الخلاصة

في محاولة لادخال مجموعة الايزوميثين في تركيب حلقة النفثالديهايد المعروفة بامتلاكها لعدد من التطبيقات الدوائية بهدف التعرف على السلوك الثنائي للمركبات الجديدة تجاه ايونات العناصر الانتقالية .لهذا الغرض تم تحضير عدد من قواعد شيف الجديدة والمحتوية على ذرتي النيتروجين و الاوكسجين وذلك بتكاثف٢-هايدروكسي-١-نفثالديهايد مع الانلين و سايكلوهيكسايل امين مكونا ً المركبات β-نفثالديهايد-N-فينايل ايمين LI وβ-نفثالديهايد- N-سايكلوهيكسايل ايمين LII على التوالي .

ثم استخدم قواعد شيف المحضرة (LI , LII) كليكندات لتحضير عدد من المعقدات الجديدة مع ايونات بعض العناصر الانتقالية التي تشمل
[V(IV), Hg(II), Cr(III), Cu(II), Co(II), Fe(III) ,Cd(II)]

شخصت الليكندات المحضرة بواسطة الاشعة تحت الحمراء (FT-IR) , ودرجات الانصهار . تم عزل المعقدات الفلزية لليكندات في الحالة الصلبة وكانت مستقرة تجاه الضوء والحرارة والرطوبة . شخصت المعقدات الجديدة بواسطة اطياف الاشعة تحت الحمراء (FT-IR) , والاشعة الفوق البنفسجية-المرئية (UV-Vis) , والقياسات المغناطيسية والتوصيلية الكهربائية اضافة الى تحليل العناصر.

استناداً الى نتائج القياسات اعلاه تم اقتراح الصيغ التركيبية وكاللاتي:-

١- معقدات الايونات V(IV), Hg(II), Cr(III), Cu(II), Co(II), Fe(III) ,Cd(II)

مع الليكند (LI) اعطى الصيغ التالية:

$[Cd\ LI\ CL\ H_2O]\ .4H_2O$, $[Fe\ LI\ (H_2O)_2\ SO_4]\ .4H_2O$,

$[Co\ (LI)_2\ CL_2]\ .H_2O$, $[Cu\ (LI)_2\ CL_2]\ .2H_2O$,
$[Cr\ (LI)_2\ CL\ H_2O]\ .C_2H_5OH$,$[Hg\ (LI)_2\ CL_2].2C_2H_5OH$
$[VO(LI)SO_4].H_2O$

٢- معقدات الايونات V(IV), Hg(II), Cu(II), Co(II), Fe(III), Cd(II) مع

الليكند(LII) اعطى الصيغ التالية :

$[Cd\ LII\ CL_2]\ .C_2H_5OH$, $[Fe_2\ (LII)_2\ (OH)_2(SO_4)_2].2H_2O$,
$[Cu\ (LII)_2\ CL_2]\ .8H_2O$, $[Co\ (LII)_2].3H_2O$,
$[Hg_2\ (LII)_2\ CL_4]$, $[VO\ LII\ SO_4]\ .H_2O$

برزت الخصائص التركيبية والتآصرية المختلفة من خلال دراسة الكيمياء التناسقية بمعقدات الليكاندات الجديدة .

فسرت طبيعة التآصر بين ايون الفلز والذرات المانحة في الليكند بمعامل راكاح ومقاييس المجال الليكندي الاخرى والتي تم احتسابها بواسطة مخطط (تنابا-سوكانو) لـ ايون الحديد الثلاثي و الكروم الثلاثي والكوبلت الثنائي .

Abstract

In an attempt to introduce the azomethine group in the structure of naphthaldehyde ring , which is known to posses a number of therapeutical applications , and in a purpose of investigating the coordination behavior of the new compounds towards transition metal ions . a number of new Schiff-bases , containing nitrogen and oxygen atoms , have been prepared by condensation of 2-Hydroxy-1-Naphthaldehyde with Aniline and Cyclohexylamine forming β-Naphthaldehyde N-Phenyl Imine (LI) and β-Naphthaldehyde N-Cyclohexyl Imine (LII) respectively.

The new Schiff-bases (LI and LII) have been used as ligands to prepare a number of transition metal complexes , which include [Cd(II), Fe(III), Co(II), Cu(II), Cr(III), Hg(II) and V(IV)] ions .

The ligands were characterized by FT-IR spectroscopy , and their melting points . The metal complexes of the obtained ligands have been obtained in solid state and were stable towards light, heat and moisture . They were characterized by FT-IR , UV-Vis spectra , conductivity , magnetic susceptibility measurements, and metal analysis .

On the basis of these techniques the structural formula of the complexes have been suggested which include :-

1- Complexes of Cd(II), Fe(III), Co(II), Cu(II), Cr(III), Hg(II) and V(IV) ions with (LI) show to have the formulas :-

$[Cd\ LI\ CL\ H_2O].4H_2O$, $[Fe\ LI\ (H_2O)_2\ SO_4].4H_2O$

$[Co\ (LI)_2\ CL_2].H_2O$, $[Cu\ (LI)_2\ CL_2\ ]\ .2H_2O$

$[Cr\ (LI)_2\ CL\ H_2O\ ]\ .C_2H_5OH$, $[Hg\ (LI)_2\ CL_2]\ .2C_2H_5OH$

$[VO\ LI\ SO_4]\ .H_2O$

2- Complexes of Cd(II), Fe(III), Co(II), Cu(II), Hg(II) and V(IV) ions with (LII) show to have the formulas :-

$[Cd\ LII\ CL_2]\ .C_2H_5OH$, $[Fe_2(LII)_2\ (OH)_2\ (SO_4)_2]\ .2H_2O$

$[Co\ (LII)_2\ ].3H_2O$, $[Cu\ (LII)_2\ CL_2]\ .3H_2O$

$[Hg_2(LII)_2\ CL_4]$, $[VO\ LI\ SO_4]\ .H_2O$

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

Symbols and Abbreviations

UV-Vis	Ultraviolet –Visible
FT-IR	Fourier transform infrared
m.p.	Melting point
D.W.	Distill water
DMSO	Dimethyl Sulfoxide
DMF	Dimethyl Formamide
υ	Stretching
δ	Bending
O.h	Octahedral
B.M	Bohr Magneton

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I would like to thank my family for their moral sport.

Sham

Chapter One

Introduction

Chapter Two

Experimental part

Chapter Three

Results and Discussion

References

(2-1) Chemicals and techniques

1- Chemicals:

The following chemicals are used in this work..

Compounds	***Purity***	***Supplied from***
Aniline	99%	Fluka
Acetone	99%	Fluka
Chromium chloride $CrCl_3.6H_2O$	98%	Fluka
Copper chloride $CuCl_2. 2H_2O$	95%	Fluka
Cobalt chloride $CoCl_2. 2H_2O$	99%	Fluka
Cadmium chloride $CdCl_2. 2H_2O$	98%	BDH
Cyclohexylamine	95%	BDH
Dimethylformamide (DMF)	99%	BDH
Ether	98%	BDH
Ethanol (absolute)	99.99%	Fluka
Ferric ammonium sulfate $Fe NH_4 (SO4)_2. 6H_2O$	Purim	Fluka
2-Hydroxy-1-naphthaldehyde	90%	Merck
Mercury chloride $HgCl_2$	99%	BDH
Vanadyl sulphate $VOSO_4. H_2O$	90%	Merck

2. Techniques:

A- Fourier Transform Infrared Spectrophotometer (FT-IR)

The Infrared Spectra were recorded on a Shimadzu 8300 Fourier Transform Infrared Spectrophotometer (FT-IR) by using the (KBr) in the wave number range (4000-400) cm^{-1}.

B- Electronic Absorption Spectra

The electronic spectra of the complexes were obtained using: (Shimadzu UV-Vis 160A) Ultraviolet Spectrophotometer using the quartz cell in the range (1100-200) nm.

C- Magnetic Susceptibility Measurements

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

D- 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.

E- 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 metal ions .

F- Conductivity measurements

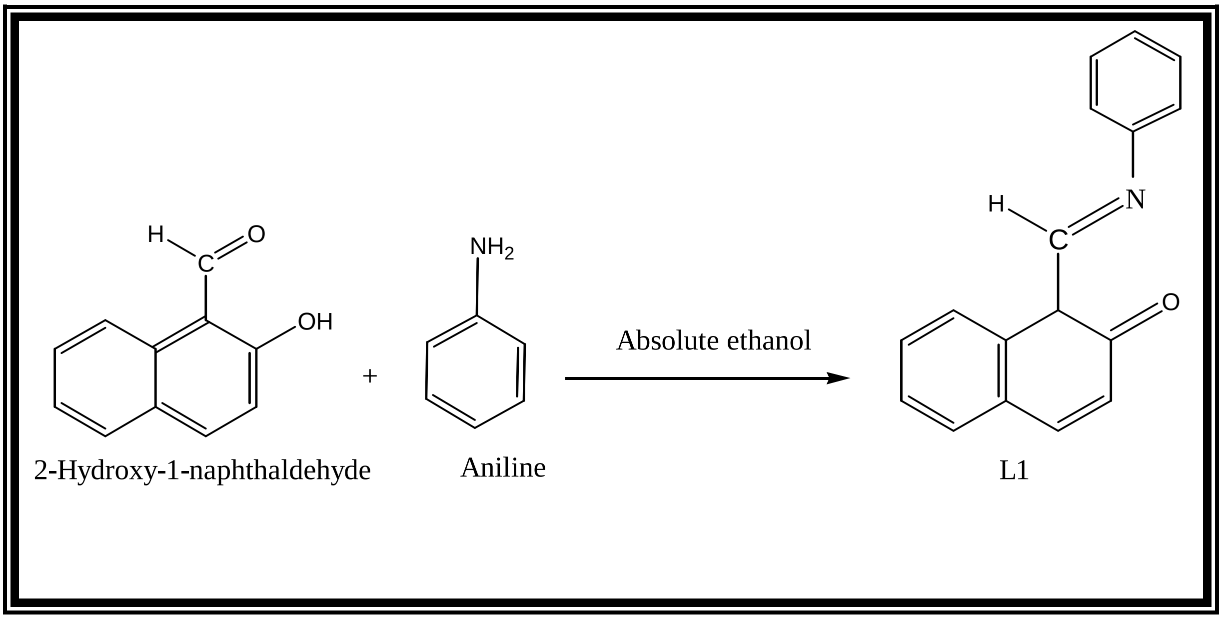
The conductivity measurements were obtained using Corning Conductivity Meter 220.

(2-2) Methods of Preparation

1-Preparation of Ligands

A- β-Naphthaldehyde N-phenyl imine (LI):

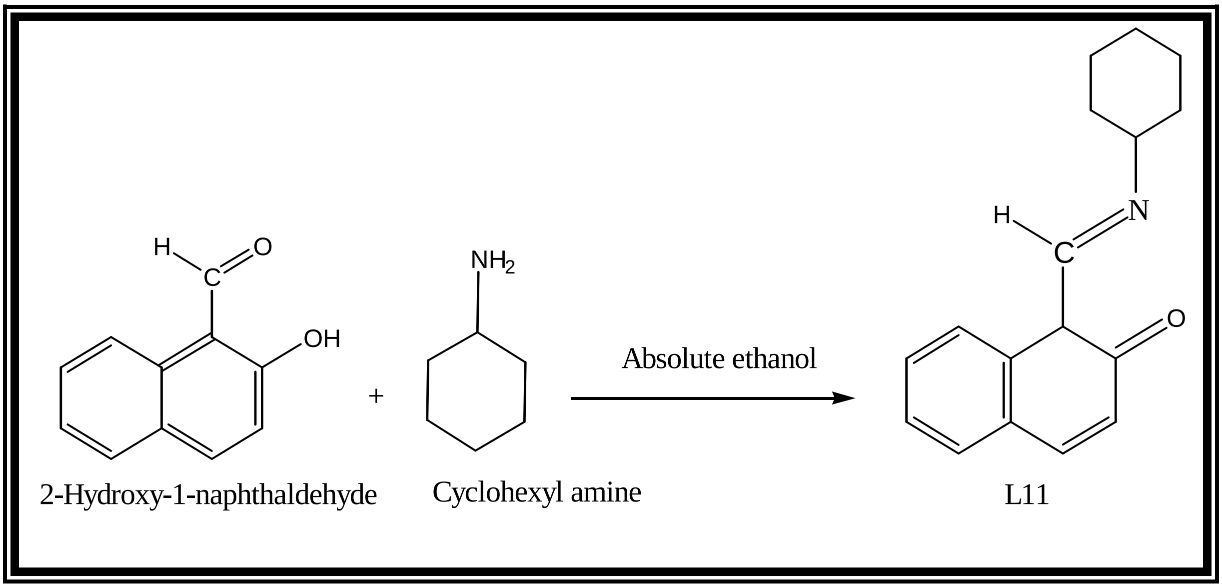
A mixture of (2g , 1.16×10 $^{-2}$ mole) 2-hydroxy-1-naphthaldehyde and (1.08g , 1.06 ml , 1.16×10 $^{-2}$ mole)of Aniline suspended in absolute ethanol (40 ml) in round bottom flask and then reflexed for 12 hours with continuous stirring . After cooling to room temperature the precipitate was filtered and dried under vaccum, The product was recrystalized from absolute ethanol as yellow product, 85.3% yield, m.p. (80-82 c°).



Scheme (2.1)
Reaction for The preparation of LI

B-β-Naphthaldehyde N-cyclohexyl imine (LII):

A mixture of (4g , 2.3×10^{-2} mole) 2-hydroxy-1- naphthaldehyde and (2.2g , 2.6 ml , 2.3×10^{-2} mole)of Cyclohexyl amine suspended in absolute ethanol (40 ml) in round bottom flask and then reflexed for 72 hours with continuous stirring .Then the reaction mixture is concentrated to half by heating gentally and then add appropriate amount of petroleum ether and heating was continue for few minute . After cooling to zero c° the precipitate was filtered and dried under vaccum, The product was recrystalized from absolute ethanol as yellow product, 75% yield, m.p. (60-62 c°).



Scheme (2.2)
Reaction for The preparation of LII

2-Preparation of the metal complexes

A-Preparation the metal complexes of the ligand LI

(1)-Cadmium (II) complex (AI_1) :

(0.1g , 4.5×10^{-4} mole)of $CdCl_2.2H_2O$ dissolved in (5 ml) mixture Of D.W and ethanol was added to (0.22g, 4.5×10^{-4} mole) of LI dissolved in (5 ml) ethanol. The precipitate is formed immediately after stirring. The resulting yellow precipitate was filtered and washed with D.W and ethanol then dried under vaccum. The prepared complex was soluble in DMSO and acetone. Melting point, colour and yield (%) are given in table (3-1).

(2)-Iron (III) complex (AI_2):

(0.1g, 2×10^{-4} mole) of $Fe\,NH_4\,(SO_4)_2.6H_2O$ dissolved in (5 ml) mixture Of D.W and ethanol was added to (0.1g, 2×10^{-4} mole) of LI dissolved in (5 ml) ethanol. The mixture was heated with stirring under –reflex for four hours .After one day the resulting yellow precipitate was filtered and washed with D.W and ethanol then dried under vaccum. The prepared complex was soluble in DMSO and acetone. Melting point, colour and yield (%) are given in table (3-1)

(3)-Cobalt(II)(AI_3),Copper(II)(AI_4),Chromium(III)(AI_5) complexes:

(0.03g, 4×10^{-4} mole) of $CoCl_2.2H_2O$, $CuCl_2.2H_2O$, or $CrCl_3.6H_2O$ dissolved in (5 ml) ethanol was added to (0.1g, 4×10^{-4} mole) of LI dissolved in (5 ml) ethanol. The mixture was heated with stirring under –reflex for four hours .The resulting precipitate was filtered and washed with ethanol then dried under vaccum. The prepared complex was soluble in DMSO and acetone. Melting point, colour and yield (%) are given in table (3-1).

(4)-Mercury (II)(AI_6) and Vanadium (IV) (AI_7)complexes:

(0.05g, 4×10^{-4} mole) of $HgCl_2$ and (0.04g, 4×10^{-4} mole) of $VOSO_4.H_2O$ dissolved in (5 ml) ethanol was added to (0.1g, 4×10^{-4} mole) of LI dissolved in (5 ml) ethanol. The mixture was heated with stirring under –reflex for 24-hours .The resulting precipitate was filtered and washed with ethanol then dried under vaccum. The prepared complex was soluble in DMSO and acetone. Melting point, colour and yield (%) are given in table (3-1).

B-Preparation the metal complexes of the ligand LII

(1)-Cadmium (II) complex (AII_1):

(0.04g, 4×10^{-4} mole)of $CdCl_2.2H_2O$ dissolved in (5 ml) mixture Of D.W and ethanol was added to (0.1g, 4×10^{-4} mole) of LII dissolved in (5 ml) ethanol. The precipitate is formed immediately after stirring. The resulting yellow precipitate was filtered and washed with D.W and ethanol then dried under vaccum. The prepared complex was soluble in DMSO and acetone. Melting point, colour and yield (%) are given in table (3-2).

(2)-Iron (III) complex (AII_2):

(0.1g, 4×10^{-4} mole) of Fe $NH_4(SO_4)_2.6H_2O$ dissolved in (5 ml) mixture Of D.W and ethanol was added to (0.1g, 4×10^{-4} mole) of LII dissolved in (5 ml) ethanol. The mixture was heated with stirring under –reflex for four hours .After one day the resulting brown precipitate was filtered and washed with D.W and ethanol then dried under vaccum. The prepared complex was soluble in DMSO and acetone. Melting point, colour and yield (%) are given in table (3-2).

(3)-Cobalt (II)(AII_3), Copper (II)(AII_4) complexes:

(0.03g, 4×10^{-4} mole) of $CoCl_2.2H_2O$ or $CuCl_2.2H_2O$ dissolved in (5 ml) ethanol was added to (0.1g, 4×10^{-4} mole) of LII dissolved in (5 ml) ethanol. The mixture was heated with stirring under –reflex for four hours .The resulting precipitate was filtered and washed with ethanol then dried under vaccum. The prepared complex was soluble in DMSO and acetone. Melting point, colour and yield (%) are given in table (3-2).

4)-Mercury (II)(AII_5) and Vanadium (IV)(AII_6) complexes:

(0.05g, 4×10^{-4} mole) of $HgCl_2$ and (0.03g, 4×10^{-4} mole) of $VOSO_4.H_2O$ dissolved in (5 ml) ethanol was added to (0.1g, 4×10^{-4} mole) of LII dissolved in (5 ml) ethanol. The mixture was heated with stirring under –reflex for 24-hours .The resulting precipitate was filtered and washed with ethanol then dried under vaccum. The prepared complex was soluble in DMSO and acetone. Melting point, colour and yield (%) are given in table (3-2).

1-1 Interaction of the ligands with the metal ions

The tendency of metal ion to form a stable complex with ligands depend on many rules such as the hard and soft acids and bases (HSAB) rule for Pearson (1).Which imply that metal ion tend to coordinate with certain functional groups of the ligand to form a stable complex.

On the other side, the tendency of transition metal ion for special oxidation states is affected by the coordination to certain ligands. This phenomena is called (symbiosis) (2).

Increasing the positive charge on the central transition metal ions strengthens the metal-ligand bonds . The metal ion prefere to bind with atoms of high electron density such as N^{-3} , O^{-2} , P^{-3}, S^{-2} and C^{-4} (3) .

The Irving Williams series of stability for a given ligand show agood criterian for the stability of complexes with dipositive metal ions which 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 across the series and in part from ligand filed effects.

A second observation is that certain ligands form their most stable complexes with metal ions such as Ag^{+}, Hg^{+2}, and Pt^{+2}, but other ligands seem to 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 preferences 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(4):

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

The ligand should have certain characteristic properties to make it convenient to form a stable complex with transition metal ions .The size, geometrical shape ,number and geometrical arrangement of ligand donor atoms play the important role in stability of the resultant complex (5).

The transition-Metal compound have certain characteristic properties which make them convenient in many aspects of life .Many biologically important reactions take place with the aid of proteins in which transition-metal atoms play important roles (6).

1-2 Metal in medicine

Bioinorganic chemistry is a rapidly developing field and there is enormous potential for applications in medicine ,not only for the 24 or so essential elements ,but also for nonessential and even radioactive elements . Biomedical inorganic chemistry ("elemental medicine") is an important new area of chemistry . It offers the potential for the design of novel therapeutic and diagnostic agents and hence for the treatment and understanding of diseases which are currently intractable [Fig. (1-1)] (7)

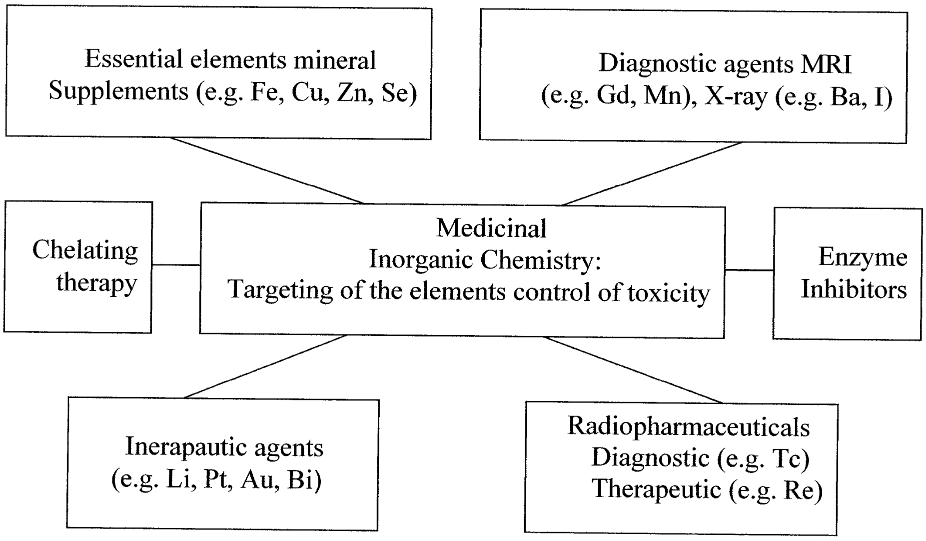


Fig. (1-1) The major key areas of medical inorganic chemistry

The field has been stimulated by the success of cisplatin , the world's best stelling anticancer drug , and platinum complexes with reducing toxicity , oral activity , and activity against resistant tumors are currently on clinical trial (8).

The ability of metal ion to coordinate with (bind) and then release ligands in some processes,and to oxidize and reduce in other processes makes them ideal for use in biological systems . The most common metal used in the body is Iron , and it plays a central role in almost all living cells , for example, Iron complexes are used in the transport of oxygen in the blood and tissues (9).

The metal cadmium is known to damage kidneys and have carcinogenic effects. Researchers have recently learned that cadmium also causes estrogen-like responses in laboratory animals . The metals estrogen-mimicking effects may lead to reproductive disorders and contribute to hormone-related cancers (10) .

It is relevant to notice that cobalt compounds have been under the increased interest as potential radio sensitizers during the last 10 years. It was observed that Co(II) complexes have shown specific hypoxic radiosensitization and thermosensitization as well as antitumour activity in vivo . some current observations have suggested that further investigations with cobalt-containing complexes are warranted (11).

It was discovered nearly 20 years ago that V^{V} as vanadate and V^{IV} as Vanadyl can mimic some of the effects of insulin (stimulate glucose uptake and oxidation as well as glycogen synthesis) . Vanadium complexes with organic ligands are often less toxic and can have improved aqueous solubility and lipophilicity(7).

Also Cr(III) is an essential dietary nutrient, it is required to potentiate insulin and for normal glucose metabolism. Chromium deficiency has been associated with impaired glucose tolerance, fasting hyperglycemia , glucosuria, elevated percent body fat, decreased lean body mass , maturity-onset diabetes, cardiovascular disease, decreased sperm count, and impaired fertility (12) .

Increasing knowledge of metal biochemistry will provide for the design of new drugs (both inorganic and organic) in many other areas too, for example neuropharma-ceutical and antiinfective agents .Progress in medicinal coordination chemistry is heavily dependant on understanding not only the thermodynamic (equilibria and structure) but also the kinetics (and mechanisms)of reactions of metal complexes ,especially under biologically relevant condition (7) .

Other example about the biological activity for the metal complexes are oxine (8 –hydroxyl quinoline) which has antifungal and antibacterial properties when chelated to Fe(III) . They have been shown that the ligand and Fe(III)ion are both inactive when separated from each other but are highly effective together (13) .

A correlation has been drawn between active tetracyclines and the ability to form 2:1 complexes with Cu^{+2} , Ni^{+2} and Zn^{+2} ,while the presence of excess metal ions inhibits the action of the tetracyclines(2) .

Recently , a platinum(II) complex with a thiourea ligand fig (1-2) was reported that showed excellent cytotoxicity against a leukemia cell line .The complex may bind to DNA in a dual manner involving platinum coordination and acridine intercalation . The complex exhibited activity against two ovarian cancer cell lines at micromolar concentration , but slightly less activity than that of the free ligand (14,15).

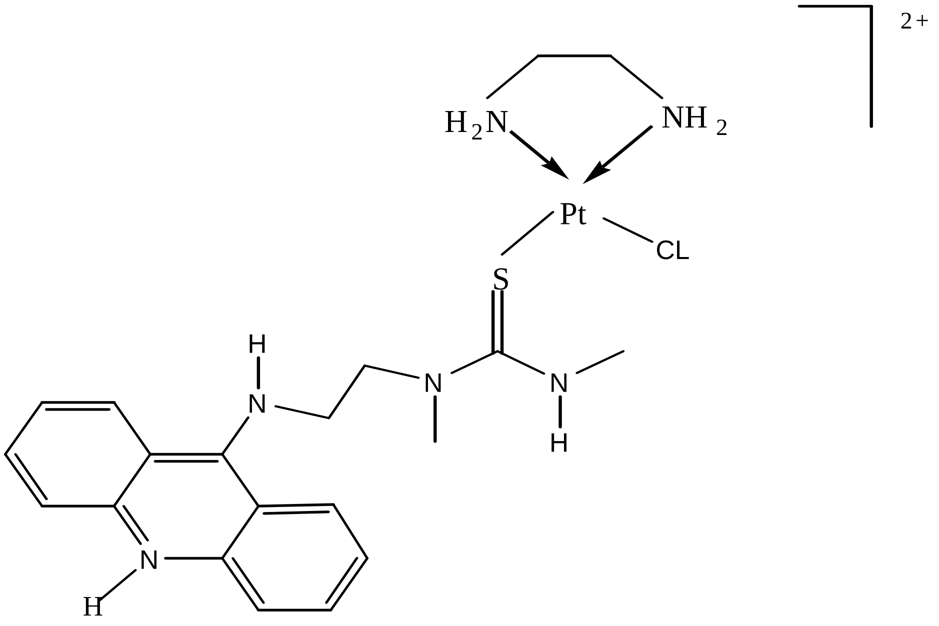


Fig (1-2) Structure of Pt(II) complex with acridinylthiourea ligands .

1-3 Schiff Bases

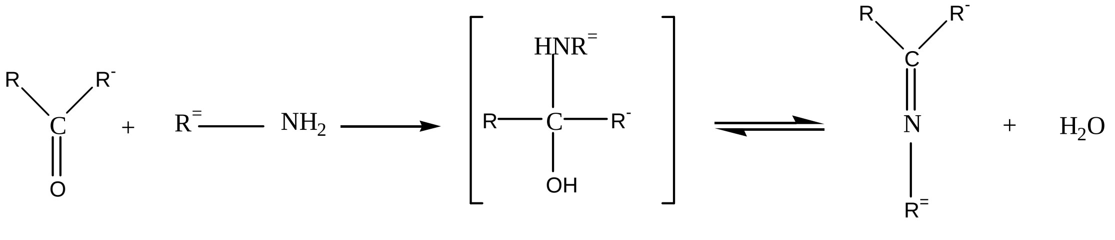
1-3-1 Synthesis of Schiff Bases:

The term "Schiff base" used to define those organic compounds which contain the functional group $\left(-\overset{|}{C}=N-\right)$ Schiff bases were firstly prepared by Schiff in 1864 $^{(16-19)}$.from condensation reaction of aldehydes or ketones with primary amines . Schiff bases have several nomenclature such as anils , imines , azomethines , benzanils and benzyildeneaniline$^{(20)}$.

Imines ,Schiff bases and other C=N compound can be reduced with $LiALH_4$,$NaBH_4$, Na-EtOH ,hydrogen and a catalysit ,as well as with other reducing agents $^{(21)}$.

Schiff bases rapidly decomposed in aqueous acidic media , but they are very stable in basic solutions(22).

Schiff base 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 .



(1) (2) (3)

Scheme (1-1)

Preparation of Schiff base

These bases can also be prepared by refluxing of equimolar quantities of aldehyde or ketone with amine or by slow melting for 10 minutes and then isolating and purifying the product by recrystallization , or sublimation under reduced pressure (20,23).

Staab (24) prepared Schiff bases by removing water which is formed by condensation of aldehydes with amine by reflex in benzene this is done by mixing the amine and the aldehydes 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 .

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 (25,26).

1-3-2 The Metal Complexes of Schiff Bases as Biologically Important Compounds

Schiff bases and their metal complexes received a great deal of attention during the last decade from many workers to prepare new sets of these bases and their transition metal complexes (27).

These complexes have proven to be antitumer and have carcinostatic activities (27,28) .they show leukaemetic activity . Schiff bases , on the other side , have a great importance in biological reactions like (visual process)(29) . and in the reaction that involve removing the amine group by enzymic effect (enzymatic transition reaction)and some B_6-catalysed reaction (30).

The biological activity of Schiff base is attributed to the formation of stable chelates with transition metal ions presents in cells (31).

Schiff bases derived from sulfa drugs have been successfully used for the bacteriostatic activities and complexation (32) . A great deal of work concerning metal complexes of Schiff bases were concentrated on the cobalt (III) complexes ,that are used as reversible of 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 in some biological systems (33) .

It has been noticed hat 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 (34),led to development of platinum complexes chemistry designed for wide biological applications (35). Palladium and platinum are regarded as soft metal , so they react with soft ligands that contain an electron –donating group like **S** and **P** ,they also can form complexes with hard ligands(36),like oxygenating molecules or molecules which contain nitrogen .

Recently many research works (37) appeared which deal with the study of palladium interaction with Schiff bases through cyclometalation 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 a starting material to improve the stereochemistry of those 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 in formation of amines that have biological origin (38).

Biological activity of complexes derived from hydrozones has been widely studied and contrasted , acting in processes such as antibacterial , antitumoral , antiviral , antimalarial and antituberculosis effect (39).

Organotin compound show a large spectrum of biological activities . In recent years ,several investigators to test their antitumour activity(40,41), 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(42).They are also used as bactericides ,fungicides and industrial and agriculture biocides(43).

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 increases on complexation with metal ion (3).

A number of new transition metal complexes of some Schiff bases derived from amino-triazole and different aromatic aldehydes have been prepared and isolated as solid compounds (44).The biological activity for these new Schiff bases complexes were evaluated against a number of bacteria . The results reflect the synergistic effect towards the increase of activity for some complexes compared with that of the corresponding ligand .

Davar et.al(45) have prepared unsymmetrical Schiff base 1-hydroxy-2-acetonaphthoneacetyl acetone-ethylendiimine and its complexes with some transition metals [Ni(II),Cu(II),Pd(II)] . These compounds were characterized 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 salicyladehyde or hydroxylacetophenone Schiff bases , due to the naphthalene nucleus possessing −OH group increases the activity fig. (1-3) .

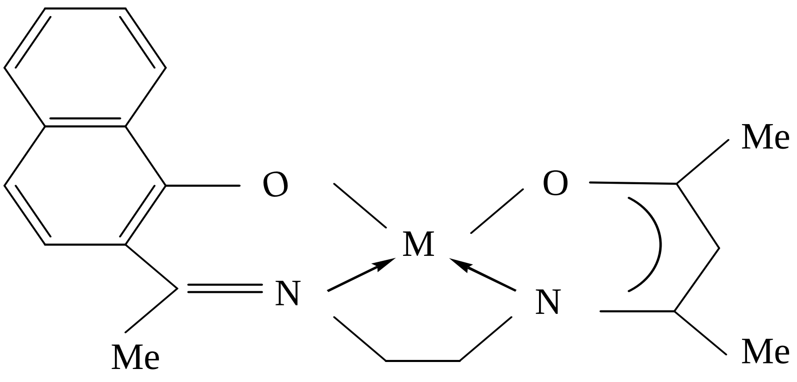


Fig. (1-3) suggested structure of the complexes .

Where M= Ni(II) , Cu(II) , Pd(II) .

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

Table (1-3) The structure and biological activities of some metal complexes of a number of Schiff bases.

Molecular formula	The name	Metal ion	Biological activity	Ref.
$C_{12}H_{15}N_5SO_2$	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	46
$C_{25}H_{16}N_4S$	4-phenyl-5-[p(α-naphthalidene) phenyl]-3-mercapto-1,2,4-trizole	Co^{+2},Cu^{+2} Pd^{+2}	Antibacterial activity	3
$C_{18}H_{15}N_3OS$	Thiocarboxyphenyl-4-allyl-5-phenyl-4H-1,2,4-trizole	Hg^{+2},Au^{+2}, Ca^{+2},Cd^{+2} Cu^{+2},Fe^{+2}	Antibacterial activity	47
$C_{12}H_{11}N_3S_2$	2-(benzylidene)-5-allylthio-1,3,4-Thiadiazole	Cu^{+2},Fe^{+2}	–	48
$C_{13}H_9N_3OCL_2$	N-isonicotinamido-2,4-dichloro benzalidimine	Co^{+2},Ni^{+2}	Antimicrobial activity	84
$C_{17}H_{14}N_2O_3S$	2-Hydroxy-1-naphthaldehyde salphanilamide	Sn^{+4}	Antimicrobial activity	49
$C_{13}H_{12}N_2O_3S$	Salicylaldehyde sulphanilamide	Sn^{+4}	Antimicrobial activity	49

1-3-2 Infrared Spectra of Schiff bases and their metal complexes

The following are a review of the γC=N assignment , as recorded for Schiff bases and their metal complexes(16-19).

1. γ(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 (50).

2. Coordination of chain polymers of Schiff bases derived from o-aminobenzic acid and terephthalaldrhyde shows C=N stretching at 1625 cm^{-1} and is shifted to (1620-1615) cm^{-1} on complex formation , indicating the involvement of azomethines nitrogen in coordination (51).

3. A strong band appeared around 1590 cm^{-1} is assigned to the C=N stretching of the free Schiff bases , bis (vanilline) ethylenediimine, bis(vanilline) propylenediimine ,bis (vanillin)o-phenylenediimine, It was found in the region (1675-1665) cm^{-1} for their complexes with Cu(II) (52).

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 γ(C=N)(53).

5. Schiff bases, oximes, thiadiazoles , iminocarbonates , and guanidines show the C=N stretch in the region (1689-1471) cm^{-1}(54).

6. The I.R. spectra of new series of Schiff bases derived from substituted ,4,5-disubstituted-2-amino-thizole, substituted-2-amino-benzothiazoles and p-hydroxybenzaldehyde show a strong sharp band in the region (1640-1625) $cm^{-1}$for γ(C=N)(55).

7. Strong band at 1600 cm^{-1} was corresponded to γ(C=N) (56) 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 (28).

8. The I.R spectrum give absorption band in the region (1640-1630)cm^{-1} for γ(C=N)of free tetraimine Schiff bases macrocycles erived from the condensation of 1,3-diamino-2-hydroxypropane with pyrrole-2,5-dicarbaldehyde and with thiophene-2,5-dicarbaldehyde (57).

9. Patai suggest that γ(C=N) appear in the region (1680-1570)cm^{-1}, the intensity of γ(C=N) is variable and it depend on the substituted groups (20).

10. The I.R spectum of Schiff bases derived from 4-phenyl-5-(p-aminophenyl)-3-mercapto-1,2,4-triazole give strong band in the region (1695-1650) cm^{-1} corresponding to γ(C=N) (3).

1-4 Aim of the present work :-

This work aims at synthesizing and characterizing some transition metal complexes with new ligands derived from naphthalene. These complexes are designed to be antibacterial and antitumour agents , according to the general drug structural requirements , This work include :-

1- preparation of β-Naphthaldehyde-N-Phenyl imine (LI) and β-Naphthaldehyde-N-Cyclohexyl imine (LII) .

2- Preparation of Cd(II), Fe(III), Co(II), Cu(II), Cr(III), Hg(II) and V(IV) complexes of ligand (LI).

3- Preparation of Cd(II), Fe(III), Co(II), Cu(II), Hg(II) and V(IV) complexes of ligand (LII).

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Synthesis and characterization of some transition metal complexes with new Schiff bases derived from naphthalene ring

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

تحضير وتشخيص بعض معقدات العناصر الانتقالية مع قواعد شيف جديدة المشتقة من حلقة النفثالين

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

من قبل
شم ولي قربان
الاركوازي
بكالوريوس ٠٠ (جامعة النهرين)

رمضان١٤٢٧ه ايلول ٢٠٠٦م

بِسم اللهِ الرَّحمنِ الرَّحيمِ

قالو سبحانك لاعلم لنا الا ماعلمتنا
انك انت العليم الحكيم

صَدَقَ اللهُ العَظيم

سورة البقرة الاية
٣١-٣٢

الاهداء

الى المعلم الاول رسول المحبة والانسانية محمد رسول الله (عليه وعلى اله الصلاة والاسلام)

الى من توج اسمي باسمه الى الذي افنى عمره ووهب لي عطفه وبره وشد من ازري في السعي لطلب العلم

والدي العزيز

الى من جعل الجنة تحت اقدامها وتأنس روحي بقربها ويستنير دربي بدعائها وتخفو احزاني بابتسامة عينيها

امي ومعلمتي

الى من احاطوني برعايتهم وشاركوني في فرحي وشجوني وقدموا لى الدعم المعنوي

اخواتي

الى عزي و سندي في الدنيا

اخي

الى زينة الحياة ....وقرة العين

لانة... بانة

ال كل من له مكانه في قلبي اليكم ما وفقني اليه ربي

شم

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3-1 Physical properties of the prepared complexes

Table (3-1) and (3-2) show the physical data for the prepared complexes . Which show different melting points , all of them were higher than the parent ligand, The colour which are shown in table (3-1) and (3-2) were useful in structural determination . All the prepared compounds were stable towards air, moisture and light .

All reactions were carried out at room under heating conditions and the solvent was abs. ethanol . Recrystallization solvent was ethanol/ water mixture (1:1) for all reactions .

Identification and study of these complexes were carried out by metal analysis [The results are shown in tables (3-1) and (3-2)], infra-red, ultra-visible spectrophotometer , 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) and (3-7).

Table(3-1)

Physical properties for the LI and its metal complexes

Symbol	Colour	Melting point °C	Yield ٪	Metal analysis ٪	
				Calc.	Found
LI	Yellow	80 - 82	85.3	−	−
AI_1 , Cd(II)	Yellow	188(dec.)	75	23.08	22.75
AI_2 , Fe(III)	Brown	170 -172	72	11.01	11.02
AI_3 , Co(II)	Yellowish-green	250 (dec.)	60	9.18	9.55
AI_4 , Cu(II)	Green	112-114	78	9.55	10.11
AI_5 , Cr(III)	Brown	150-152	64	7.84	7.99
AI_6 , Hg(II)	Deep-yellow	101-103	61	23.40	21.44
AI_7 , V(IV)	Green	123-125	70	11.89	12.05

Table(3-2)

Physical properties for the LII and its metal complexes

Symbol	Colour	Melting point °C	Yield %	Metal analysis %	
				Calc.	Found
LII	Deep-Yellow	60 -62	75	–	–
AII_1 , Cd(II)	Brown	250(dec.)	78	23.38	24.01
AII_2 , Fe(III)	Light- Brown	176 -178	74	12.52	12.76
AII_3 , Co(II)	Green	200 (dec.)	68	9.54	9.87
AII_4 , Cu(II)	Brownish-Green	98-100	66	8.12	9.11
AII_5 , Hg(II)	Brown	115-117	70	19.18	20.52
AII_6 , V(IV)	Greenish-blue	130-132	72	11.75	11.79

3-2 Infra – red spectra

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

3-2-1 The FT-IR spectra of LI and their metal Complexes

The ligand LI has 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 (20,44) . the compound containing azomethine group show basic coordination 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 (58,59,3), or toward lower frequency in others(60,61).

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 (58). 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 (62,63) .

The I.R. spectra of the ligand LI ,Fig(3-1), Table(3-3), showed the absence of the band at ~1735 cm^{-1} and ~3315 cm^{-1} due to the carbonyl υ(C=O) and υ(NH_2) stretching vibration (64), and a strong new band appeared at 1640 cm^{-1} assigned to azomethine υ(HC=N) linkage , showing that amino and aldehyde moieties of the starting material are absent and have been converted in to the azomethine group (65).

A broad band appearing at (3420 cm^{-1}) have been assigned to the hydrogen bonded OH group in the ligand LI . Medium to strong intensity bands appear at (1344 cm^{-1}) which may be assigned to the phenolic C—O stretching mode . This band is slightly shifted to higher frequency side in the spectra of the complexes showing chelation of the phenolic oxygen to the metal atom (66).

The band appear at 1587, 1518 and 1485 cm^{-1} refer to υ(C=C) of aromatic ring , and the band at 2920 and 2852 cm^{-1} refer to υ_{C-H} of aromatic ring (67).

A- Cadmium(II) Complex (AI_1)

The spectra of AI_1 complex , Fig(3-3), Table(3-3), which show the shifting of the azomethine band to lower frequency by (12) cm^{-1} indicating the participation of azomethine nitrogen in the interaction with the cadmium (II)ion .

Another difference appeared which was the red shifting of the phenolic C—O band by (10)cm^{-1}in the spectra of AI_1 complex referring to chelation of the phenolic oxygen to the cadmium (II)ion(65,66) .

A broad band which appeared at 3460 and another medium sharp band at 746 cm^{-1} indicate the presence of both coordinating and lattice H_2O molecules in the structure of AI_1 complex .

B- Iron(III) Complex (AI_2)

The molecular formula of Iron (III) complex (AI_2) includes six water molecules , two of them may be coordinated to the metal and the other four were considered to be lattice water . The presence of this large number of water molecules expected due to the high tendency of Fe(III) to bind to water through a strong bond which affected the i.r. spectrum of the complex(4a) , so the band at 3452 and 663 cm^{-1} refer to the presence of both coordination and lattice H_2O molecules .

The spectrum of Fe (III) ion ,Fig(3-4) , show the azomethine band to be shifted to lower frequency by (20)cm^{-1} indicating the interaction of the metal ion with the azomethine nitrogen and also the shifting of phenolic υ(C—O) band to higher frequency showing the participation of phenolic oxygen with the Fe (III) ion (65,66).

The weak band at 565 and 504 cm^{-1} refer to υ(Fe—N) and υ(Fe—O) bands respectively (69,70).

Another bands appeared at 1170 , 1082 and 1028 cm^{-1} refer to the sulphate group bonded to ferric ion as a bi-dentate ligand (69,71). Table (3-3) shows the most characteristic bands of LI and its complexes .

C- Cobalt(II) (AI_3) and Copper(II) (AI_4) Complexes

The spectra of these complexes , Fig(3-5) and (3-6), showed similar behavior with no much difference compared to that of the ligand .

The i.r. spectrum show a blue shift of the azomethine band by (20) cm^{-1} and red shift of phenolic υ(C—O) band to higher frequency which mean the involvement of both nitrogen and oxygen in coordination with both metal ions Co(II) and Cu(II)(65,66) .

Further condusive evidence of the coordination of the ligand with the studied metal ions was shown by the appearance of new weak low frequency band at (400-600) cm^{-1} these were assigned to υ(M—O) and υ(M—N) vibrations . The new band were only observable in the spectra of metal complexes and not in the spectra of uncomplexed ligand thus confirming the participation of groups (O and N) in coordination (72).

The broad band found in the region (3000-3600) cm^{-1} refer to the presence of water molecules out of the coordination sphere for AI_3 and AI_4 complexes (67).

Table (3-3) shows the most characteristic band of AI_3 and AI_4 .

D- Chromium (III) Complex (AI_5)

On comparison of the chromium (III)complex (AI_5) spectrum , Fig(3-7), Table(3-3) , with that of the free ligand , the following changes were observed . First , the υ (C=N) band was shifted to lower frequency by (18) cm^{-1} , and the second was the disappearance of the broad band of υ(O−H) which indicates the complexation with Cr(III) ion .and the shifting of υ (C—O) band to higher frequency by 12 cm^{-1}.

From the above information would indicate that the coordination of LI with chromium(III) ion took place through nitrogen and oxygen atoms.

The presence of new weak band observed at (567 cm^{-1}) and (516 cm^{-1}) which assigned to υ (Cr—N) and υ(Cr—O) respectively .

The broad band appear at (3749 cm^{-1}) which refer to the presence of ethanol molecule in the structure .

The appearance of weak band at (657 cm^{-1}) indicated the presence of coordinated water molecules in the structure (69,67).

E- Mercury (II) Complex (AI_6)

Mercury (II) ion is known to have different geometrical shapes ranging from linear to tetrahedral or octahedral (4a,73). For octahedral complexes, the shape is distorted with two bonds much shorter than the other four , which can some times regarded as linear complex (68).

In this work , a mercury (II) complex (AI_6) , Fig (3-8) , was prepared and characterized by the shift of azomethine band to a lower frequency by (15)cm^{-1} which appeared at (1625 cm^{-1}) , also the shifting of υ(C—O) band to higher frequency by (10) cm^{-1} and appeared at (1354 cm^{-1})

From the above information , it can be concluded that the coordination took place through nitrogen and oxygen atom present in ligand LI with mercury(II) ion (65,66).

A broad band appeared at (3749 cm^{-1}) indicate the presence of ethanol molecule in the structure of the complex .

F- Vanadium(IV) Complex (AI_7)

The FT-IR spectrum of (AI_7) complex is show in Fig (3-9), the stretching frequency of azomethine group was shifted to lower frequency by (10) cm^{-1} and appeared at (1630 cm^{-1}), the band for the υ(C−O) was shifted to higher frequency by (6 cm^{-1}) and appeared at (1350 cm^{-1}). This indicate the participation of azomethine nitrogen and phenolic oxygen with the V(IV) ion (72).

The band at (977 cm^{-1})can be assigned to υ(V=O) (73). The sulphate group have been shown to be bonded with V(IV) through two oxygen atoms (bidentate behavior) due to the appearance of medium band at 1180,1157 and 1099 cm^{-1} (69,71). The broad band found in the region (3000-3600cm^{-1}) refer to the presence of water molecules out of the coordination sphere (67)

The band at 563 and 505 cm^{-1} can be attributed to υ(V—N) and υ(V—O) respectively (69) .

3-2-2 The FT-IR Spectra of LII and their metal complexes

The I.R. spectrum of LII show the same behavior of the LI , which contain the same group (azomethine group and phenolic oxygen) that used to characterize the spectra of the complexes .

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

The azomethine band appeared at (1650 cm^{-1}) and the(1235 cm^{-1})refer to the υ(C—O) stretching vibration (65,66) .

The broad band at (3247 cm^{-1}) assigned to the υ(O−H) (67) 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 (72) .

The band appear at 1500 ,1450 and 1407 cm^{-1}refer to υ(C=C) aromatic ring , and the band at 3049 cm^{-1} refer to the υ_{C-H} of cyclohexane , the band 2929 and 2854 cm^{-1} refer to the υ_{C-H} of aromatic ring (67).

A- Cadmium(II) Complex (AII_1)

The i.r. spectra of (AII_2) complex , Fig (3-10) , Table (3-3), show the shifting of υ(C=N) to lower frequency by (20) cm^{-1} which appear at (1631cm^{-1}) .

Also the band at (1255 cm^{-1}) which corresponded to υ(C—O) shift to a lower frequency by (20) cm^{-1} . These observation indicated the participation of both oxygen and nitrogen in the complex .

A broad band appeared at (3516 cm^{-1}) indicating the presence of ethanol molecule in the structure .

B- Iron (II) Complex (AII_2)

The spectrum of Fe(III) complex (AII_2) , Fig (3-11) , Table(3-3), show the azomethine band was shifted to lower frequency which appeared at (1635cm^{-1}) ,and the υ(C—O) was shifted to higher frequency which appeared at (1250 cm^{-1}) , This indicating the participation of azomethine and phenolic oxygen in complexation (65,66) .

The weak band at 553 and 507 cm^{-1} refer to υ(Fe—N) and υ(Fe—O) band respectively (69,70) .

Other band appeared at 1172 , 1142 and 1035 cm^{-1} refer to the sulphate group bonded to Ferric ion as a bidentate ligand (69,71) . In general the compounds of Fe(III) usually tend to form brigdinghydroxy group , this group can be assigned at (989 cm^{-1}) which refer to its stretching vibration (4a,68) .another band at 3462 and 682 cm^{-1} refer to the presence of both coordination and lattice H_2O molecules

C- Cobalt(II) (AII_3) and Copper(II) (AII_4) Complexes

The spectra of Co(II) and Cu(II) complexes , Fig (3-12) and Fig (3-13) , show similar behavior and were characterize by the shifting of υ(C=N) to lower frequency by 10 cm^{-1} and shifting of υ(C—O) to higher frequency by 10 cm^{-1} . These observation indicate the coordination of the metals ion with azomethine nitrogen and phenolic oxygen atom.

Two weak band appear at 569 and 513 cm $^{-1}$ refer to υ(Co—N) and υ(Co—O) respectively and at 574 and 522 cm^{-1} refer to υ(Cu—N) and υ(Cu—O) respectively (69) .

The broad band appear at (3460 cm^{-1}) in the spectra of Cu(II) complex indicate the presence of water molecule in (AII_4) complex .Table(3-3) show the most characteristic band of AII_3 and AII_4 complexes.

D- Mercury (II) Complex (AII_5)

The i.r. spectrum of AII_5 complex , Fig (3-14) , show the shifting of azomethine band to a lower frequency and appear at (1635 cm^{-1}) which indicate the participation of azomethine- nitrogen with Hg(II) atom (the high basisity of the N of the naphthalene ring allow the coordination with the metal (74)).

Since the υ(C—O) band in the spectra of AII_5 complex show no difference and appear at (1235 cm^{-1}) which indicate that phenolic-oxygen did not participate in the coordination with the mercury ion.

E- Vanadium (IV) Complex (AII_6)

The FT-IR spectrum of (AII_6) complex , Fig (3-15), show the shifting of azomethine band to lower frequency by 22 cm^{-1} and the shifting of υ(C—O) band to higher frequency by 15 cm^{-1}, which indicate the participation of both oxygen and nitrogen in the coordination of the (AII_6) complex (72).

The band at 989 cm^{-1} can be assigned to υ (V=O) band (73) . the sulphate group have been shown to be bonded with V(IV) ion through two oxygen atom (bidentate) due to the appearance of medium band at 1182, 1139 and 1060 cm^{-1} (69,71). The broad band appear at 3425 cm^{-1} refer to the presence of water molecules out of the coordination sphere (67).

The band at 563 and 515 cm^{-1} can be attributed to υ(V—N) and υ(V—O) respectively (69) .

Table (3-3): The most significant bands of FT-IR of the LI & LII and its metal complexes .

Symbol	υ(C=N)	υ(O−H)	υ(C−H)	υ(C−O)	υ(M−N)	υ(M−O)	δ(O−H)
LI	1640	3420	2920 2852	1344	_	_	968
AI_1	1628	3460	2926 2858	1355	545	506	980
AI_2	1622	3452	2939 2838	1369	565	504	970
AI_3	1622	3458	2927	1375	550	508	966
AI_4	1624	3458 3298	2926 2860	1362	568	509	961
AI_5	1622	3749	2962 2831	1357	567	516	982
AI_6	1625	3749	2927	1354	588	534	977
AI_7	1630	3454	2925 2856	1371	563	505	955
LII	1650	3247	2929 2854	1235	_	_	947
AII_1	1631	3516	2927 2852	1255	553	503	948
AII_2	1635	3462	2925 2850	1250	553	507	950
AII_3	1641	_	2929 2854	1245	569	513	_
AII_4	1638	3460	2933 2862	1251	574	522	950
AII_5	1635	_	2929 2850	1235	586	523	_
AII_6	1628	3425	2927 2852	1250	563	515	931

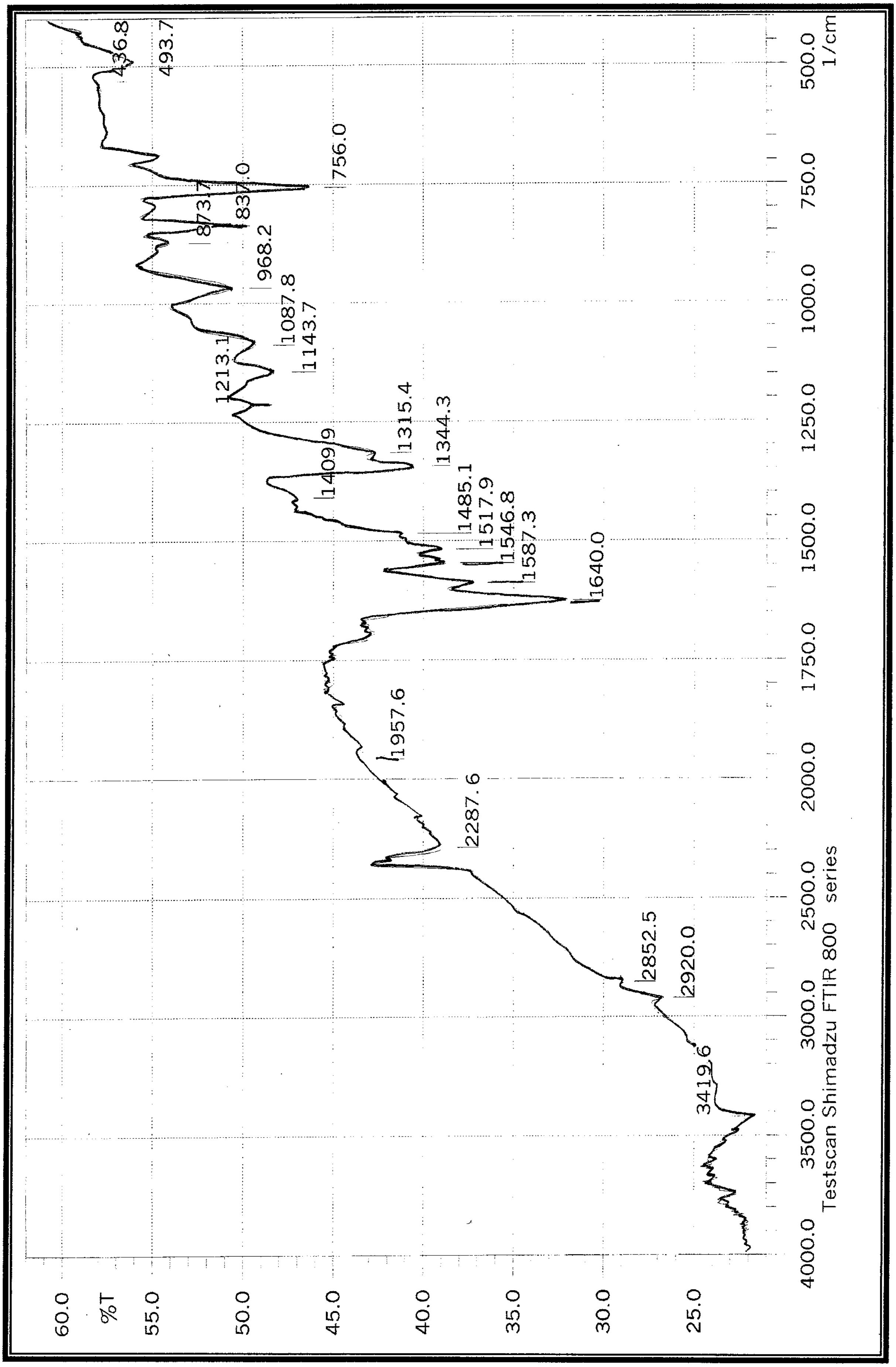


Fig (3-1) FT-IR spectra of LI

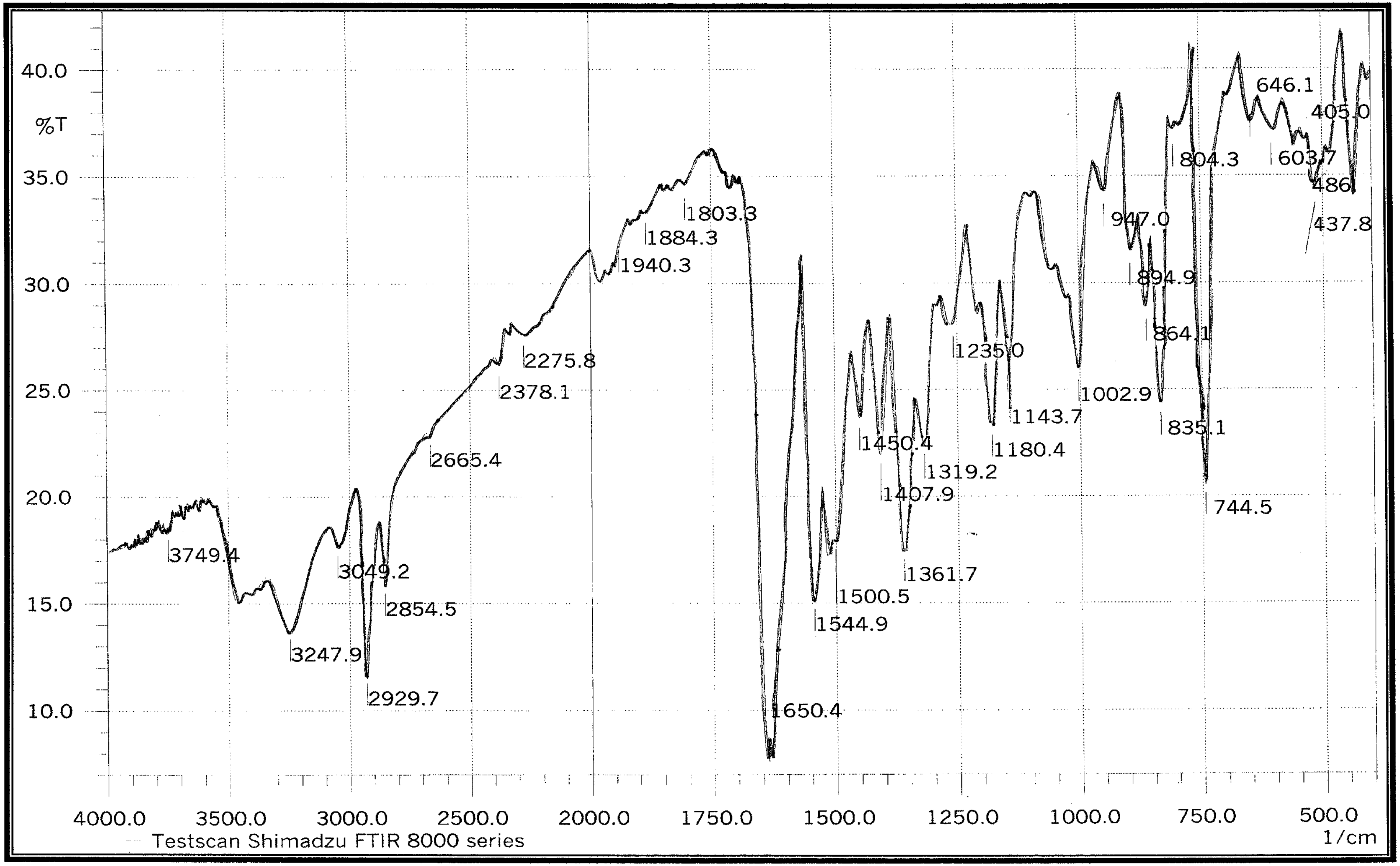
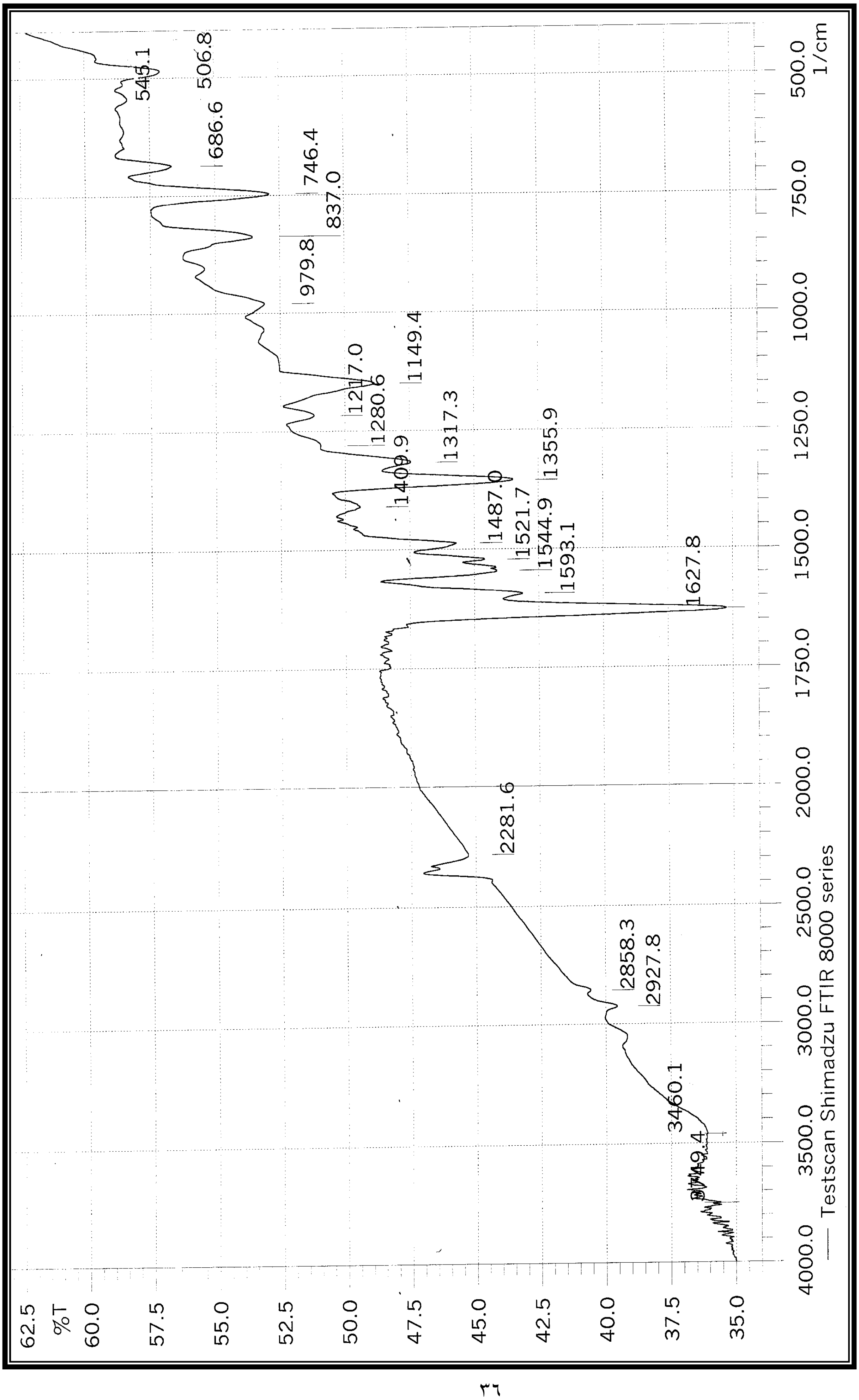


Fig (3-2) FT-IR spectra of LII



Fig(3-3) FT-IR spectra of AL$_1$

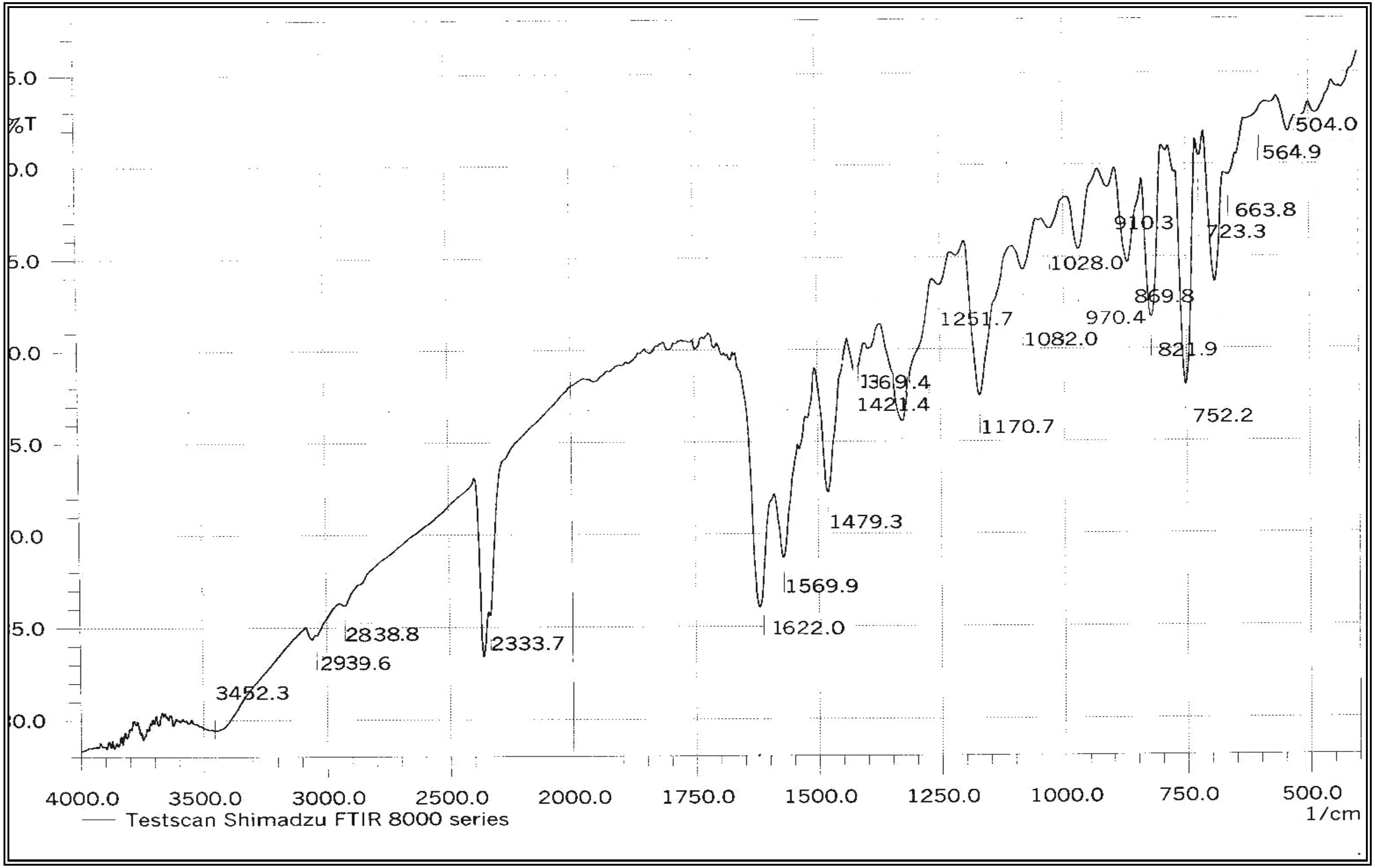


Fig (3-4) FT-IR spectra of AI_2

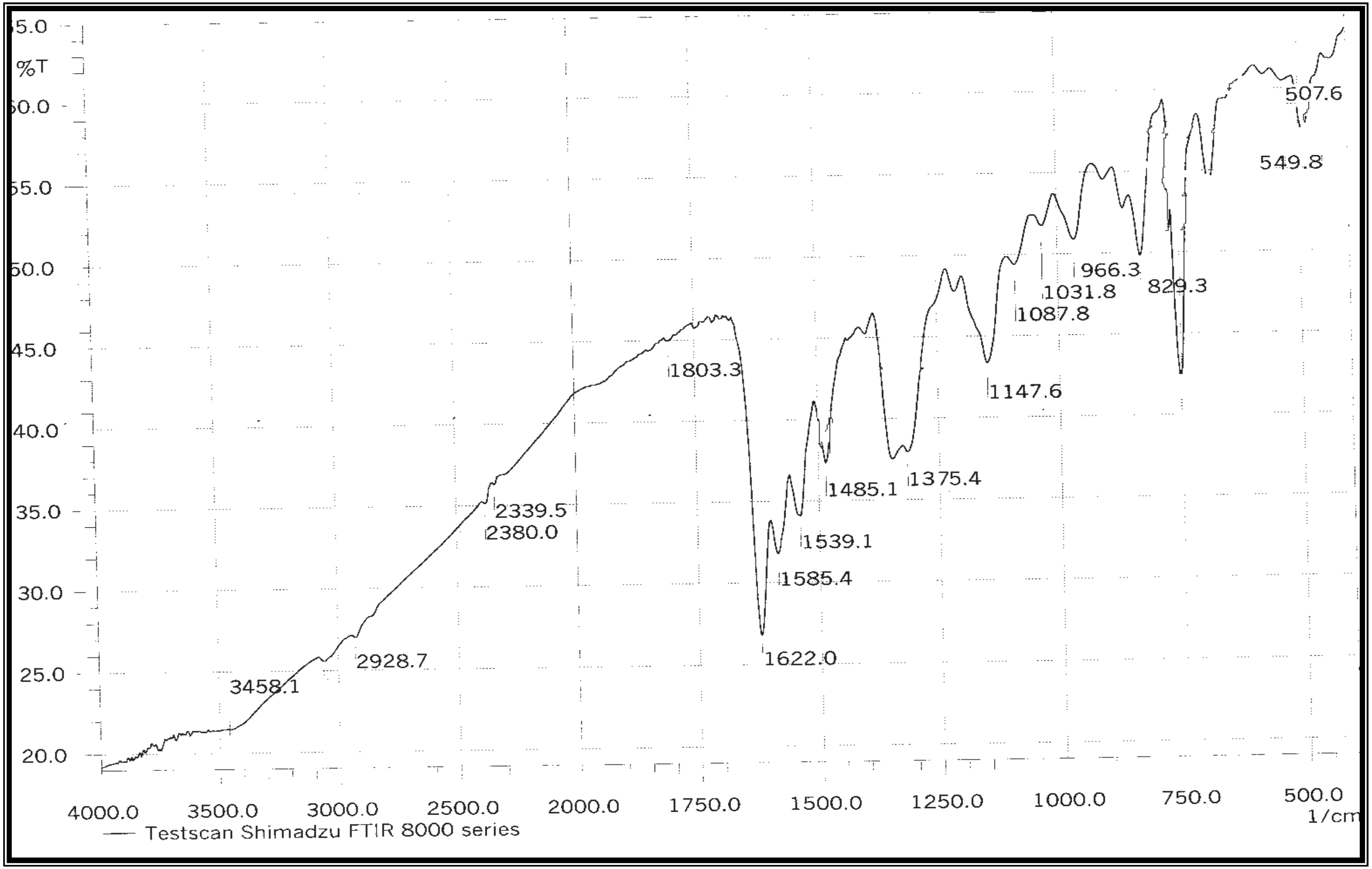


Fig (3-5) FT-IR spectra of AI_3

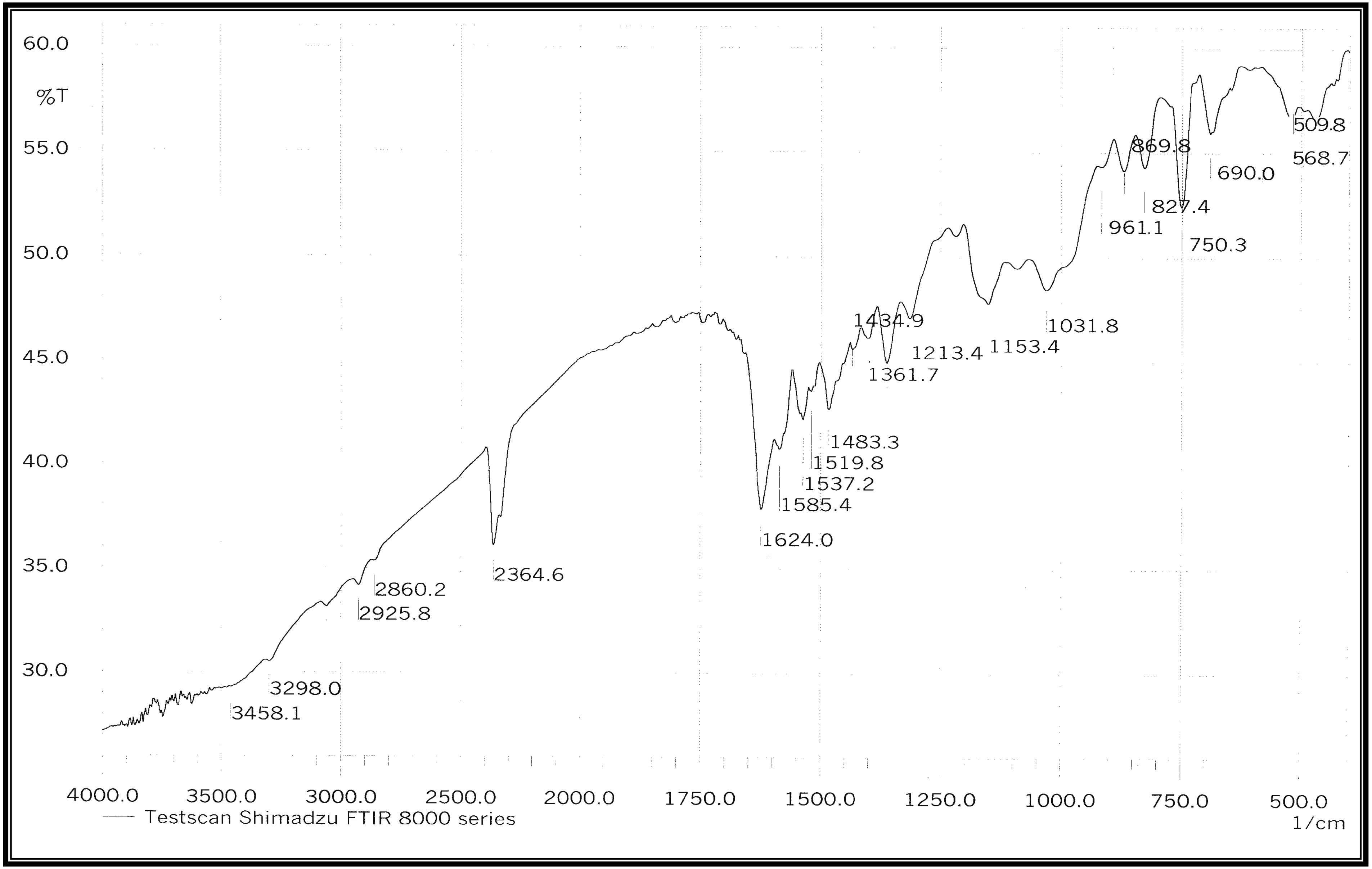


Fig (3-6) FT-IR spectra of AI_4

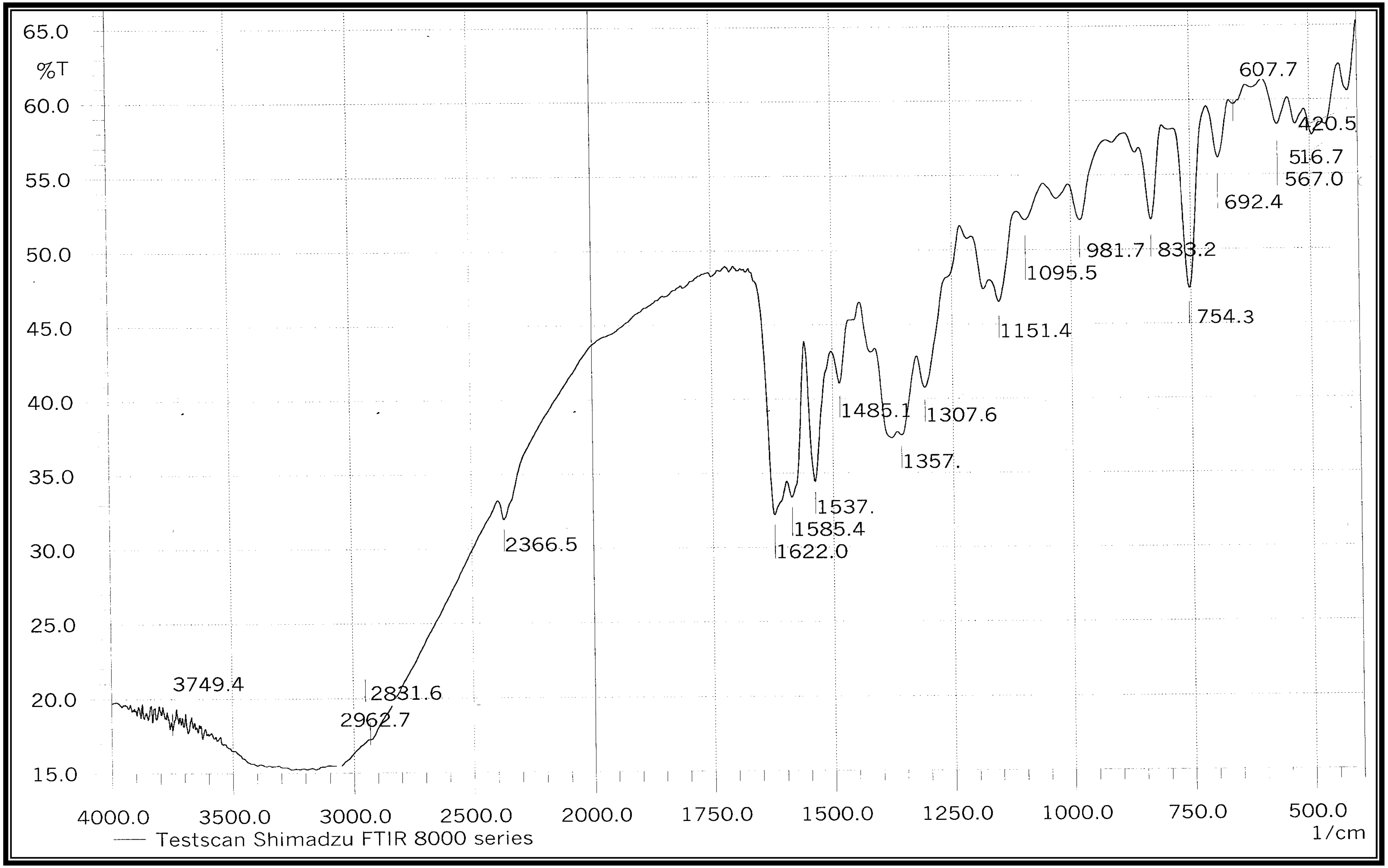


Fig (3-7) FT-IR spectra of AI_5

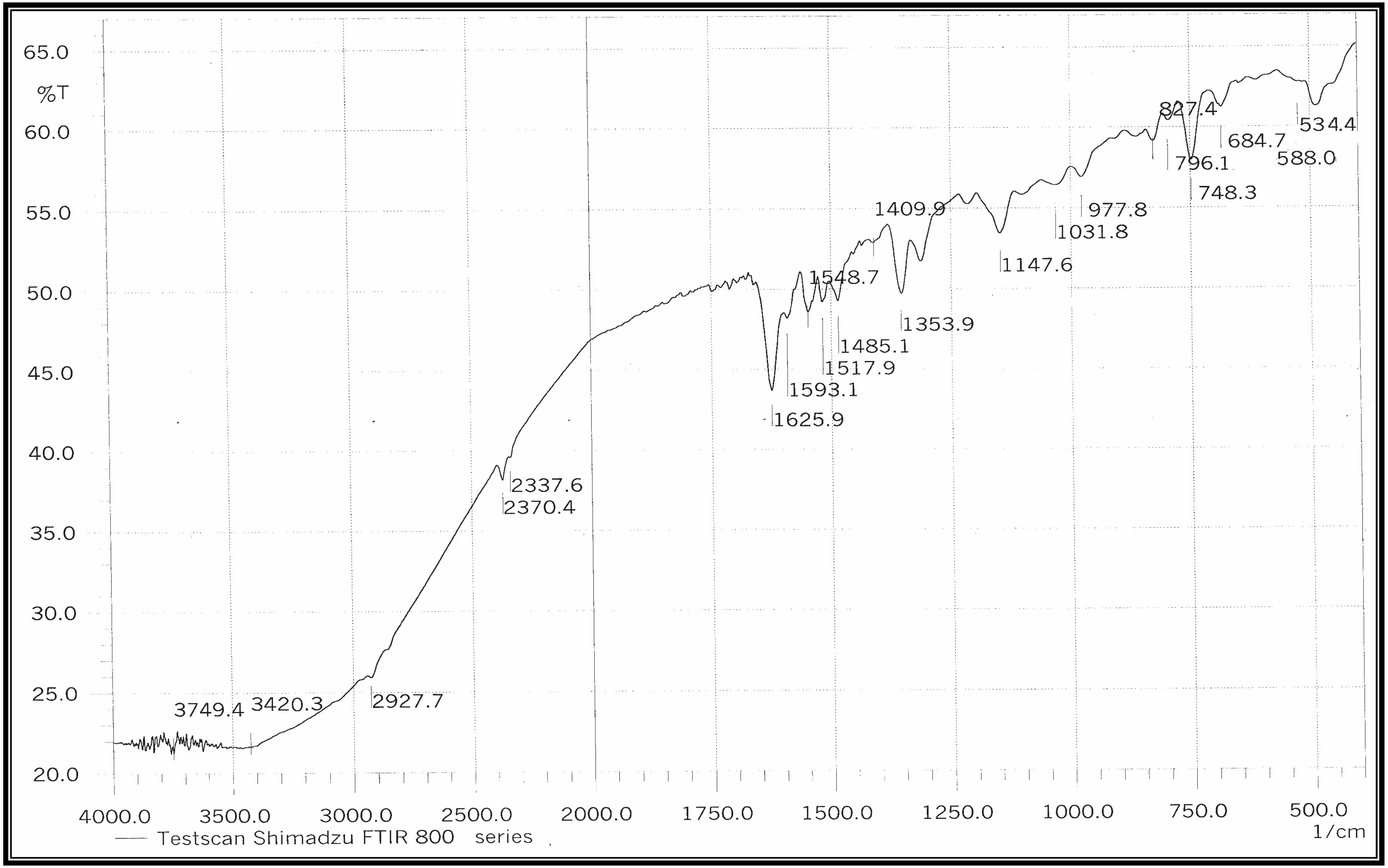


Fig (3-8) FT-IR spectra of AI$_6$

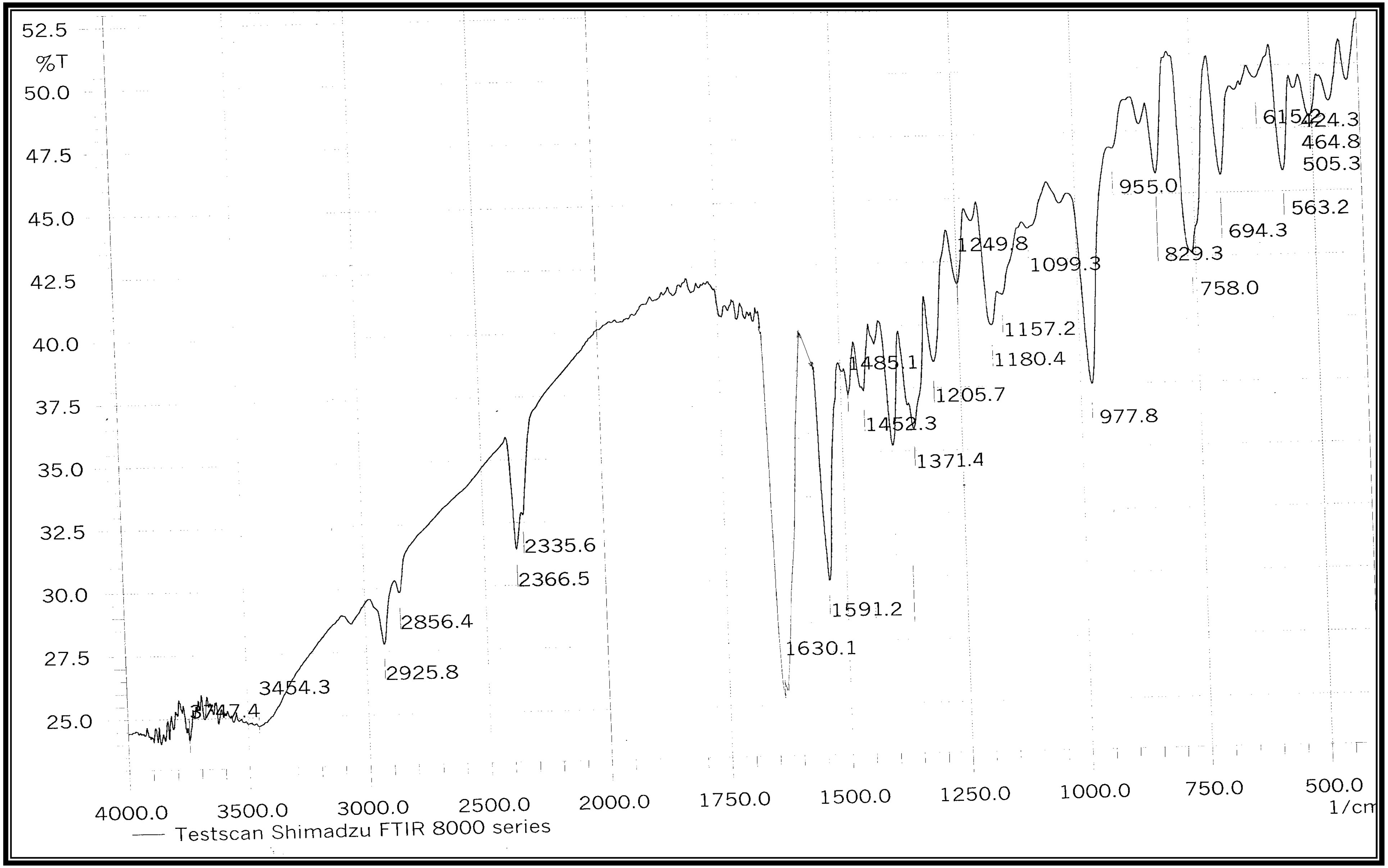


Fig (3-9) FT-IR spectra of AI_7

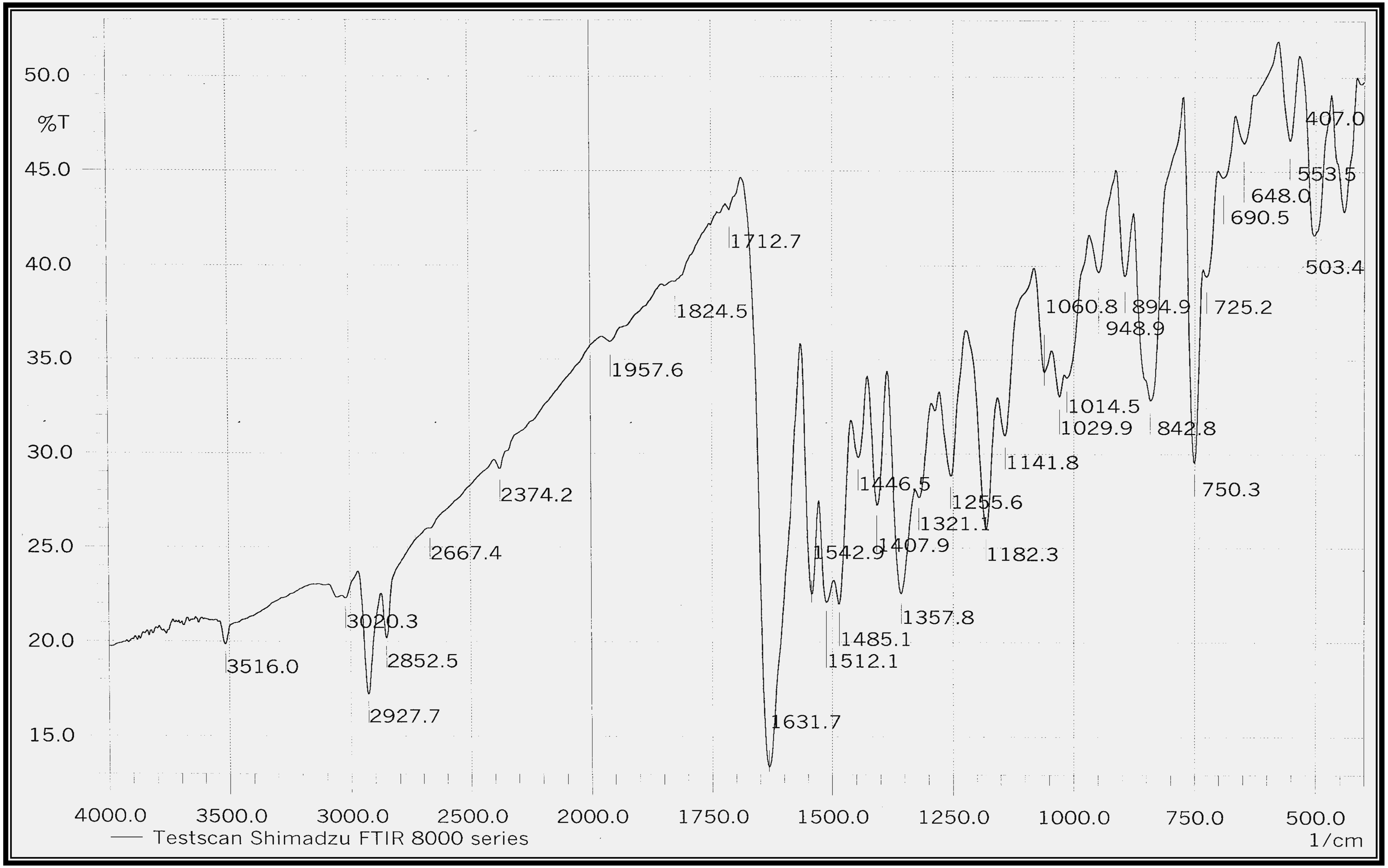
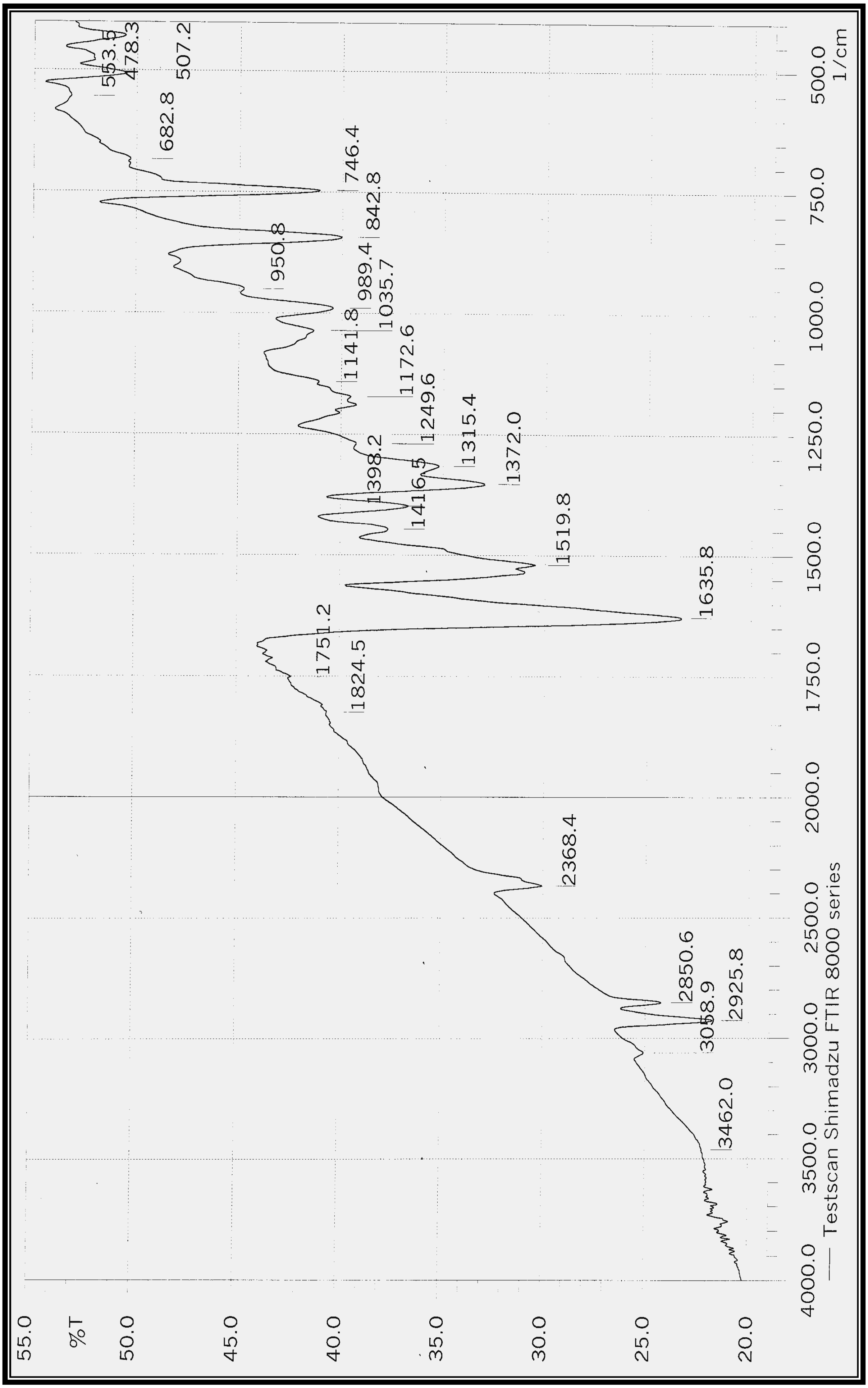
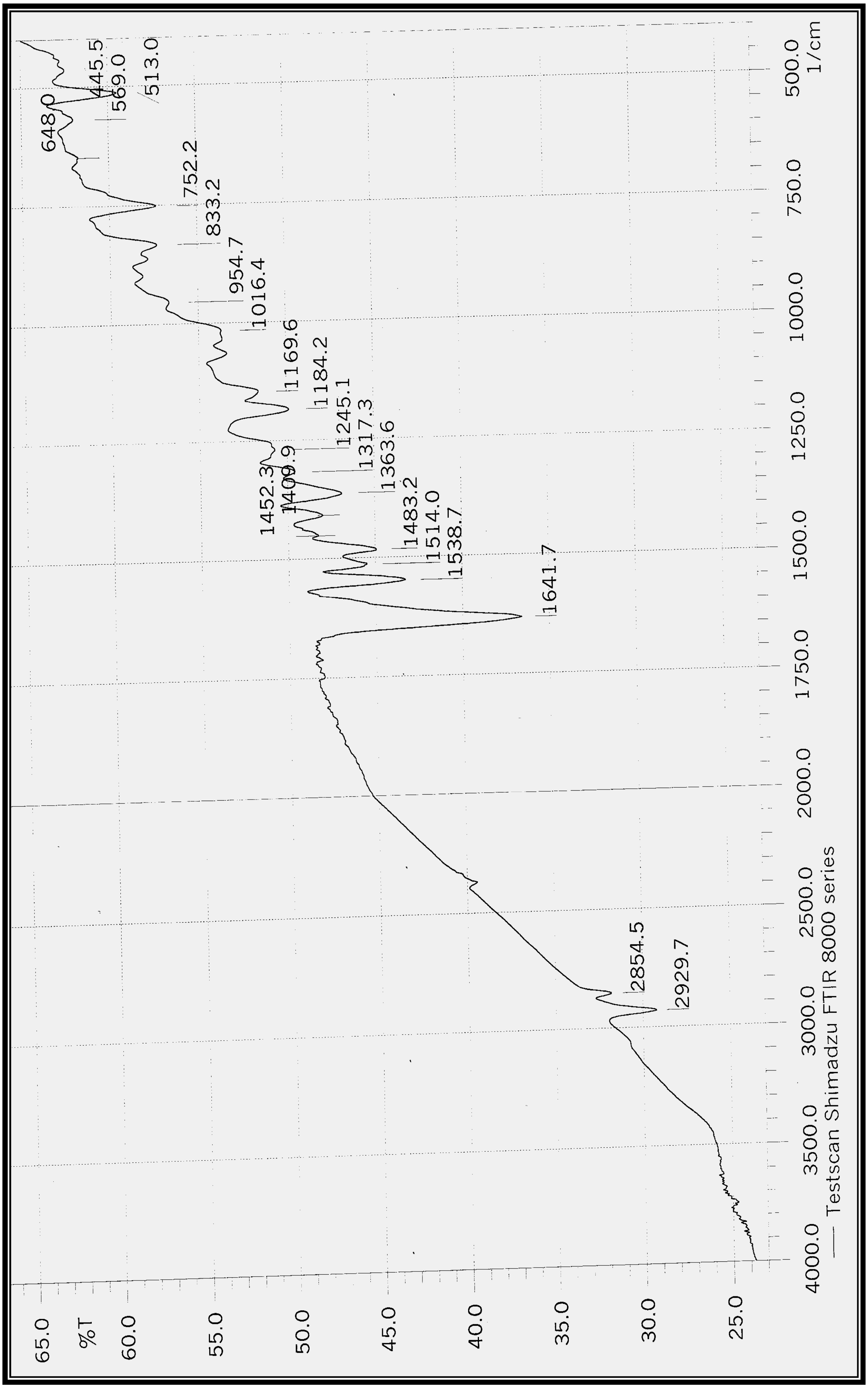


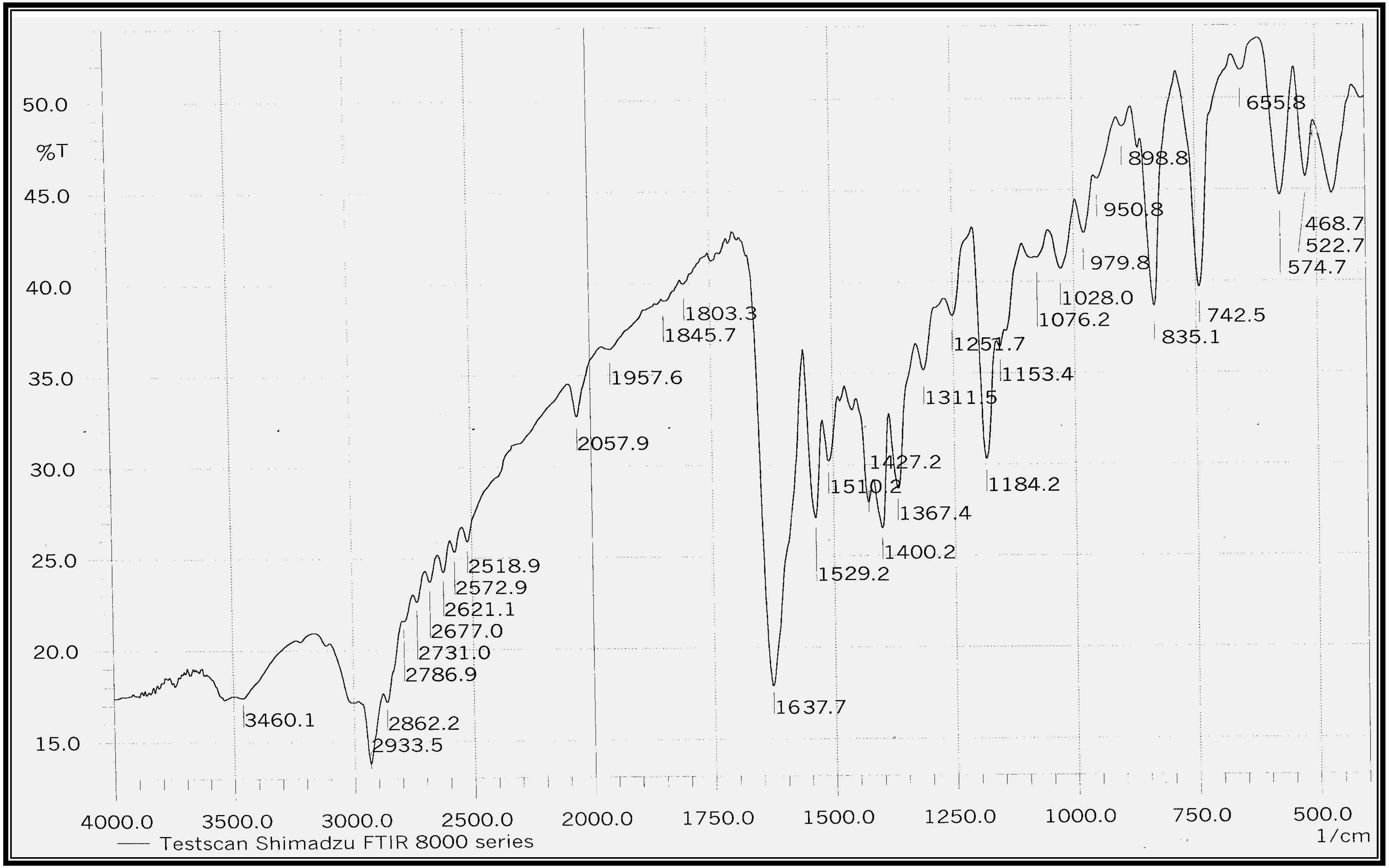
Fig (3-10)FT-IR spectra of AII_1



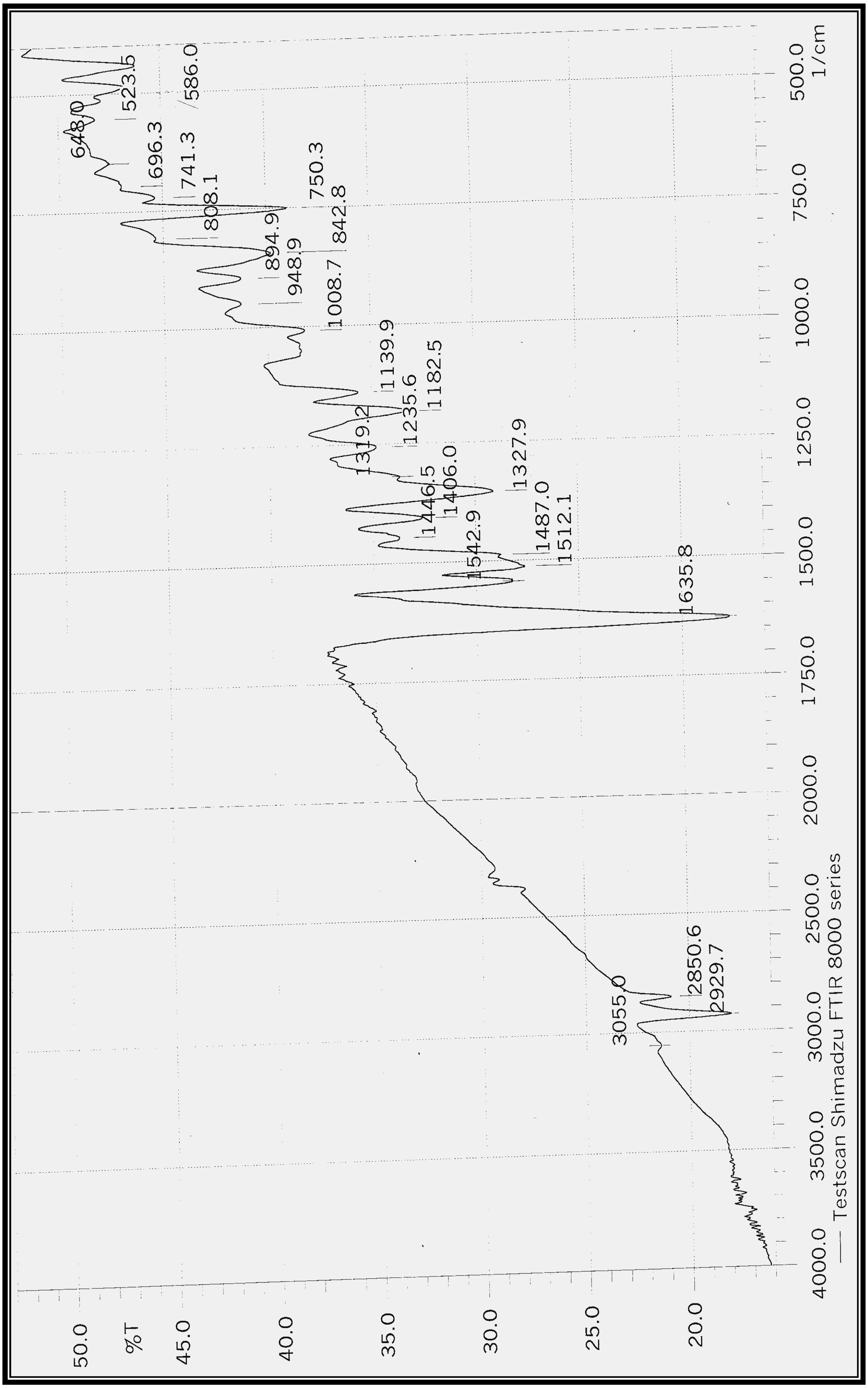
Fig(3-11) FT-IR spectra of AII$_2$



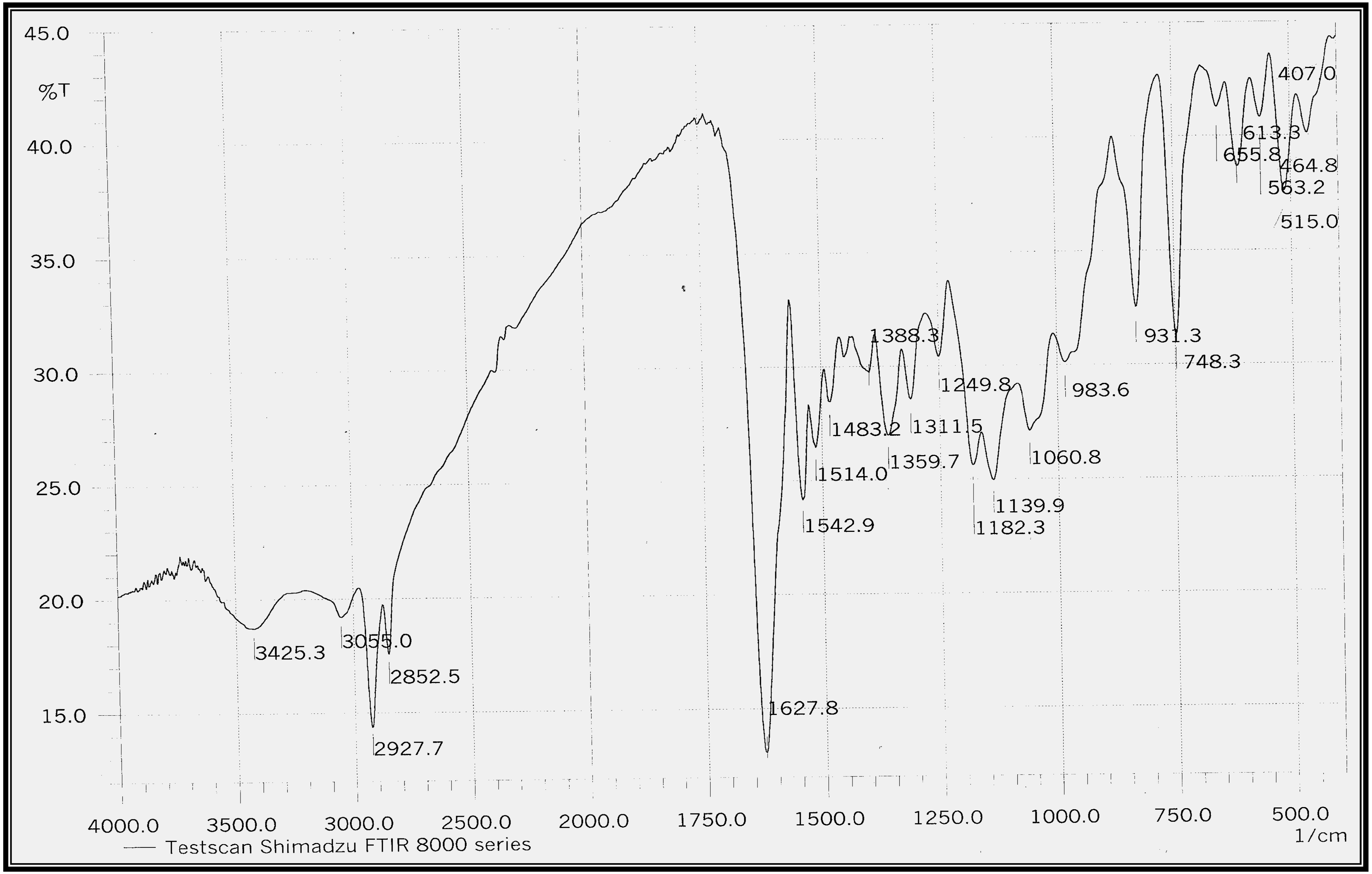
Fig(3-12) FT-IR spectra of AII$_3$



Fig(3-13) FT-IR spectra of AII_4



Fig(3-14) FT-IR spectra of AII_5



Fig(3-15) FT-IR spectra of AII_6

3-3 Electronic spectra, magnetic properties and conductivity measurement

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 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 rang (200-1100) nm, using dimethylformamide (DMF) as a solvent.

Measurement magnetic susceptibility contributes to the determination of structure 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 (75) .

$$\mu s.o = 2\sqrt{S(S+1)}$$

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

The results obtained from this equation were compared to the actual values obtained through magnetic measurements.

These values were corrected for diamagnetic effects using the following relationship:-

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

$X_A = X_M – D$

$X_M = X_g \times M.wt.$

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 is usually grater than the calculated value of magnetic moment.

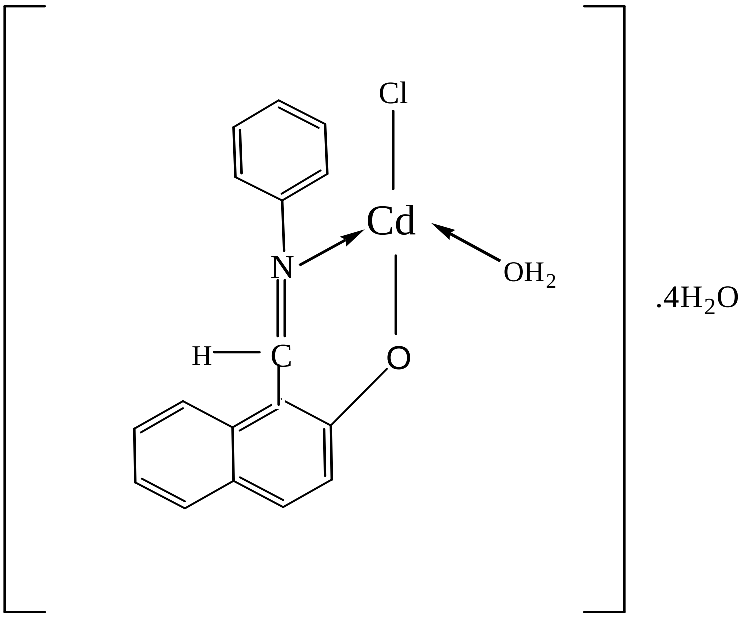
Conductivity measurements of the prepared complexes in the appropriate solvent are used to decide whether a complex is electrolyte or neutral (76,77). Table (3-4) show the positions of electronic absorption bands and it’s transitions, and also include the calculated value of **Racah** parameter ($\bar{B}$), 10Dq and nephelauxetic factor (β) , table (3-5) showed the magnetic moment and conductivity measurement 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 position of the infra-red spectra, electronic absorption band, atomic absorption, magnetic properties and electronic conductivity measured for these complexes.

3-3-1 <u>**Complexes of LI**</u>

A- <u>**Cd(II) Complex (AI$_1$)**</u>

Since the UV-Vis spectra of these d^{10} ion do not furnish a lot of information , just some shifting and change in the shape of band compare with the band of the ligand , so the possible geometry around these ions can be suggested considering the metal analysis , FT-IR spectra and available structures found in the literature (4-68).

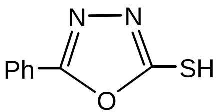
These observations lead us to suppose tetrahedral geometry for AI_1 complex :-



Conductivity measurements showed that the AI_1 complex is non-conductive , Table (3-5) .

B- Fe(III) Complex (AI_2)

Mishra and Said studied the electronic spectra of $[Fe(L)\ py(OH)_2]_2$,

where , L = , and found that the spectrum could not be recorded due to its poor soluibility , while the spectra of the solid complexes showed bands in the range of (19,230-18,182)cm^{-1} in addition to a shoulder observed at (15,625-15,151)cm^{-1} (78). These bands were assigned to Spin forbidden d-d transitions . The higher energy ligand field bands were obscured by the intense charge-transfer bands observed at 24,390 cm^{-1} . these assignments are comparable to the other earlier report made for Fe(III) complexes (79) .the shoulder observed at 15,384 cm^{-1} in the solid state spectra disappeared in the solution spectra and a new band at (18,050-17,094) cm^{-1} appeared . This shift , observed in the solution $^{(80)}$ may be due to the rearrangement in the first coordination sphere around the metal ion , it has been claimed that it was quite possible that solvent (DMSO) molecules might be substituting either aquo or chloro group present in the complexes . However the substitution of chloro group by DMSO as discarded on the ground that conductance of the complex measured in the same solvent did not lie in the range at least for 1:1 electrolyte due to setting of Cl$^-$ ion in the solution . But in the complexes containing H_2O , the substitution of H_2O group by DMSO is possible as DMSO is a better donor than water .

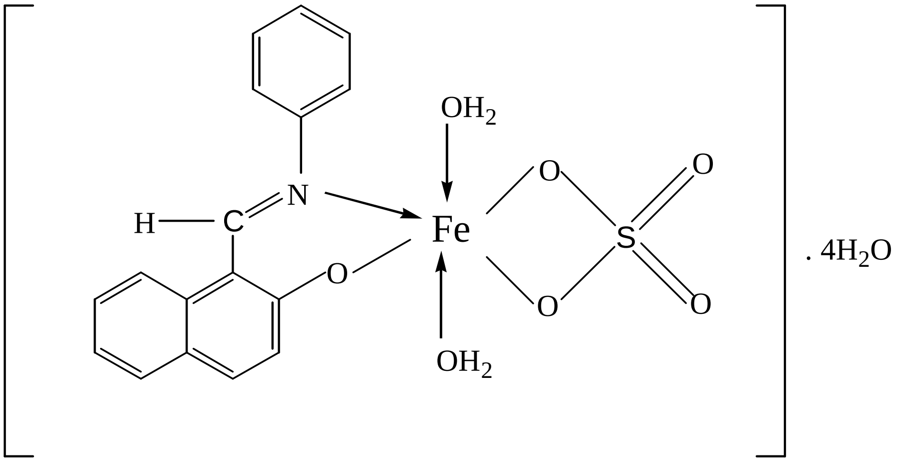
The UV-Vis spectrum of the present complex showed two bands in the d-d transition region at 28,577 cm^{-1} and 20,000 cm^{-1} both as a shoulder to higher energy band which are comparable to that bands which were discussed above bands can be assigned to the following transitions:-

$$^6A_{1}g \longrightarrow {}^4T_{1}g \quad (20,000\ \text{cm}^{-1})$$

$$^6A_{1}g \longrightarrow {}^4T_{2}g \quad (28,577\ \text{cm}^{-1})$$

To the above complex and came in accordance to other available data so an octahedral geometry was suggested to the (AI_2) complex $^{(81)}$. The value of the measured magnetic moment for (AI_2) is (5.9 B.M..) in accordance with the presumption of high-spin d^5 ferric ion in octahedral geometry $^{(68)}$.

From Tanabe-Sugano diagram for d^5 octahedral field Fig (3-16), the value of 10Dq equal to 25,800 cm^{-1} and the high value of nephelauxetic factor (β) (0.99) indicted the ionic character between Iron(III) ion and the ligand ,Table (3-4),Therefore the following structure is suggested for the (AI_2) complex :



The above complex is non-ionic due to the conductivity measurement table (3-5).

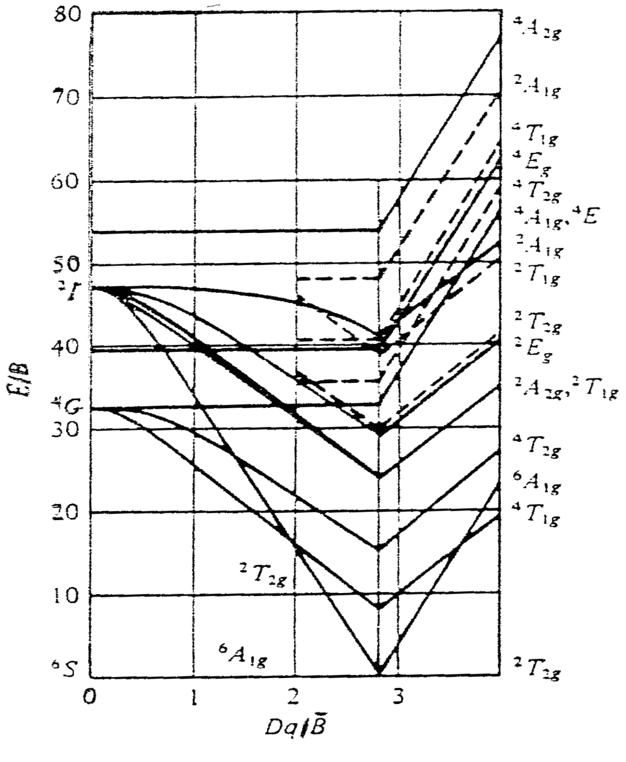


Fig. (3-16) Tanabe-Sugano diagram for d^5 system

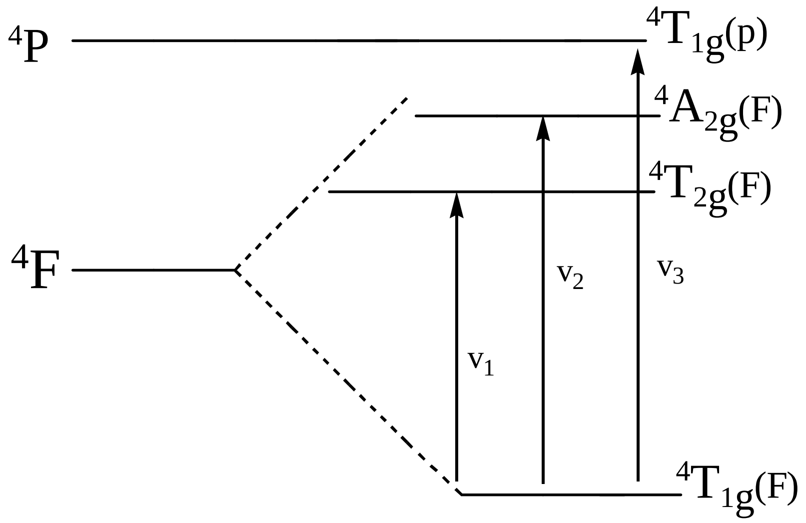
C- Co(II) complex (AI_3)

Electronic spectra of cobalt(II)complex show three transition but these transition cannot be assigned because of the greater overlapping of them (82,83,4b). Octahedral complex of Co(II) consist of two band one in the (15,400-15,500 cm^{-1}) and the other in the (20,000-20,830 cm^{-1}) regions (84) .

In present work two band appear one at (15,384 cm^{-1})and the other at (20,618cm^{-1}) which is assigned to the transition υ_1 and υ_2 respectively .

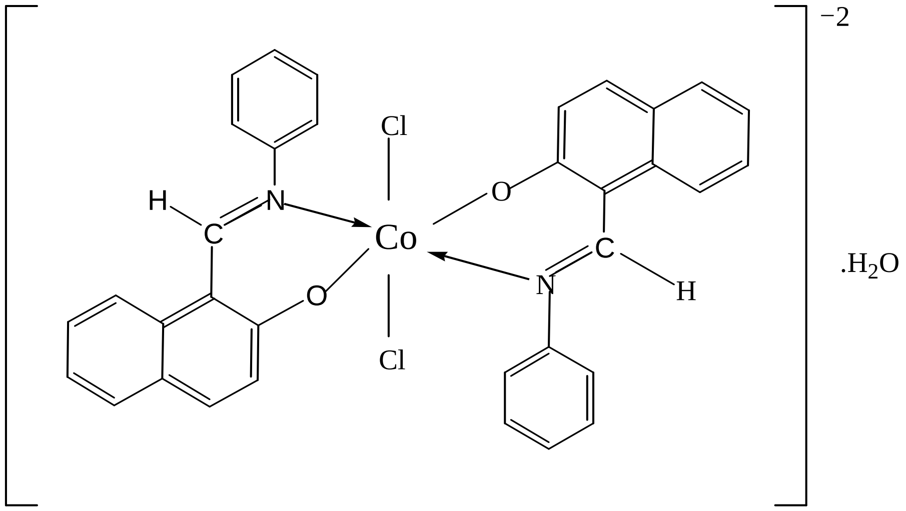
The value of υ_3 can be calculated using Tanabe-Sugano diagram for d^7 system, Fig(3-17), and found to be (25,723 cm^{-1})which is refer to $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition . The different ligand field parameters have been calculated using the same diagram, the result are found in table (3-4).

The term symbol for the ground state of Co(II) ion ^4F which can split in octahedral crystal field as fellow (83).



Octahedral cobalt (II) complex however maintain a large contribution due to ^4T_g ground term and exhibit $\mu_{eff.}$ In the range (4.8-5.6 B.M .)(85) The magnetic measurement of the (AI_3)complex is (4.93 B.M .) show the complex are 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 illustratd in the following structure :-



The formulae was further confirmed to be ionic by conductivity measurement .

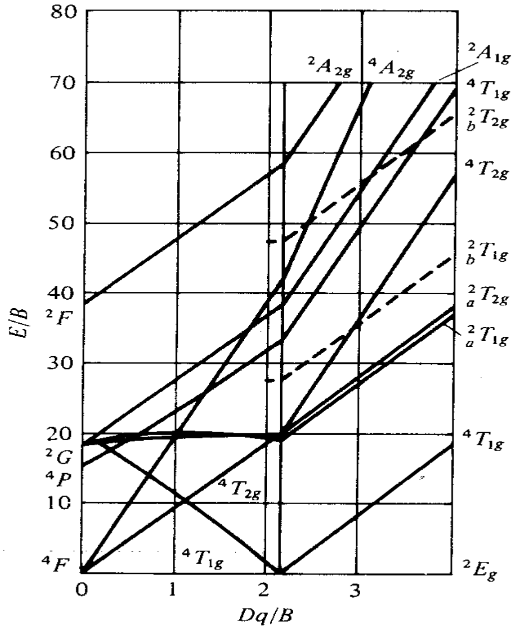
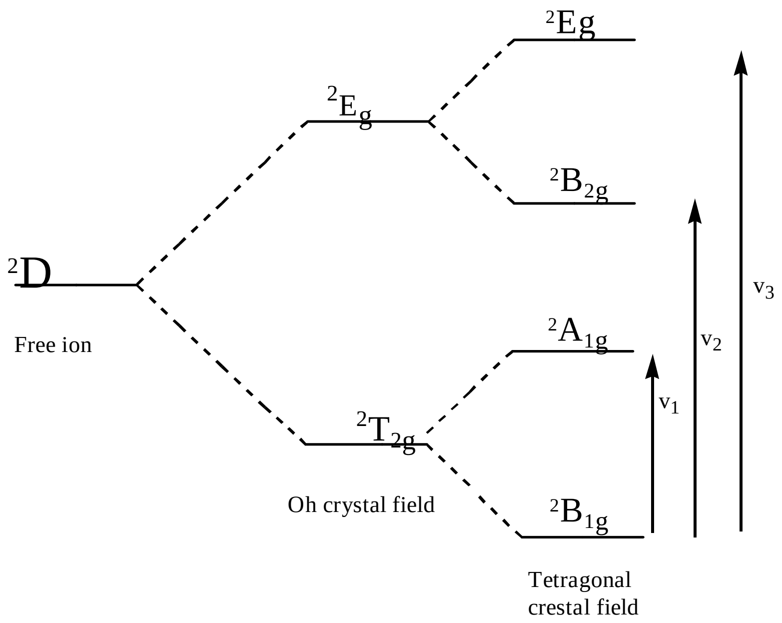


Fig. (3-17) Tanabe-Sugano diagram for d^7 system

D- Cu(II) complex (AI_4)

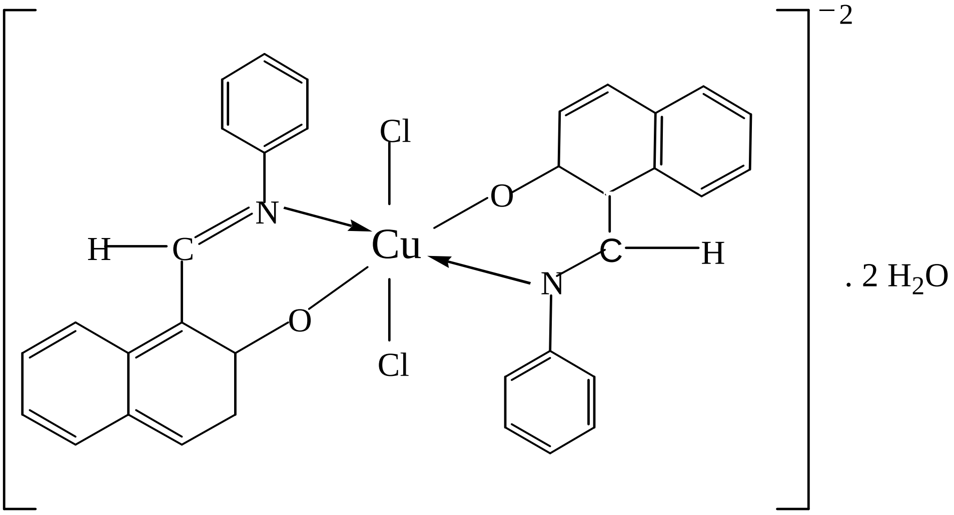
Cu(II) compound are blue or green because of single broad absorption band in the region (11,000-16,000 cm^{-1}) (68) . The d^9 ion is characterized by large distortion from octahedral symmetry and the bond is unsymmetrical , being the result of a number of transition , which are by no means easy to assign 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 (4a,68):-



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 AI_4 complex show a broad band (68) at (15,873 cm^{-1}) which can be assigned to $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions , Fig (3-20).

The value of $\mu_{eff.}$ That have been measured for (AI_4)complex was 1.9 B.M . this value is in the range of octahedral geometry (87,88).Therefore the expected geometry of AI_4 complex is :-



Conductivity measurements show that the complex is ionic ,Table (3-5).

E- Cr(III) Complex (AI_5)

Cr(III) complex spectrum in DMF shows three bands , the first two band at (22,935 cm^{-1}) and (29,985 cm^{-1}) were assigned as belonging to transitions:-

$^4A_{2g}(F) \longrightarrow {}^4T_{2g}(F)$ (υ_1 which is equal to10Dq)

$^4A_{2g}(F) \longrightarrow {}^4T_{1g}(F)$ (υ_2) (68)

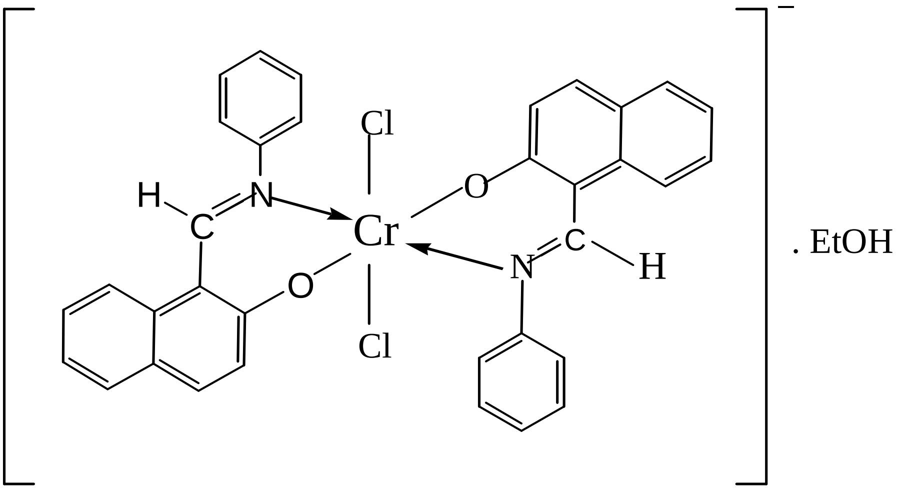
The third band was expected to appear in the ligand or charge transfer absorption region , so it was found at (31,545 cm^{-1}) which assigned to the transition

$^4A_{2g}(F) \longrightarrow {}^4T_{1g}(P)$ (υ_3) (89)

The value of $\overline{B}$ is calculated from Tanabe-Sugano diagram , Fig (3-18),and was found to be (485 cm^{-1})from which the value of the nephelauxetic factor (β) was calculated taking the value of the free ion (918 cm^{-1}) and as found to be (0.528). The law value of β refer to the relatively great expansion of d-electron charge upon complexation which reduces the inter electronic repulsion . The internal consisting of this interpretation were checked using Tanabe-Sugano diagram by calculating υ_1 and 10Dq .

The magnetic moment of the AI_5 complex is found to be (3.80 B.M .) which is in good agreement with other octahedral Cr(III) complex .

The above result indicate an octahedral geometry of AI_5 complex which can be depicted as fellows :-



This fourmula was further confirmed to be ionic by conductivity measurement .

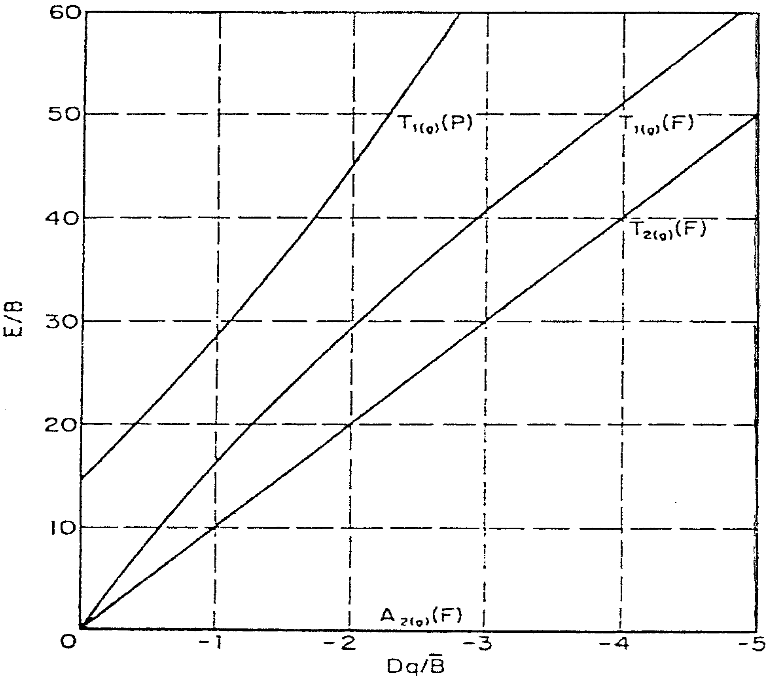
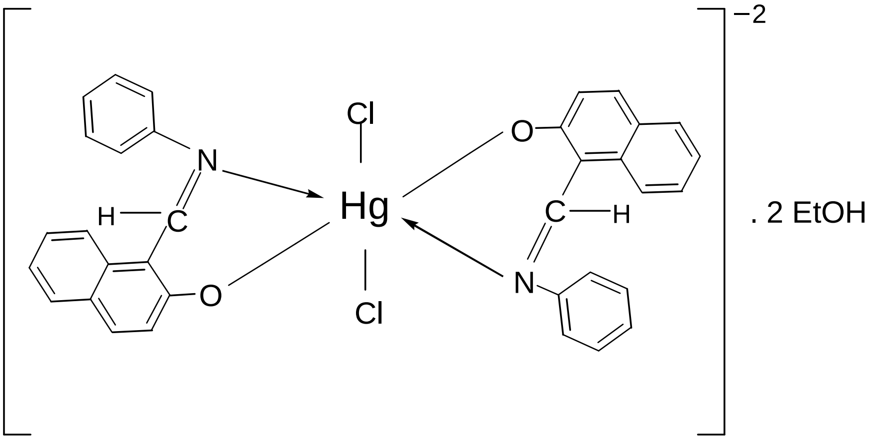


Fig. (3-18) Tanabe-Sugano diagram for d^3 system

F- Hg(II) Complex (AI_6)

The UV-Vis spectrum of Hg(II) ion have some transition found in the region 200-400 n.m , can be assigned as intraligand transitions , 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 :-



Conductivity measurement showed that complex was conductive , Table (3-5).

G- V(IV) Complex (AI_7)

The V(IV) ion is usually represented by the VO(II) molecular ion , VO(II) behaves as a class-action forming stable compounds with F ,Cl,O and N donor ligands . These "Vanadyl" complexes are generally green or blue –green and can be cationic , neutral or anionic ,. They are very frequently 5-coordinate in which are the stereochemistry is almost invariably square pyramidal . The Vanadyl (II) ion has one unpaired d-electron (90) .

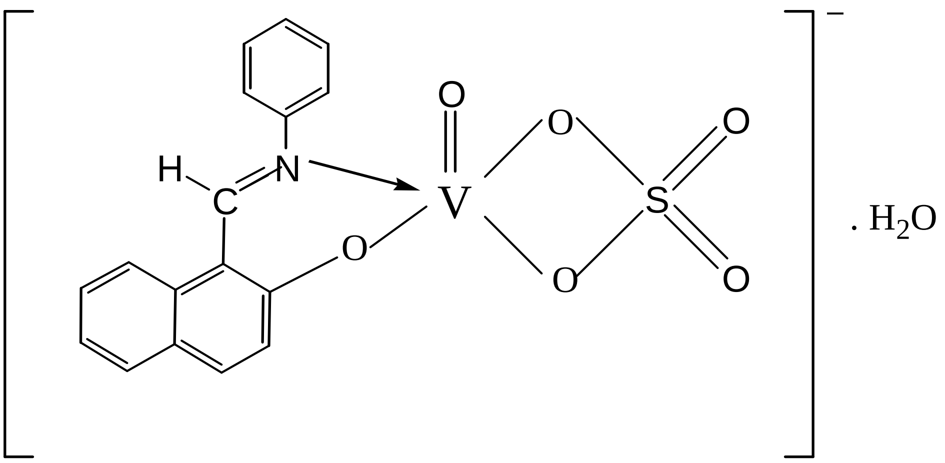
The electronic spectra of Vanadyl complex are less easily understood . This is primarily due to the presence of a strong π contribution to the bond between the vanadium and the oxygen (68).

In the several Vanadyl (VO(II)) ion complexes studied (91,92) , at room temperature , three ligand field absorption bands are reported with the first in the spectral range (11,000-14,700 cm^{-1}) , the second in the range (14,800-20,400cm^{-1}) and the third in the range (21,000-31,250cm^{-1})

In the present work, only one band was observed at (22,857cm^{-1}),Fig (3-21) which can be assigned to υ_3 ($^2B_2 \rightarrow ^2A_1$).

Most Vanadyl (II)complex are magnetically simple having virtually "spin-only" moments of (1.73 B.M .) (93) . corresponding to 1 unpaired electron . The value of the present AI_7 complex was found to be (1.40 B.M .)showing quardivalent state of vanadium ion which contain VO(II)ion (94).

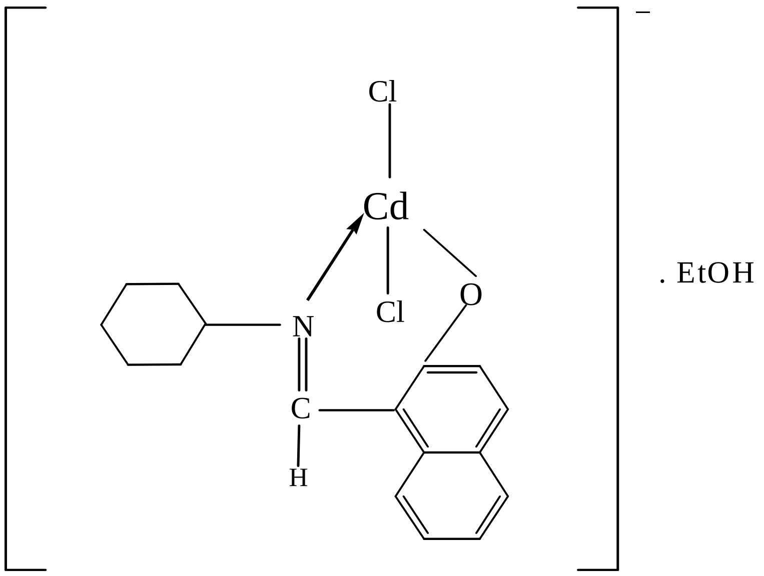
Conductivity measurement show the AI_7 complex to be electrolyte , Table (3-5) , Therefore square-pyramidal can be assumed :-



3-3-2 Complexes of LII

A- Cd(II) Complex (AII_1)

Conductivity measurement showed that the complex is ionic , and from FT-IR study the structure of this complex can be regarded as tetrahedral geometry :-



B- Fe(III) Complex (AII_2)

The electronic spectrum of (AII_2) complex, Fig(3-21) Table(3-4) . shows two bands ; the first one at (20,408 cm^{-1}) and the second at (26,455 cm^{-1})which is assigned to the transitions :-

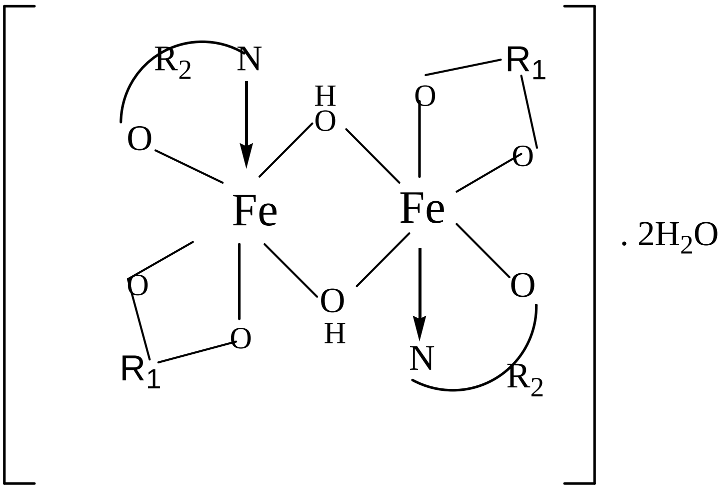
$$^{6}A_{1g} \longrightarrow {}^{4}T_{1g} \quad (20,408\ cm^{-1})$$

$$^{6}A_{1g} \longrightarrow {}^{4}T_{2g} \quad (G)\ \ (26,455\ cm^{-1})$$

These are similar to that shown by (AI_2) complex so an octahedral geometry was suggested to the (AII_2)complex $^{(81)}$.

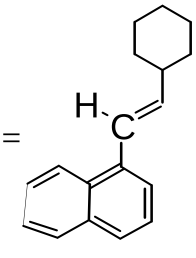
The value of the measured magnetic moment for (AII_2) complex is (5.15 B.M .), which could be related to high-spin d^5 ferric ion in octahedral geometry .

From Tanabe-Sugano diagram for d^5 octahedral field Fig (3-16), the value of 10Dq equal to(20,695 cm^{-1}) and the high value of nephelauxetic factor (β) (0.88) indicated the ionic character between Iron(III) ion and the ligand . Therefore the following structure is suggested for the (AII_2) complex :-



R_1= SO_2

R_2=



Conductivity measurements show the complex to be non-ionic , Table(3-5).

C- Co(II) Complex (AII$_3$)

Cobalt (II) complex spectrum in DMF , Fig(3-22), shows three bands . The first two bands at (16,611cm^{-1})and (14,880 cm^{-1}) were assigned to the transition $^4A_{2g} \longrightarrow {}^4T_{1g(P)}$ (υ_3) , since this transition is known to be a triplet in the range (14,000-17,500 cm^{-1}) in divalent cobalt of tetrahedral geometry . This splitting is due to spin orbit coupling (95). Therefore υ_3 have been calculated as the average of these two bands .

The third band which appears as a weak band at (9,345 cm^{-1}) was assigned to the transition υ_2 ($^4A_{2g} \rightarrow {}^4T_{1g(F)}$), while υ_1 could not be observed since it is expected to appear in a range out of the instrument scale so it was calculated using Tanabe-Sugano diagram for d^7 system and found to be(6,266 cm^{-1}) which belong to the transition $^4A_{2g} \longrightarrow {}^4T_{2g(F)}$ (68).

The different ligand field parameters have been calculated using the same diagram , the result are found in table (3-4) . comparison of the results obtained in this work with the literature data suggests high spin tetrahedral geometry around Cobalt (II) ion . Magnetic measurements show that the complex is paramagnetic ($\mu_{eff.}$ =4.35 B.M .), Table(3-5) which in accordance with the high spin tetrahedral .(96-98)

The reported magnetic moment values for tetrahedral Co(II) complexes are greater than the spin –only values ($\mu_{s.o}$=3.873 B.M .)(99-102) ,this was ascribed to the orbital contribution and degeneracy in energy .

The relatively high value of 10Dq and the low value of β(0.54) indicate the participation of the nitrogen and oxygen atoms in the coordination with the Co(II) ion through a bond of high covalent character .

The low ratio of υ_2/υ_1 (1.49) indicates the tetrahedral geometry (103) to show weather the shape is regular or distorted , the value of spin orbit coupling constant (λ)has been calculated , and compared with the value of free ion (-178 cm^{-1}), This constant has been calculated using the following equation :-

$$\mu_{obs}=\mu_{s.o}-15.49\,\lambda/\,10Dq$$

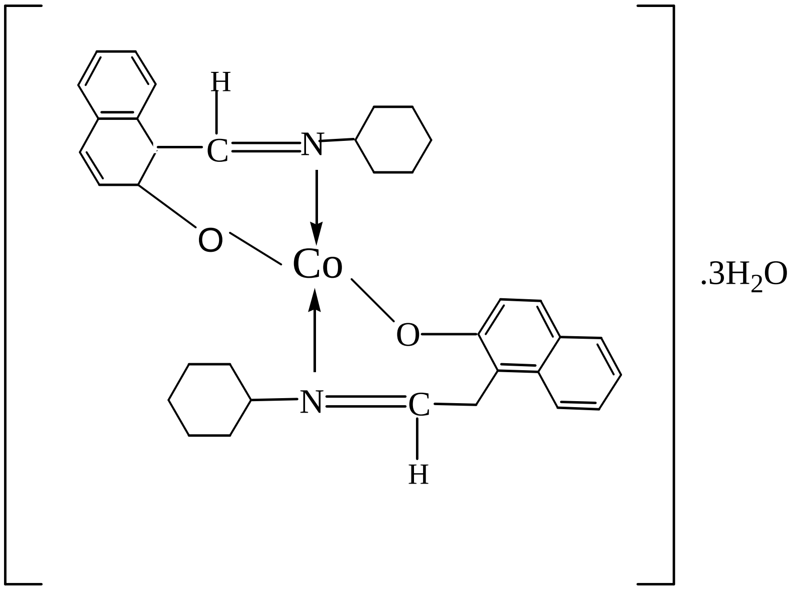
$$4.35 = 3.873-15.49\,\lambda/6256$$

Where , μ_{obs} = The observed effective magnetic moment .

$\mu_{s.o}$ = The electronic spin only magnetic moment .

The observed value of λ for the (AII_3) was (-193.87) and it is less than the value for the free ion and dose not fit in the range of the regular geometry , rather it fit with value for the distorted tetrahedral (101,104,105).

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

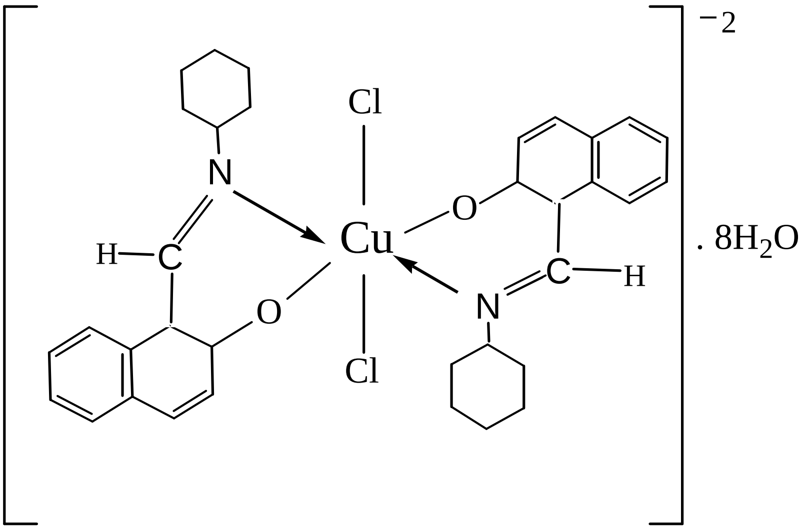


D- Cu (II) Complex (AII_4)

The spectral behavior of this complex , Fig(3-22) , is identical with that of (AI_4) (86) , which also show a broad band at (16,625 cm^{-1}) that refer to $^2B_{1g} \longrightarrow {}^2B_{2g}$ and $^2B_{1g} \longrightarrow {}^2E_g$ transition .

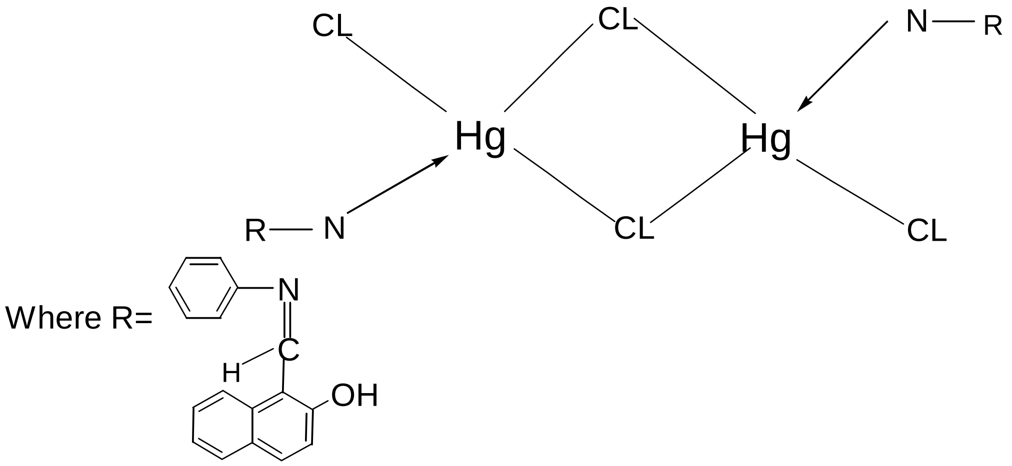
The magnetic moment of the (AII_4) complex is (2.14 B.M .),Table (3-5). Therefore an octahedral geometry was assumed for Cu (II)complex.

Conductivity measurement show the (AII_4) complex is ionic , Table (3-5) . The following structure can be suggested:-

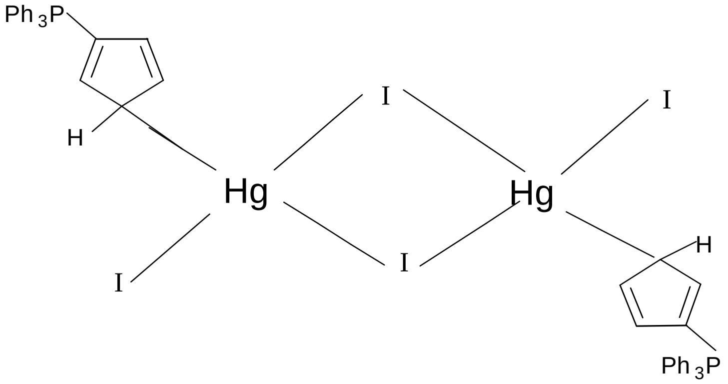


E- Hg(II) Complex (AII_5)

Conductivity measurement showed the complex is non-ionic , from the FT-IR study the following structure can be suggested :-



And it is known for mercury to form such bridging compounds through halides according to the following example (4a):-



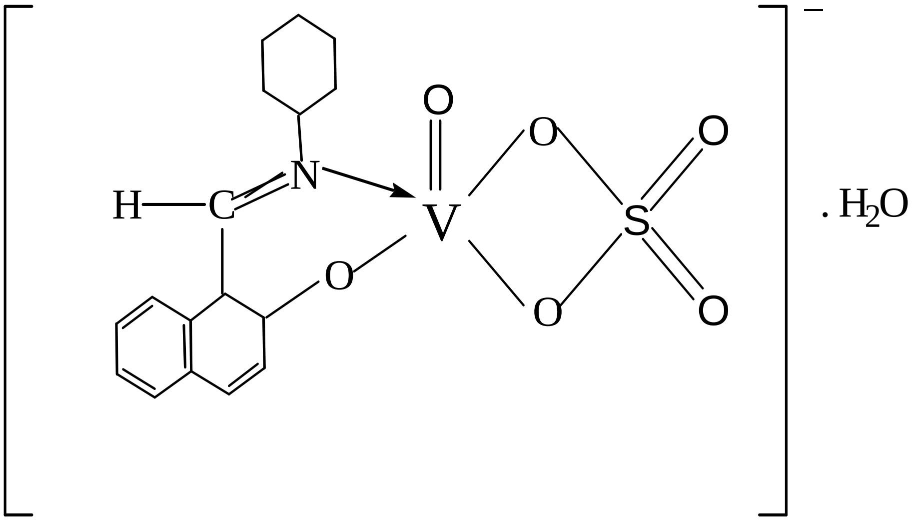
F- V(IV) Complex (AII_6)

The greenish-blue complex may refer to squarpyramidly structure(106) The electronic spectra for the Vanadium complex cannot be assigned unambiguously due to the presence of strong π-bond between the vanadium and oxygen (90). In this work only one broad band was observed (24,038 cm^{-1}) , Fig (3-23), which can be assigned to υ_3 ($^2B_2 \rightarrow {}^2A_1$).

These are similar to that shown by (AI_7) complex so an square-pyramidal structure was suggested to the (AII_6) complex .

The magnetic moment of the Vanadyl (II) complex (94) was found to be(1.36 B.M .).

Conductivity measurement show the (AII_6) complex to be electrolyte , Table (3-5) , According to these result an square-pyramidal structure can be proposed :-



3-4 Conclusions

1. The different Schiff bases which have been prepared showed different physical properties , where the cyclohexyl derivative LII show to have lower melting point with lower yield of product .

2. The reaction conditions for the preparation of the cyclohexyl derivative LII were more vigorous than the other derivative .

3. The reaction of both ligands (LI and LII) with the selected transition metal ions gave complexes of comparable geometry , except those of Fe(III) and Hg(II) , where they gave dimeric structure with LII only.

4. The new complexes of LI were ionic for Co(II) , Cu(II) , Cr(III) , Hg(II) , V(IV) , and non ionic for Cd(II) , Fe(III) , But the complexes of LII were ionic for Cd(II) , Cu(II) , V(IV) , and non ionic for Fe(III) , Co(II) , Hg(II) .

5. All the prepared complexes were soluble in DMF .

6. The ligand field calculations showed different field strength (according to the 10Dq value) and different electron-repulsion parameter (β) , which refer to different ionic character between the metal and donor atoms of the ligand .

Table (3-4) Electronic spectra for complexes of LI and LII in DMF solvent (cm^{-1})

Symbol	Absorption bands cm^{-1}	Transitions	B	Dq/ $\bar{B}$	$\bar{B}$	β	10Dq	15$\bar{B}$
AI_2 Fe(III)	20,000 28,577	υ_1 $^6A_{1g} \rightarrow {}^4T_{1g}$ υ_2 $^6A_{1g} \rightarrow {}^4T_{2g}$	1300	2.0	1,290	0.99	25,800	19,350
AI_3 Co(II)	15,384 20,618 25,723(cal)	υ_1 $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ υ_2 $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ υ_3 $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	971	5.3	288	0.29	15,384	4,320
AI_4 Cu(II)	15,873	$^2B_{1g} \rightarrow {}^2B_{2g}$ $^2B_{1g} \rightarrow {}^2E_g$						
AI_5 Cr(III)	22,935 29,985 31,545	υ_1 $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ υ_2 $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ υ_3 $^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$	918	4.7	485	0.52	22,935	7,275
AI_7 V(IV)	22,857	$^2B_2 \rightarrow {}^2A_1$						
AII_2 Fe(III)	20,408 26,455	υ_1 $^6A_{1g} \rightarrow {}^4T_{1g}$ υ_2 $^6A_{1g} \rightarrow {}^4T_{2g}$	1300	1.8	1,497	0.88	20,695	17,245
AII_3 Co(II)	6,266 9,345 15,756	υ_1 $^4A_{2g} \rightarrow {}^4T_{2g}(P)$ υ_2 $^4A_{2g} \rightarrow {}^4T_{1g}(F)$ υ_3 $^4A_{2g} \rightarrow {}^4T_{1g}(P)$	971	1.2	522	0.54	6,266	16,920
AII_4 Cu(II)	16,625	$^2B_{1g} \rightarrow {}^2B_{2g}$ $^2B_{1g} \rightarrow {}^2E_g$						
AII_6 V(IV)	24,038	$^2B_2 \rightarrow {}^2A_1$						

Table (3-5) Magnetic moment, Conductivity and suggested Structure for complexes of LI and LII

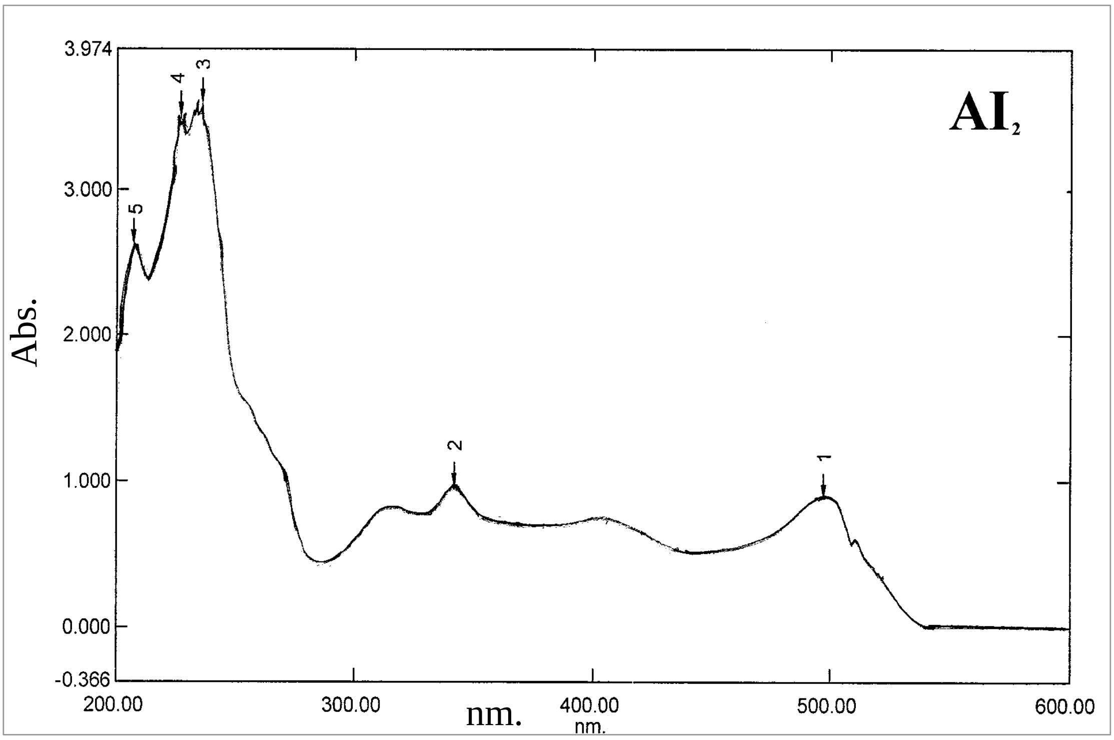
Complex	Magnetic moment $\mu_{eff.}$ (B.M.)	Conductivity µs.cm^{-1}	Suggested structure
AI$_1$, Cd(II)	Diamagnetic	20	Tetrahedral
AI$_2$, Fe(III)	5.90	44	Octahedral
AI$_3$, Co(II)	4.93	67	Octahedral
AI$_4$, Cu(II)	1.90	79	Octahedral
AI$_5$, Cr(III)	3.80	53	Octahedral
AI$_6$, Hg(II)	Diamagnetic	60	Octahedral
AI$_7$, V(IV)	1.40	74	Square pyramidal
AII$_1$, Cd(II)	Diamagnetic	26	Tetrahedral
AII$_2$, Fe(III)	5.15	21	Octahedral
AII$_3$, Co(II)	4.35	25	Tetrahedral
AII$_4$, Cu(II)	2.14	62	Octahedral
AII$_5$, Hg(II)	Diamagnetic	37	Tetrahedral
AII$_6$, V(IV)	1.36	69	Square pyramidal

Table(3-6) The Chemical Formula and the name of the LI and their complexes

Symbol	Chemical Formula	Name of the Compound
LI	$C_{17}H_{15}NO$	β-Naphthaldehyde N-Phenyl imine
AI_1	$[\,Cd\ LI\ CL\ H_2O]\ .\ 4H_2O$	Aquo chloro [β-Naphthaldehyde N-Phenyl imine] Cadmium (II) . Water(4)
AI_2	$[Fe\ LI\ (H_2O)_2\ SO_4]\ .\ 4H_2O$	Diaquo [β-Naphthaldehyde N-Phenyl imine] sulphato Iron (III) . Water(4)
AI_3	$[\,CO(LI)_2\ CL_2]\ .H_2O$	Dichloro bis [β-Naphthaldehyde N-Phenyl imine] Cobalt(II) . Water(1)
AI_4	$[\,Cu(LI)_2\ CL_2]\ .\ 2H_2O$	Dichloro bis [β-Naphthaldehyde N-Phenyl imine] Copper(II) . Water(2)
AI_5	$[Cr(LI)_2\ CL\ H_2O]C_2H_5OH$	Aquo chloro bis [β-Naphthaldehyde N-Phenyl imine] Chromium(III) . Ethanol(1)
AI_6	$[Hg(LI)_2CL_2].2\ C_2H_5OH$	Dichloro bis [β-Naphthaldehyde N-Phenyl imine] Mercury(II) . Ethanol(2)
AI_7	$[VO(LI)\ SO_4]\ .\ H_2O$	[β-Naphthaldehyde N-phenyl imine] sulphato oxovanadium (IV). Water(1)

Table(3-7) The Chemical Formula and the name of the LII and their complexes

Symbol	Chemical Formula	Name of the Compound
LII	$C_{17}H_{21}NO$	β-Naphthaldehyde N- cyclohexyl imine
AII_1	$[\,Cd\ LII\ CL_2]\ .C_2H_5O$	Dichloro [β-Naphthaldehyde N-cyclohexyl imine] Cadmium (II) . Ethanol(1)
AII_2	$[Fe_2\ (LII)_2\ (OH)_2\ (SO_4)_2]\ .\ 2H_2O$	Di-µ-hydroxo-bis[β-Naphthaldehyde N-cyclohexyl imine] disulphato Iron (III) . Water(2)
AII_3	$[\,CO(LII)_2\,]\ .3H_2O$	bis [β-Naphthaldehyde N-cyclohexyl imine] Cobalt(II) . Water(3)
AII_4	$[\,Cu(LII)_2\ CL_2]\ .\ 8H_2O$	Dichloro bis [β-Naphthaldehyde N-cyclohexyl imine] Copper(II) . Water(8)
AII_5	$[Hg_2(LII)_2CL_4]$	Tetrachloro bis [β-Naphthaldehyde N-cyclohexyl imine] dimercury(II) .
AII_6	$[VO(LII)\ SO_4]\ .\ H_2O$	[β-Naphthaldehyde N-cyclohexyl imine] sulphato oxovanadium (IV). Water(1)



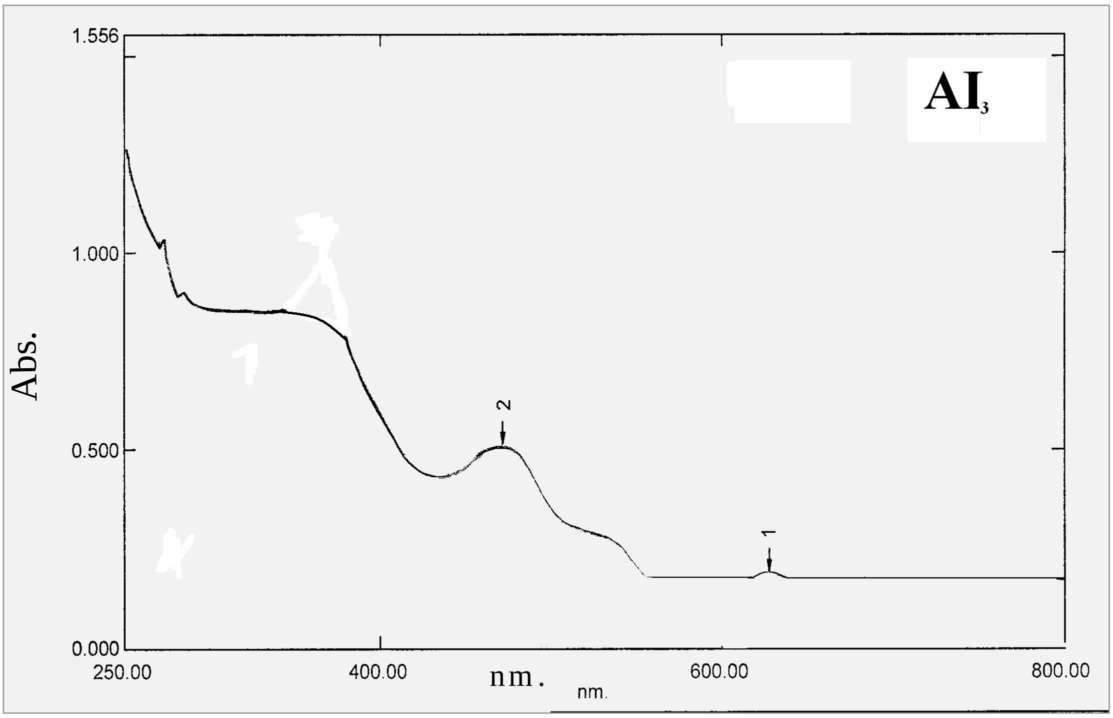
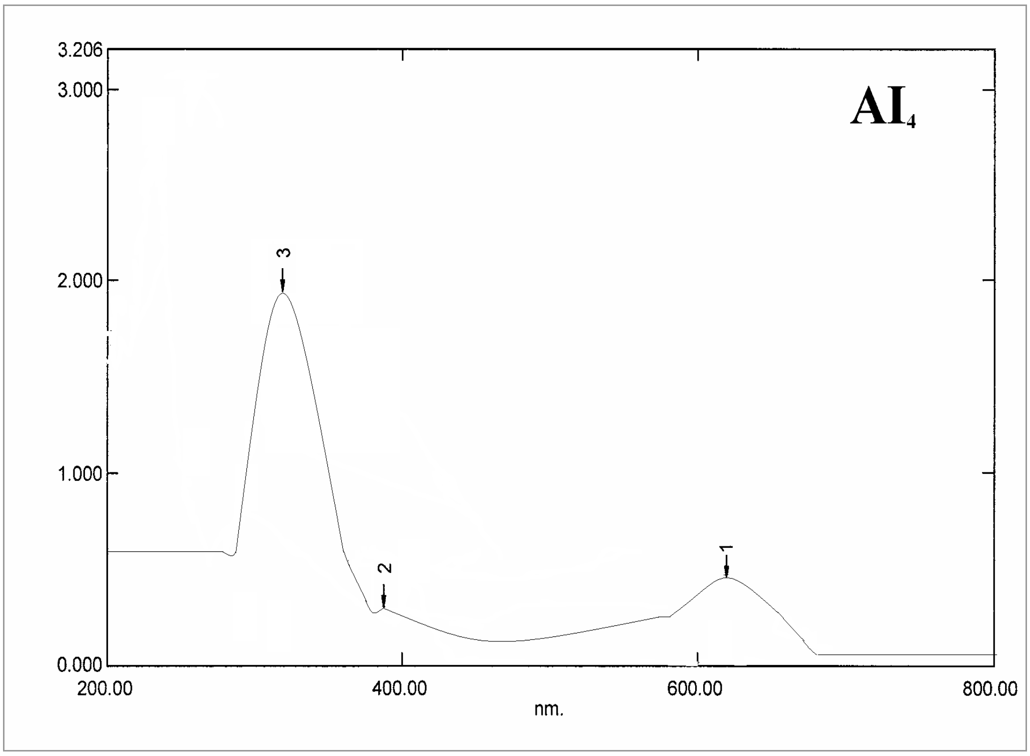


Fig (3-19) Electronic spectra of AI$_2$ and AI$_3$



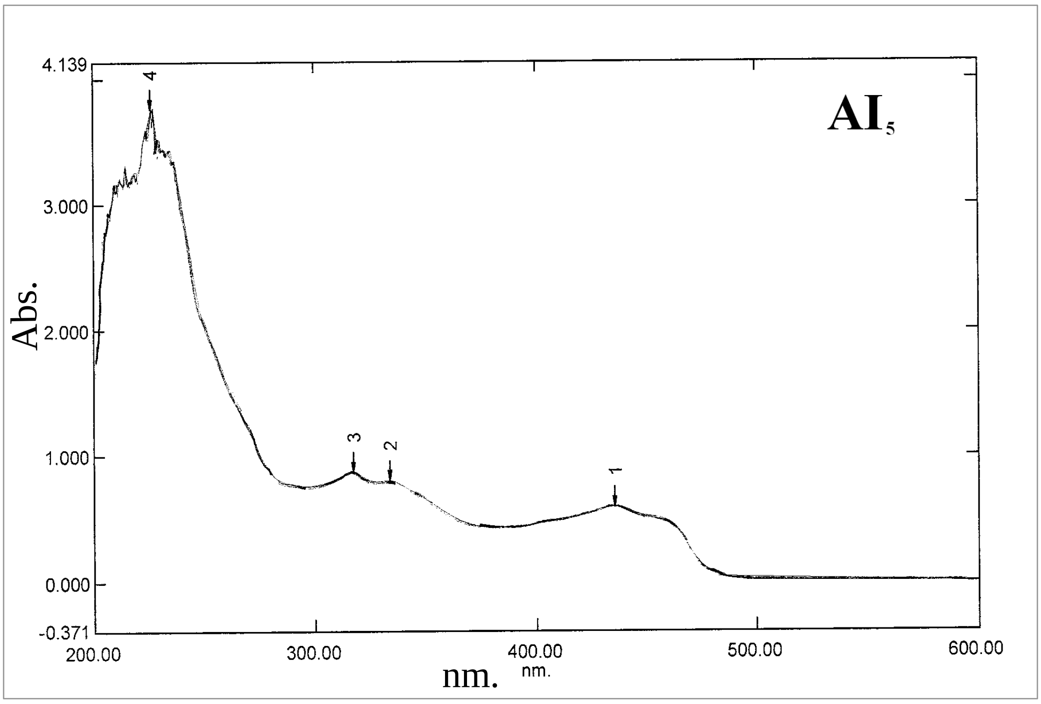
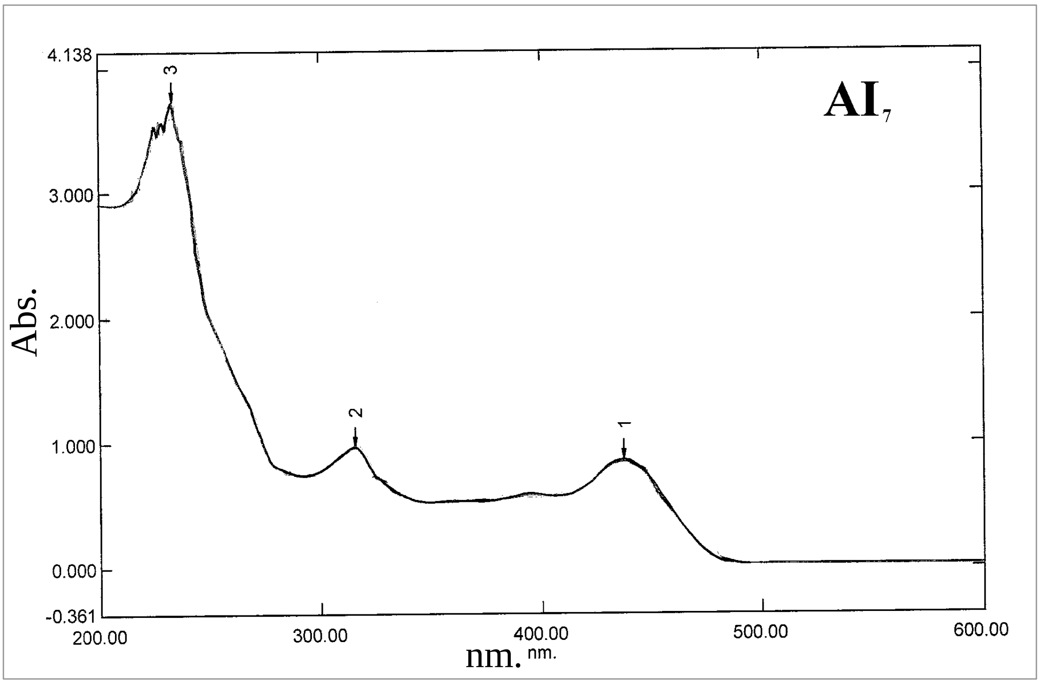


Fig (3-20) Electronic spectra of AI_4 and AI_5



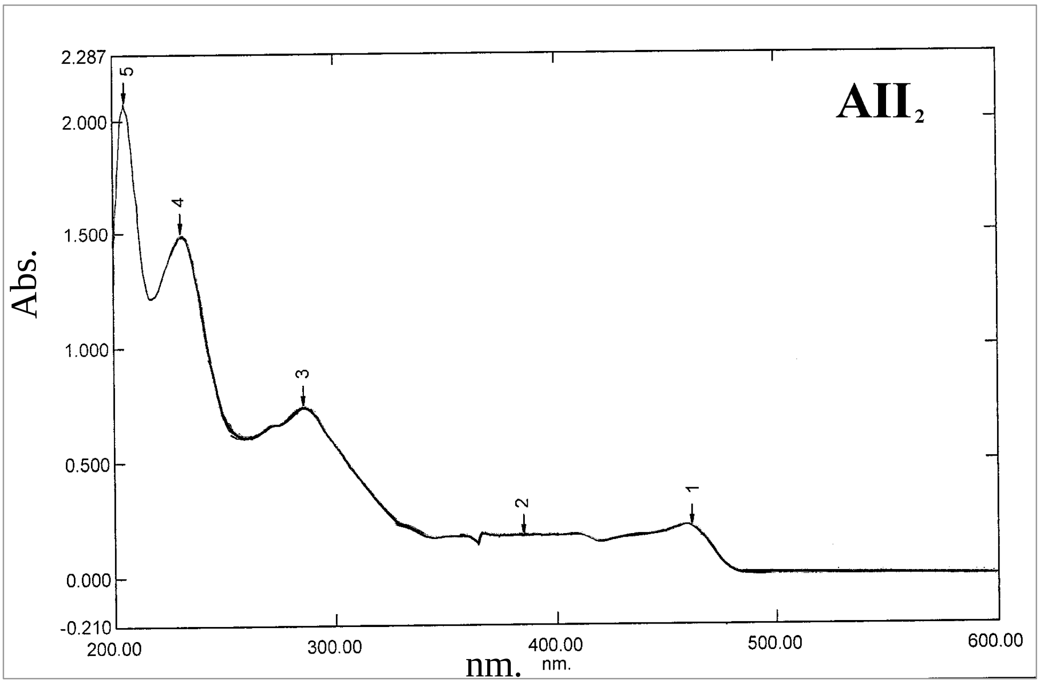
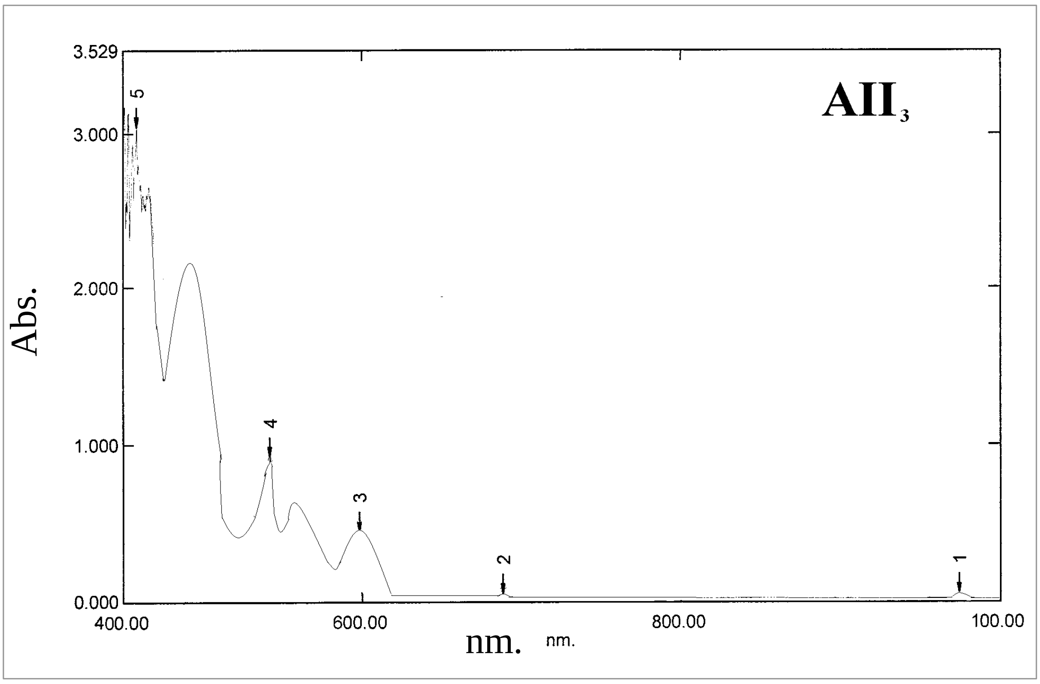


Fig (3-21) Electronic spectra of AI_7 and AII_2



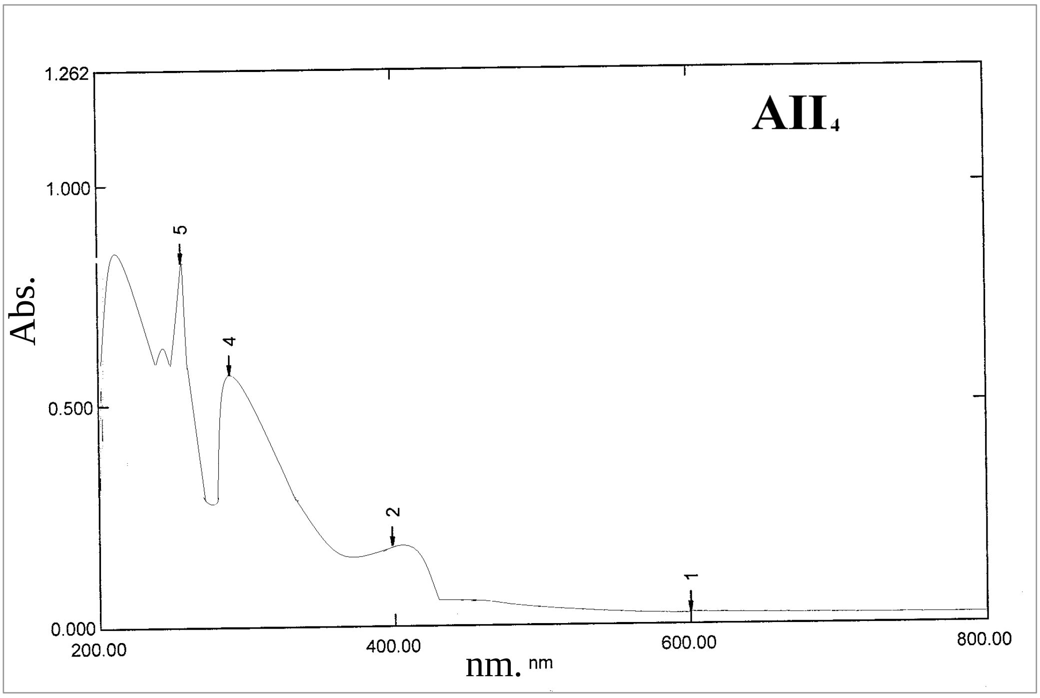


Fig (3-22) Electronic spectra of AII_3 and AII_4

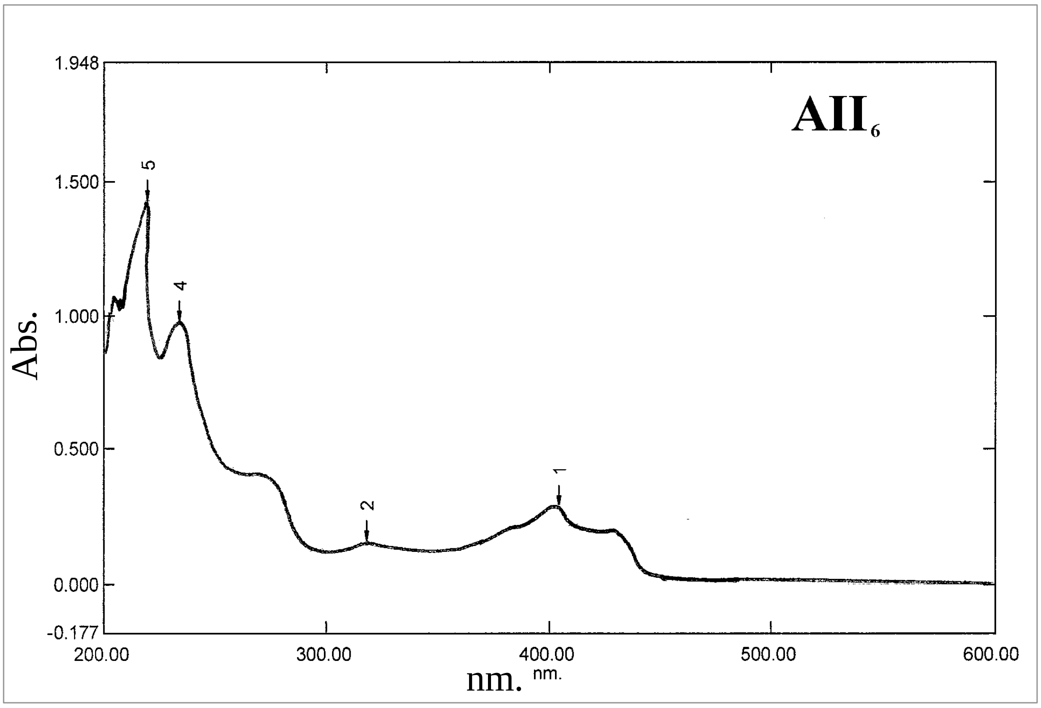


Fig (3-23) Electronic spectra of AII$_6$

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عنوان الرسالة:
تحضير وتشخيص بعض معقدات العناصر الانتقالية مع قواعد شيف جديدة المشتقة من حلقة النفثالين

اسم المشرف:
د. أياد حمزة جاسم