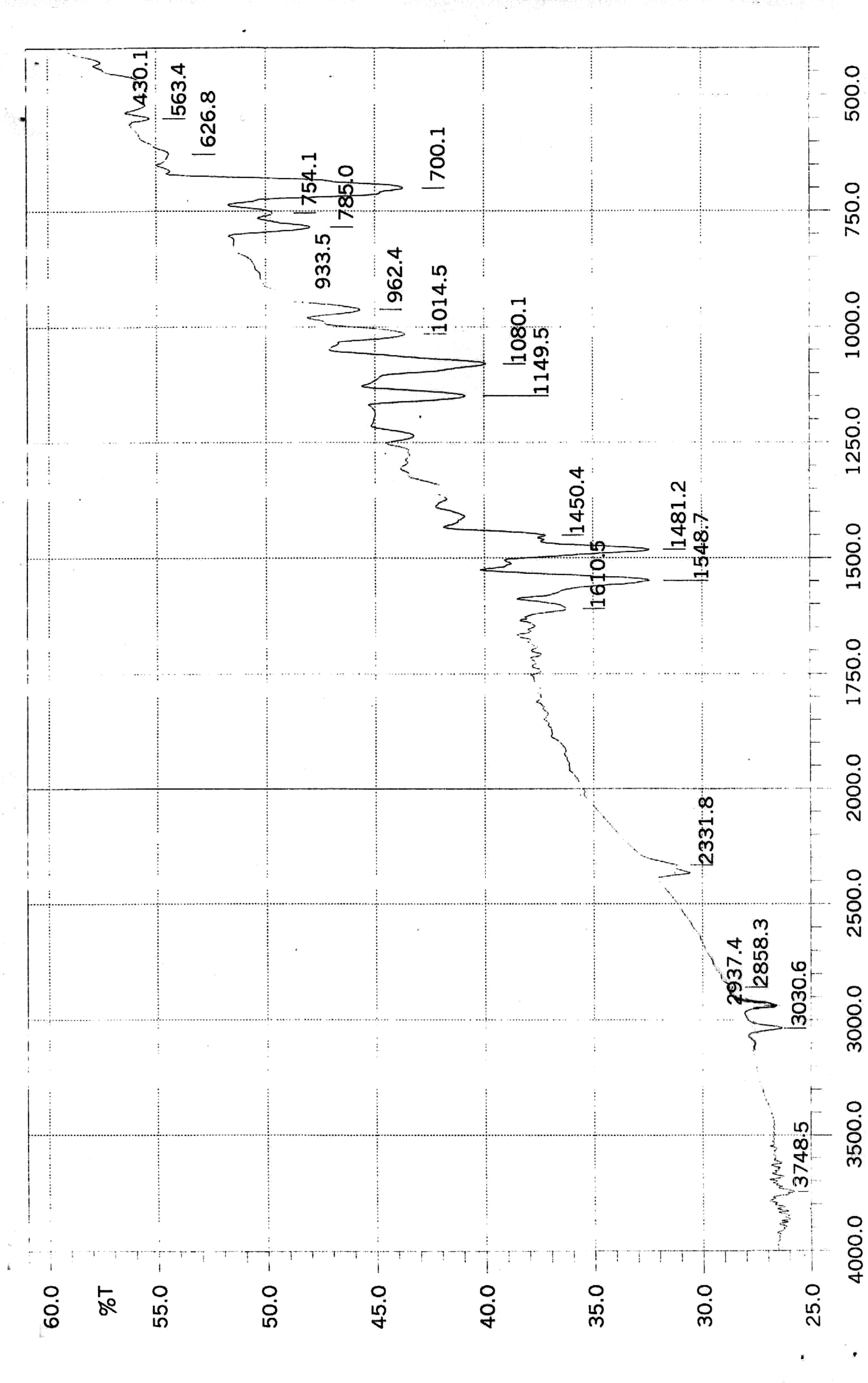


Figure (3-6): F.T.IR spectrum of LICo.

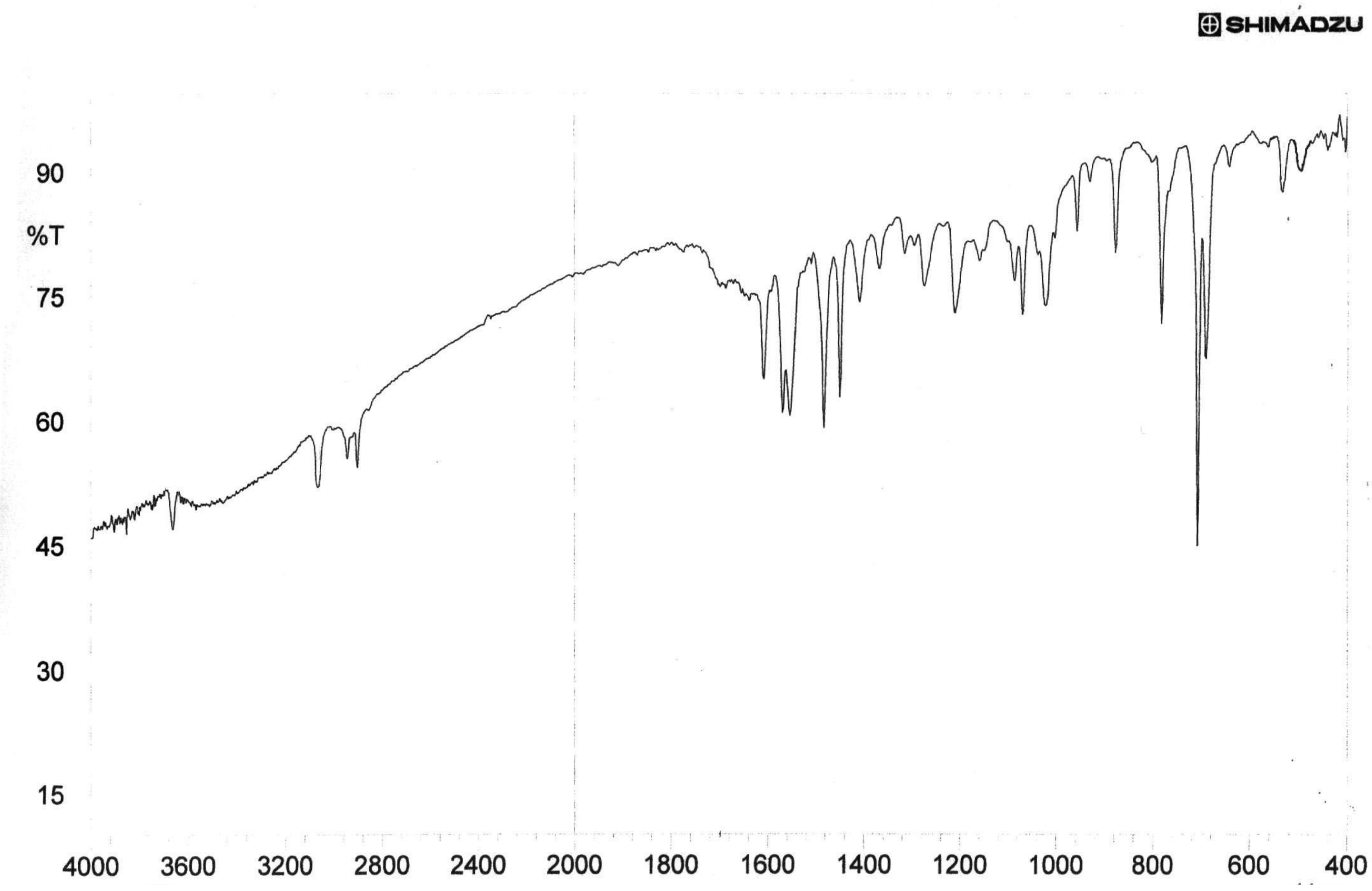


Figure (3-7): F.T.IR spectrum of LIHg.

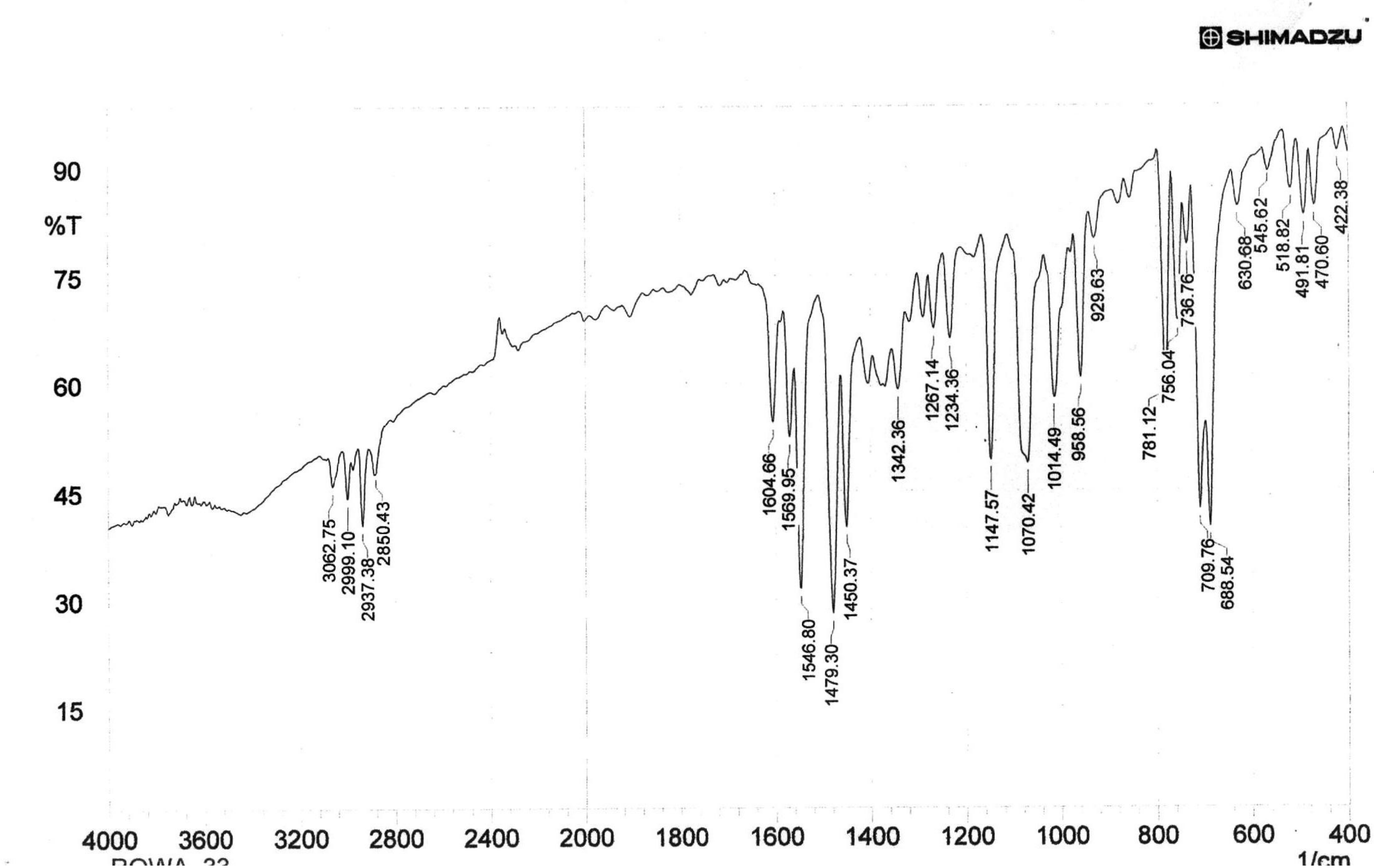


Figure (3-8): F.T.IR spectrum of LINi.

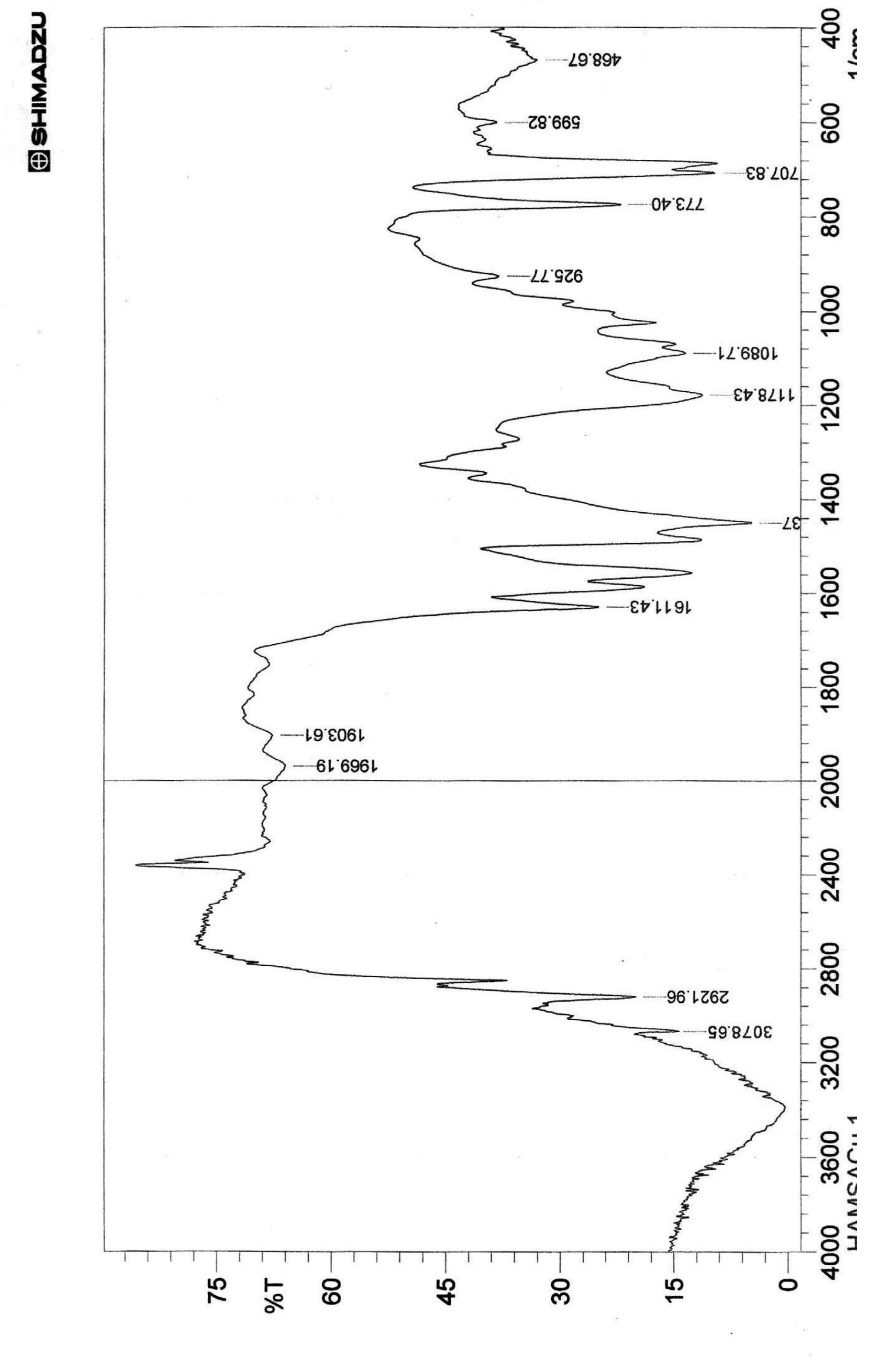


Figure (3-9): F.T.IR spectrum of LICu.

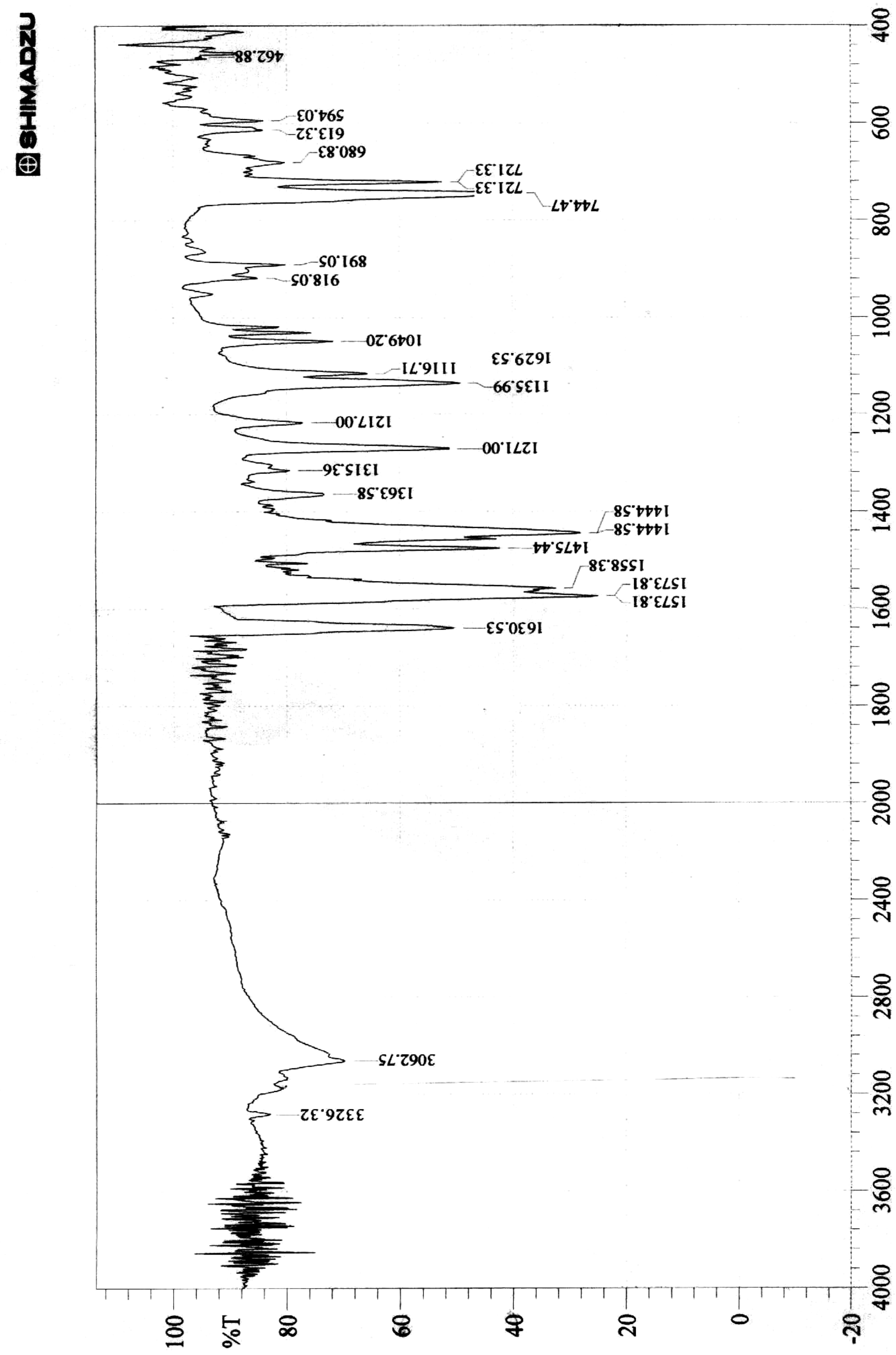


Figure (3-10): F.T.IR spectrum of LII.

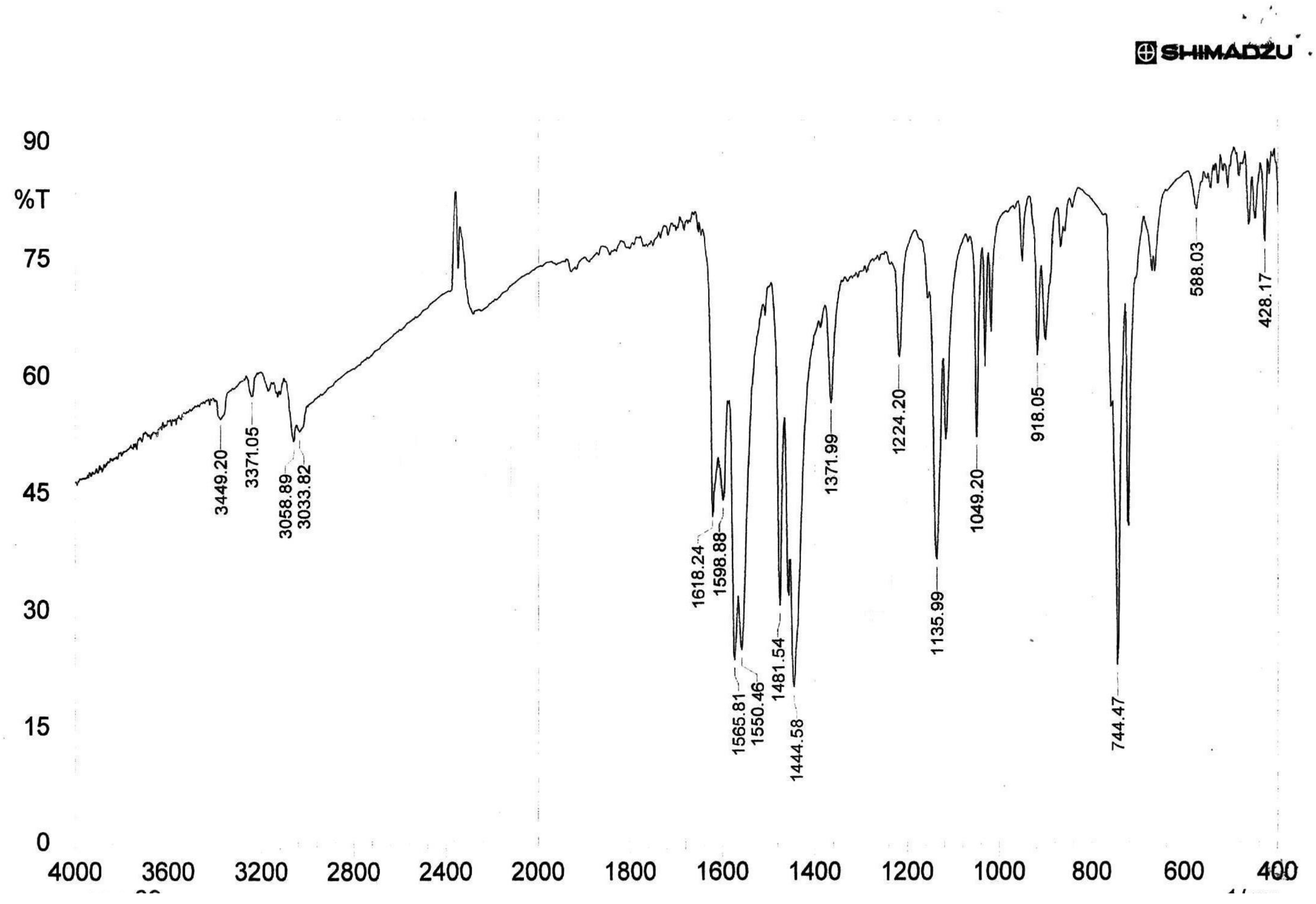


Figure (3-11): F.T.IR spectrum of LIICd.

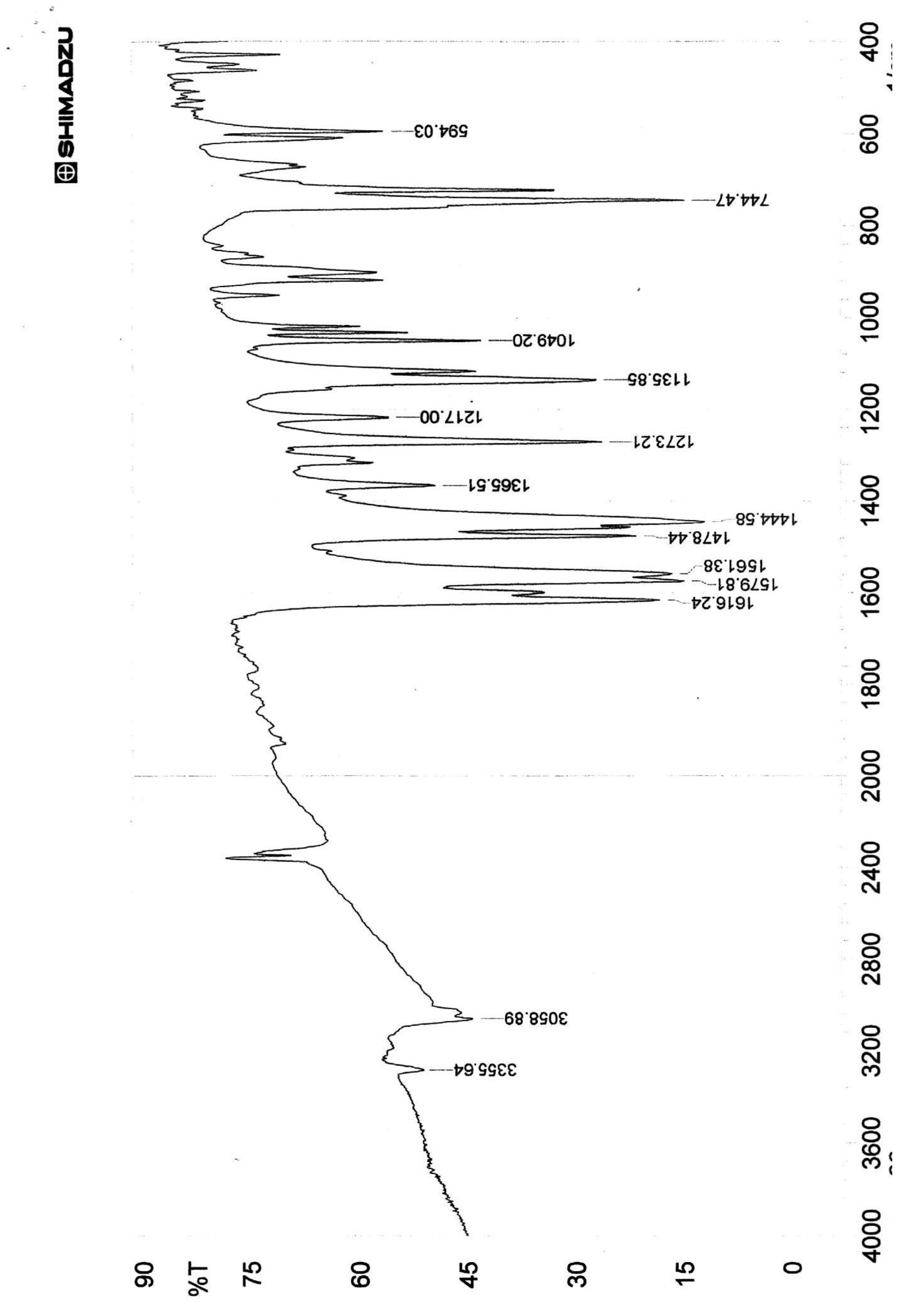


Figure (3-12): F.T.IR spectrum of LIICo.

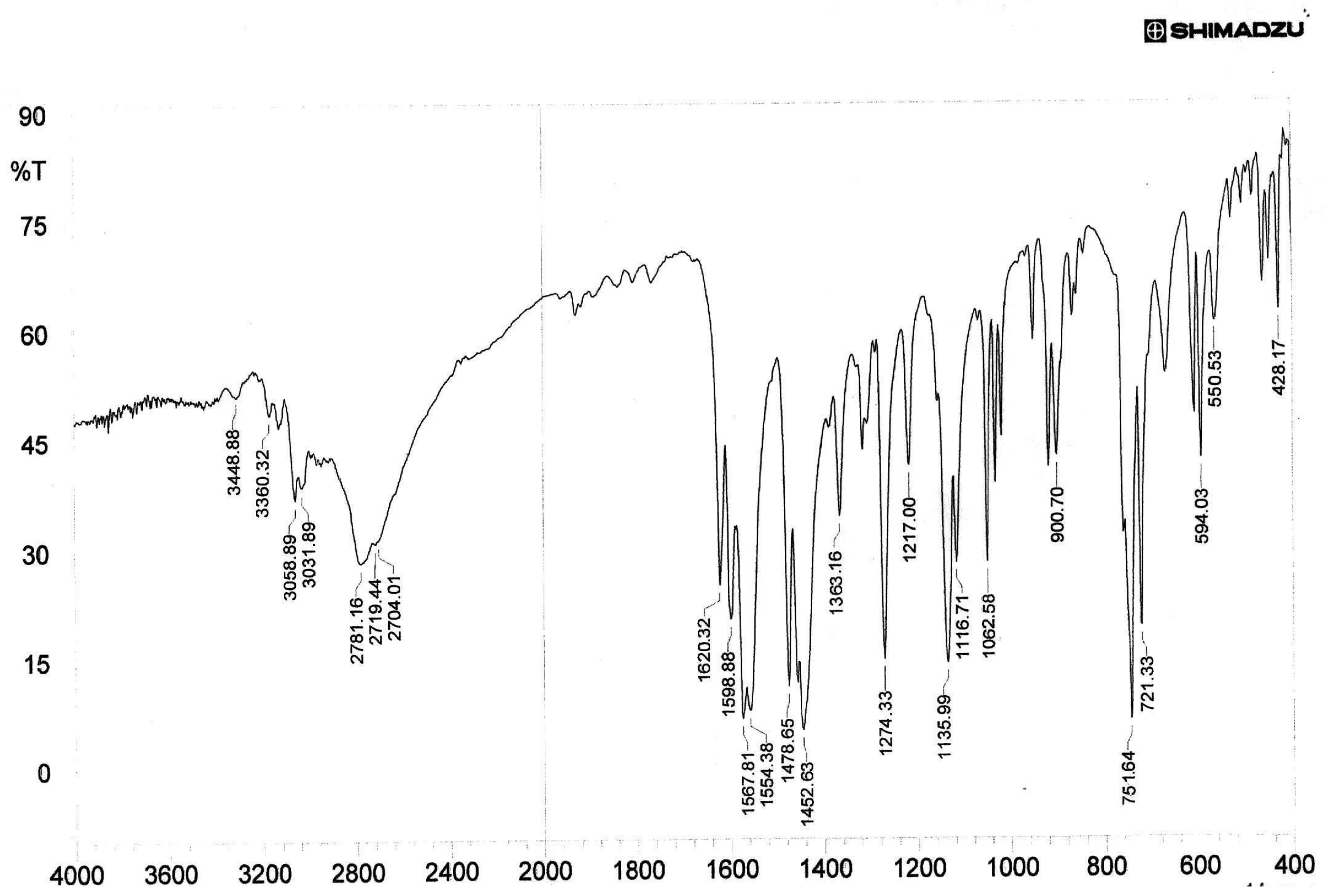


Figure (3-13): F.T.IR spectrum of LIINi.

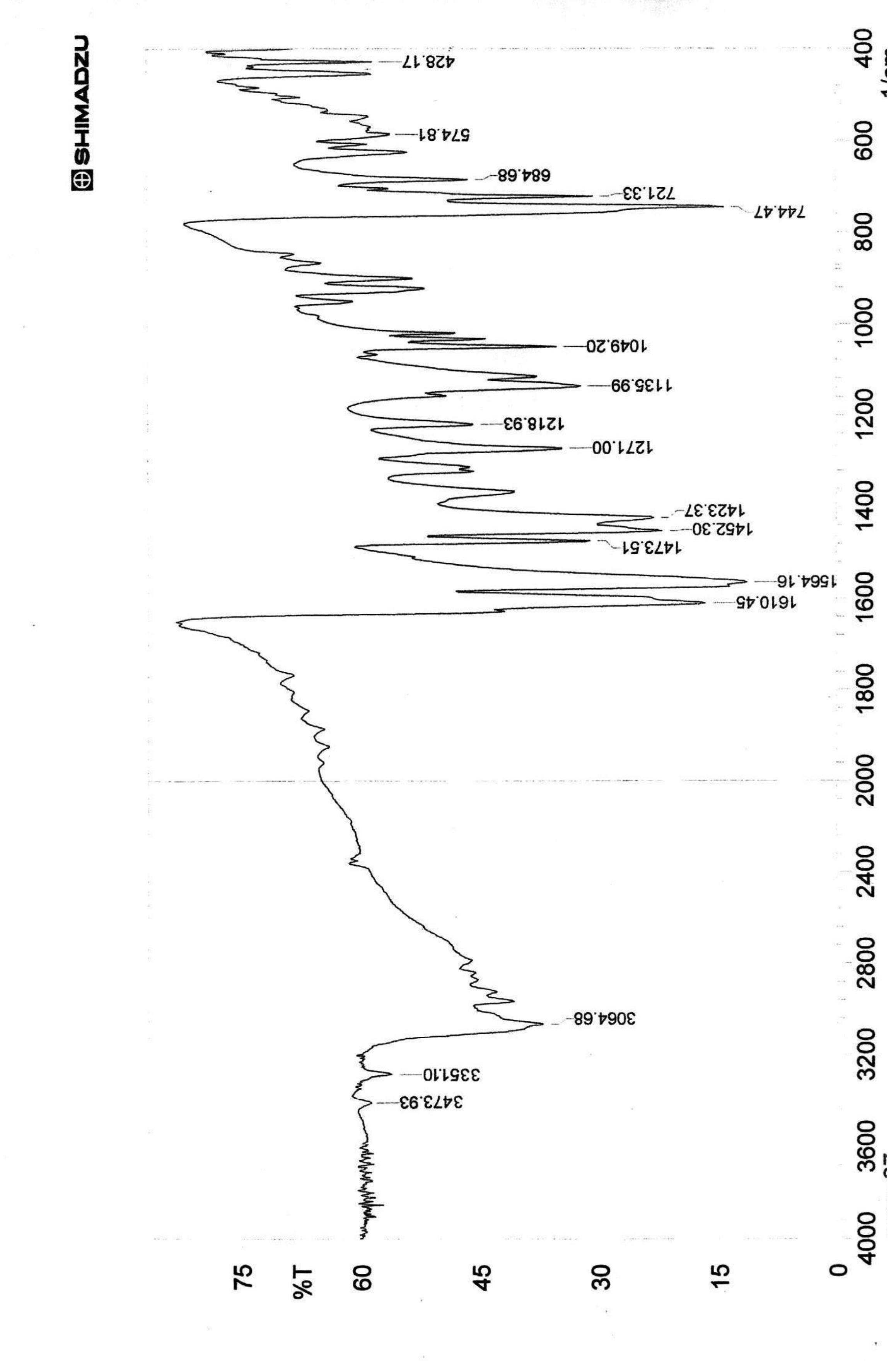


Figure (3-14): F.T.IR spectrum of LIICu.

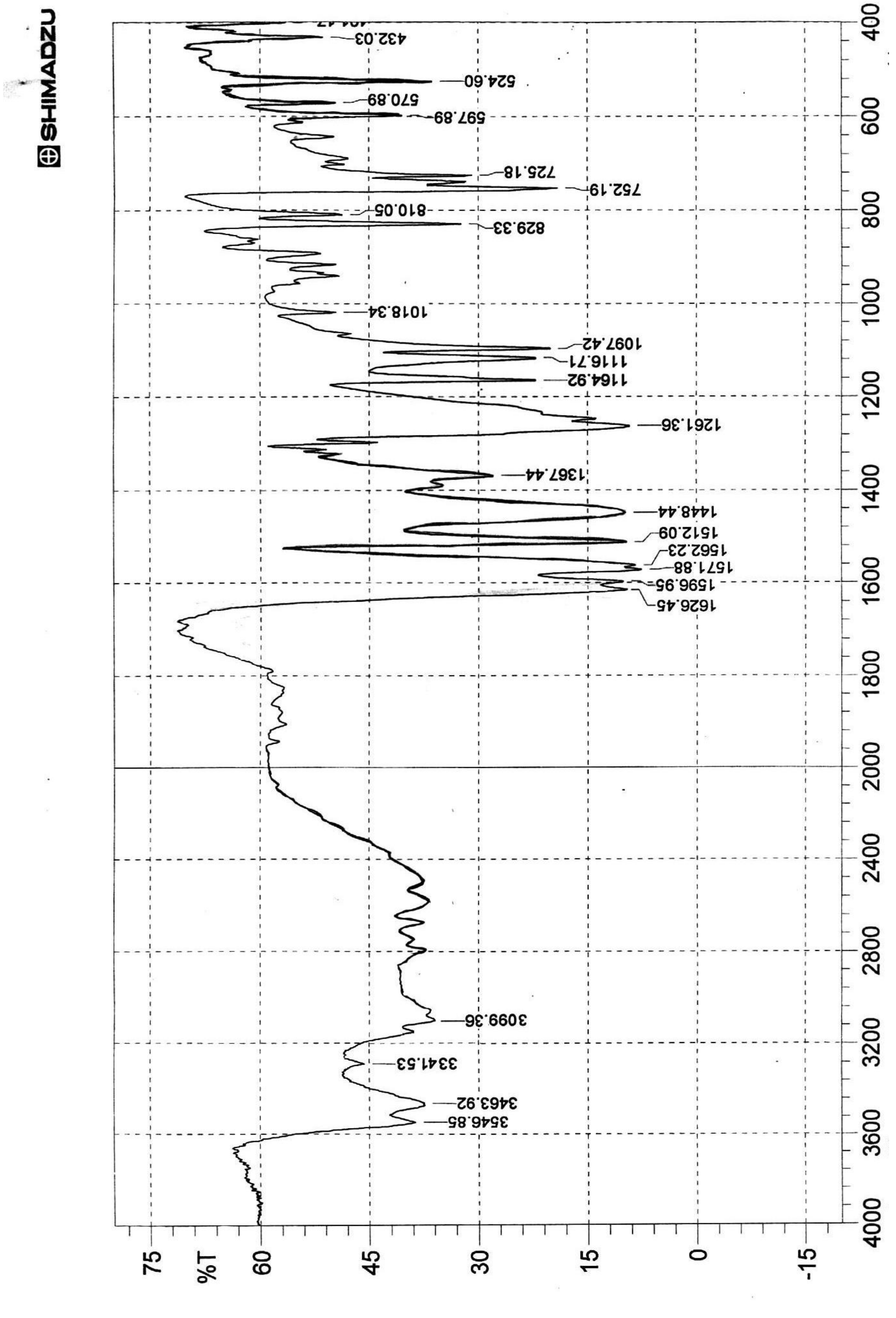


Figure (3-15): F.T.IR spectrum of L.III.

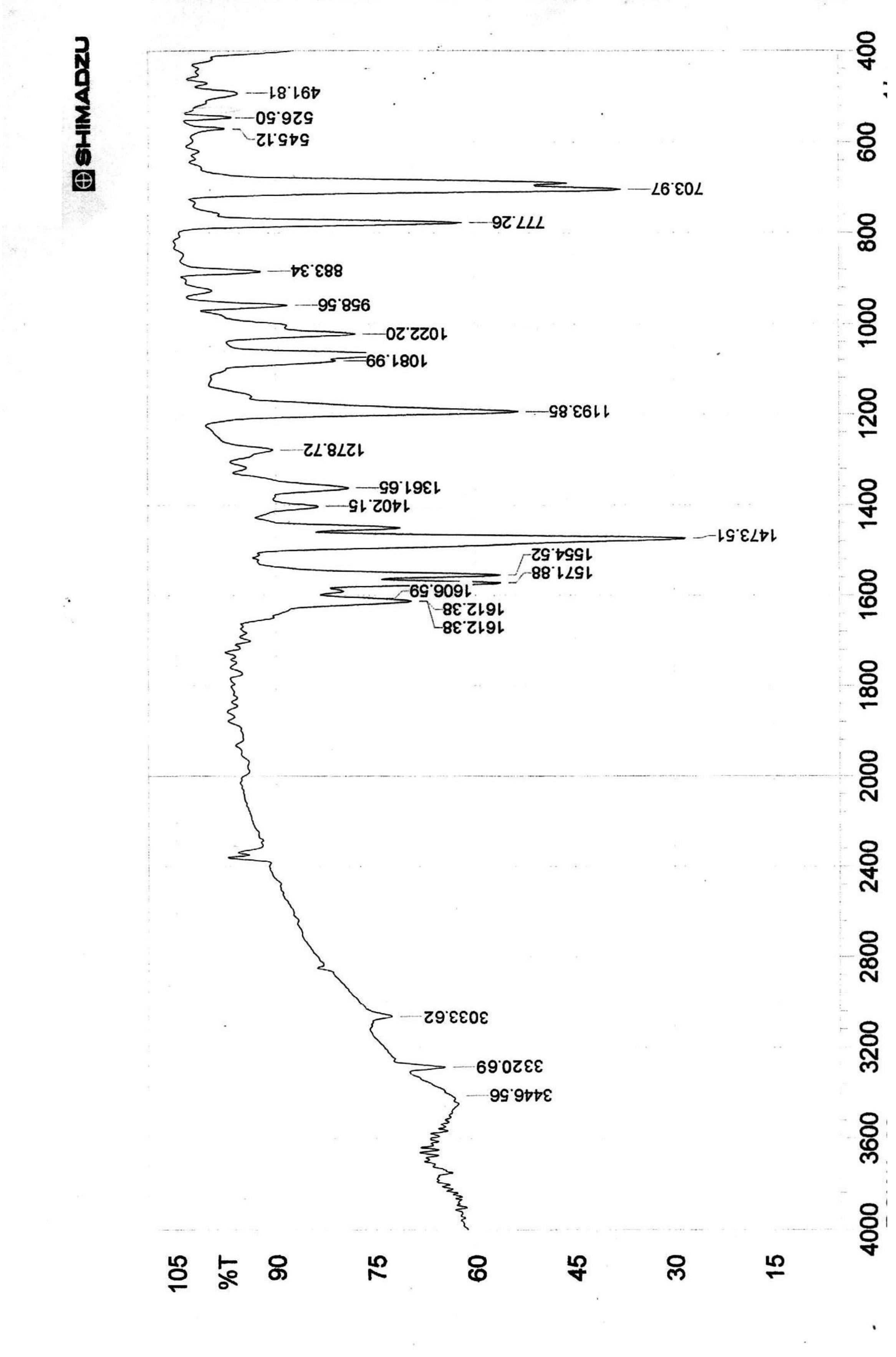


Figure (3-16): F.T.IR spectrum of LIIICd.

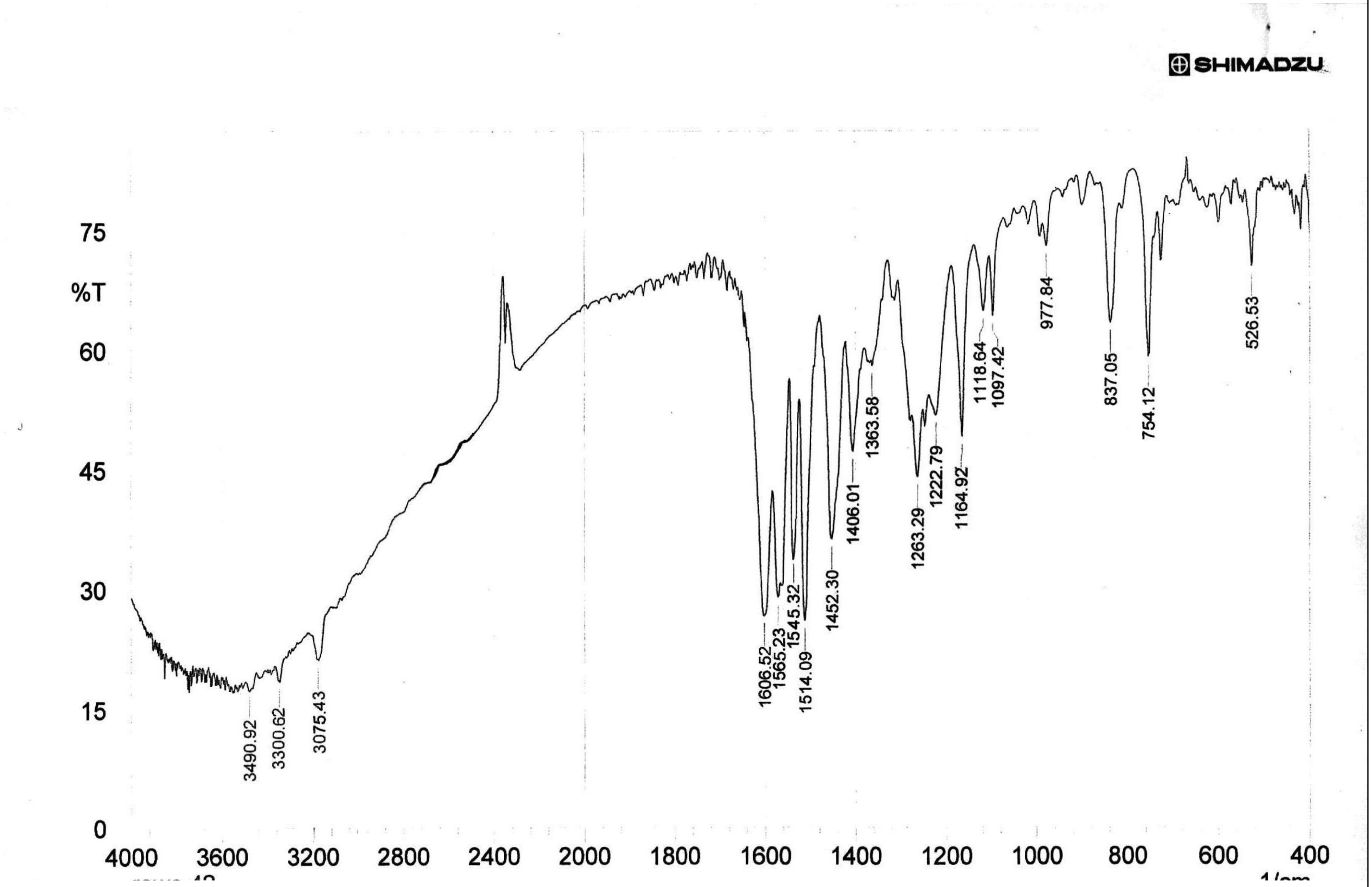


Figure (3-17): F.T.IR spectrum of LIIICo.

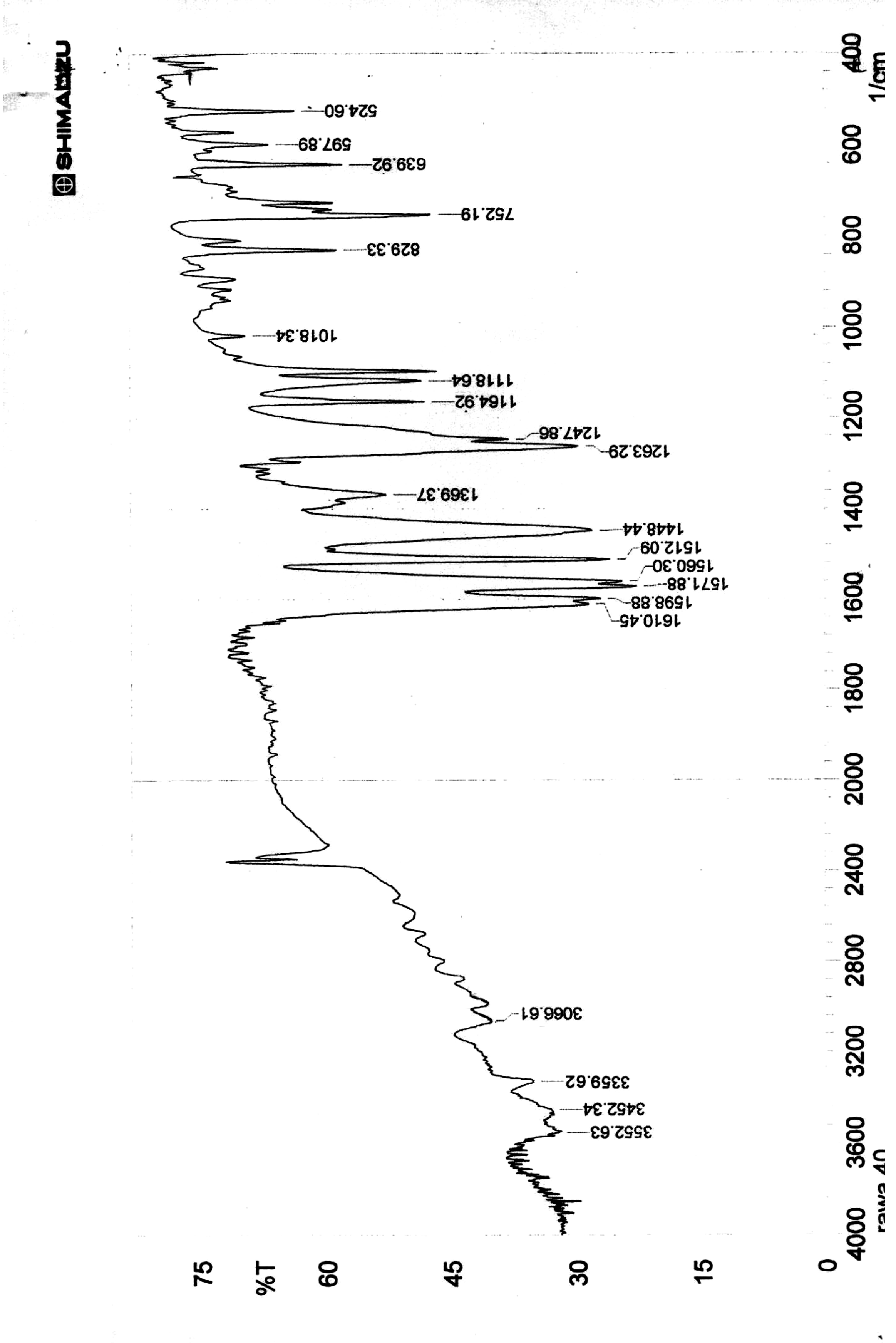


Figure (3-18): F.T.IR spectrum of LIIINi.

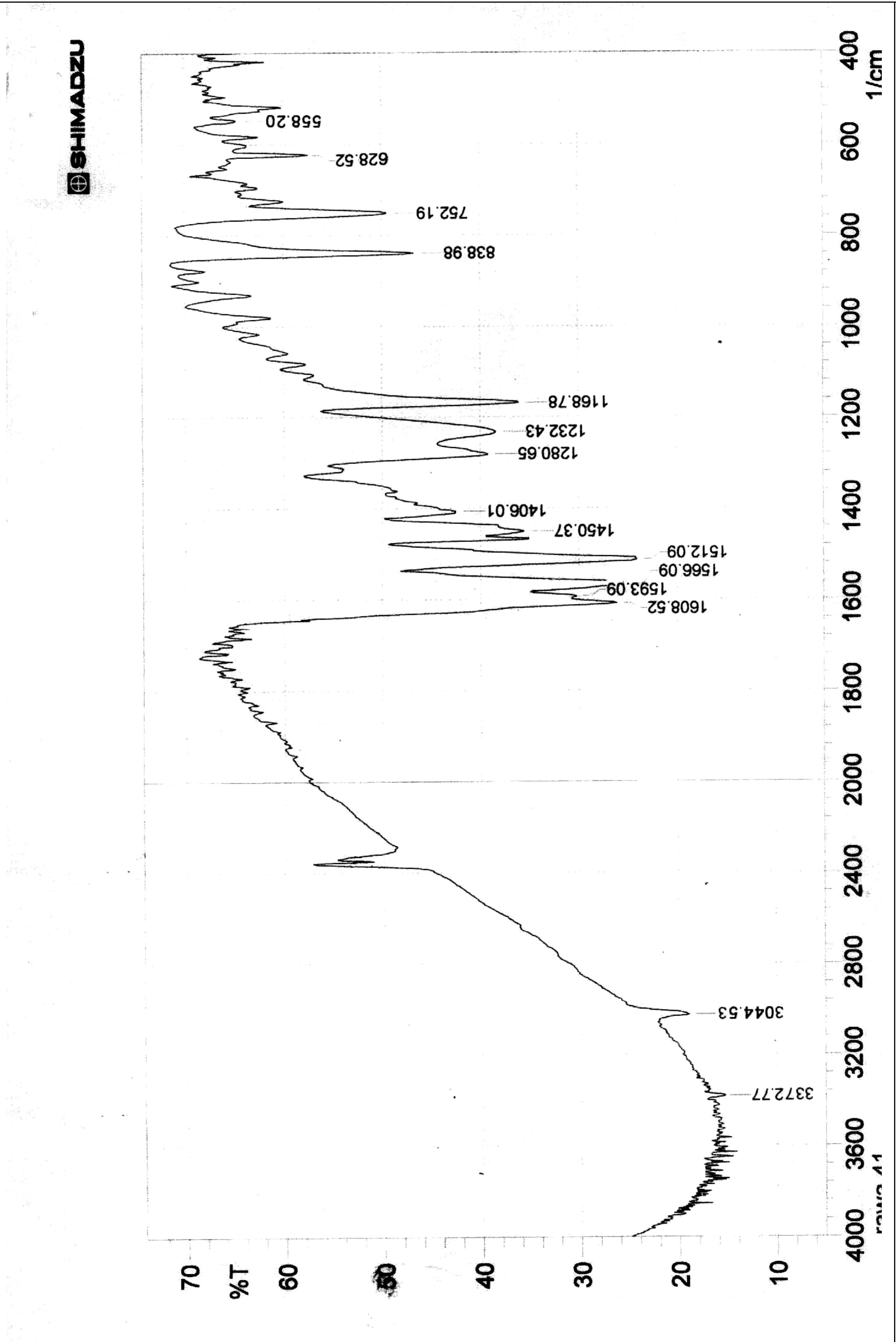


Figure (3-19): F.T.IR spectrum of LIIICu.

3.5 Electronic spectral study, magnetic properties and conductivity measurements:

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 U.V. and visible region. Charge transfer spectra are due to transitions between metal and ligand. Study of electronic spectra of complexes helps 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. Measurements of the magnetic susceptibility contributes to the determination of the complexes. In addition these measurements provide information about the type of bonding and strength of ligand field of complexes by giving information about the number of the unpaired electrons.

The effective magnetic spin of the complexes was measured using spin-only magnetic moment according to the following equation (80).

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

Where s= n/2 (n=number of unpaired electrons).

The results obtained from this equation were compared with the actual values obtained through magnetic measurement. These values were corrected for diamagnetic effects using the following relationships:

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

$$X_A = X_M - D$$

$$X_M = X_g \times M.wt$$

Where:

T= Absolute temperature (298 K).

D = Correction factor.

X_A = Atomic susceptibility.

X_g = gram susceptibility.

X_M = molar susceptibility.

The experimental values of magnetic moment are usually greater than calculated values of magnetic moment.

Conductivity measurements of the prepared complexes in the appropriate solvent are used to decide whether a complex is electrolyte or neutral(81, 82), Table (3-5) show the positions of the electronic absorption bands and their transitions, and also include the calculated values of Racah parameter (B^-), 10 Dq and neuphelauxetic factor (β), Table (3-6) showed the magnetic moment and 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:

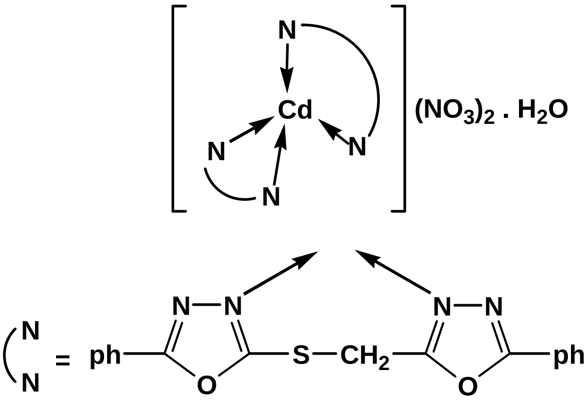
A) Cadmium(II) complex (LI Cd):

Since the UV-Vis 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 those of the ligand. therefore the possible geometry around these ions can be suggested considering the metal analysis, F.T.IR spectra and in account the available structures found in the literature(69, 70, 83).

The magnetic moment of the (LI Cd) complex was (μ=0 B.M) which show the complex to be Diamagnetic.

Conductivity measurements showed that the LICd complex was conducting, Table (3-6).

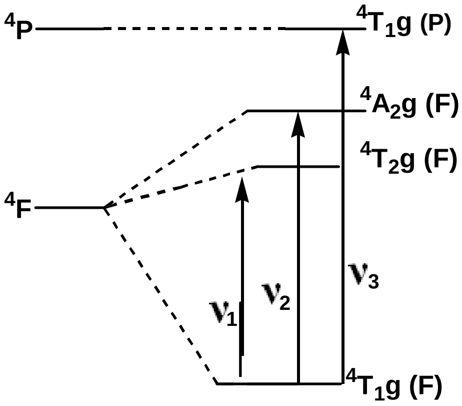
These observations led us to suppose tetrahedral geometry for (LI Cd) complex:



B) Cobalt(II) Complex (LI Co):

Electronic spectrum of cobalt (II) complex usually shows three transitions, but these transitions cannot be assigned easily because of their greater overlapping (83,89, 90). Octahedral complexes of Co (II) are reported to consist of two bands one in the (15,400- 15,000 cm $^{-1}$) and the other in the (20,000- 20,830 cm $^{-1}$) regions (91).

The term symbol for the ground state of Co (II) ion ^4F which can split in octahedral crystal field as follow (90).

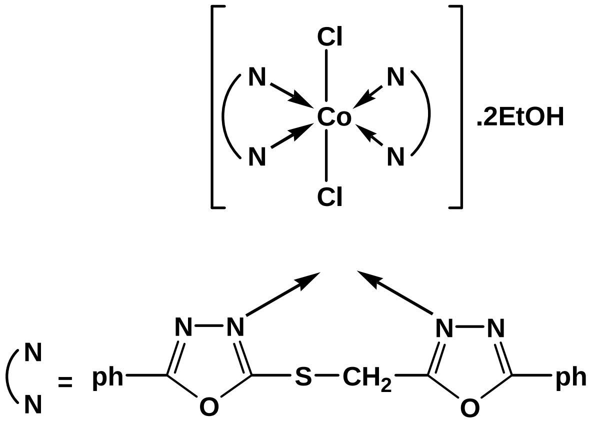


In the present work the greenish blue complex shows, two bands, one at (15,432 cm^{-1}) and the other at (20,242cm^{-1}) Fig (3-20), which were assigned to the transitions ν_2 and ν_3 respectively. The value of ν_1 was calculated by using Tanabe-Sugano diagram for d^7 system, Fig (3-21), the band found at (8034 cm^{-1}) refers to $^4T_1g_{(F)} \rightarrow {}^4T_2g_{(F)}$ transition. The different ligand field parameters have been calculated using the same diagram, the results are found in Table (3-5). The calculated neuphelauxetic factor (β) was of the value (0.8), 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.

Octahedral cobalt (II) complex however maintain a large contribution due to ^{4}Tg ground term and exhibit μeff in the range (4.8-5.6 B.M) (92). The magnetic moment of the (LI Co) complex was (5.13 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 (3-6).

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



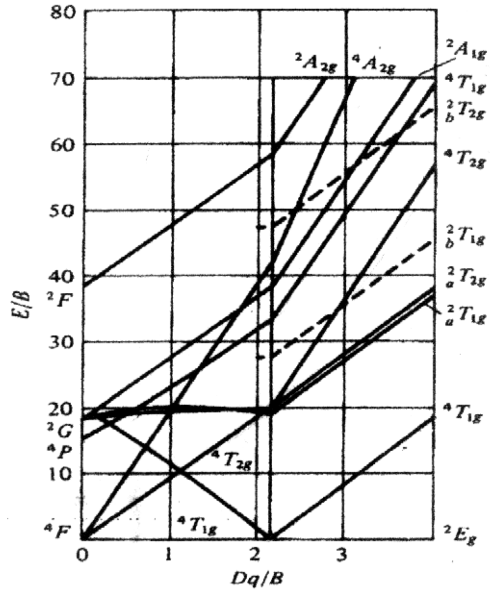
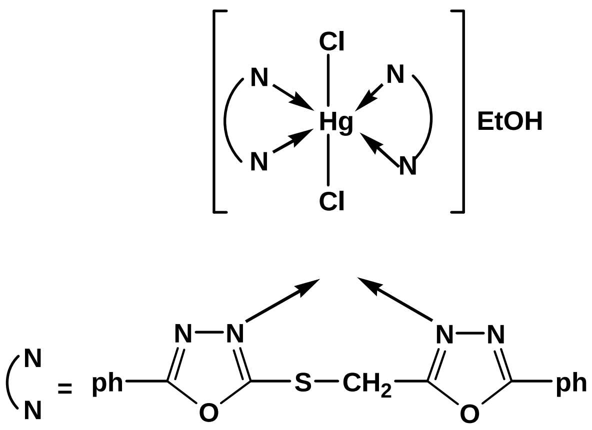


Figure (3-21): Tanabe-Sugano diagram for d^7 system.

C) Mercury(II) complex (LI Hg):

The UV-Vis spectrum of Hg (II) ion have some transition found in the region (200-400 n.m), can be assigned as intraligand transition, The magnetic moment of the (LI Hg) complex was (μ=0 B.M) which show the complex to be Diamagnetic.

Conductivity measurement showed that complex was non-conductive, and this transition of d^{10} ion do not furnish a lot of information. So from the FT.IR study an octahedral geometry structure can be suggested:



D) Nickel(II) complex (LI Ni):

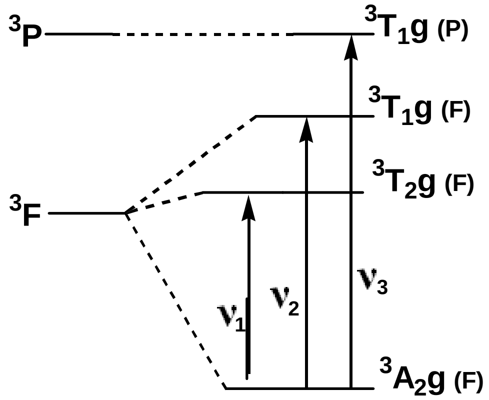
In octahedral field three spin-allowed transitions are expected to appear because of the splitting of the free-ion ,ground ^{3}F term and the presence of the ^{3}P term, these bands can be assigned as

$\nu_1\ ^3A_2g_{\ (F)} \rightarrow\ ^3T_2g_{\ (F)}$ = 10 Dq

$\nu_2\ ^3A_2g_{\ (F)} \rightarrow\ ^3T_1g_{\ (F)}$

$\nu_3\ ^3A_2g_{\ (F)} \rightarrow\ ^3T_1g_{\ (P)}$

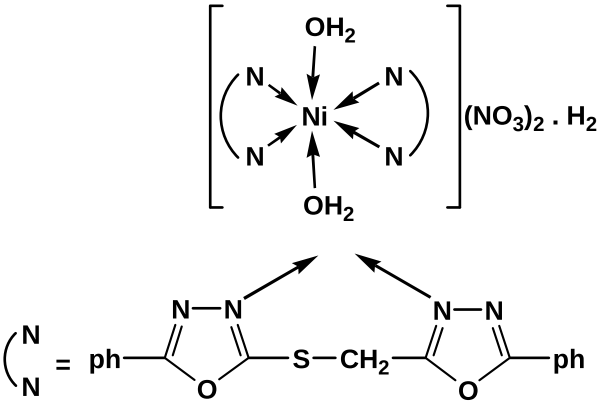
The term symbol for the ground stare of Ni (II) ion ^{3}F which can split in octahedral crystal as follow:



The UV-Visible spectrum of the present brown Ni^{+2} complex, (LI Ni), Figure (3-22), show two bands at (15,723 cm^{-1} and 25,706 cm^{-1}) can be assigned ν_2 and ν_3 respectively$^{(70, 102)}$.

The value of ν_1 was calculated using Tanabe-Sugano diagram for d^8 system, Figure (3-23), and found to be (10,400 cm^{-1}) which refer to $^3A_2g_{\ (F)} \rightarrow\ ^3T_2g_{\ (F)}$ transition.

The value of the calculated μeff (LI Ni) complex was (2.77 B.M.) this value is in the range of octahedral geometry (70). The conductivity measurement showed the complex to be ionic, therefore the following structure can be postulated:



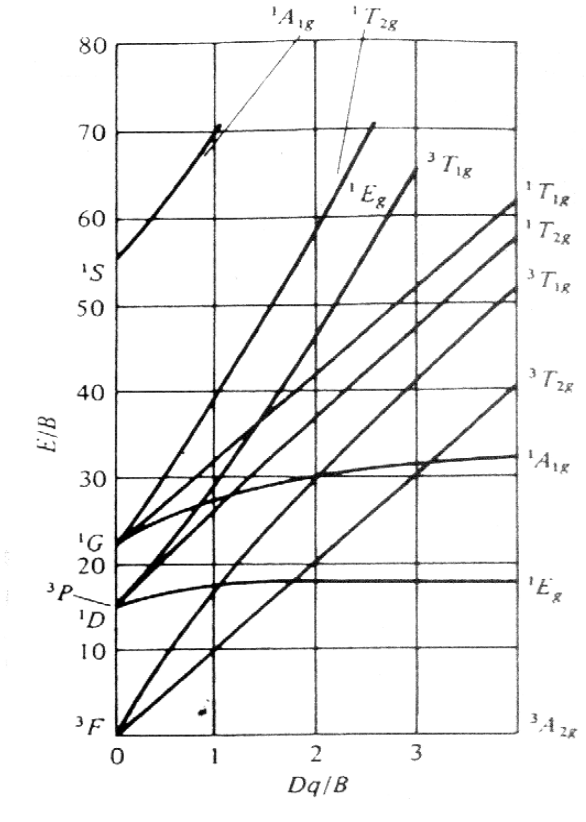
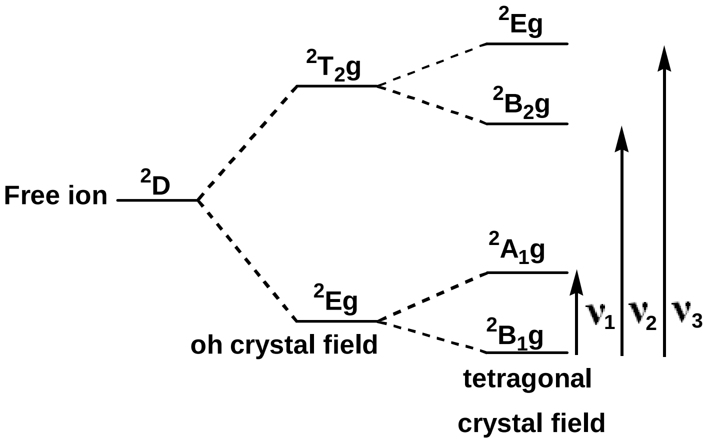


Figure (3-23): Tanabe-Sugano diagram for d^8 system.

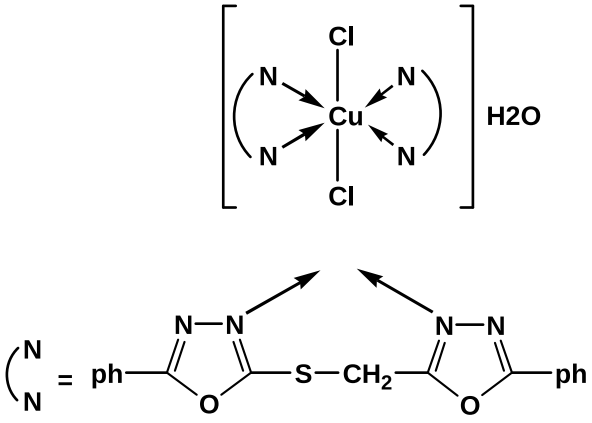
E) Copper(II) complex (LI Cu):

Cu(II) compounds are blue or green because of single broad absorption band in the region (11,000-16,000 cm^{-1})$^{(70)}$. The d^9 ion is characterized by large distortion from octahedral symmetry and the band is unsymmetrical, being the result of a number of transitions, which are no means easy to assign unambiguously. 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 (69, 70) diagram:



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 bright green (LI Cu) complex show a broad band (70) at (15,873 cm^{-1}) can be a ssigned to $^2B_1g \rightarrow {}^2B_2g$ and $^2B_1g \rightarrow {}^2Eg$ transitions, Figure (3-24). Conductivity measurement shows that the complex was non-ionic, table (3-6).

The value of μeff. that have been measured for (LI Cu) complex was (1.81 B.M.).This value is in the range of octahedral geometry(84,85). Therefore the expected geometry of (LI Cu) complex is:

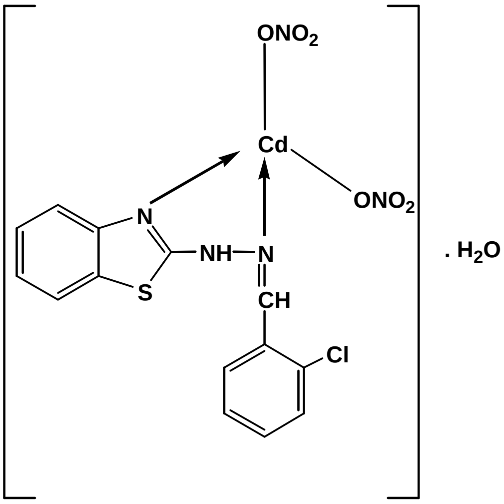


3.5.2 Complexes of (LII):

A) Cadmium(II) complex (LII Cd):

Conductivity measurement showed that the complex is non-ionic, and the magnetic moment of the (LII Cd) complex was (μ=0 B.M) which show the complex to be Diamagnetic.

And from FT.IR study the structure of this complex can be regarded as tetrahedral geometry:



B) Cobalt(II) complex (LII Co):

The spectral behavior of this complex, fig (3-26), showed that the Co(II) was converted to Co(III). Octahedral Co(III) complexes was recorded that the two bands at (16.615cm^{-1}) and (14.884cm^{-1}) were assigned to the transition $^1A_1g \rightarrow {}^1T_1g$ (ν_1), this splitting is due to spin orbit coupling (93). Therefore ν_1 have been calculated as the average of these two bands.

The second band appears as a weak band at (23.809 cm $^{-1}$) was assigned to the transition $^1A_1g \rightarrow {}^1T_2g$ (ν_2). from These transitions that happened for low spin Co(III) complexes in octahedral geometry we would expect following transitions (70)

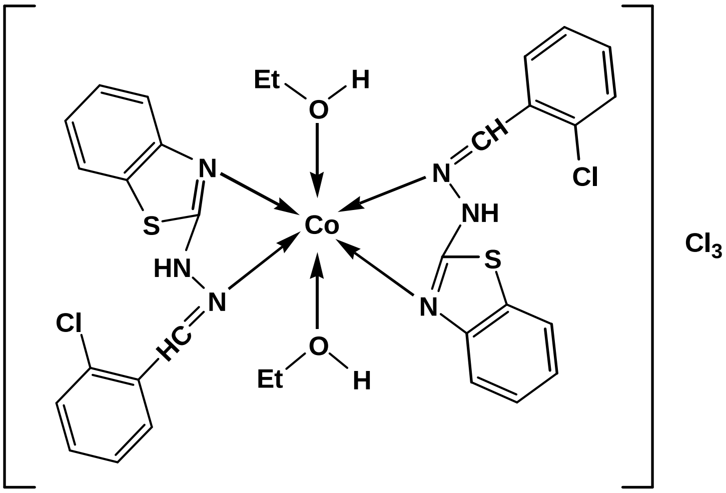
ν_1 $^1A_1g \rightarrow {}^1T_1g$

ν_2 $^1A_1g \rightarrow {}^1T_2g$.

These peaks should appear more widely spaced at large values of Dq (83).

The values of B^- , 10 Dq have been calculated using Tanabe-Sugano diagram for d^6 system, fig (3-25).

The molar conductivity measurements in DMSO show that the complex was electrolyte. According to these results the following structure can be proposed:



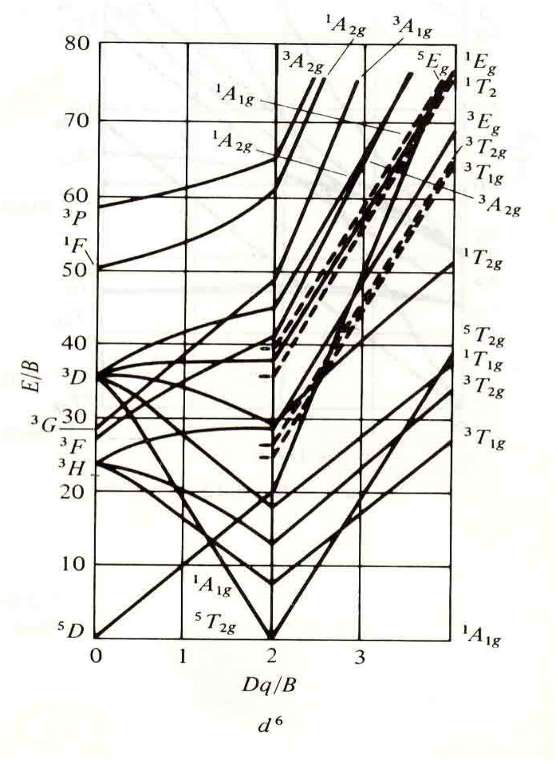


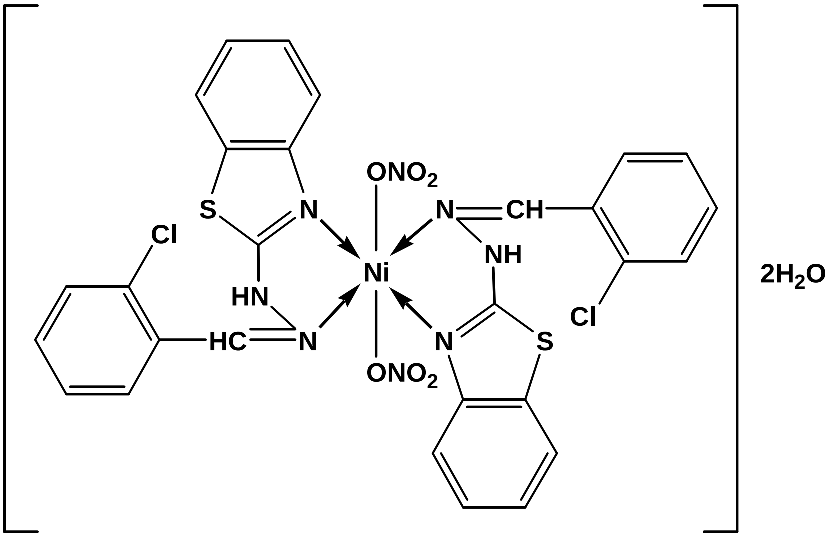
Figure (3-25): Tanabe-Sugano diagram for d^6 system.

C) Nickel(II) complex (LII Ni):

The spectral behavior of this complex, Figure (3-27), was identical with that of (LI Ni). Which also shows two bands one at (15,576 cm^{-1}) and the other at (24,937 cm^{-1}) which was assigned to the transition ν_2 and ν_3 respectively. ν_1 was calculated using Tanabo-Sugano diagram for d^8 system and found to be (8,500 cm^{-1}) this belongs to the transition $^3A_2g_{\,(F)} \rightarrow {}^3T_1g_{(F)}$.

The magnetic moment of the (LII Ni) complex was (2.69 B.M.), Table (3-6). Therefor an octahedral geometry was assumed for Ni(II) complex.

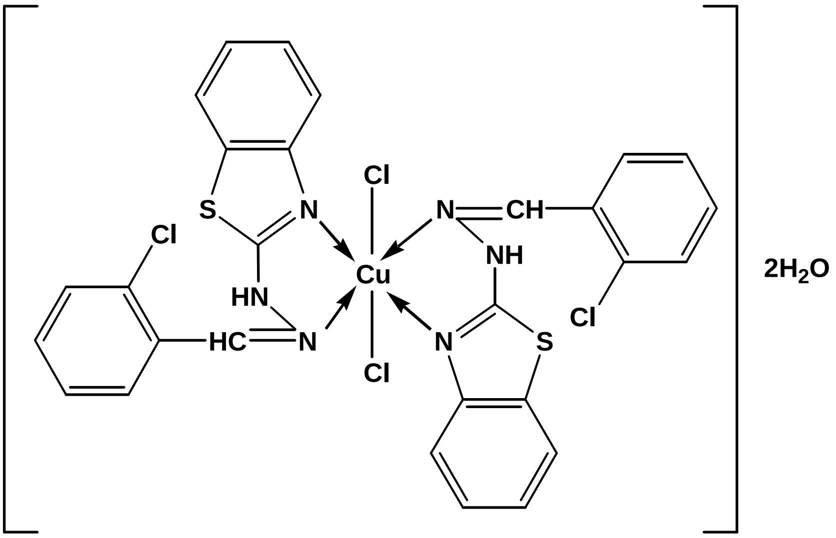
Conductivity measurement shows the (LII Ni) complex was non-ionic; Table (3-6). The following structure can be suggested:



D) Copper(II) complex (LII Cu):

Electronic spectrum of the dark green complex (LIICu) is shown in Fig (3-28), Table (3-5). The dark green color was attributed to the single broad absorption band in the region 625-500 nm (16,000-20,000 cm^{-1}) $^{(87)}$, the d^9 ion characterized by large distortion from octahedral geometry. Oh. 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 624 nm (16.025 cm^{-1}), this band refers to the distorted octahedral geometry (Jahn-Teller distortion) (47, 88), and can be assigned as $^2Eg \rightarrow {}^2T_2g$. The other bands found in the region 350-200 nm (28,571-50,000 cm^{-1}), can be assigned as intraligand or charge transfer. The magnetic susceptibility of the (LII Cu) complex was (2.05 B.M.), Table (3-6). Therefor an octahedral geometry was assumed for Cu(II) complex. Conductivity measurements show the (LII Cu) complex was non ionic, Table (3-6), the following structure can be suggested:

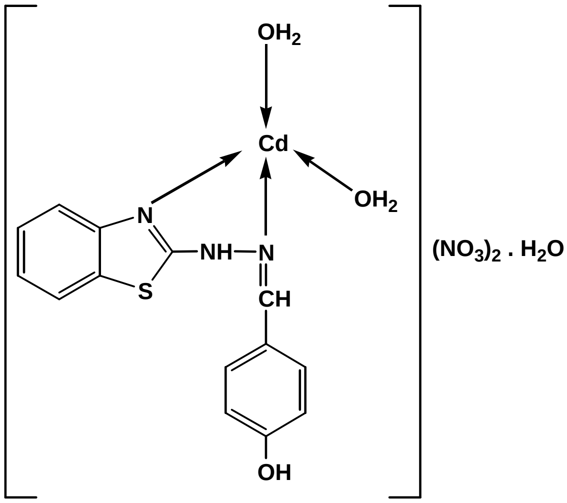


3.5.3 Complexes of LIII:

A) Cadmium(II) complex (LIII Cd):

Conductivity measurement showed that the complex was ionic, The magnetic moment of the (LIII Cd) complex was (μ=0 B.M) which show the complex to be Diamagnetic.

and from FT. IR study the structure of this complex can be regarded as of tetrahedral geometry:



B) Cobalt(II) complex (LIII Co):

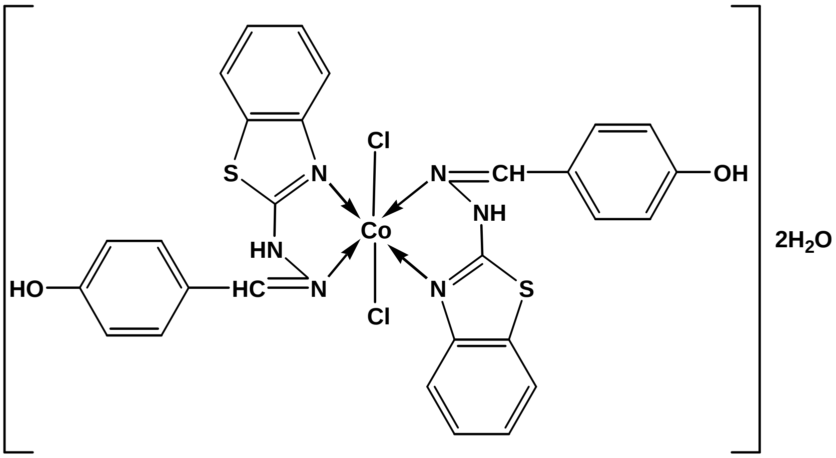
The spectral behavior of this complex, Fig (3-29), was identical with that of (LI Co), which also show two bands one at (15,408 cm^{-1}), and the other at (20,000 cm^{-1}) which was assigned to the transition ν_2 and ν_3 respectively.

The value of ν_1 was calculated using Tanabe-Sugano diagram for d^7 system, and found to be (7,981 cm^{-1}) which refers to $^4T_1g_{(F)} \rightarrow {}^4T_1g_{(P)}$ transition, 10Dq Value was also calculated from the diagram and found to be (9,976 cm^{-1}) referring to a weak field state.

The magnetic moment of the (LIII Co) complex was (4.91 B.M.) that shows the complex are paramagnetic and have three unpaired electrons indicating a high spin octahedral configuration.

The formula was further confirmed to be non-ionic by conductivity measurement.

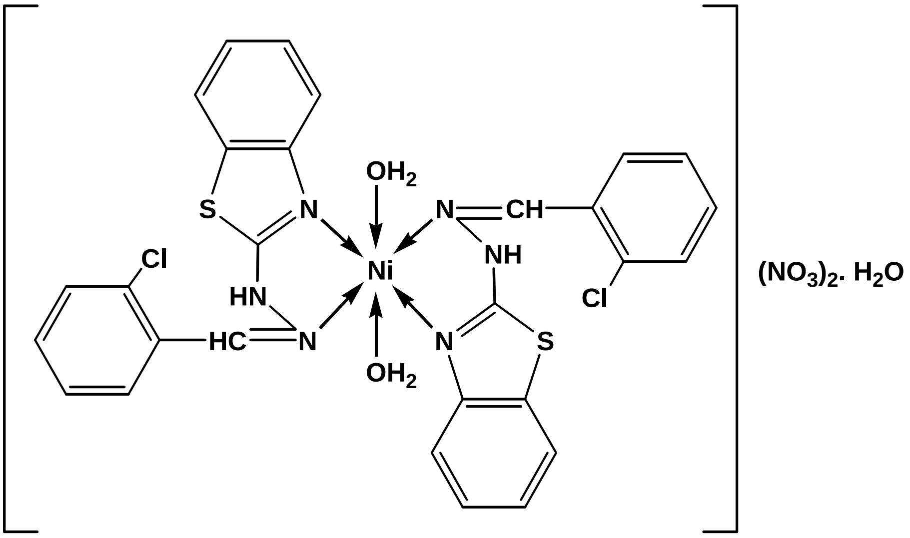
From these results an octahedral geometry around Co(II) ion can be suggested as illustrated in the following structure:



C) Nickel(II) complex (LIII Ni):

Electronic spectrum of (LIII Ni), Fig (3-30), shows two bands, One at (15,673 cm^{-1}) and the other at (25,316 cm^{-1}) which refers to the transitions $^3A_2g_{(F)} \rightarrow {}^3T_1g_{(F)}$ and $^3A_2g_{(F)} \rightarrow {}^3T_1g_{(p)}$ respectively. The value of ν_1 was calculated using Tanabe-Sugano diagram for d^8 system and found to be (8,856 cm^{-1}) referring to $^3A_2g_{(F)} \rightarrow {}^3T_2g_{(F)}$ transition, which is also equal to 10Dq value indicating a high spin complex. The magnetic moment of the (LIII Ni) complex was (2.71 B.M.) Table (3-6). Therefore an octahedral geometry was assumed for Ni (II) complex.

Conductivity measurement show the (LIII Ni) complex was ionic. Table (3-6). The following structure can be suggested:



D) Copper(II) complex (LIII Cu):

The spectral behavior of this complex, Fig (3-31), was identical with that of (LI Cu) (86), was also show abroad band at (13,404 cm^{-1}).That refer to $^2B_1g \rightarrow {}^2B_2g$ and $^2B_1g \rightarrow {}^2Eg$ transitions. The magnetic moment of the (LIII Cu) complex was (2.45 B.M.), Table (3-6). There fore an octahedral geometry was assumed for Cu(II) complex.

Conductivity measurement shows the (LIII Cu) complex was ionic, Table (3-6). The following structure can be suggested:

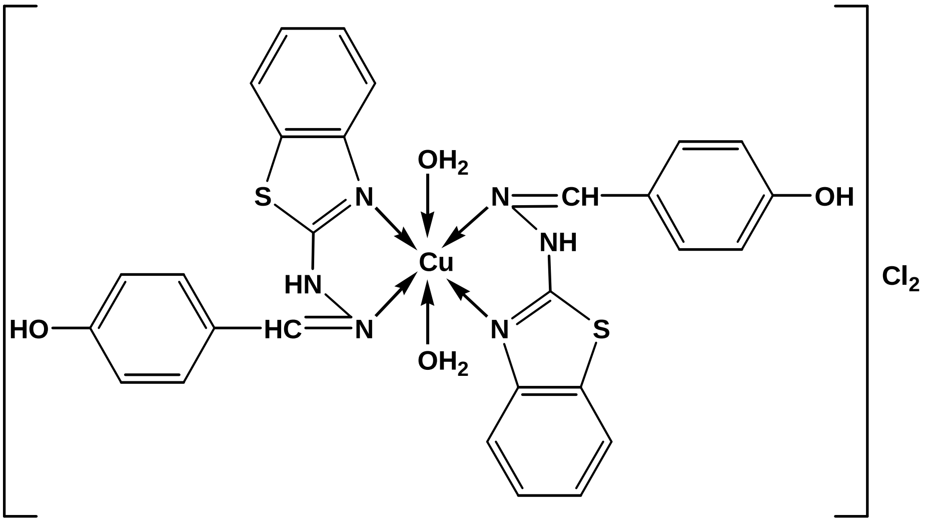


Table (3-5). Electronic spectra data for complexes of LI, LII and LIII in DMSO solvent (cm^{-1}).

Complex	Absorption bands(cm^{-1})	transition	B	B^-	β	10Dq	15 B^-
LICo	8,034 15,432 20,242	$\nu_1\,{}^4T_1g(F)\rightarrow{}^4T_2g(F)$ $\nu_2\,{}^4T_1g(F)\rightarrow{}^4A_2g(F)$ $\nu_3\,{}^4T_1g(F)\rightarrow{}^4T_2g(P)$	971	772	0.8	7,768	11,580
LI Ni	10,400 15,723 25,706	$\nu_1\,{}^3A_2g(F)\rightarrow{}^3T_2g(F)$ $\nu_2\,{}^3A_2g(F)\rightarrow{}^3T_1g(F)$ $\nu_3\,{}^3A_2g(F)\rightarrow{}^3T_1g(P)$	1030	681	0.66	10,400	10,229
LI Cu	15,873	${}^2B_1g\rightarrow{}^2B_2g$ ${}^2B_1g\rightarrow{}^2Eg$					
LII Co	15,749 23,809	$\nu_1\,{}^1A_1g\rightarrow{}^1T_1g$ $\nu_2\,{}^1A_1g\rightarrow{}^1T_2g$	1100	540	0.5	18,000	8,100
LII Ni	8,500 15,576 24,937	$\nu_1\,{}^3A_2g(F)\rightarrow{}^3T_2g(F)$ $\nu_2\,{}^3A_2g(F)\rightarrow{}^3T_1g(F)$ $\nu_3\,{}^3A_2g(F)\rightarrow{}^3T_1g(P)$	1030	1,001	0.97	8,500	15,013
LII Cu	16,025	${}^2B_1g\rightarrow{}^2B_2g$ ${}^2B_1g\rightarrow{}^2Eg$					
LIII Co	7,981 15,408 20,576	$\nu_1\,{}^4T_1g(F)\rightarrow{}^4T_2g(F)$ $\nu_2\,{}^4T_1g(F)\rightarrow{}^4A_2g(F)$ $\nu_3\,{}^4T_1g(F)\rightarrow{}^4T_2g(P)$	971	802	0.82	9,976	12,041
LIII Ni	8,856 15,673 25,316	$\nu_1\,{}^3A_2g(F)\rightarrow{}^3T_2g(F)$ $\nu_2\,{}^3A_2g(F)\rightarrow{}^3T_1g(F)$ $\nu_3\,{}^3A_2g(F))\rightarrow{}^3T_1g(P)$	1030	962	0.93	8,856	14,421
LIII Cu	13,404	${}^2B_1g\rightarrow{}^2B_2g$ ${}^2B_1g\rightarrow{}^2Eg$					

Table (3-6). Magnetic moment, conductivity and suggested structure for complexes of LI, LII and LIII.

Complex	Magnetic moment µeff. (B.M.)	Conductivity µs. cm^{-1}	Suggested structure
LI Cd	**Diamagnetic**	**32**	**Tetrahedral**
LI Co	**5.13**	**20**	**Octahedral**
LI Hg	**Diamagnetic**	**21**	**Octahedral**
LI Ni	**2.77**	**38**	**Octahedral**
LI Cu	**1.81**	**19**	**Octahedral**
LII Cd	**Diamagnetic**	**17**	**Tetrahedral**
LII Co	**-**	**40**	**Octahedral**
LII Ni	**2.69**	**18**	**Octahedral**
LII Cu	**2.05**	**20**	**Octahedral**
LIII Cd	**Diamagnetic**	**34**	**Tetrahedral**
LIII Co	**4.91**	**19**	**Octahedral**
LIII Ni	**2.71**	**31**	**Octahedral**
LIII Cu	**2.45**	**36**	**Octahedral**

Table (3-7): The Chemical Formula and the name of the LI and their metal complexes.

Complex	Chemical Formula	Name of the Compound
LI	**$C_{17}H_{12}N_4O_2S$**	**2-(5-phenyl-2-methylthio1,3,4oxadia- zole)-5-phenyl-1,3,4-oxadiazole**
LICd	**$[Cd (LI)_2] (NO_3)_{2.} H_2O$**	**bis [2-(5-phenyl-2-methylthio-1,3.4-oxadiazole)-5-phenyl-1,3,4-oxadiazole]Cadmium(II).nitrate .water(1)**
LICo	**$[Co (LI)_2 Cl_2].2\ C_2H_5OH$**	**Dichloro bis [2-(5-phenyl-2-methylt-hio-1,3.4-oxadiazole)-5-phenyl-1,3,4-oxadiazole]Cobalt(II).Ethanol(2).**
LIHg	**$[Hg (LI)_2 Cl_2].2\ C_2H_5OH$**	**Dichloro bis [2-(5-phenyl-2-methyl thio -1,3.4-oxadiazole)-5-phenyl-1,3,4-oxadiazole]Mercury(II).Ethanol(2)**
LINi	**$[Ni (LI)_2 (H_2O)_2] (NO_3)_{2.} H_2O$**	**Diaqua bis [2-(5-phenyl-2-methylth-io-1,3.4-oxadiazole)-5-phenyl-1,3,4-oxadiazole]Nickel(II).nitrate.water (1)**
LICu	**$[Cu (LI)_2 Cl_2] .H_2O$**	**Dichloro bis [2-(5-phenyl-2-methyl-thio-1,3,4-oxadiazole)-5-phenyl-1,3,4 -oxadiazole] Copper(II). water(1)**

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

Complex	Chemical Formula	Name of the Compound
LII	**$C_{14}H_{10}N_3SCl$**	**2-(O-chloro benzylidine) hydrazino benzothiazole.**
LIICd	**$[\ Cd\ LII\ (NO_3)_2]\ .H_2O$**	**Di nitrato [2-(O-chloro benzylidine)-hydrazino benzothiazole] Cadmium(II). Water(1).**
LIICo	**$[\ Co\ (LII)_2\ (EtOH)_2]\ Cl_3$**	**Di ethanol bis [2-(O-chloro benzylidine) hydrazino benzothiazole.] Cobalt(II). chloride(3).**
LIINi	**$[Ni\ (LII)_2\ (NO_3)_2].2\ H_2O$**	**Di nitrato bis [2-(O-chloro benzylidine) hydrazino benzothiazole] Nickel(II). water (2).**
LIICu	**$[\ Cu\ (LII)_2\ Cl_2]\ .2\ H_2O$**	**Dichloro bis [2-(O-chloro benzylidine) hydrazino benzothiazole] Copper(II). water(2).**

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

Complex	Chemical Formula	Name of the Compound
LIII	$C_{14}H_{11}N_3OS$	**2-(P-hydroxy benzylidine) hydrazino benzothiazole.**
LIIICd	$[\ Cd\ LIII\ (H_2O)_2]\ (NO_3)_2\ .H_2O$	**Diaqua [2-(P- hydroxy benzylidine)-hydrazino benzothiazole] Cadmium(II). nitrate. water (1).**
LIIICo	$[\ Co\ (LIII)_2\ Cl_2].2H_2O$	**Di chloro bis [2-(P-hydroxy benzylidin-e) hydrazino benzothiazole] Cobalt(II). water(2).**
LIIINi	$[Ni\ (LIII)_2\ (H_2O)_2]\ (NO_3)_2\ .H_2O$	**Di nitrato bis [2-(P-hydroxy benzylidine) hydrazino benzothiazole] Nickel(II). nitrate. water (1).**
LIIICu	$[\ Cu\ (LIII)_2\ (H_2O)_2]\ Cl_2$	**Diaqua [2-(P- hydroxy benzylidine)-hydrazino benzothiazole] Copper(II). Chloride(2).**

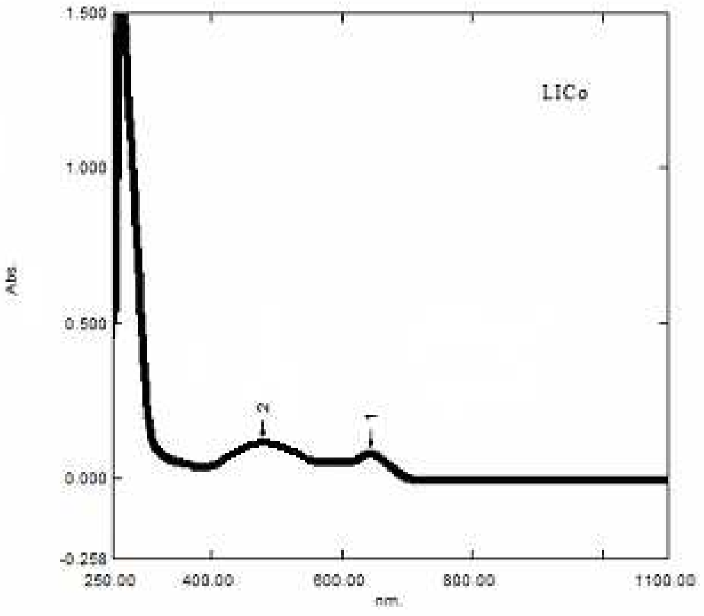


Figure (3-20): Electronic Spectrum of LICo

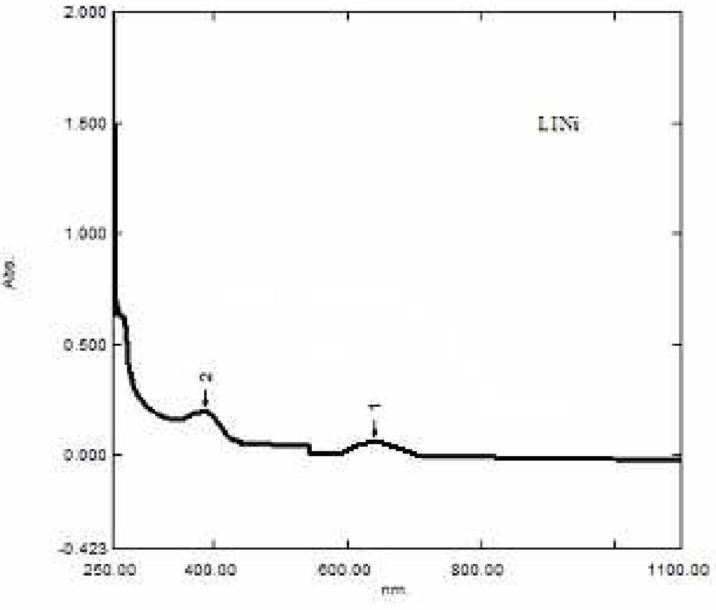


Figure (3-22): Electronic Spectrum of LINi

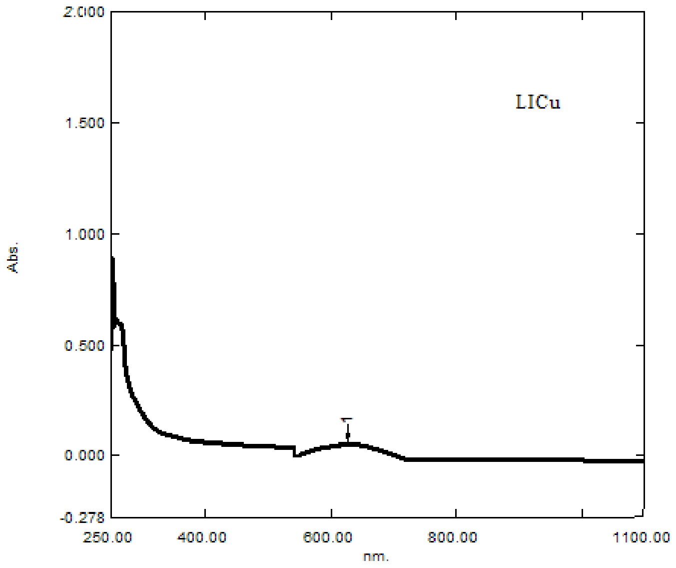


Figure (3-24): Electronic Spectrum of LICu

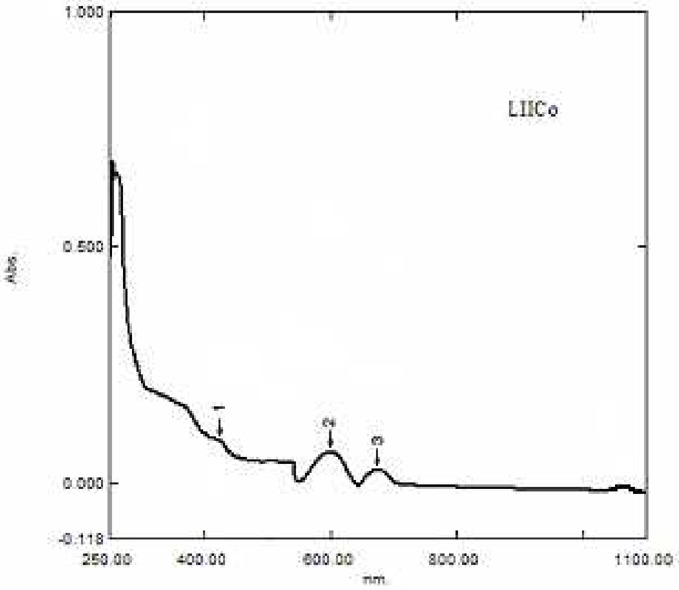


Figure (3-26): Electronic Spectrum of LIICo

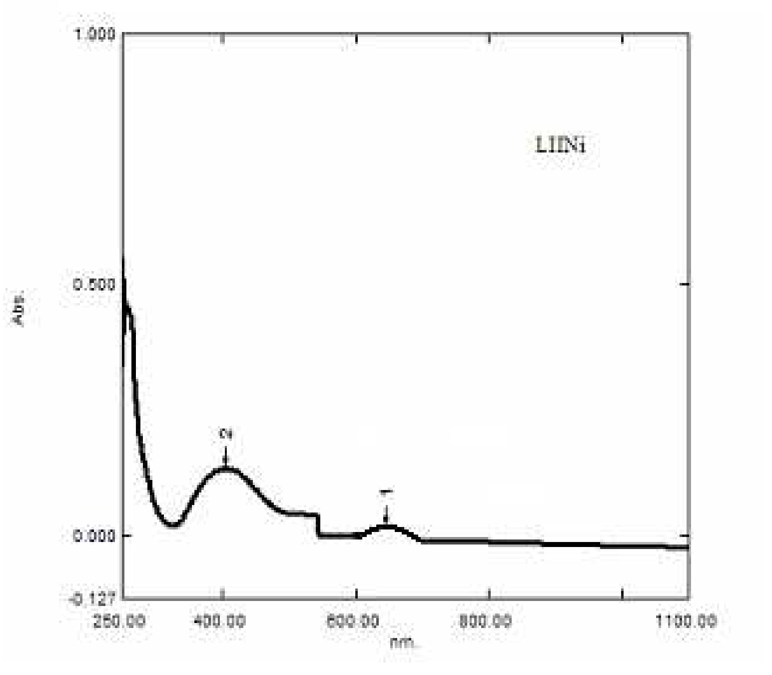


Figure (3-27): Electronic Spectrum of LIINi

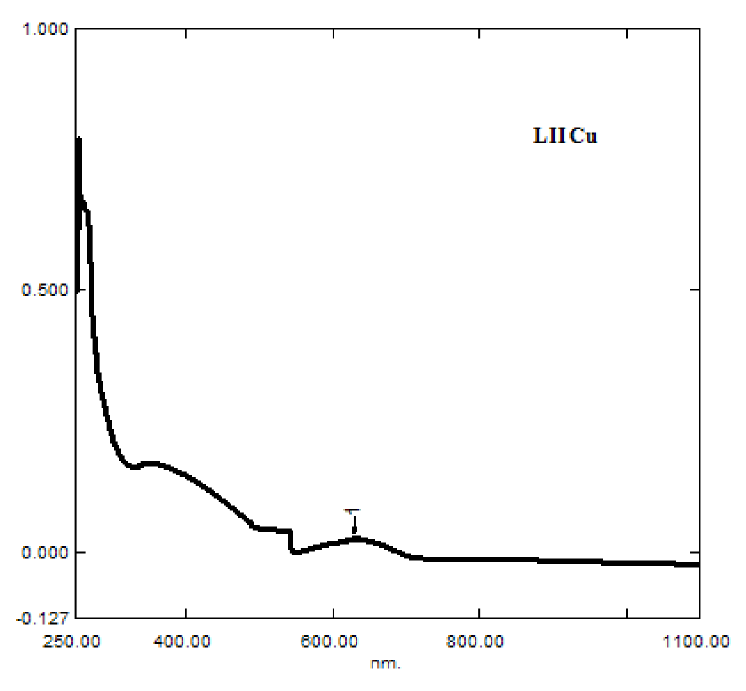


Figure (3-28): Electronic Spectrum of LIICu

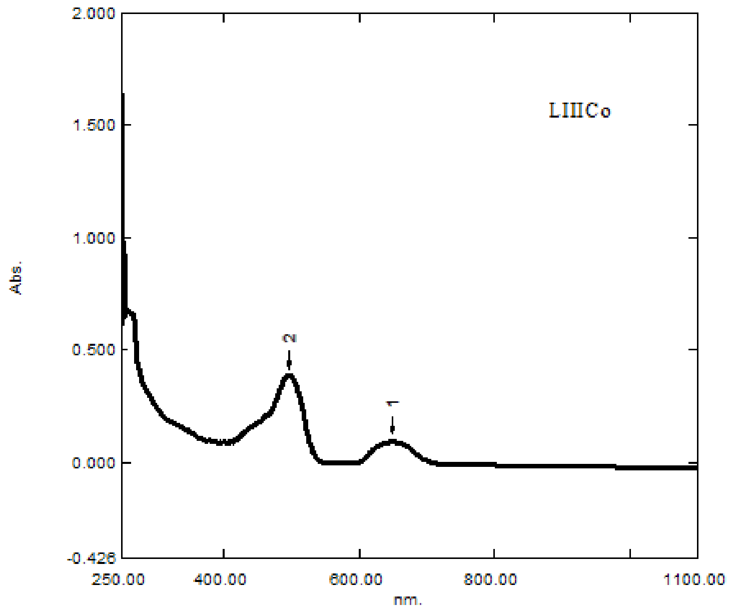


Figure (3-29): Electronic Spectrum of LIIICo

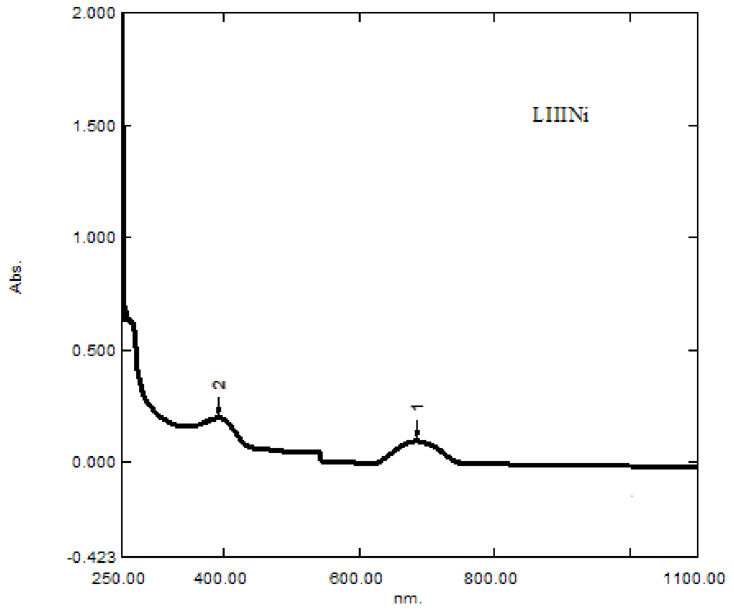


Figure (3-30): Electronic Spectrum of LIIINi

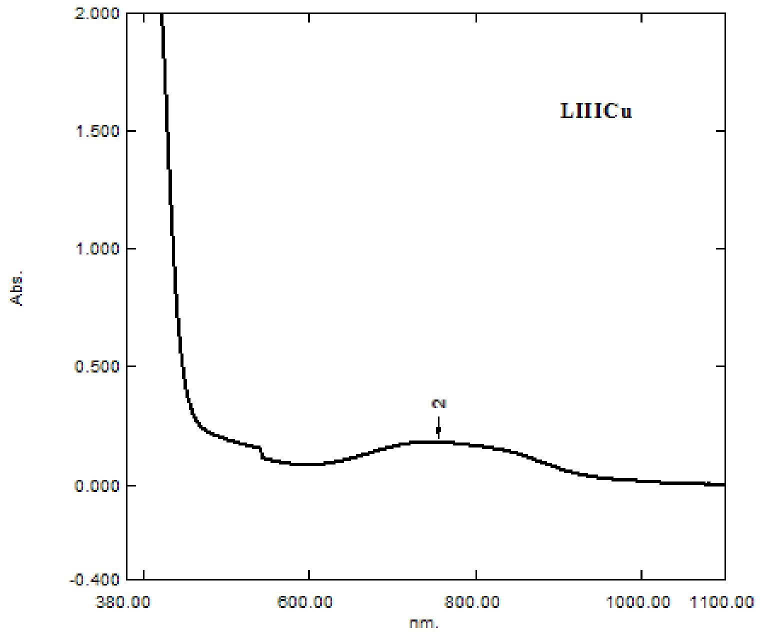


Figure (3-31): Electronic Spectrum of LIIICu

Suggestion for future work:

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

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

2) Using C.H.N. Microanalysis and NMR techniques to completely identify the structures of the ligands and its metal complexes.

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

Chapter one

Introduction

1.1 Interaction of the ligand with metal ion:

The tendency of metal ion to form stable complex with ligands depend on many rules such as the hard and soft acid and base (HSAB) rule of Pearson(1) which simply state that metal ions tend to coordinate with certain donor atoms of the ligand to form stable complex.

Hardness and softness refer to special stability of hard-hard and soft-soft interaction and should be carefully distinguished from inherent acid or base. The Irving Williams series of stability for a given ligand is a good criterion for the stability of complexes with dipositive metal ions which follows the order:

$Ba^{+2} < Sr^{+2} < Mg^{+2} < Mn^{+2} < Fe^{+2} < Co^{+2} < Ni^{+2} < Cu^{+2} > Zn^{+2}$.

This order arises in part from decrease in size across the series and in part from ligand field effects. The tendency of transition metal ions for special oxidation states is affected by coordinating to certain ligands, this phenomena is called (Symboiosis)(2).

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}, C^{-4} (3).

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 and donor atoms play the important role in the stability of the resultant complex.

Metal centers, begin positively charged, are favored to bind to negative charged biomolecules, the constituents of proteins and nucleic acid offer excellent ligands for binding to metal ions(4).

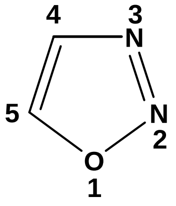
1.2 Metal complexes; chemistry of polydentate ligands:

Large molecules which contain a number of donating atoms, have the ability to bind to the metal ion through more than one atom, polydentate ligand, especially those which have equivalent atoms with respect to their coordination ability, show different behavior with respect to the number of binding sites with the central metal, e.g. (ethylene-diamine tetraacetate may have coordination number between 2 and 6). The pH of the reaction mixture has also a large effect on the bonding properties of the polydentate ligands. In addition to that the type of solvent and the metal, concentration of the ligand and other factors which may affect the mechanism of the ligand exchange, have also important role in this respect(5).

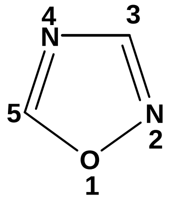
The chemistry of metal complexes containing polydentate ligands which have delocalized π-orbitals like Schiff bases, triazole and porphyrins, have recently attracted the attention of many scientist due to their use in many biomodels, like respiratory pigments and vitamin B_{12} co-enzymes. In the case of Schiff base metal complexes the work were carried out on cobalt (III) complexes, because they are considered to be a reversal molecular oxygen carriers or vitamin B_{12} co-enzyme models. This interest extends to iron (II) and (III) complexes since iron is found in many living systems like hemoglobine. On the other hand transition metal (especially vanadium) complexes of Schiff bases are also used industrially as catalyst in the co-polymerization of acetylene-propylene the method of Ziegler-Nata process(6).

1.3 Oxadiazoles:

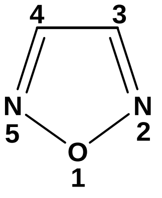
Oxadiazoles are five-membered ring compounds with three hetero atoms: one oxygen atom and two nitrogen atoms. There are four isomeric types of oxadiazoles: 1,2,3-oxadiazole (I); 1,2,4-oxadiazole (II); 1,2,5-oxadiazole (III); and 1,3,4-oxadiazole (IV), as shown below(7):



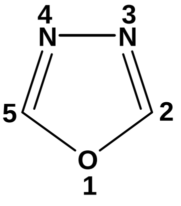
[I]



[II]



[III]



[IV]

1.3.1 1,3,4-Oxadiazoles:

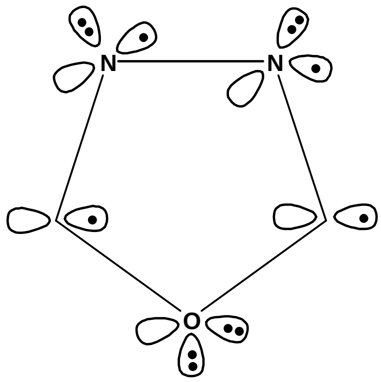


Figure (1-1): Orbital structure of 1,3,4-oxadiazole.

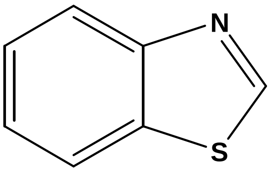
1,3,4-Oxadiazole ring has three pairs of delocalized π-electrons. Two of the pairs are shown as π-bonds through the overlapping of unhybridized *p*-orbital of nitrogen atom and one pair of non-bonding electrons on the hetero oxygen atom. 1,3,4-oxadiazole has three pairs of non-bonding electrons that are not part of the π-cloud. These electrons are in sp^2 prependicular to the *p*-orbital .

The growing literature in the past years demonstrates that 1,3,4 Oxadiazoles are becoming of great interest stems mainly from their wide range of applications

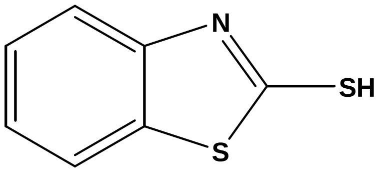
The 1,3,4-oxadiazoles have been reported to be biologically versatile compounds having bactericidal(8), fungicidal(9), herbicidal(10), analgesic(11), hypoglycemic(12), anti-inflammatory(13), and transqualizing agents (14,15), moreover, various 1,3,4-oxadiazoles are suitable for uses in photography(16),Scintillation materials, dyestuffs industry(17),corrosion inhibitors(18), and as thermal stabilizers for rigid polyvinyl chloride(16).

1.4. Benzothiazoles:

Benzothiazoles are bicyclic system (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 4,5 position of thiazole ring like the structure(A).



(A)



(B)

2-Mercaptobenzothiazole are derivatives in which the 2-position is linked 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 (19).

In 1922, 2-mercaptobenzothiazole was developed as a rubber vulcanization accelerators, thus the early impetus to the study of thiazole chemistry came from the practical importance of the benzothiazole(20).

Further more, the ease with which a large variety of such derivative can be prepared and the reactivity of the mercapto group make these compound valuable starting materials for the preparation of many other benzothiazoles.

The biological importance of benzothiazole derivatives was further emphasized during the period 1941- 1945 When work on the structure of antibiotics, penicillin, which has showed the presence of a thiazolidine ring in this important therapeutic agent (21).

1.5 Schiff bases:

1.5.1 Synthesis of Schiff bases:

The term "Schiff bases" used to define those organic compounds which contain the functional group (-C=N-).

Schiff bases were firstly prepared by Schiff in 1864(22-23) .from condensation reaction of aldehydes or ketones with primary amine.

Schiff bases have several nomenclature such as anils, imines, azomethines, benzanils and benzyildeneaniline(24).

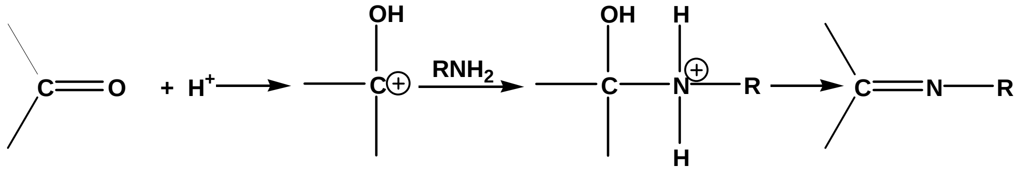
Imines ,Schiff bases and other (C=N) compounds can be reduced with $LiAlH_4$, $NaBH_4$, Na-EtOH, hydrogen and a catalyst, as well as with other reducing agents(25) .

Schiff bases rapidly decomposed in aqueous acidic media, but they are very stable in basic solution (26).

Schiff bases can be obtained by condensation reaction between carbonyl compound (1) and amine (2) with the formation of amino alcohol as intermediate (3).

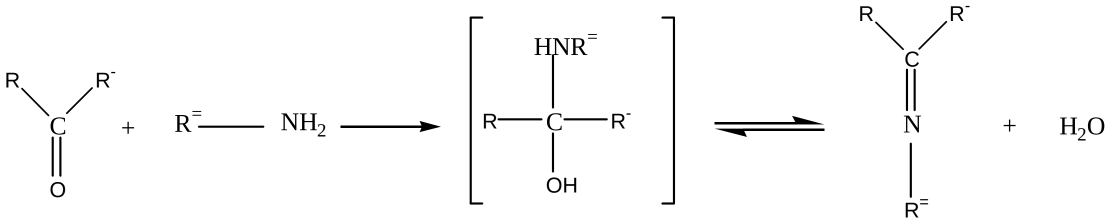
The experimental conditions depend on the nature of the amine and especially of the carbonyl compound which determine the position of the equilibrium.

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).



..... 1.1

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

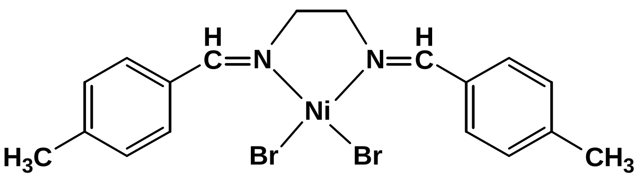


(1) (2) (3)

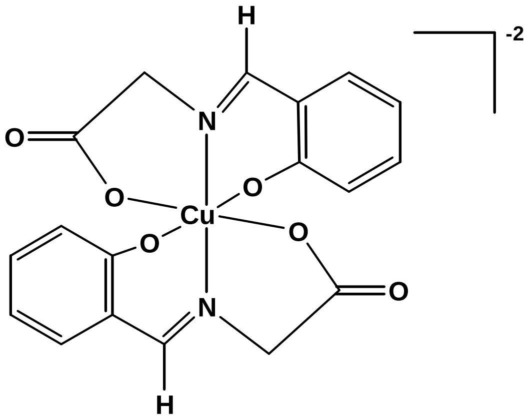
These bases can also be prepared by refluxing of equimolar quantities of aldehyde or ketone with amine by slow melting for 10 minutes and then isolating and purifying the product by recrystallization, or sublimation under reduced pressure(24,27).

Staab(28) prepared Schiff bases by removing water which is formed by condensation of aldehyde with the amine and by reflux in benzene this is done by mixing the amine and the aldehyde in benzene and then the residual solution is distilled under vacuum.

Bidentate Schiff bases have been among ligands that are extensively used for preparing metal complexes. These ligands are described according to their donor set N,N-donor Schiff bases and N,O-donor Schiff bases for example.



Tridentate Schiff bases may be generally considered as derived from the bidentate analogues by adding another donor group. These have been utilized as an ionic ligands having (N,N,O),(N,N,S), (N,O,O) and (N,S,O) donor sets(29,30) for example.



1.5.2 *The metal complexes of Schiff bases as biologically important compounds:*

Schiff bases and their metal complexes have received a great deal of attention during the last decade by many workers to prepare new sets of these bases and their transition metal complexes(31).

These complexes have proven to be antitumer and have carcinostatatic activities(31,32). They show leukaemetic activity. Schiff bases, on the other side, have a great importance in biological reactions like (visual process)(33), and in the reaction that involve removing the amine group by enzymic effect (enzymatic transition reaction) and some B_6-catalysed reaction(34).

The biological activity of Schiff bases is attributed to the formation of stable chelates with transition metal ions presents in cells(35).

Schiff bases derived from sulfa drugs have been successfully used for the bacteriostatic activities and complexes(36). A great deal of work concerning metal complexes of Schiff bases were concentrated on the cobalt(III) complexes, that are used as reversible of oxygen carriers or amodel for vitamin B_{12} Co-enzymes, the attention is also extended to Fe(II) and Fe(III) complexes which are included in the hemoglobin found in some biological systems(37).

It has been noticed that 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(38),led to dev - elopement of platinum complexes chemistry designed for wide biological applications(39). Palladium and platinum are regarded as soft metals, so they react with soft ligands that contain an electron-donating group like S and P, they also can form complexes with hard ligands(40), like oxygenating molecules or molecules which contain nitrogen.

Recently many research works(41) appeared which deal with the study of palladium interaction with Schiff bases through cyclometalation reaction (this include metal containing cyclic in which the metal is bonded to a carbon atom). This reaction plays an important role in preparation of some organometalic compounds in which these complexes are used as starting materials to improve the stereochemistry of these compounds. Also these complexes are used in photochemical reactions.

Schiff bases and their analogues have great importance as catalysts in racemic reactions in peptide syntheses and information of amines that have biological origin(42). Recently a new set of Schiff bases have been prepared

Table (1-1): The molecular formula, and biological activities of some metal complexes of a number of Schiff bases.

Name	Molecular formula	Metal ion	Biological activity	Ref
Thiocarboxy phenyl-4-allyl-5-phenyl-4H-1,2,4-triazole	$C_{18}H_{15}N_3OS$	Hg^{+2}, Au^{+2}, Ca^{+2}, Cd^{+2}, Cu^{+2}, Fe^{+2}	**Antibacterial activity**	**43**
2-(benzylidene)-5-allylthio-1,3,4-thiadiazole	$C_{12}H_{11}N_3S_2$	Cu^{+2}, Fe^{+2}	-	**44**
β-naphthaldehyde N-phenyl imine	$C_{17}H_{15}NO$	Cd^{+2}, Fe^{+2} Co^{+2}, Cu^{+2}, Cr^{+2}, Hg^{+2} V (IV)	-	**45**
β-naphthaldehyde-N-cyclohexyl imine	$C_{17}H_{21}NO$	Cd^{+2}, Fe^{+3} Co^{+2}, Cu^{+2}, Hg^{+2},V (IV)	-	**45**

1.6 Infrared spectra of Schiff bases and their metal complexes:

The following are a review of the νC=N assignment, as recorded for Schiff bases and their metal complexes$^{(22-23)}$.

1) ν(C=N) appeare 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$^{(46)}$.

2) Coordination of chain polymers of Schiff bases derived from *o*-amino benzoic acid and terphthalaldehyde shows C=N stretching at 1625 cm^{-1} and is shifted to (1620-1615) cm^{-1}on complex formation, indicating the involvement of azomethine nitrogen in coordination$^{(47)}$.

3) A strong band appeared around 1590 cm^{-1} is assigned to the C=N stretching of the free Schiff bases, bis (Vaniline) ethylenediimine, bis (Vanilline) propylenediimine, bis (Vanillin) *o*-phenylenediimine, it was found in the region (1675-1665) cm^{-1} for their complexes with Cu(II)(48).

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 ν(C=N)(49).

5) Schiff bases, oximes, thiadiazoles, iminocarbonates and guanidines show the C=N strength in the region (1689-1471) cm^{-1}(50).

6) The IR spectra of new series of Schiff bases derived from substituted,4,5-disubstituted-2-amino-thizole and *p*-hydroxybenzaldehyde show a strong sharp band in the region (1640-1625) cm^{-1} for ν (C=N)(51).

7) Strong band at 1600 $cm^{-1}$was corresponded to ν(C=N)(52) 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 azomethines nitrogen in coordination(32).

8) The IR spectrum give absorption band in the region (1640-1630) cm^{-1} for ν(C=N) of free tetraimine Schiff bases macrocycles derived from the condensation of 1,3-diamine-2-hydroxypropane with pyrrole-2,5-dicarbaldehyde and with thiophene-2,5-dicarbaldehyde(53).

9) Patai suggest that ν(C=N) appear in the region (1680-1570) cm^{-1}. The intensity of ν(C=N) is variable and it depend on the substituted groups(24).

10) The IR spectrum of Schiff bases derived from 4-phenyl-5-(*p*-aminophenyl)-3-merapto-1,2,4-triazole give strong band in the region (1695-1650) cm^{-1} corresponding to ν(C=N)(54).

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.

In the presence of conjugation, the electronic spectra of, for example $CH_2=CH-CH=N-C_4H_9$, show n→π* transition at 219 nm but the electronic spectra of benzylidene aniline show a very important phenomena since it is iso-electronic with stilibene and they have a different spectra.

The following interpretation of the first four electronic absorption band systems of the benzylidene aniline molecule seen to be accepted by many authors:-

a) The band centered at 322 nm is assigned to a π → π* transition extending over the whole molecule but taking origin from the ph-C-N moiety(52,56,57,58,59,60).

b) The band at 262 nm is characterized for the $C_6H_5CH=N$ fragment and has been interpreted by some authors as a transition to a charge-transfer state in which the ph-ring moiety is the electron donor and the azomethine group acts as an electron acceptor(52,56,57,58,59,60).

c) The band at 237 nm has been assigned to a local excitation in the ph-C-N moiety in which the lone pair on the nitrogen atom interacts with the π-electrons of the ph-C-N ring, on the other band local excitation in the ph- ring has also been proposed to explain absorptions in the same region in the spectrum(56,57,59,61).

d) A fourth band system exists at 218 nm has been assigned to a local excitation in the ph-ring(57,58). The electronic spectra of all other Schiff base like heterocyclic hydroxy, β-diketones(62,63) and those derived form α-diketones have been interpreted on this bases unless indicated otherwise.

1.8 Aim of the present work:

This work aims to synthesizing and characterizing some transition metal complexes with new ligands derived form oxadiazole and benzothiazole. These complexes are designed to be anti bacterial and antitumour agent, according to the general drug structural requirements, This work include:

1)Synthesis of 2-[5-phenyl-2-methylthio-1,3,4-oxadiazole]-5-phenyl-1,3,4-oxadiazole(LI), 2-[O-chloro benzylidine] hydrazino benzothiazole (LII), and 2-[p-hedroxy benzylidine] hydrazino benzothiazole (LIII) .

2) Synthesis of Cu (II), Co (II), Cd(II), Ni(II) and Hg(II) complexes with (LI).

3) Synthesis of Cu(II), Co (II), Cd(II) and Ni(II) complexes with (LII) and (LIII).

4) In order to verify the proposed structures of the prepared complexes spectroscopic methods have been used .these include FT.IR and UV-Vis spectroscopy . The prepared complexes were further studied using conductivity and magnetic susceptibility measurements . Metal analysis was used to identify these complexes.