Chapter One

Introduction

Chapter Tow

Experimental Work

Chapter Three

Results and Discussion

1.1 Bioinorganic Chemistry :

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

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

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

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

Inorganic biochemistry is the most growing field which is based on the role of coordination compounds in the living system.(1)

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

1.2 Interaction of The ligand with metal ions :

The tendcy 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 (2) , which simply state that metal ions tend to coordinate with certain donor atoms of the ligand to form stable complex.

The Iwring Williams series of stability for a given ligand is a good 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 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 symbiosis.(3,4)

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

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

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

Metal centers , begin positively charged, are favored to bind to negatively charged bioimolecules , the constituents of protines and nucleic acid offer excellect ligands for binding to metal ions.(1)

1.3 ***Metal Complexes; Chemistry Of Polydentate Ligands:***

Large molecules which contain a number of donating atoms, have the abiliting to bind to the metal ion through more than one atom, polydentate ligand, especially those ligands which have equivelent 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 alarge effect on the bonding properities 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 mechanisim of the ligand exchange , have also important role in this respect.(5)

The chemistry of metal complexes contaning polydentat ligands which have delocalized π orbitals like schiff bases, triazole and porphyrins, have recently attracted the interest of many scientist due to their use in many biomodels , like respiretory pigments and vitamine B12 CO-enzymes, in the case of schiff base metal complexes the work were carried out on cobalt(III)complexes, because they are considerd to be areversal molecular oxygen carriers or vitamin B12 CO-enzyme models. This interest extend to iron (II) and (III) complexes since iron is found in many living systems like hemeoglobine.

On the other hand transition metal (especially vanadium) complexes of schiff bases are also used industrially as catalyst in the Co-polymerzation of acetylene-propylen by the method of Zygler-Nata process.(6)

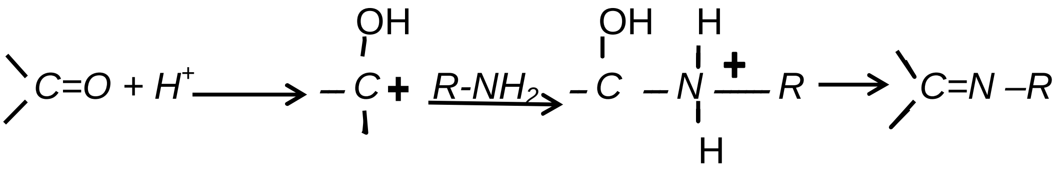
1.4 Schiff bases:

The term schiff base is used to define those organic compounds which contain the functional group$(-\overset{|}{C}=N-)$ and can be designated structurally as R'' R' C=NR.

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

The schiff bases were first prepared by schiff in 1864(7,8) from the condensation reaction of aldehyde or ketones with primary amines by refluxing the mixture in absolute ethanol, benzen , or any other suitable solvent for half or one hour some times, The reaction may be catalyzed by acid.(9,10)

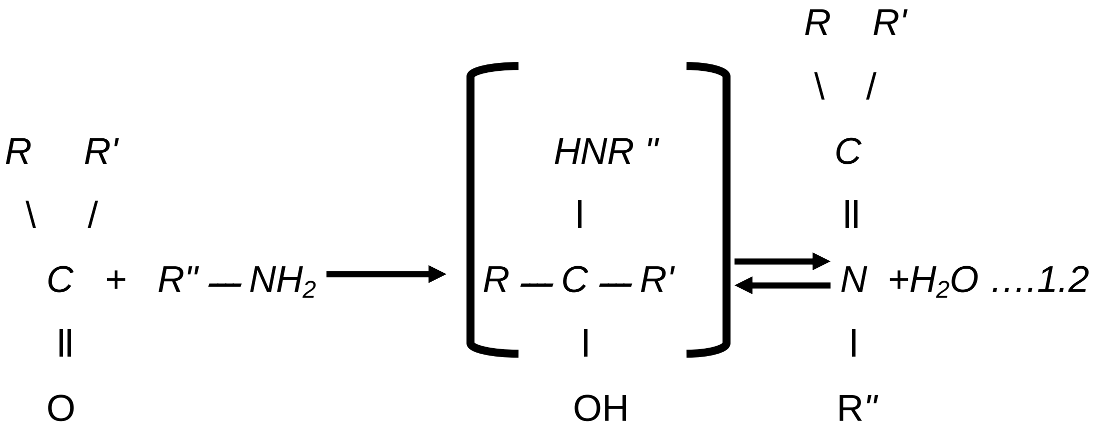
The addition of proton to the carbonyl group yield the conjugated acid in which the carbon of the carbonyl group is more electrophilic , Thus facilitating the attack of the amine on the carbonyl group.The added acid will enhance elimination of water molecule to give the final product (schiff base) ……………



$$>C=O + H^{+} \longrightarrow -\overset{OH}{\underset{|}{\overset{|}{C}}}{+} \;\xrightarrow{R\text{-}NH_2} -\overset{OH}{\overset{|}{C}} - \overset{H}{\underset{H}{N}}{}^{+} - R \longrightarrow\ >C=N-R$$

$+H_2O$……….1.1

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



$$\overset{R\quad R'}{\overset{\backslash\ /}{\underset{\underset{O}{\|}}{C}}} + R''-NH_2 \longrightarrow \left[\underset{\underset{OH}{|}}{\overset{\overset{HNR''}{|}}{R-C-R'}}\right] \rightleftharpoons \overset{\overset{\overset{R\quad R'}{\backslash\ /}}{C}}{\underset{\underset{R''}{|}}{\overset{\|}{N}}} + H_2O$$

….1.2

These bases can also be prepared by refluxing of equimolar quantities of aldehyde or keton with amine without solvent or by slow melting for 10 minutes and then isolating and purifying the product by recrystallization or sublimation under reduced pressure.(11)

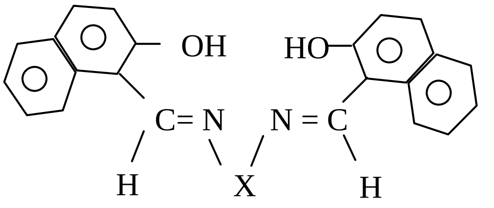
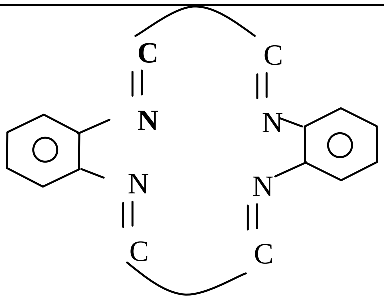
Staab prepared schiff bases by removing water which is formed by condensation of aldehyde with the amine by reflux in benzene , This is done by mixing the amine and the aldehyde in benzen and then the residual solution is distilled under vacuum .(12)

Imine schiff bases and other C=N compound can be reduced by $LiALH_4$,$NaBH_4$, Na-EtoH, hydrogen and catalyst, as well as with other reducting agents.

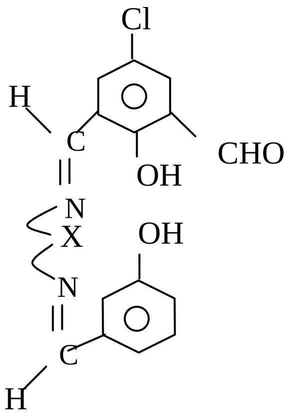
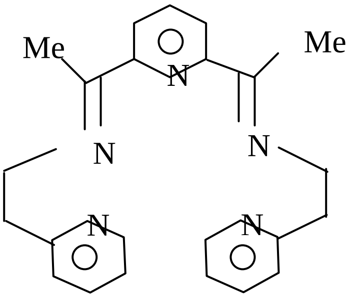
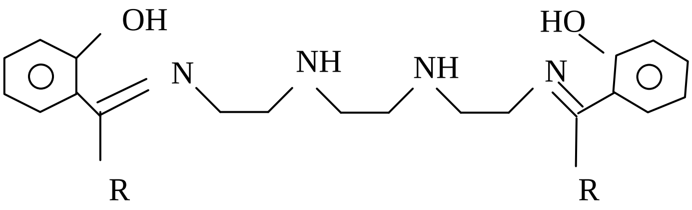
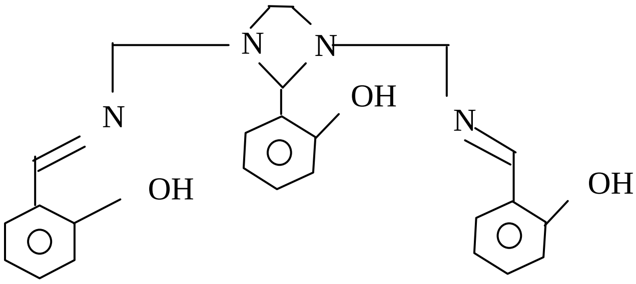
Schiff bases can be classified according to the number of coordinating sites, type of bonding,Type of donor atom (rather than azomethin nitrogen), number of donated electron paires and other method of ligand classification.

Of these methods the one which depend on the coordination site is considered to be the most important ,the following table show exampeles of schiff bases classified according to this method.

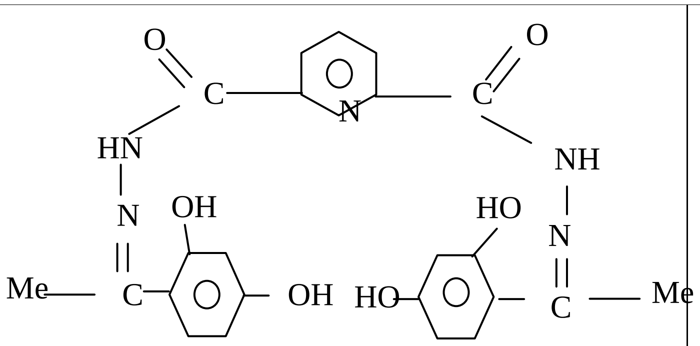
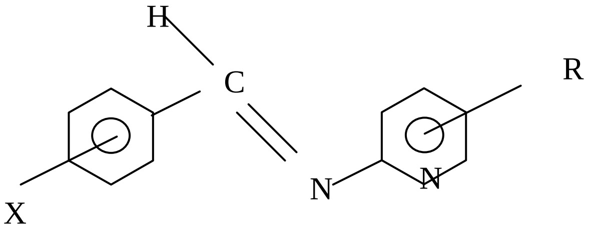
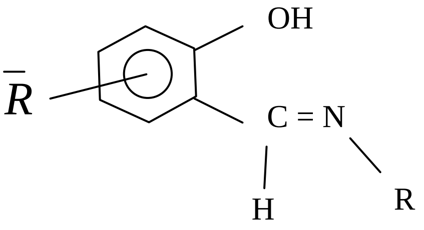
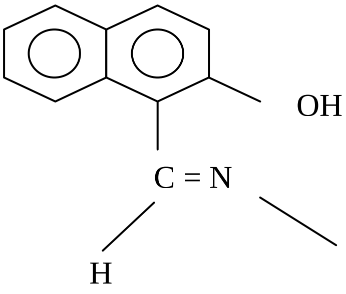
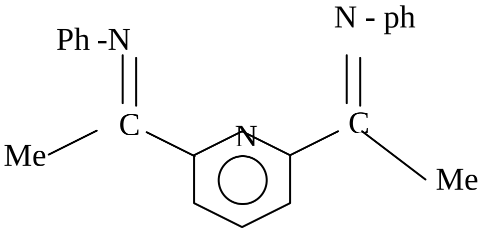
<u>Table(1-1)Some schiff bases with different donor atoms</u>

Complex	***Donar atoms***	***Type of donor***	***Refer-ence***
 X=S, NH, NCH_3	N_2O_2	Tetradentate	23
	NNNN	Tetradentate	24

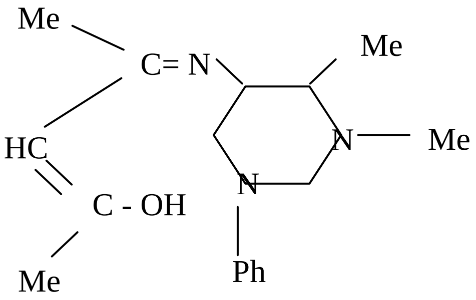
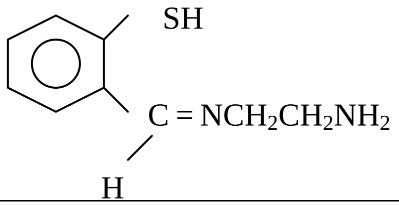
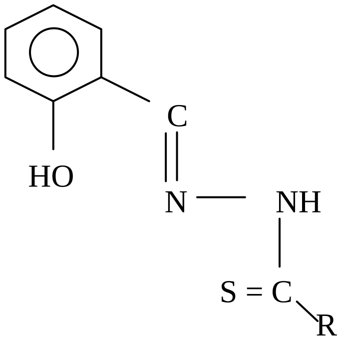
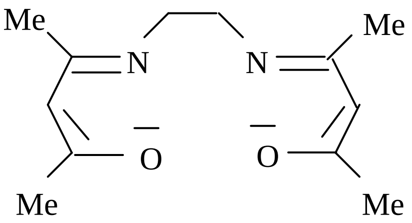
Table(1-1) :….continued

 X = S, NH, NCH_3	N_3O_2 N_2O_2S	Pentdentate	25
	NNNNN	Pentdentate	26
	N_4O_2	Hexadentate	27
	N_4O_3	Heptadentate	28

Table(1-1) :….continued

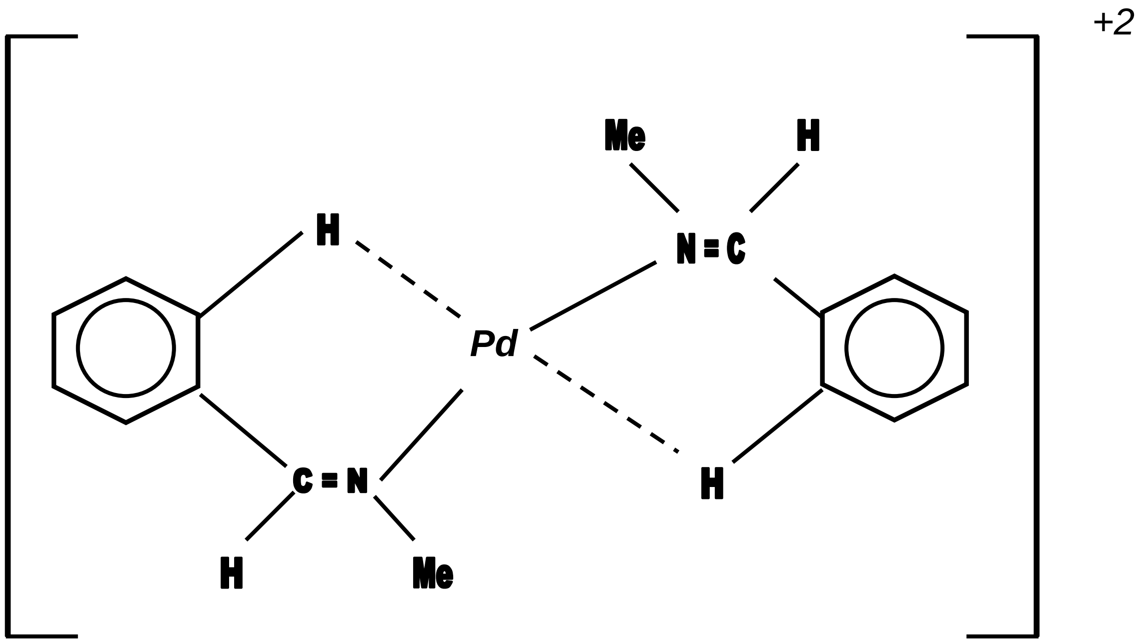
	N_5O_4	Nanodentate	29
	N N	Bidentate	13-14
Ph – C = N – ph | Ph – C = N – ph	N N	Bidentate	15
	N O	Bidentate	16
	N O	Bidentate	17
	NNN	Tridentate	18

Table(1-1) :….continued

	NOO	Tridentate	19
	NNS	Tridentate	20
	NSO	Tridenatae	21
	N_2O_2	Tetradentate	22

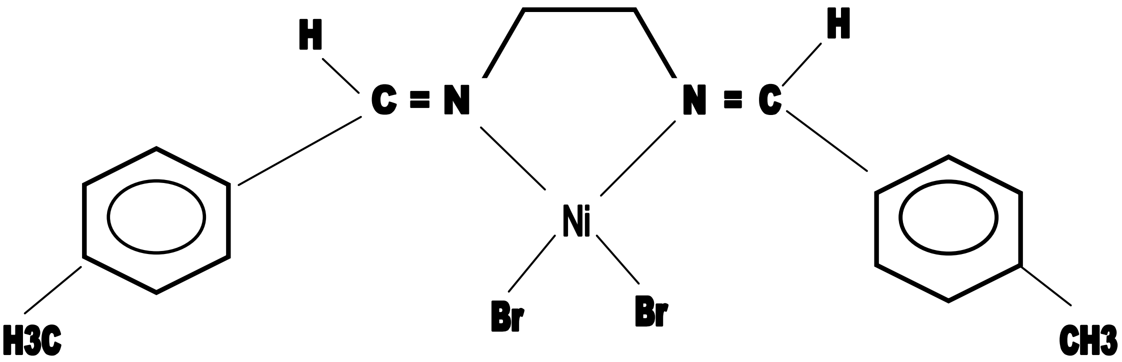
As mentioned previously (section 1.2), the way the ligand coordinate to the metal ion .Is affected by the type and oxidation state of the metal ion in addition to the ligand structure, This can shown by the following examples.

1-The monodentate schiff base phCH=NMe from the weak M…H bond which make extra stability for its complexes(16),as in the following palladium complex.



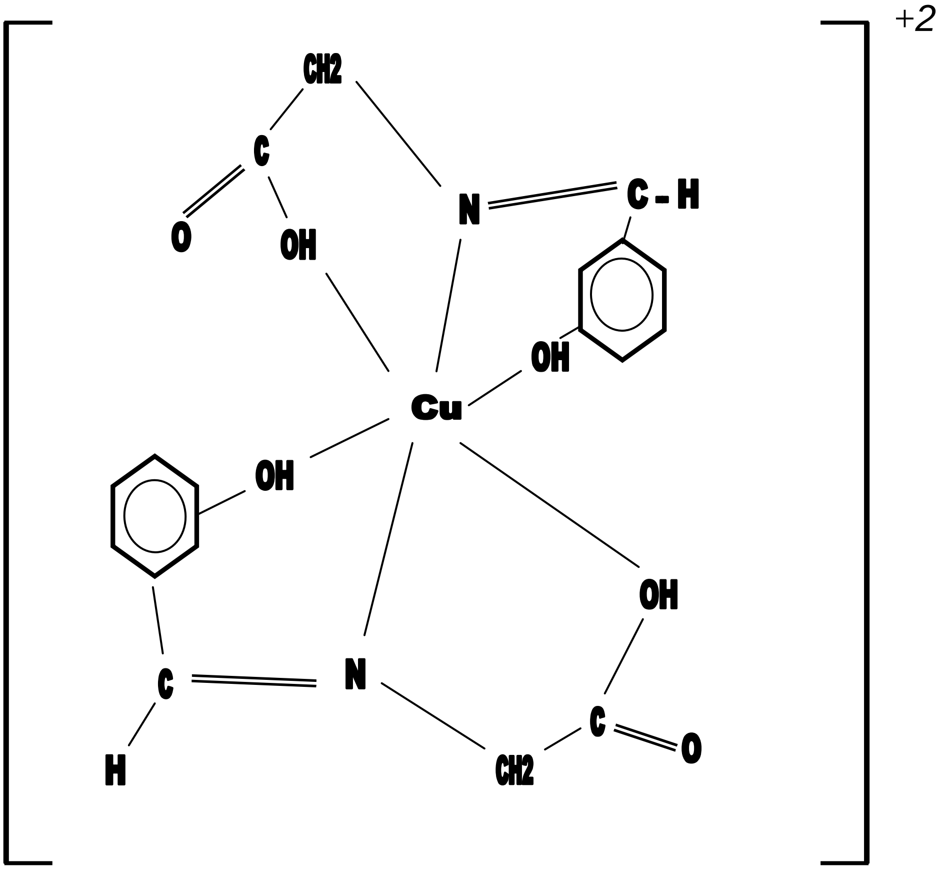
Figure(1-1) The complex palladium (II) with methyl benazalidine imine.

2-Bidentate Schiff bases containing two nitrogen atoms form more stable chelating rings with the central metal ion as in the following nickel(II) complex:(23)



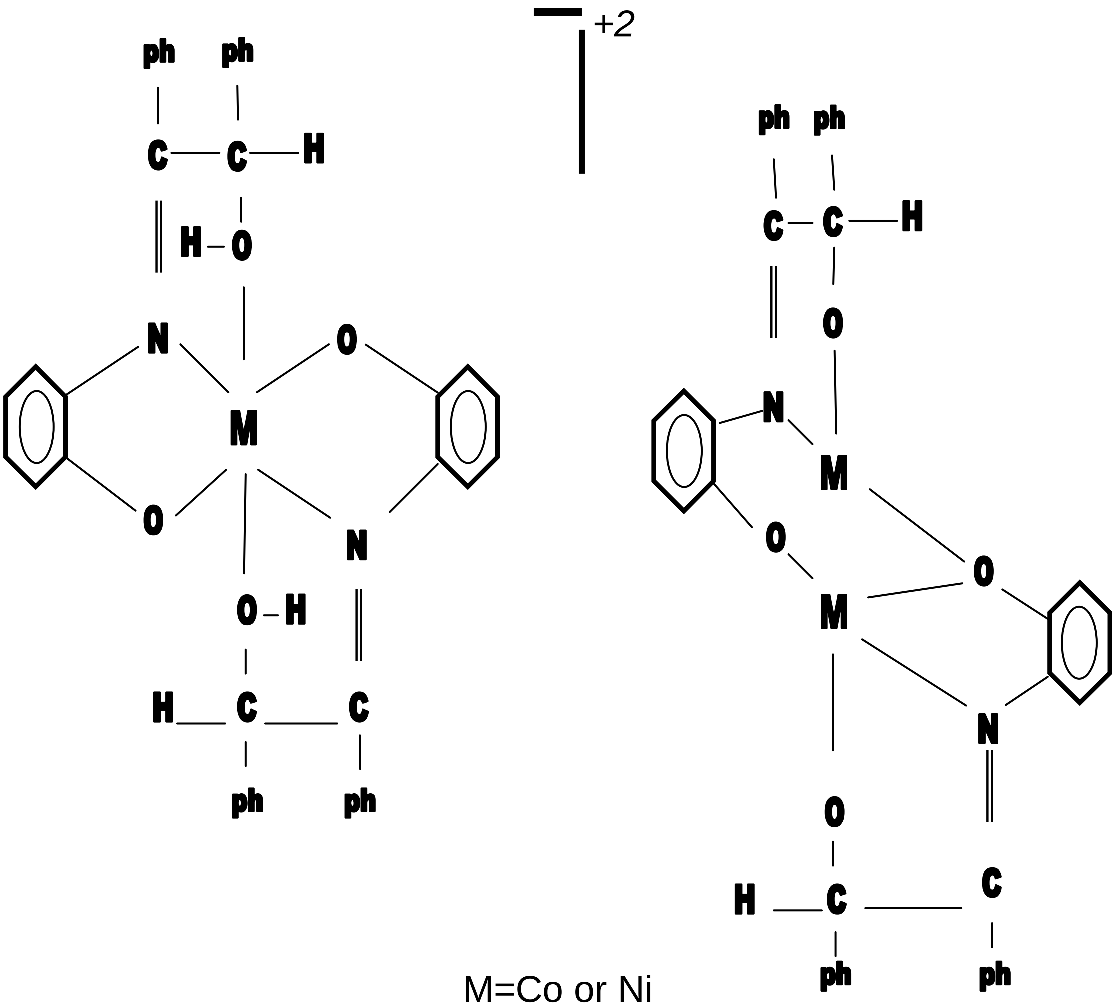
Figure(1-2) The complex of Ni(II) with bis (p-Methylen aldehyde) ethylene dimine

3-As an example of Tridentate neutral schiff base complexes is the following cupper (II) complex.(22)



figure(1-3)

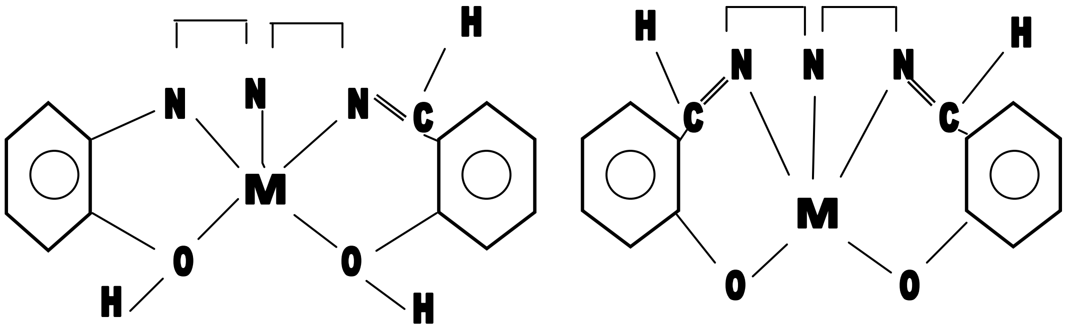
4-It was found that the ligands derived from benzoin and or the amino phenol(30) give mononuclear complex ions in neutral media, while binuclear brigded complexes were formed in basic media as in the following structures .



M=Co or Ni

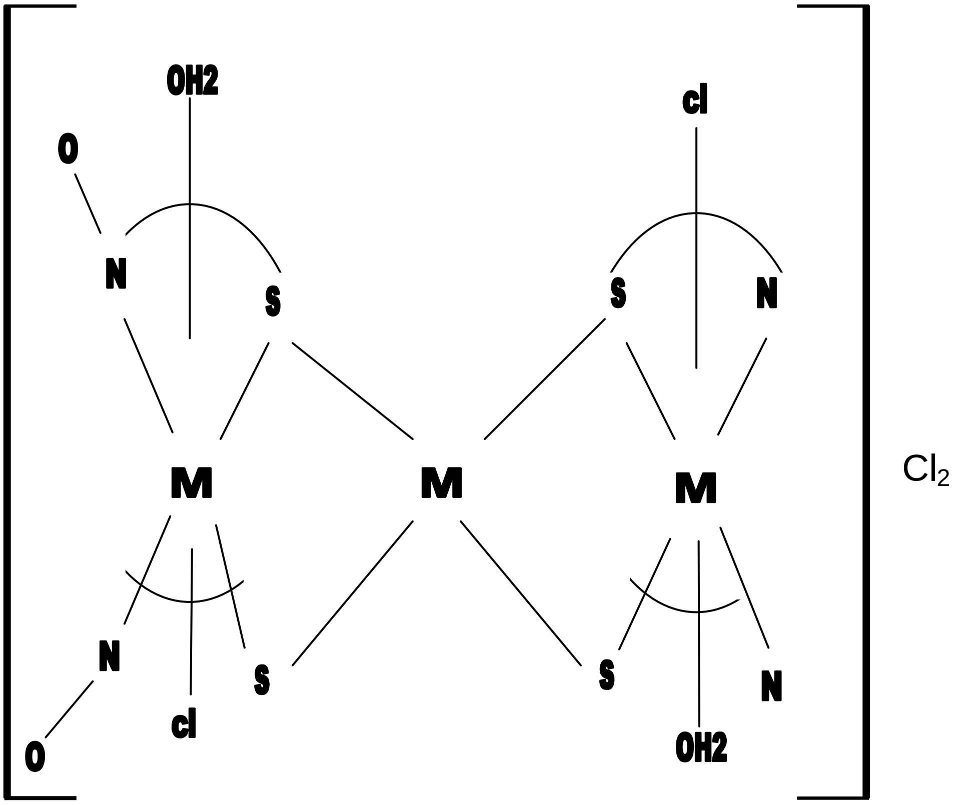
figure(1- 4)

5-Some schiff bases show high coordination number as that of bis (salysilidin) diethylene triamine(31) which form complexes with cobalt(II) and nickel (II) having octahedral geometry in which the ligand behave as pentdentate in the neutral and basic media respectively.



figure(1-5)

6-There are some polynuclear complexes(32) of the schiff bases which show different geometrical shapes around the metal ions as in the following complex, where the central metal has square planar geometry, which the other two metal atoms have octahedral geometry.



figure(1-6)

1.5 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 in order to prepare a new sets of these bases and their transition metal complexes.(33)

These complexes have proven it be antitumer and have carcinostatic activities (33,34), they show leukaemetic activity. Schiff bases, on the other hand, have a great importance in bioligical reactions like (visual process)(35) and in the reaction that involve removing the amino group by enzymic effect (enzymatic transition reaction) and some B6-Catalysed reactions.(36)

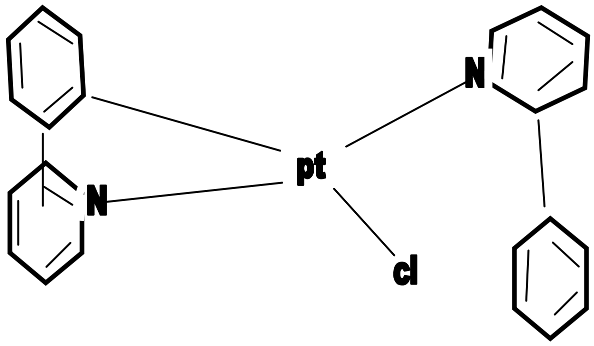
The Biological activity of schiff base is attributed to the formation of stable chelate with transition metal ion present in cells.(37) Schiff bases derived from sulfa drugs have been successfully used for the bacteriostatic activites and complxation.(38)

A great deal of work concerning metal complexes of schiff bases were focused on the cobalt (III) complexes.

The discovery of cis-platinum complexes, cis-[pt$(NH_3)_2$ cl_2], as an antitumer agent by Rosenberg (39,40) , lead to development of the chemistry of platinum complexes toward biological applications.(41) Palladium and platinum are regarded as soft metals, so they react with soft ligands that contain on electron-donating group like S and P,they also can form complexes with hard ligands(42) , like oxygen-contaning or nitrogen-contaning molecules.

Recently many research works appeared which deal with the study of palladium interacting with schiff bases through cyclometalation reaction(this include metal containing cycle in which the metal is bonded to a carbon atom).An example of such compounds is the mono functional platinum (II) complexe with one normal and one cyclometelated 2-phenyl pyridine ligand (figure

(1-7)),which was discovered to exhibited high antitumer efficacy against the cisplatine-resistant mouse sarcoma 180 cell lines.(39)

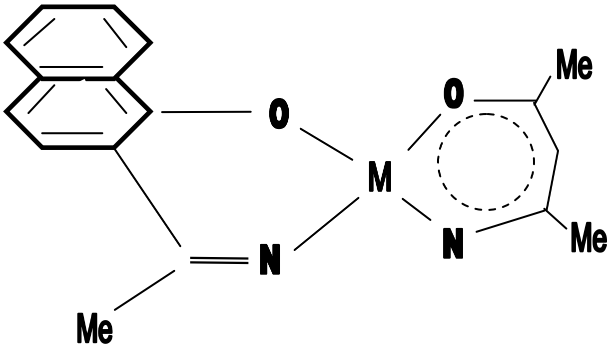


Figure(1-7) structure Pt (II) complex with 2-phenyl pyridine ligand

Cyclometallation reaction play an important role in preparation of some organometallic compounds 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.(43)

Schiff bases and their analogous have great important as catalysts in racemic reactions in peptide synthises and in the formation of amines that have biological origin.(44) Daravet et.al.(45)have prepared unsymmetrical schiff base 1-hydroxy-2 acetonaphathonea (ethyl a cetone-ethylen diimine)and its complexes with some transition metals[Ni(II), Cu(II), Pd(II)].These compound were charactrized by elemental analyisis, 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 activites figure(1-8).



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

Figure(1-8) suggested structure of the complexes.

1.6 Infrared Spectra of Schiff Bases and their metal complexes.

The following are a review of the C=N group assignment as recorded for schiff bases, and their metal complexes:

1-ע(C=N) appear around 1630cm^{-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.(46)

2-Coordination chain polymers of schiff base, derived from o-amino benzoic acid and terephthaldehyde shows C=N stretching at 1625 cm^{-1} which shifts to (1620-1615)cm^{-1} on complexes indicating the involvement of azomethine nitrogen in coordination.(47)

3-A strong band around 1590cm^{-1} is also assigned to the C=N stretch of the free schiff base of bis (vanillin)-ethylendiimine, bis (vanilline) propylene diimine and bis(vanillin) o-phenyl diimine, this band was found in the region (1675-1665)cm^{-1} for their complexes with Cu(II) ion.$^{(48)}$

4-The IR spectra recorded by others show astrong sharp band in the region (1630-1615)cm^{-1} for ע(C=N).$^{(49)}$

5- Schiff bases of oximes,thiazoles,imino carbonate,and quanidines showed the C=N stretch in the region (1689-1471)cm^{-1}.$^{(50)}$

6- The IR spectra of new series of schiff bases derived from 4,5-disubstituted-2-amino-thiazoles,substituted-2-aminobenzo-thiazoles and p-hydroxy benzaldehyde showed astrong sharp band in the region(1640-1625)cm^{-1} for ע(C=N).$^{(51)}$

7-Strong band at 1600cm^{-1} corresponding to ע(C=N) in some schiff bases derived from 2-furylglyoxyl and 2-amino pyridine was observed.$^{(52)}$ This band shift to lower frequencies in the spectra of the Mn(II) ,Co(II), Ni (II) and Cu(II) complexes indicating the involvement of a zomethine nitrogen in the coordination.

8-The IR spectrum gave absorption band in the region (1640-1630cm^{-1}) for ע(C=N) of free tetraimine schiff base macrocycles derived from the condensation of 1,3 diamine-2- hydroxypropane with pyrole-2,5-dicarbaldehyde and with thiophene-2,5 dicarbaldehyde.$^{(53)}$

9-Patai suggest that ע(C=N) appeared in the region(1680-1570) cm^{-1}.The intensity of this band is variable and it depend on the substituted group.$^{(9)}$

10-The IR spectrum of schiff base derived from 4-phenyl-5-(p-aminophenyl)-3-mercapto-1,2,4-triazole gave strong band in the region (1695-1650)cm^{-1} corresponding to ν(C=N).(7)

Layer study Raman spectra of imine compounds and found that a number of N-alkylidene alkyl amines give rise to a Raman line near 1670cm^{-1} .Centeral also find that imines have aRaman line in the same region and compares their characteristic frequency with those of C=C and C=O and find it to be close to the latter

	Δr, cm^{-1}
C=C	1600-1650
C=N	1650-1670
C=O	1710-1750

The C=N bond distance for several imines has been deduced from the corresponding Raman frequencies by comparsion with the C=O distance for several ketons .(54)

The average distance for the C=O band is close to the accepted value of 1.25Aº, so the imines are considered to be perfectly covalent and the bond is close to the expected value of 1.25A°, so the imines are considered to be perfectly covalent and the bond distance of 1.24A° was adopted .The N-radius is to be 0.575A° and the c-radius is 0.665A°.

1.7 Electronic Spectra Of Schiff Bases :-

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

In the presence of conjugation, the electronic spectra of, for example $CH_2=CH-CH=N-C_4H_9$,show $n \rightarrow \pi^*$ transition at 219nm.But the electronic spectra of benzylidene aniline show avery important phenomena since it is also electronic with stilbene and they have a different spectra.

The following interpretation of the first four electronic absorption band systems of the benzylidene aniline molecule seem 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_N moiety.(55,56,57,58,59)

b-The band at 262nm is characterised 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_C moiety is the electron donor and the azomethine group acts as an electron acceptor. (53,56,57,58,59,50)

c- The band at 237nm has been assigned to a local excitation in the ph_N moiety in which the lone pair on the nitrogen a tom interacts with the π electrons of the ph_N ring , on the other band local excitation in the ph_C ring has also been proposed to explain absorptions in the some region in the spectrum.(56,57,59,60)

d- A fourth band system exists at 218nm has been assigned to a local excitation in the ph_C ring .(57,58) The electronic spectra of all other schiff base like heterocyclic hydroxy , β-diketones (61,62) and those derived form α-diketones have been interpreted on this bases unless indicated other wise .

1.8 Aim of the work

Considering the biological activities of the schiff-bases and their metal complexes, in addition to the diversity of coordination behavior of substituted schiff bases, the fallowing goals are to be satisfied:

1- Preparation of a chelating schiff base with alicyclic moiety (cyclohexyl group) and aromatic moiety (phenyl group).

2- Preparation of a series of transition metal complexes with the new schiff base, these transition metals include partially filled and completely filled ions.

3- Characterization of the schiff-base and it's metal complexes using the available techniques.

2.1 Instrumentation

A) Fourier Transform Infrared spectrophotometer (FT-IR)

The infrared spectra of the prepared compound were recorded using FT-IR 8300 fourier transform infrared spectrophotometer of Shimadzn company as a (KBR) discs .

B) Electronic Absorption spectra

The electronic spectra of the prepared complexes were obtained using Shimadzn uv-vis 160A ultraviolet spectrophotometer ,using 1cm quratz cell in the range of weve length (200-1100) nm .

C) Magnetic Susceptibility Measurments .

The magnetic susceptibility values for the prepared complexes were obtained at room temperature using (magnetic susceptibility Balance) of Jhonson Mattey catalytic system division .

D) Melting Point :

Callen kamp M.F.B,600.01 melting point apparatus was used it measure the melting points of all the prepared compounds .

E) Molar Conductivity

Molar conductivity measurement were carried out at 25c° with concentration of (10^{-3} M) using Wissenschaftlich-Technische werkstatten 8120 Weilheim I.O.B ,Drucker-Printer,W.Germany. All the complexes were dissolved in absolute ethanol .

F) Atomic Absorbance Measurments

The metal content of the complexes was measured using atomic absorption technique by Berkin-Elmer 5000 atomic absorption spectrophotometer for the determination of (V^{+4},Cr^{+3},Fe^{+2},Co^{+2},Ni^{+2},Cu^{+2}, Zn^{+2} ,Cd^{+2},Hg^{+2},Pd^{+2})

2.2-Chemicals

All the chemicals used in this work were of highest purity available and the supplied without further purification .The following Table shows the purity the reagents and the companies which supply themes .

	Chemical	***Assay %***	***Company***
1	$NiCl_2.6H_2O$	*96.00*	*BDH*
2	$Cu(NO_3)_2.6H_2O$	*97.50 %*	*BDH*
3	$Fe(NH_4)_2.(SO)_4.\ 6H_2O$	*95 %*	*Fluka*
4	$ZnCl_2$	*Dry pure*	*Merck*
5	$CO(NO_3)_2.\ 6H_2O$	*97 to 101 %*	*BDH*
6	$CrCl_3$	*99 %*	*Fluka*
7	$VOSO_4.H_2O$	*95 %*	*BDH*
8	$Pd(DMSO)_2Cl_2$	*93 %*	*Fluka*
9	$HgCl_2$	*98 %*	*BDH*
10	$CdCl_2.2H_2O$	*99.00 %*	*BDH*
11	*Cyclohexylamine*	*99.00 %*	*Fluka*
12	*Salicylaldehyale*	*97 %*	*Merk*
13	*Absolute ethanol*	*99.99 %*	*Hyman Limited*

2.3 Methods of Preparation :

2.3.1*- Preparation 0.1 M alcoholic KoH solution 0.11 g of KoH was* dissolved in 20ml of absolute ethanol .

2.3.2*- Preparation of the Schiff base ligand (CSSB)*

A mixture of 0.9918 g of cyclohexylamine (0.01 mmole)with 1.22 g (0.01mmole) of salicyladehyde was dissolved in 25 ml of absolute ethanol. To this solution small amount of P-. Toluene sulfonic acid was added ,The resulting mixture was heated with stirring under reflux for two hours ,the result was a yellowish viscous liquid ,from which the ethanol was removed under vaccum .

2.3.3 *- Preparation of Metal complexes*

A- ***VO^{+2} complex****.*

To a mixture of 0.2g(1.15mmole) of $VOSO_4.H_2O$ with 0.23g (1.15mmol) CSSB dissolved in 5 ml absolute ethanol, 2 ml alcoholic KOH (0.1M) was added . The mixture was heated with stirring under-reflux for three hours ,The resulting olive green precipitate was filtered,washed with water and ethanol then it was dried under vaccum , the prepared complex was partially soluble in warm absolute ethanol.

B- ***Cr (III) complex***

To the mixture of 0.2g (0.75 mmole) $CrCl_3 . 6H_2O$ with 0.15g (0.75 mmole) of the (CSSB), (CSSB) dissolved in 5 ml absolute ethanol ,2 ml of alcoholic KoH (0.1M) was added,the mixture was heated with stirring under – reflux for three hours ,the resulting deep green precipitate was filtered ,washed with water then with absolute ethanol several time,then dried under vaccum . The prepared complex was partially soluble in warm absolute ethanol .

C- ***Fe(II) complex***

To the mixture of 0.2g (0.51mmole) $Fe(NH_4)_2(So_4).6H_2O$ with 1.03g (0.51mmol) of (CSSB) in 5 ml absolute ethanol(0.1M) was added. 2 ml alcoholic KOH(0.1M) was added. Reflux for three hours. The resulting red brown precipitated was filtered and wash with water the water and absolute ethanol then dried under vaccum. The resulting complex was partially soluble in warm absolute ethanol.

D- ***Co(II) complex***.

To the mixture of 0.2g (1.45mmole) of Co $(No_3)_2$. $6H_2O$ with 0.292g (1.45mmole) of (CSSB) dissolved in 5 ml absolute ethanol (0.1M) was added ,2 ml of alcoholic KoH . The mixture was heated with stirring under – reflux for three hours.The resulting light red precipitate was filtered, washed with water then absolute ethanol several times and dried under vaccum. The resulting complex was partially soluble in warm absolute ethanol.

E- ***Ni(II)Complex.***

To amixture of 0.2 g(0.84mmol) of $NiCl_2.6H_2O$ with 0.16g (0.84mmol) of (CSSB) in 5 ml absolute ethanol,2 ml alcoholic KoH (0.1M) was added. The mixture was heated with stirring under-reflux for three hours.The resulting bright yellowish green precipitate was filtered, washed with water the absolute ethanol and dried under vaccum. The resulting complex was partially soluble in warm absolute ethanol.

F- ***Cu(II) complex***

To a mixture of 0.2g (0.67mmole) of $Cu(NO_3)_2,6H_2O$ with 0.13g (0.67mmole) (CSSB) in 5 ml absolute ethanol ,2 ml alcoholic KoH (0.1)M was added . The mixture was heated with stirring under–

reflex for three hours, the resulting olive green , precipitated washed with water and ethanol than filtered and dried under vaccum . the prepared complex was partially soluble in warm absolute ethanol.

G- *Zn(II) complex*

To the mixture of 0.2g(1.46mmol) of $ZnCl_2$ with 0.29g of (1.46mmol) of (CSSB) dissolved in 5 ml absolute ethanol,2 ml alcoholic KOH(0.1M) was added .The mixture was heated with stirring under-reflux. For three hours ,the resulting yellow precipitated was filtered, washed with water then ethanol and dried under vaccum.The resulting complex was partially soluble in hot absolute ethanol.

H- *Cd(II)complex*

To a mixture of 0.2g(1.12mmole) of $CdCl_2.2H_2o$ with 0.22g (1.12mmole) of (CSSB) dissolved in 5 ml absolute ethanol , 2 ml alcoholic KOH (0.1M) was added. The mixture was heated with stirring under-reflux for five hours , the resulting yellowish white Precipitate, was heated with water and then it was dried under vaccum, it was partially soluble in warm ethanol.

I- *Hg(II) complex*

The mixture of 0.2g (0.58mmole) of $HgCl_2$ with 0.11g (0.58 mmol) dissolved in 5 ml absolute ethanol was heated with stirring under - reflux for three hours. The resulting dark precipitate was filtered,washed with water and ethanol than dried under vaccum .The resulting precipitate was partially soluble in hot absolute ethanol .

G- *Pd(II) complex*

A soultion of [Pd(DMSO)$_2$Cl$_2$],2mmole(0.666g),dissolved in 5 ml absolute ethanol was added drop wise to the ligand, 4mmole(0.807g) dissolved in absolute ethanol , the mixture was refluxed for one hour . After cooling the solution was precipitate ,was filtered off ,washed several times with absolute ethanol then recrystallized by diethyl ether , ayellowish green fine crystalline powder was obtained.

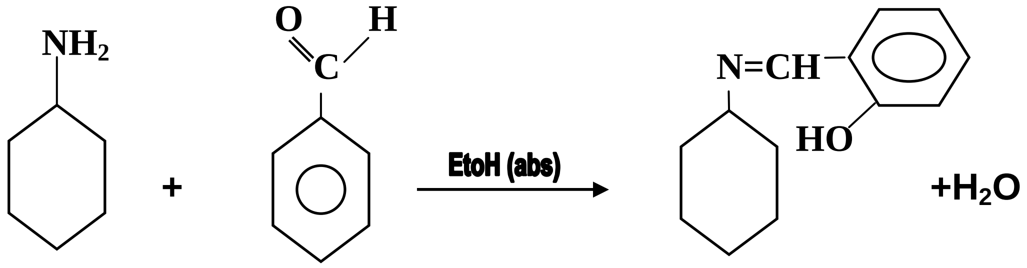
Schiff bases are considered to be good coordinating ligands because they involve hard nitrogen atom as azomethine group . The ligand prepared in this work . i.e.P- hydroxy benzyliden phenylimine (CSSB) is reported for the first time .

CSSB has two donor atoms ,i.e . N of the imine group and the O of the hydroxyl group .

A number of transition metals belonging to the first,second and third series were chosen to prepare a set of complexes ,which were characterized by following spectral changes of the above groups , in addition to other techniques .

3.1 Preperation and identification of CSSB

CSSB was prepared a ccording to the following equation .



The reaction is believed to proceed according to the general mechanism mensioned in section (1.4). Higher yield product with higher purity was obtained following this method, This was obtained by making some modification to a reported method (63,64) in last method(65) salicylaldehyde was reacted with cyclohexylamine in the presence of small a mount of p-toluene sulfonic acid using absolute ethanol as solvent under reflux conditions, but the isolated schiff base was of low yield and was impure .

The ligand CSSB is a yellow colored viscous liquid which is miscible with absolute ethanol and immiscible with water ,with boiling point of 320 C°. It was characterized by UV-Vis and FT-IR spectroscopy.

3.2-Preparation of Transition-Metal Complexes of CSSB.

The reaction of CSSB with Vanadium(IV), Chromium(III), Iron(II), Cobalt(II), Nickel(II),Copper(II), Zinc(II), Cadmium(II) and Mercury(II), Palladium (II)salts.

Using absolute ethanol as solvent with the addittion of ethanolic potassium hydroxide, except in the case of Hg(II) complex.All the reactions were carried out under reflux conditions for at least 3 hours to ensure completion of reaction.

New fine crystalline complexes were obtained which were of high stability toward air and moisture, these complexes were characterized by their UV-Vis and FT-IR spectra, conductivity measurement,metal analysis using atomic absorption spectroscopy , magnetic susceptibility measurment,and their melting points.

Table(3-1) shows the physical data and metal analysis data of the prepared CSSB and its metal complexes.

Table(3-1)-The physical data and metal content of the of the ligand and it's metal complexe

Symbol	**Color**	**Melting point C°**	**M% Calc**	**M% found**
CSSB	Yellow	(B.P.320)	—	—
V0(II)	Olive green	240-242	11.19	13.21
Cr(III)	deep green	220-250	11.4	11.33
Fe(II)	Red brown	210-211	12.6	11.61
Co(II)	Light Red	160-163	10.86	11.72
Ni(II)	Bright Yellow green	300-330	11.82	12.51
Cu(II)	Olive green	120-150	12.6	11.72
Zn(II)	Yellow	140-147	13.9	13.34
Cd(II)	Yellowish white	110-114	16.41	16.34
Hg(II)	Dark	208-210	26.24	23.1
Pd(II)	Yellowish green	210-214	10.76	10.33

According to these results the following general formula can be suggested:

1-[M L_2 (X) (M)].S

X=M=zero S=Zero when M= Vo(II)

X=Cl,M=H_2O S= Zero when M= Cr(III)

X=M=H_2O S=2H_2O when M=Fe(II)

X=NO_3 ,M=H_2O S=Zero when M= Co(II)

X=M=H_2O S=Zero when M=Ni(II)

X=M=H_2O S=Zero when M=Cu(II)

X=M=Zero S=2Cl when M= Zn(II)

X=M=Zero S=2Cl.C_2H_5OH when M= Cd(II)

X=M=Zero S= 2Cl.C_2H_5OH when M= Hg(II)

X=M=Zero S=2Cl when M= Pd(II)

3.3- Infrared Spectral Study.

Infrared spectrum of CSSB was recorded and compared with those of its metal complexes, all the spectra were recorded using KBr disk in the case of complexes and Nacl window for the ligand, in the range (4000-200)cm^{-1}.

3.3.1-*The Spectrum of CSSB*

The spectrum of the CSSB, figure(3-1),show stretching frequency of the imine group at 1627.8 cm^{-1}as strong and sharp band which in accord with the published data which have been discussed in section (1.6)$^{(66)}$. The ע C-H of the aromatic ring appeared at 3058.9cm^{-1} and that of the aliphatic ring (cyclohexyl group) appeared as strong and sharp band at 2929.7cm^{-1}. The OH group should show itself through two vibrational bands ,i.e stretching and bending frequencies , these bands appeared at 2220cm^{-1} as week band and at 1413.7cm^{-1} as medium sharp band respectively.

The עC=C of the phenyl group appeared at 1581.5cm^{-1}.These data confirm the formation of the desired schiff base.

3.3.2- *The Spectra Of The Metal Complexes*

The changes in the position and shape of the vibrational spectral bands of the imine and the hydroxyl moities were followed to examine the formation of the complexes.

Birdar and Kukanni$^{(67)}$ studied Ti (IV) complexes with aromatic schiff bases and found that the free izomethine group absorbed in the regin (1610-1630)cm^{-1}. Which were schifted to the region (1630-1650)cm^{-1} upon the formation of the complexes, they attributed to the coordination of the metal with the nitrogen atom of the azomethine group, and explained this blue schift to the increase in C=N double bond character. Which was (68) also noticed by Bursch and Bailor.While panda et.al.(69) recorded a red shift for the izomethine group in the complexes of the nickel(II) cobalt(II) copper(II) with a number of schiff bases.This red shift was also found during the preparation of schiff base complexes with a number of first series transition metal.(70)

Mahapatra also found a red shift by ($5cm^{-1}$) for the izomethine group upon the coordination metal ion . Maida(71) also recorded a red schift of the azomethine group in the formation of a number of transition metal complexes with p-hydroxy benzyliden phenylimine. In our present work a red shift was observed in all the new complexes which depend on the metal ion. figure (3-2)(3-3)(3-4)(3-5) (3-6) (3-7)(3-8)(3-9)(3-10)(3-11) Table(3-2) show the position of the new bands in addition to the other most diagnostic bands. This shift confirm the coordination of the N-atom with all the studies metal ions.

On the other side the oxygen of the hydroxyl group can also be excpected to coordinats with metal ions,since the ν O-H and δ O-H bands were not noticed in the spectra of the complexes, this was more confirmed by the red shift in the position of the ν C-O band in all the new complexes as show in table(3-2) , the value of the shift was variable and depend on the type of the studied metal ion. Examination of the lower energy region show the appearance of M-N and M-O bands(72,73), this also confirms the coordination of the metal with the N and O atoms of CSSB, the values of there bands are shown in table (3-2).

ν(M-X)	—	**970(s)**									

Table (3 -2) The most diagnostic bands in the infrared spectra for CSSB and its metal complexes

Symbol	ν(C-H)	ν(C-H) aliphatic	ν(C=N)	ν(O-H)	ν(C-O)	ν(C=C)	ν(M-N)	ν(M-O)
CSSB	3058.9(w)	2929.7(s)	1627.8(s)	1413.7(m)	1078(m)	1581.5(w)	———	———
CSSBVo	3055.0(w)	2927.7(s)	1622(s)	1415.7(w)	1053.1(m)	1548.7(m)	547.7(m)	499.5(m)
CSSBCr	3078.2(m)	2927.7(m)	1620.1(s)	1436.9(m)	1028.0(m)	1529.4(m)	534(m)	450(sh,w)
CSSBFe	3018.4(m)	2925.8(m)	1624.0(s)	1404.1(w)	1026.1(m)	1523.7(m)	499.5(m)	441(w)
CSSBCo	3016.5(w)	2929.7(s)	1604.7(s)	1406.0(m)	1072.3(m)	1531.4(m)	551.6(m)	493.4(m)
CSSBNi	3022.2(w)	2923.9(m)	1651.0(s)	1411.8(w)	1033.8(m)	1527.5(m)	532.3(m)	437.8(w)
CSSBCu	3018.4(w)	2931.6(m)	1608.5(s)	1409.9(w)	1022.2(m)	1529.4(m)	549(m)	500(w)
CSSBZn	3053.1(w)	2929.7(s)	1614(s)	1407.9(m)	1070.4(m)	1537.2(m)	547.7(w)	453.2(w)
CSSBCd	3095.5(w)	2927.7(s)	1566.1(w)	1442.7(m)	1047(m)	1566.1(m)	576.7(m)	441.7(w)
CSSBHg	———	2925.8(w)	1602.7(w)	———	1082(s)	1575.7(w)	600(sh,w)	470.6(m)
CSSBPd	———	2929.7(m)	1624(w)	1444.6(s)	1037.6(w)	1595(w)	559.3(m)	515(w)

w=weak , s=strong , m=medium , sh=shoulder

3.3.3-Electronic Spectra, 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 uv and visible region. Charge transfer spectra are due to the metal under certain conditions . study of electronic spectra of complexes helps in the determination of structure of those complexes through the electronic interaction of the metal d-orbital and orbital of the ligand. In our case, the spectra were recorded in the range (200-1100) nm using absolute ethanol as a solvent .

Measuring magnetic susceptibility contributes to the determination of structure of the complexes. In addition, these measurements provide information about the number of unpaired electrons.

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

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

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, table(3-4), it’s also usually less than the values of the actual values.These values obtained from the instrument (Magnatic balance) were corrected for diamagnetic effects using the following relation ship:-

$X_g = (R – R0) cl / wt$

$X_m = X_g + M.wt$ R=Reading of the tuble with the sample

$X_A=X_m-D$ R=Reading of the empty tube

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

were C=constant , X_A=Atomic susceptibility , L=light of the sample in the tube

Wt=weight of the sample x_g=gram susceptibility

T=absolute temperature(298) D=correction faction

X_M=Molar susceptibility

Conductivity measurements of the prepared complexes in the appropriate solvent are used to decide wherther a complex is electrolyte or neutral .(75,74)

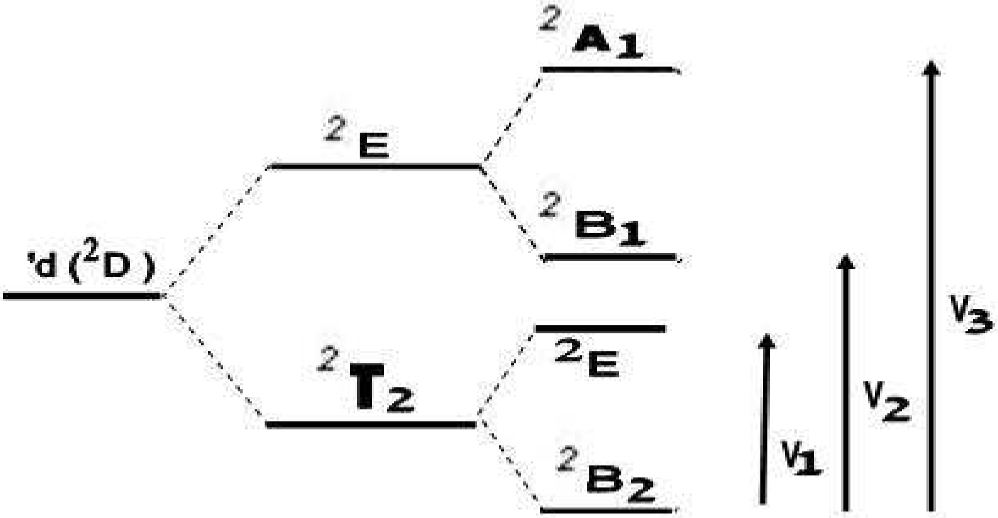
Table(3-3) , show the position of electronic absorption bands and its transition , and also include the calculated value of Racah parameter (B′) , and nephelauxetic factor (β) for all the prepared complexes, Table (3-4) show the magnetic moment(The calculated and found values) and conductivity measurement for the prepared complexes at room temperature and suggested structure for each complex , The structure were suggested for the prepared complexes according to the position of electronic absorption band , magnetic properties and electric conductivity measured for these complexes , and infrared spectra and Metal analysis .

3.4 – Metal complexes of CSSB

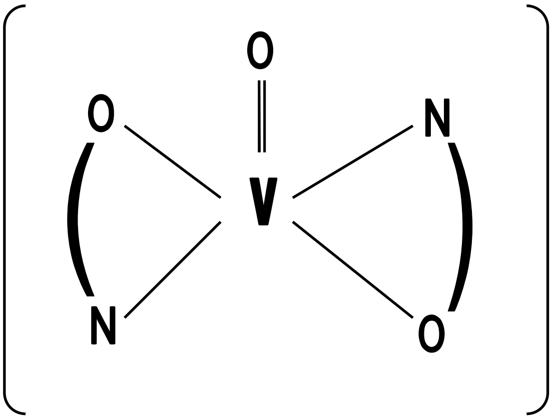
A- *Vanadyl complex (CSSBV0)*

Most vanadyl (II) coplexes are magnetically simple , having virtually " spin only " moments of 1.73 B.M (76).corresponding to one unpaired electron . the value of the present V0(II) complex was found to be(1.94B.M) showing quadrivalent state of vanadium which contain V0(II) ion . But their electronic spectra are less easily understood . This is primarily due to the presence of a strong π contribution to the band between the vanadium and the oxygen(77). The V(IV) ion is usually represented by the V0 (II) molecular ion , V0 (II) behaves as a class – action forming stable compounds with F , Cl , O and N donor ligands . These " vanadyl " complex are generally green or blue – green and can be cationic , neutral or anionic . They are very frequently 5 – coordinate in which the stereochemistry is almost invariably square pyramidal.The vanadyl (II) ion has one unpaired d – electron . In octaheadral symmetry , this d – electron occupied theT_2g orbital and gives rise to a ^2T_2g ground state for the V0(II) ion. On excitation , it goes over to the upper eg – orbital and give rise to a ^2Eg state. Thus , only one single transition $^2T_2g \rightarrow {}^2E$ and correspondingly a single band is expected for V0 (II) in octahedral symmetry . However if the symmetry is lowered , the upper and ground electronic energy levels are split and more number of bands are observed .

In a low symmetry tetragonal field , such as C_4V, the ^2T_2g and ^2E levels are split into $^2B_2$, ^2E , ^2B , A1 levels as shown in the following (78) :-



In the several vanadyl (V0(II)) ion complexes studied(79,80)at room temperature , three ligand filed absorption bands are reported with the first in the spectral range (11,000 _ 14,700) cm^{-1}, the second in the range (14,800 _ 20,400)cm^{-1} and the third in the range (21,000 _ 31,250)cm^{-1} In the present work , Two band were observed 504nm (19841 cm^{-1}) and 398nm (25123)cm^{-1}, fig.(3-12) , which can be assigned as $\nu_2(^2B_2 \rightarrow {}^2B_1)$, $(^2B_2 \rightarrow {}^2A_1)$ respectively , conductivity measurements show the complex to be non – ionic , table (3-4). There for the following structure can be assumed .



B- *Cr(III) complex (CSSBCr)*

(CSSBCr) complex spectrum in absolute ethanol , fig(3-13), show three bands. The three bands at 15,748,19,841cm and 35,714 cm^{-1} were assigned as belonging to transitions

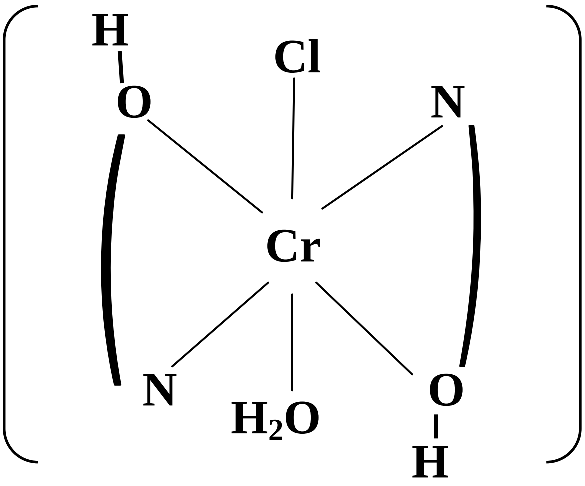
$^4A_2g(F)\rightarrow {}^4T_2g$ (F) (V_1 which is equal to 10Dq) and

$^4A_2g(F)\rightarrow {}^4T_1g$ (F) (V_2)(77)

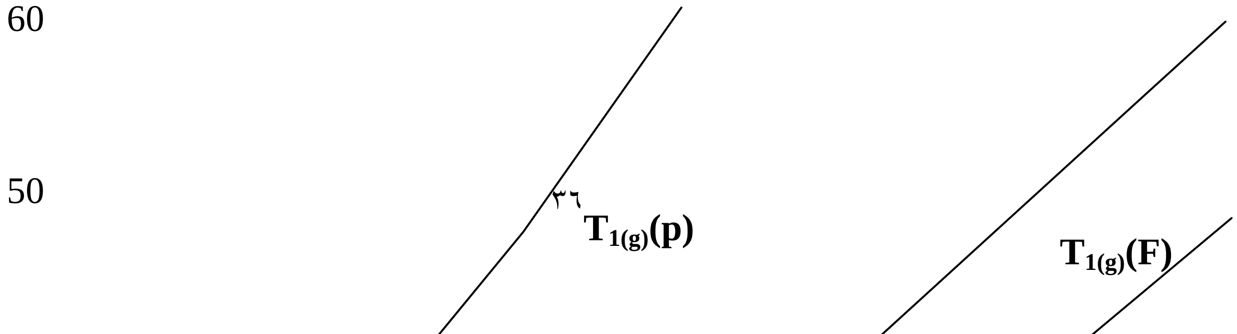
$^4A_2g(F)\rightarrow T_1g$ (P) (V_3)

The value of B′ was calculated using the following equation(81),$15B'=V_3+V_2-3V_1$ it was found to be (554)cm^{-1}from which the value of the nephelauxtic factor (β) was calculated taking the value of the free ion (1,030)cm^{-1} and was found to be (0.54), table(3-3)The low value of B refer to the relatively great expansion of d-electron charge upon complexation which reduces the internal the inter-electronic repulsion. The internal consistency of this interpretation were checked using Tanaba-Sugano diagram figure (3-22) by calculating V_1 and 10Dq.The magnetic moment of the Cr(III) complex was found to be (3-21) B.M

The above results indicate an octahedral geometry about the chromium ion which can be depicted as follows:-



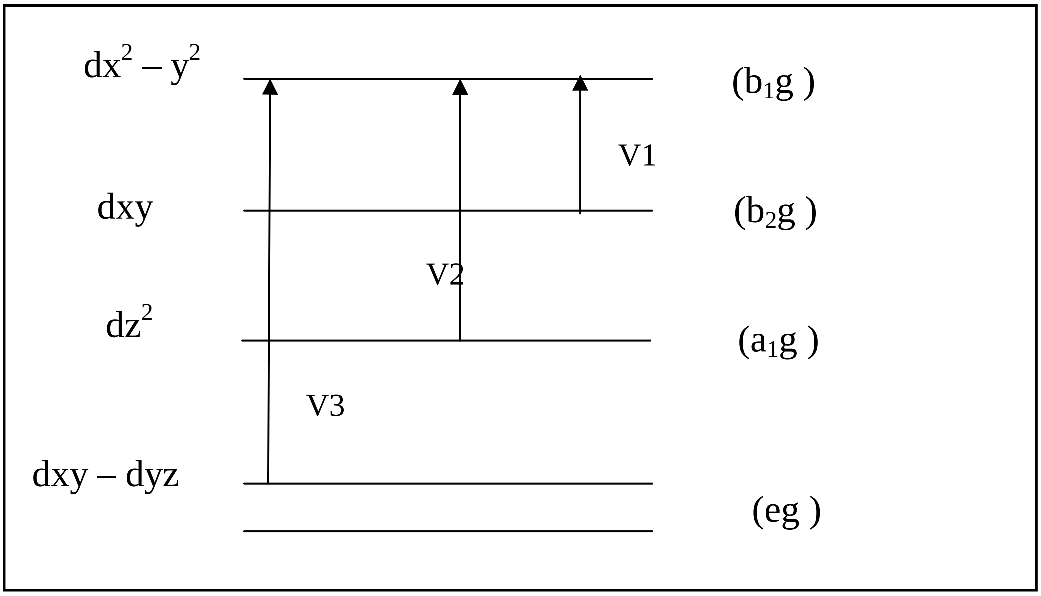
This formula was further confirmed to be non-ionic by conductivity measurement , table(3-4)



Figure(3-22):- Tanaba- Sugano diagram for d^3 system

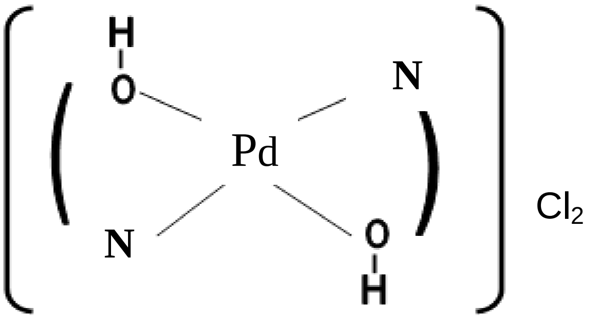
C-pd(II) complex (CSSBPd)

Most four coordinated complexes of pd(II) are diamagnetic and most of them are square planar, and in some cases it have a distorted octahedral because of the coordination of solvent molecule in vacant position(75), thus the expected allowed transition should be



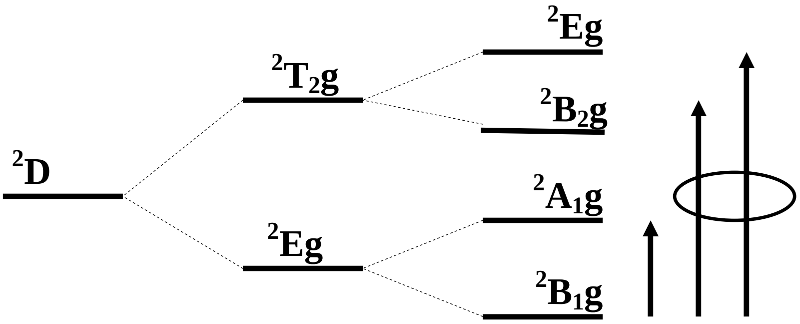
(Electronic transition in ^{8}d system for square planer geometry)

Electronic spectra of (CSSB pd) complex,Figure(3-24) was characterized by an absorption band at 27,030cm^{-1} which might beassigned to the transition $^1A_1g \rightarrow {}^1B_1g$, which same in accordance with the published data for square planar pd(II) complexes. (77,82,83)conductivity measurement showed that the complex is ionic, table(3-4).There for , the following structure can be proposed :-



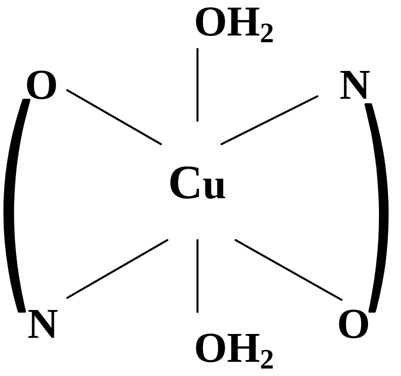
D-Cu(II) complex (CSSBCu)

Cu(II) compounds are blue or green because of a single broad absorption band in the region (11,000-16,000)cm^{-1}(77).The d^9 ion is characterized by large distortions from octahedral symmetry and the bond is unsymmetrical , being the result of a number of transitions , which are by no means easy to assign unambiguosly. The free ion ground ^2D term is expected to split in a crystal field in the same way as the ^5D term of the d^4 ion and a similar interpretation of the spectra is likewise expected, and according to the following(43,77):



Free ion octahedral crystal field tetrangonal crystak field

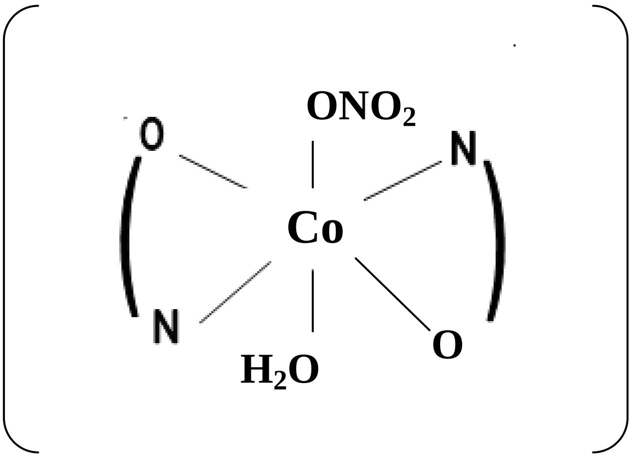
Un fortunately, this is more difficult because of the greater overlapping of bands, which occurs in the case of Cu(II).In the present work , the green (CSSBCu) complex shows two band(84)at 14,347 and 15.698cm^{-1} which can be assigned to $^2B_1g^2$→ $^2B_2g^2$ and ^2B_1g→ ^2Eg transitions, figure.(3-17).The value of magnetic moment (1.95) BM, Table(3-4) can be show the value of magnetic moment There for the expected geometry of the complex is as following:-



Conductivity measurements show that the complex is non-ionic

E- Co(III) complex (CSSBCo)

CSSB complex spectrum in absolute ethanol Fig(3-15) shows two bands. The first two bands at 15.748 and 20,000 cm^{-1} were assigned to the transition $^5A_1g \rightarrow {}^5T_1g$, $^5A_1g \rightarrow {}^5T_2g$$^{(77)}$ The molar conductivity measurements in absolute ethanol show that the complex to be non-ionic and because the complex was found to be dimagnatic in the following structure is octahedral geametry

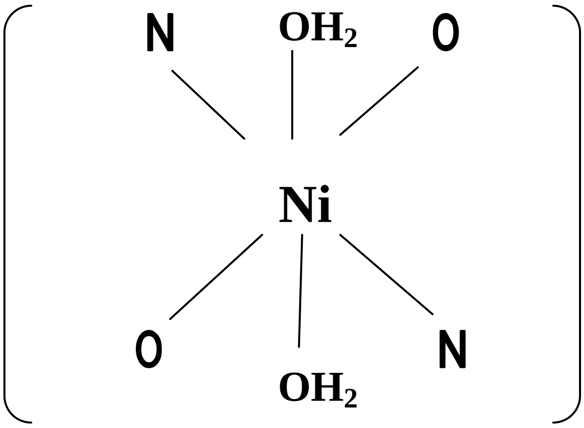


F-Ni (II) complex (CSSBNi)

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

ν_1 ^3A_2g (F) → ^3T_2g (F) =10Dq
ν_2 ^3A_2g (F)→ ^3T_1g (F)
ν_3 ^3A_2g (F)→ ^3T_1g (P)

The uv-visible spectrum of the present Ni^{+2} complex, CSSBNi , figure(3-16) show two bands at 15748 cm^{-1} and 25773 cm^{-1} which can be assigned ν_2 and ν_3 respectively(77,85)The conductivity measurement showed the complex to be non-ionic, therefore the following structure can be postulated

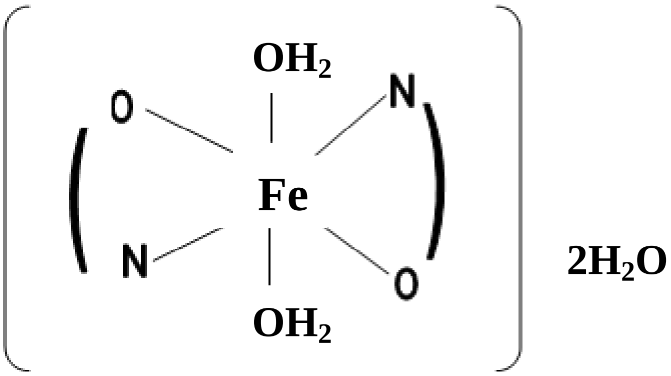


g-Fe(II) complex (CSSBFe)

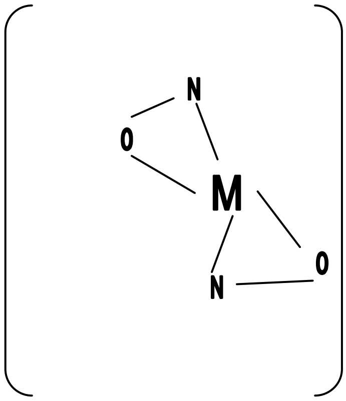
Iron (II) forms complexes with a variety of ligands, it forms stable complexes N-donor ligands. High spin octahedral complexes of Fe^{+2}have a free-ion ^5D ground Term, split by the crystal field in to ground ^5T_2g and an exited ^5Eg Term. Most Fe^{+2} complexes are octahedral. Amagnatic moment of around 5-5 BM (i.e 4.90 BM torbitel contribution) is expected for pure octahedral symmetry but, in practice, distortions produce values in the range 5.2-5.4 BM.

Similarly , in the electronic spectrum, the expected single band due to they $^5T_2g(^4T_2g^2eg) \rightarrow$ $^5Eg(^3T_2g^3eg)$ Transition is broadened or split.(77)

In our present complex the large difference in the crystal field effect of the donor atome(Nitrogen of imine, Oxygen of phenolic group and Oxygen of water molecules) beside the inequality in the electronic distripution leads to high distortion (Large-Gahn-Teller effect)The spectrum of CSSBFe ,figure an(3-14) , show a number of bands which can be assighred as follows the high energy band , 25000cm^{-1} can be assigned as charge transfer band (M→L), the two lower energy band, i.e 14326 and 15742 cm can be assigned to the splitted $^5T_2g \rightarrow$ ^5Eg single band.According to these data, in addition to the non-ionic behaviour of the complex .The following structure can be assighned

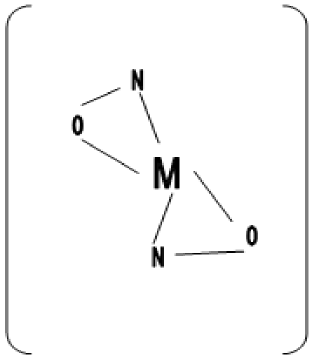


The Zn^{+2} ,Cd^{+2} and Hg^{+2} ions in their and respectively complexes CSSBZn, CSSBCd and CSSBHg, have d^{10} configuration, therefore they are not expected to show d-d transition, which is the case in the spectra of these complexes, figure (3-18) (3-19) (3-20) Since conductivity measurement for the three complexes show them to be ionic in all cases, the following structures can be suggested



$Cl_2.C_2H_5OH$

M=cd^{+2} , Hg^{+2}



cl_2

M=Zn

Table(3-3) Electronic spectra for complexes of CSSB in absolute ethanol (cm^{-1})

Symbol	*Absorption bands cm^{-1}*	*Transition*	*B*	*B´*	*β*	*15B´*
CSSBVo	19841cm^{-1}, 25,123cm^{-1}	$^{2}B_{2}\rightarrow{}^{2}B_{1}$ $^{2}B_{2}\rightarrow{}^{2}A_{1}$				
CSSBCr	15,748cm^{-1} 19841cm^{-1} 35,714cm^{-1}	$^{4}A_{2}g(F)\rightarrow{}^{4}T_{2}g(F)$ $^{4}A_{2}g(F)\rightarrow{}^{4}T_{1}g(F)$ $^{4}A_{2}g(F)\rightarrow{}^{4}T_{1}g(P)$	1.030	554	0.54	8311
CSSBPd	27,030cm^{-1}	$^{1}A_{1}g\rightarrow{}^{1}B_{1}g$				
CSSBCu	14,347cm^{-1} 15,698cm^{-1}	$^{2}B_{1}g\rightarrow{}^{2}B_{2}g$ $^{2}B_{1}g\rightarrow{}^{2}Eg$				
CSSBCo	15.748cm^{-1} 20.000cm^{-1}	$^{5}A_{1}g\rightarrow{}^{5}T_{1}g$ $^{5}A_{1}g\rightarrow{}^{5}T_{2}g$				
CSSBNi	15718cm^{-1} 25773cm^{-1}	$^{3}A_{2}g(F)\rightarrow{}^{3}T_{2}g(F)$ $^{3}A_{2}g(F)\rightarrow{}^{3}T_{1}g(F)$ $^{3}A_{2}g(F)\rightarrow{}^{3}T_{1}g(P)$				
CSSBFe	14326cm^{-1} 15742cm^{-1} 25000cm^{-1}	$^{5}T_{2}g\rightarrow{}^{5}Eg$				
CSSBZn, CSSBCd, CSSBHg	———	———	——	—	——	——

Table(3-4) Magnetic moment , conductivity and suggested structure for complexes of CSSB

Complex	***Magnatic moment***	***Conductivity μs.cm***	***Suggested structure***
1-CSSBVo	1.94	27.9	Octahedral
2-CSSBCr	3.21	26.4	Octahedral
3-CSSBPd	Diamagnatic	57.1	Square planar
4-CSSBCu	1.95	2.8	Octahedral
5-CSSBCo	Diamagnatic	7.8	Octahedral
6-CSSBNi	2.79	5.4	Octahedral
7-CSSBFe	4.95	4.5	Octahedral
8-CSSBZn	Diamagnatic	56.6	Tetrahedral
9-cssBCd	Diamagnatic	61.7	Tetrahedral
10-cssBHg	Diamagnatic	59.4	Tetrahedral

3.5 – Suggestion for further work

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

1- Using C.H.N. microanalysis and NMR techniques to completely identify the structures of the schiff base and it’s metal complexes.
2- Preparation of another set of transition metal complexes with the other transition metal ions.
3- Making a screening antibacterial and antifungat activity of the schiff base and all the metal complexes, to explore their activity and the synergic effect between the metal and the ligand.

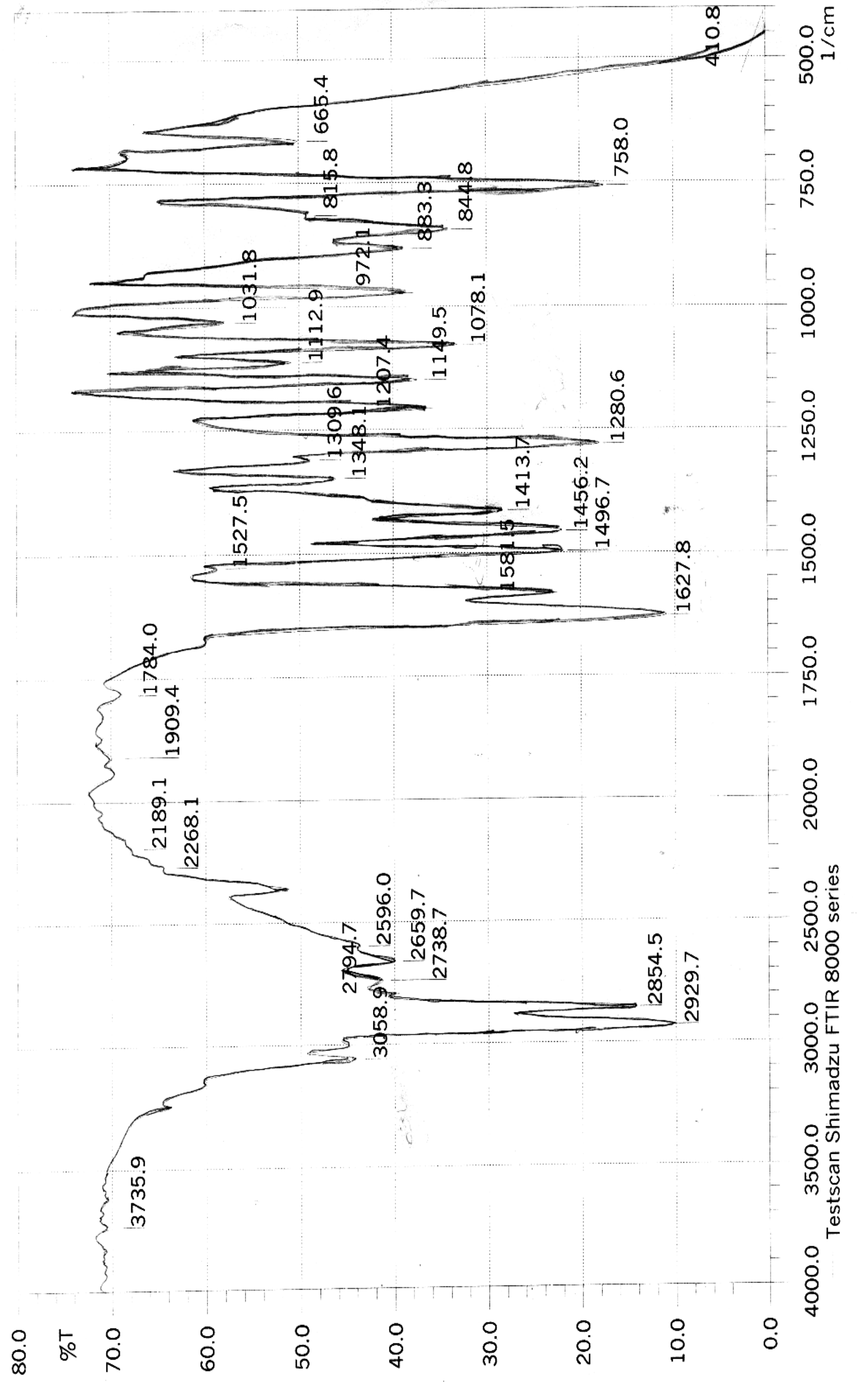


Figure (3-1): F.T.IR spectrum of Schiff base CSSB

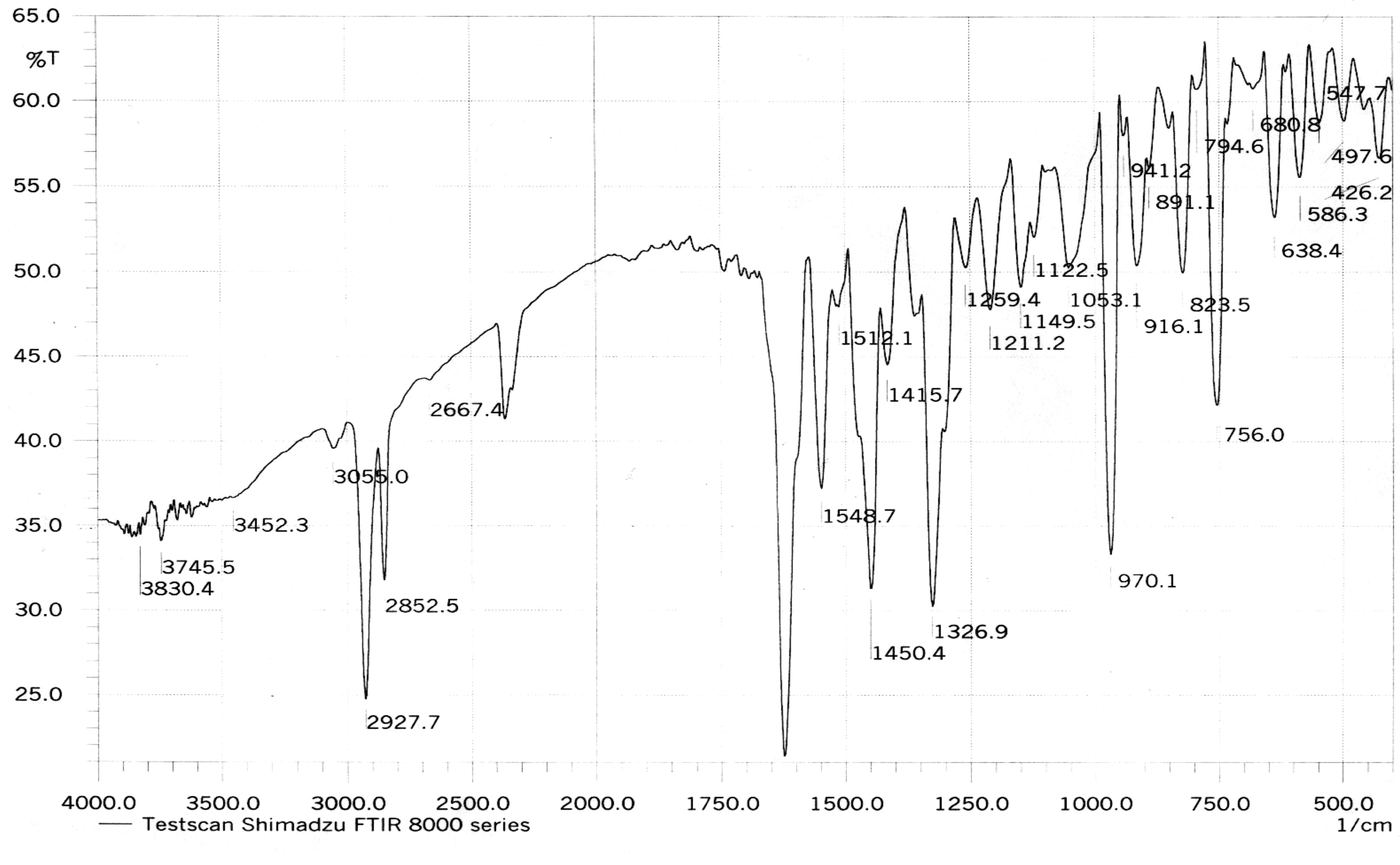


Figure (3-2): F.T.IR spectrum of CSSBVO

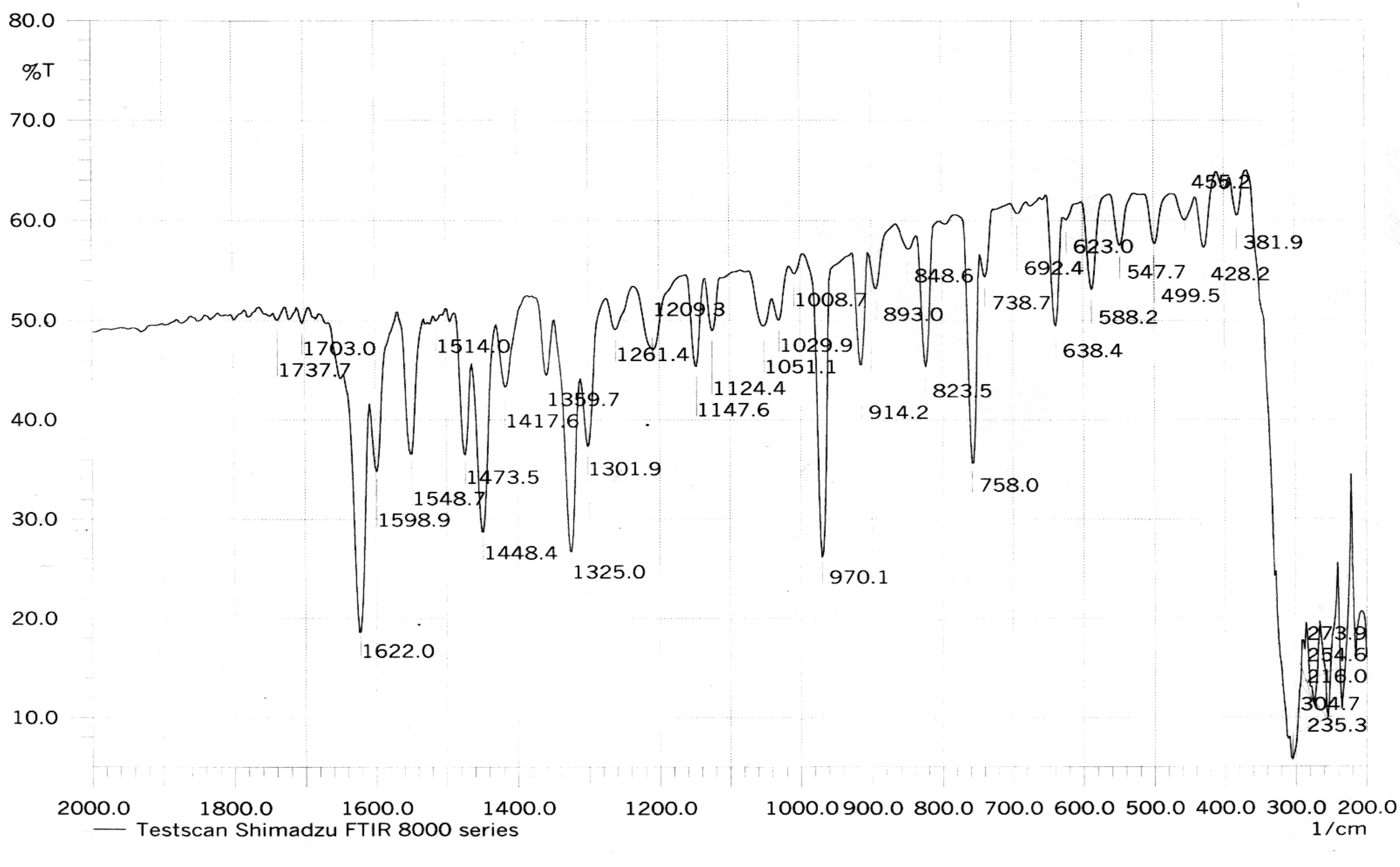


Figure (3-2): F.T.IR spectrum of CSSBVO

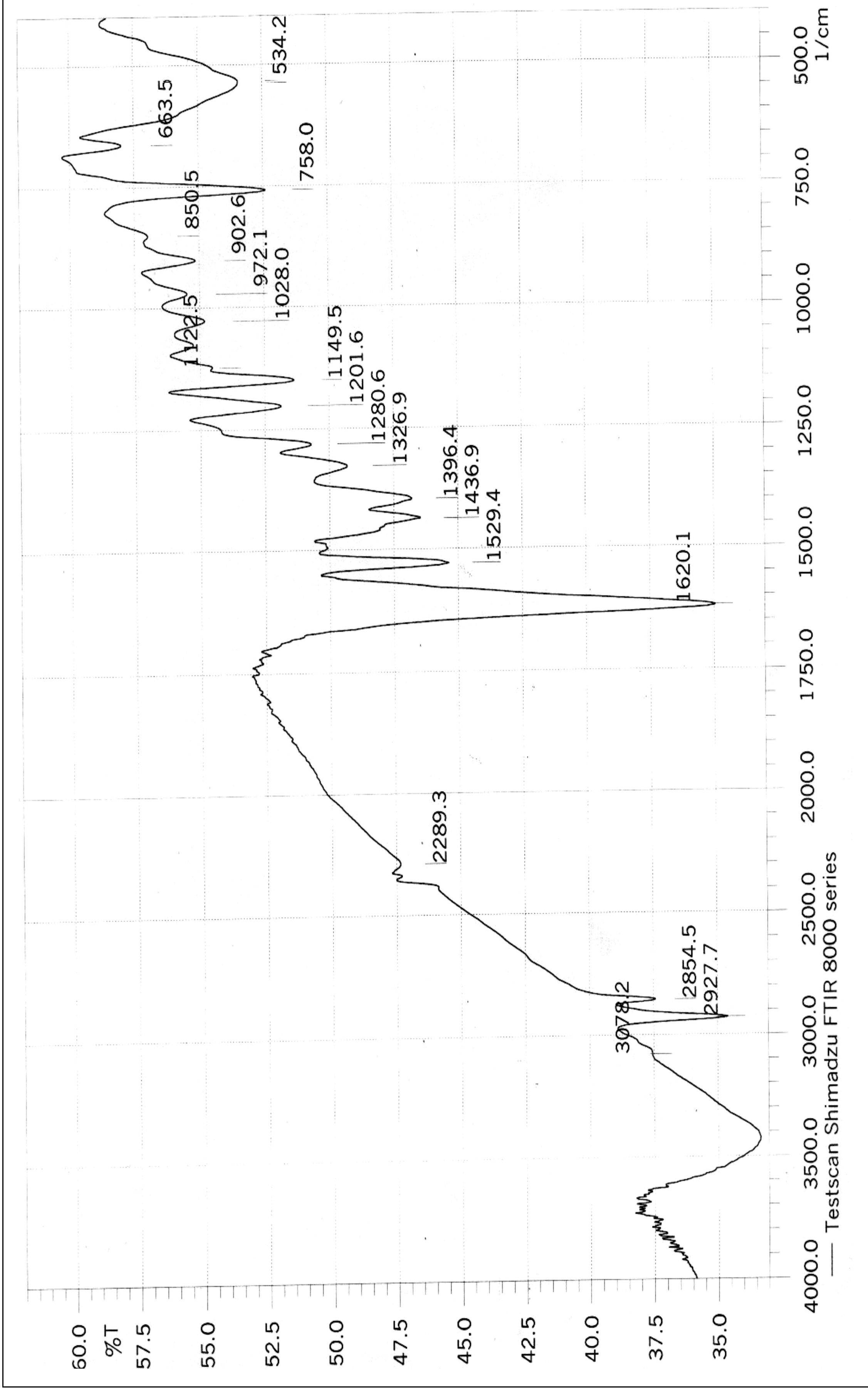


Figure (3-3): F.T.IR spectrum of CSSBCr

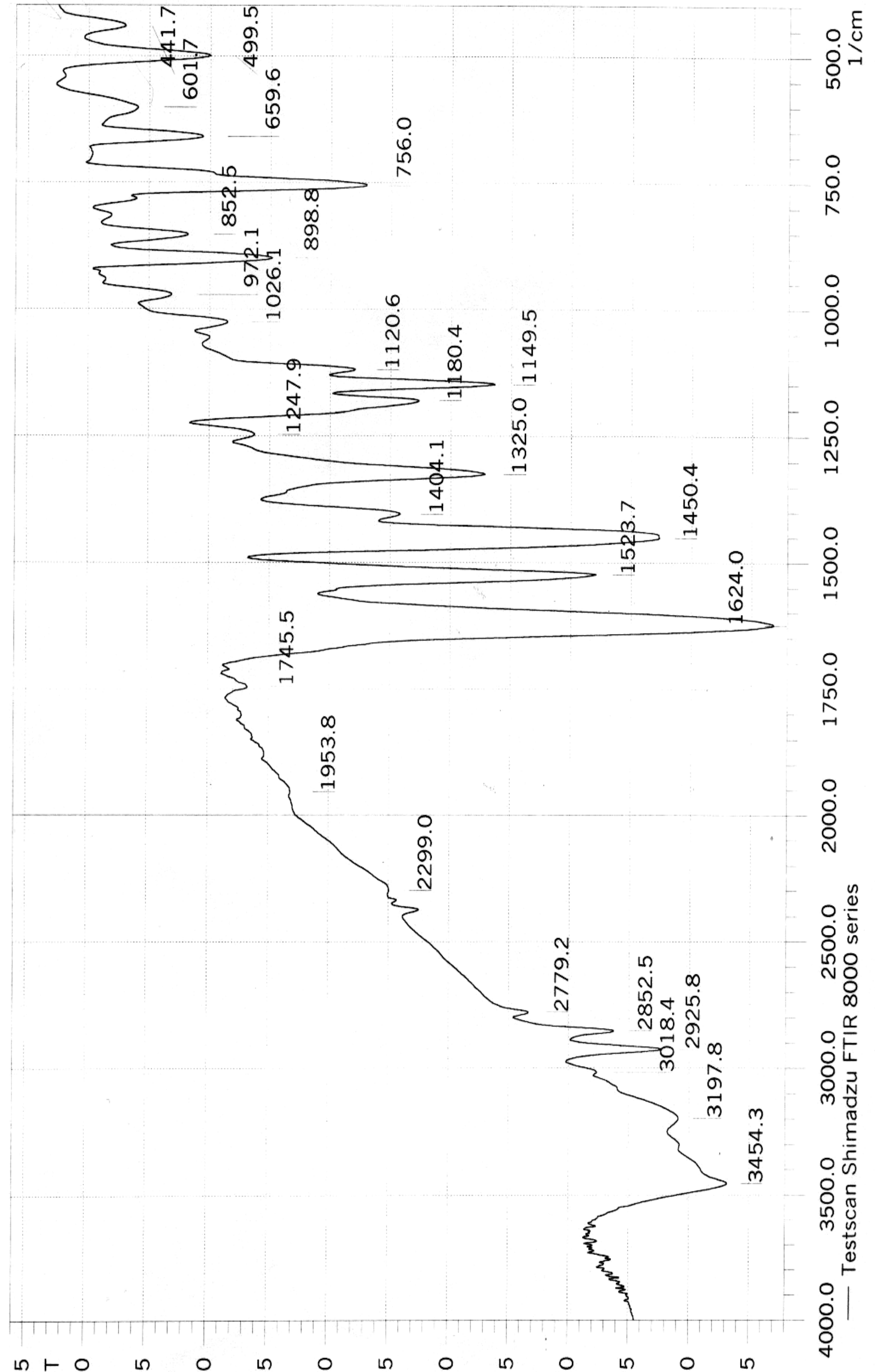


Figure (3-4): F.T.IR spectrum of CSSBFe

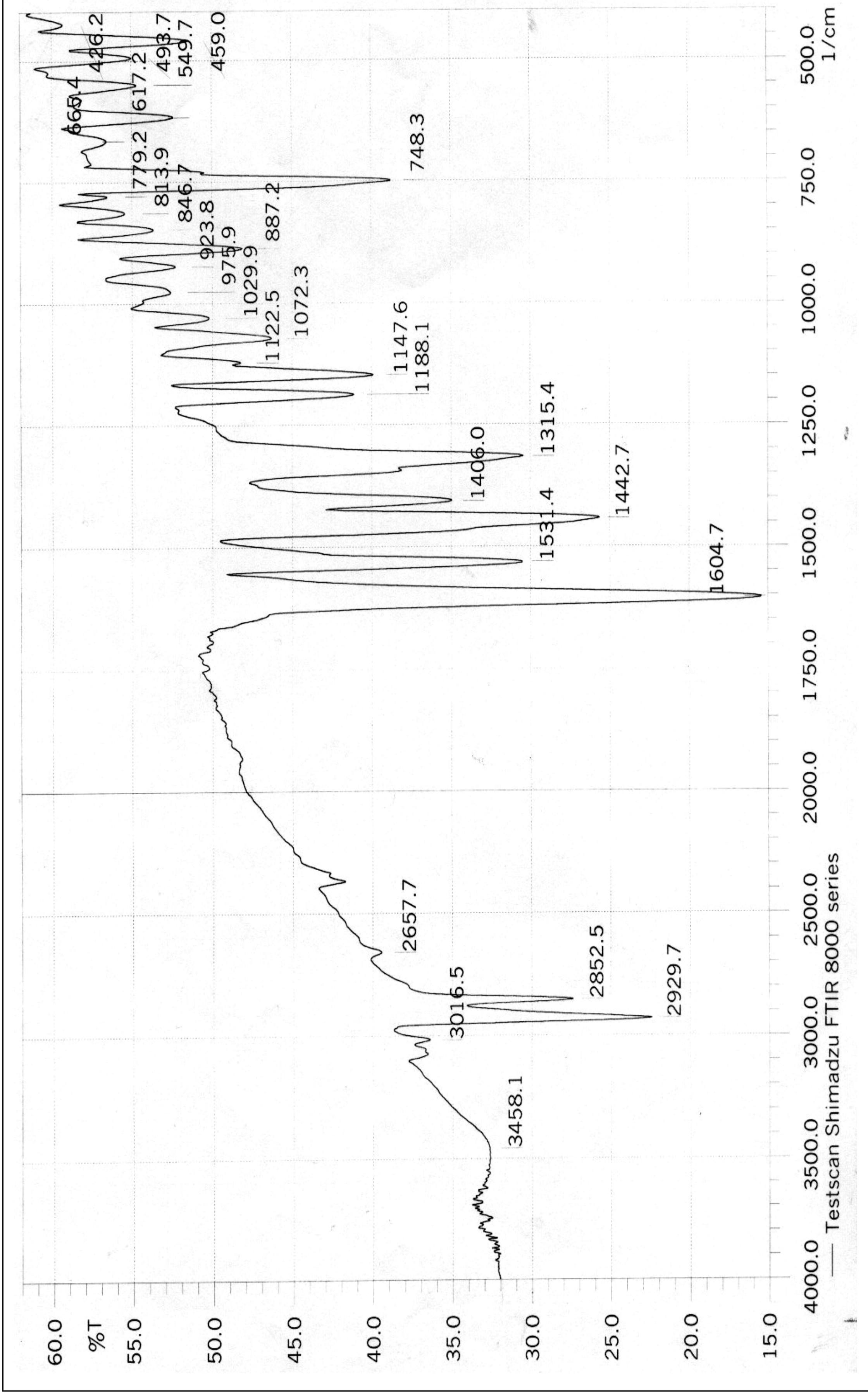


Figure (3-5): F.T.IR spectrum of CSSBCo

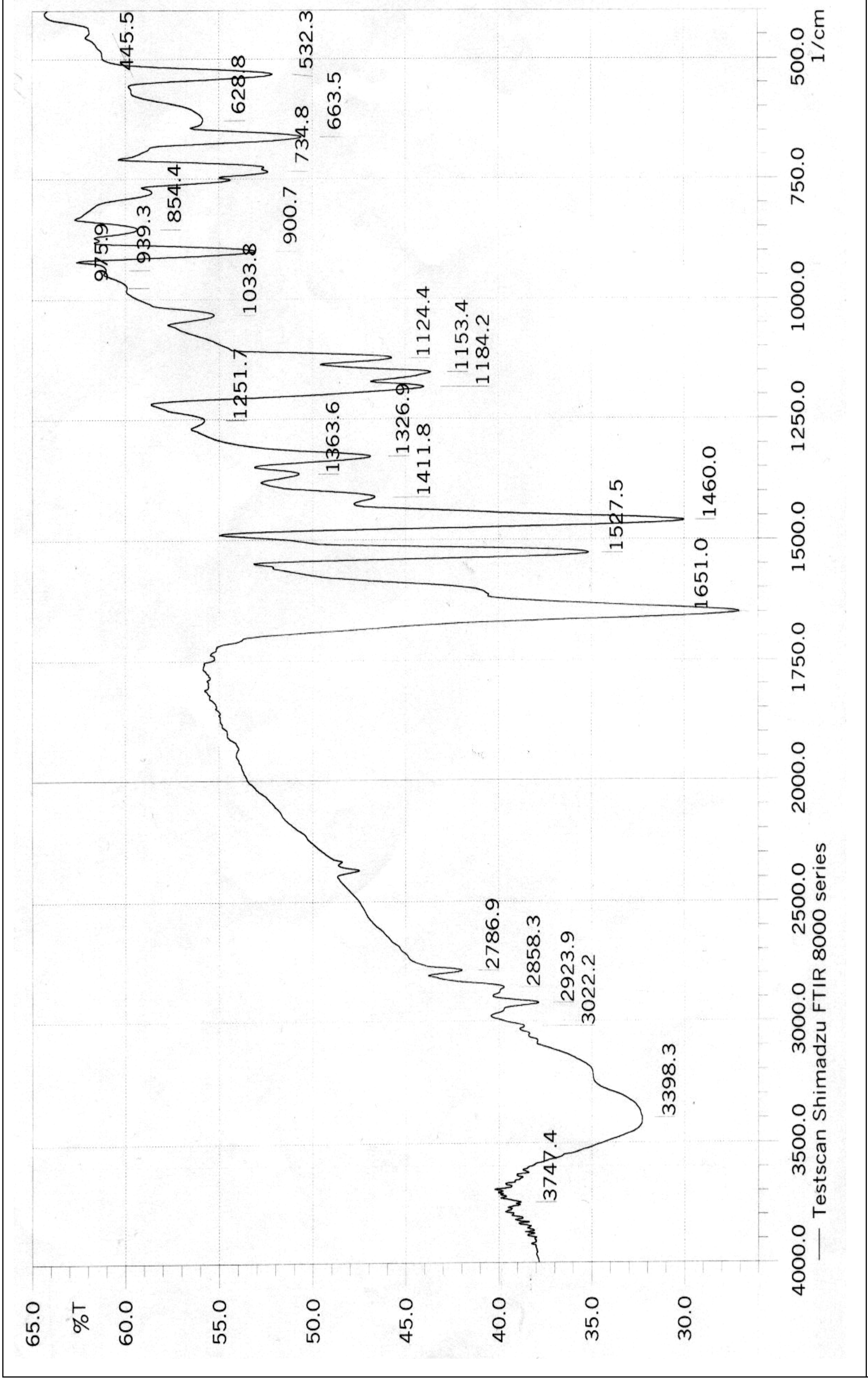


Figure (3-6): F.T.IR spectrum of CSSBNi

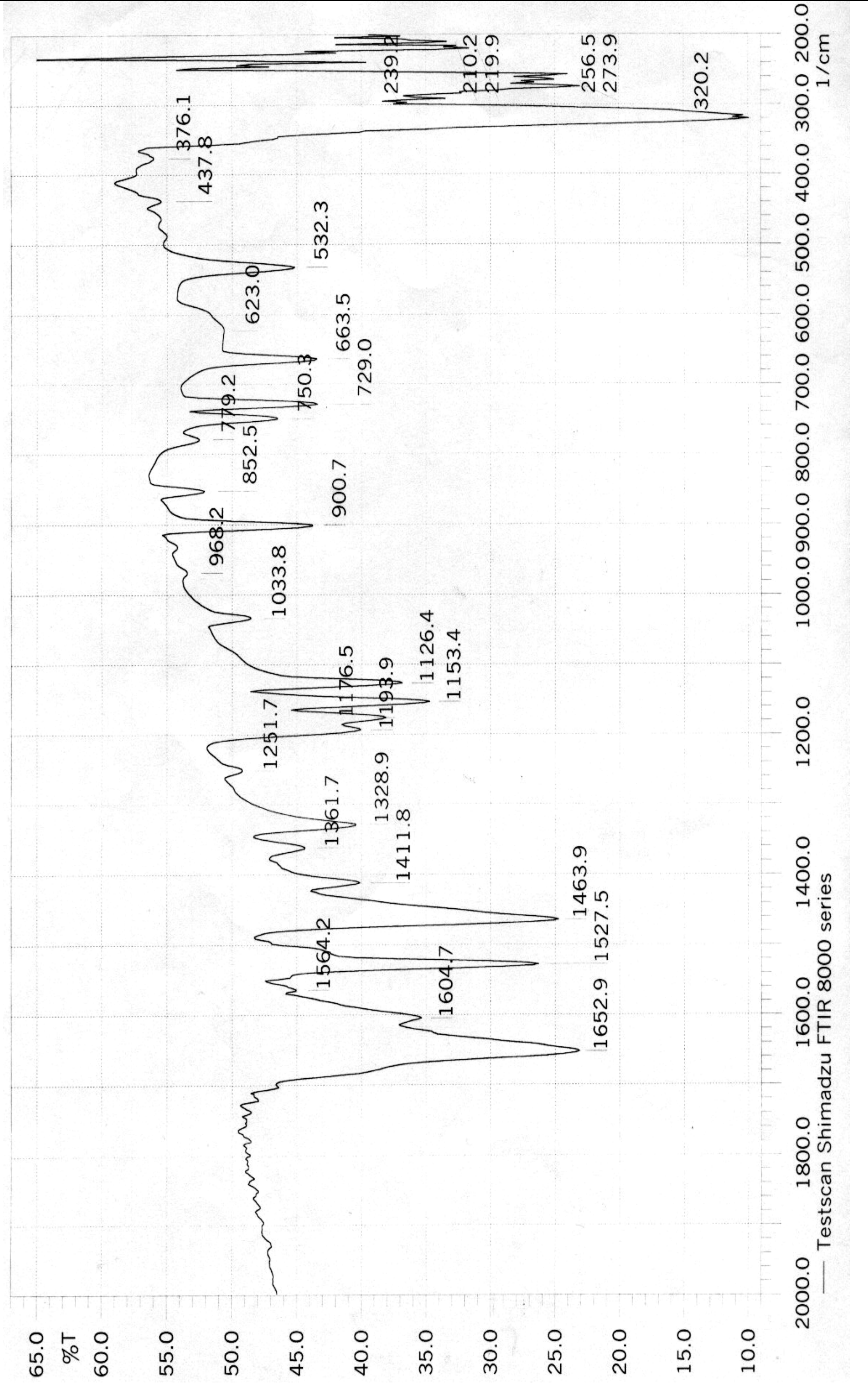


Figure (3-6): F.T.IR spectrum of CSSBNi

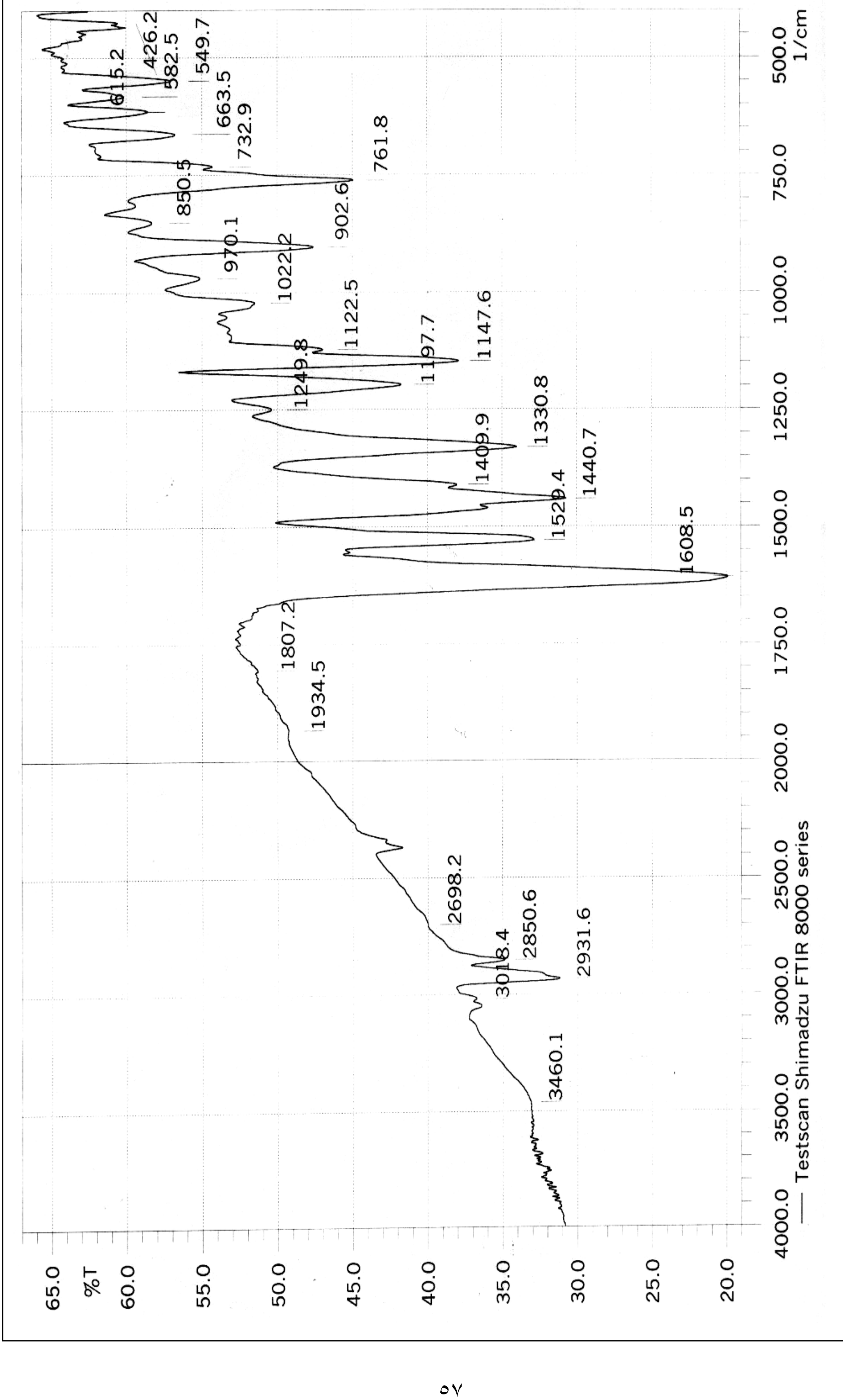


Figure (3-7): F.T.IR spectrum of CSSBCu

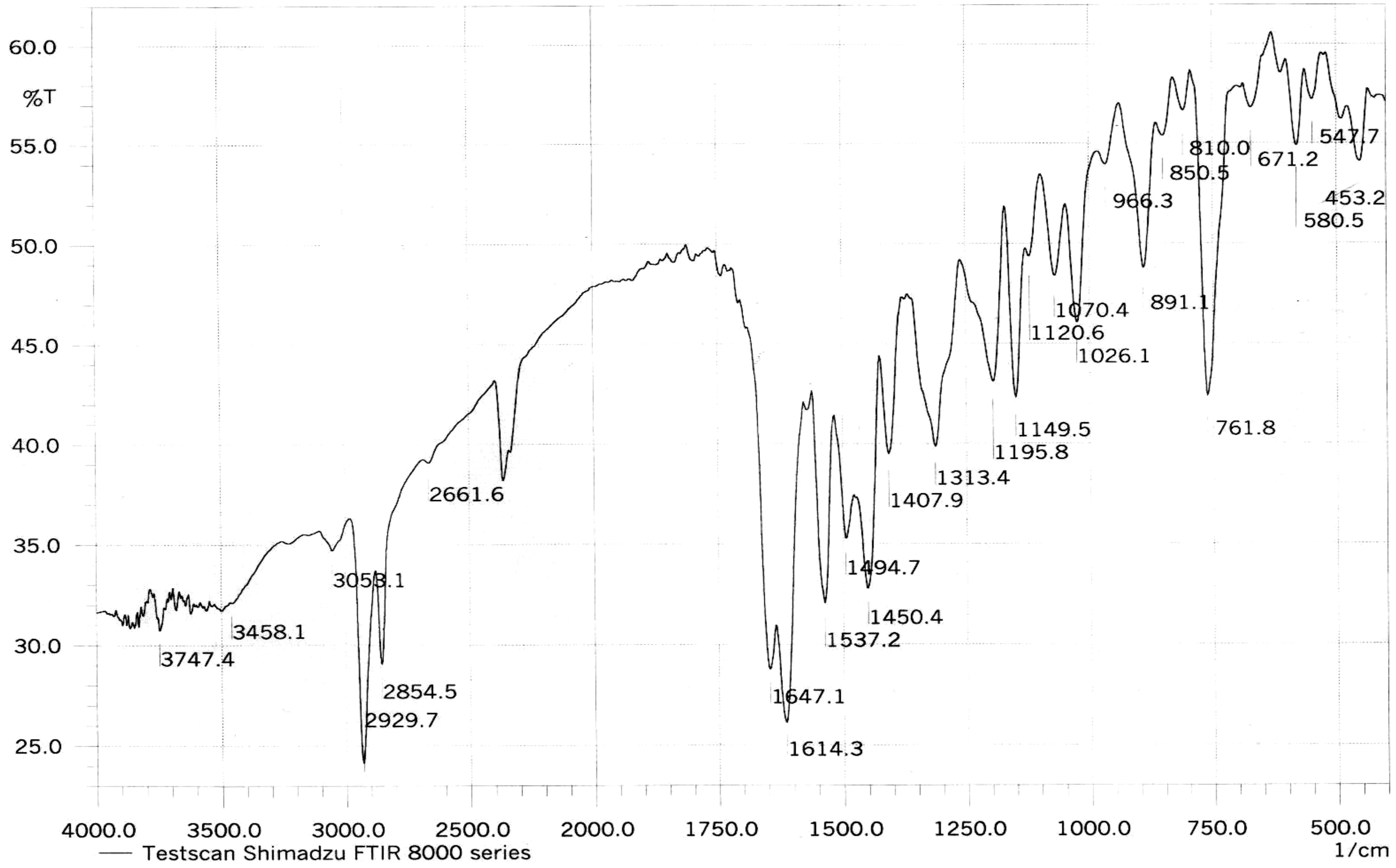


Figure (3-8): F.T.IR spectrum of CSSBZn

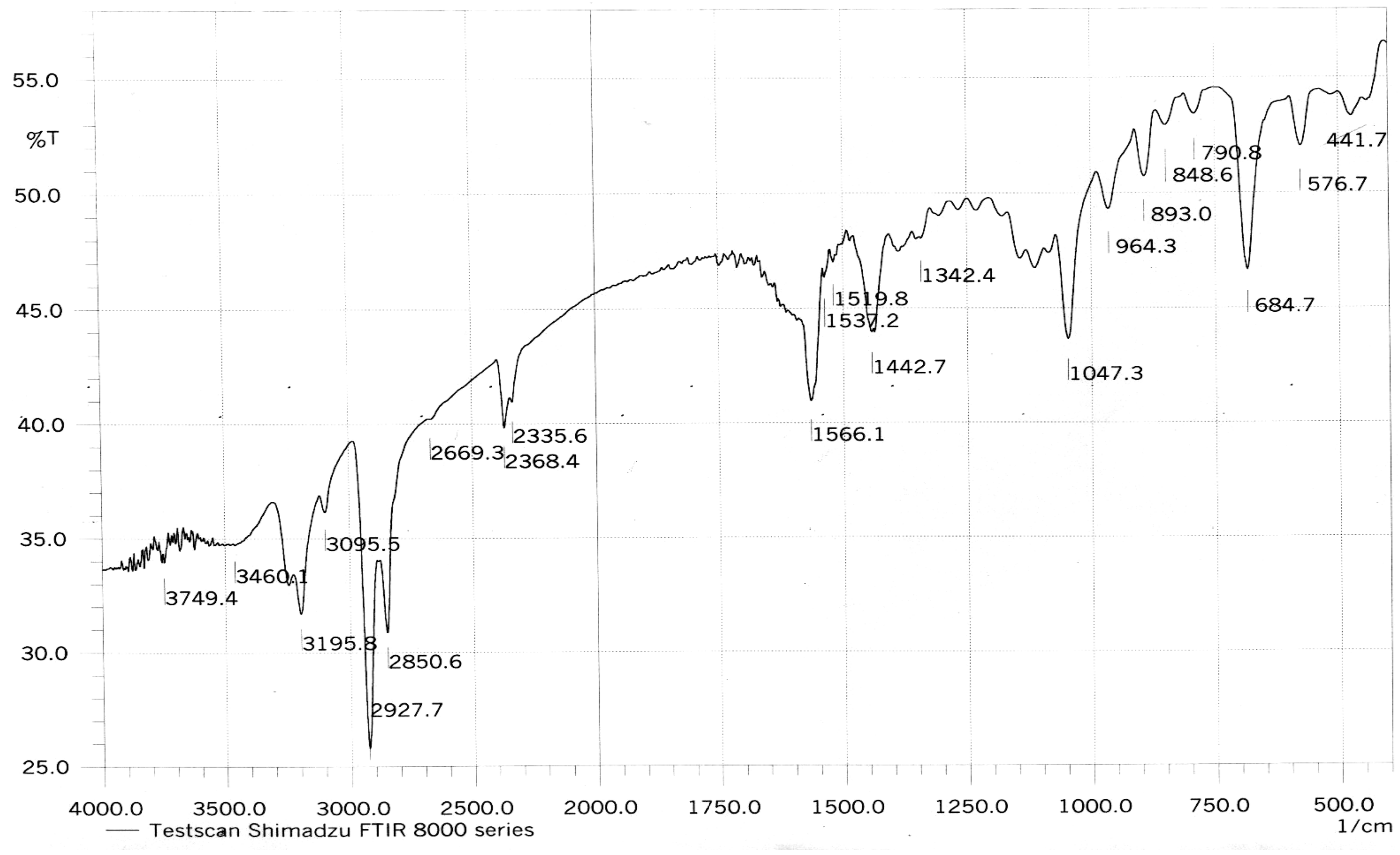


Figure (3-9): F.T.IR spectrum of CSSBCd

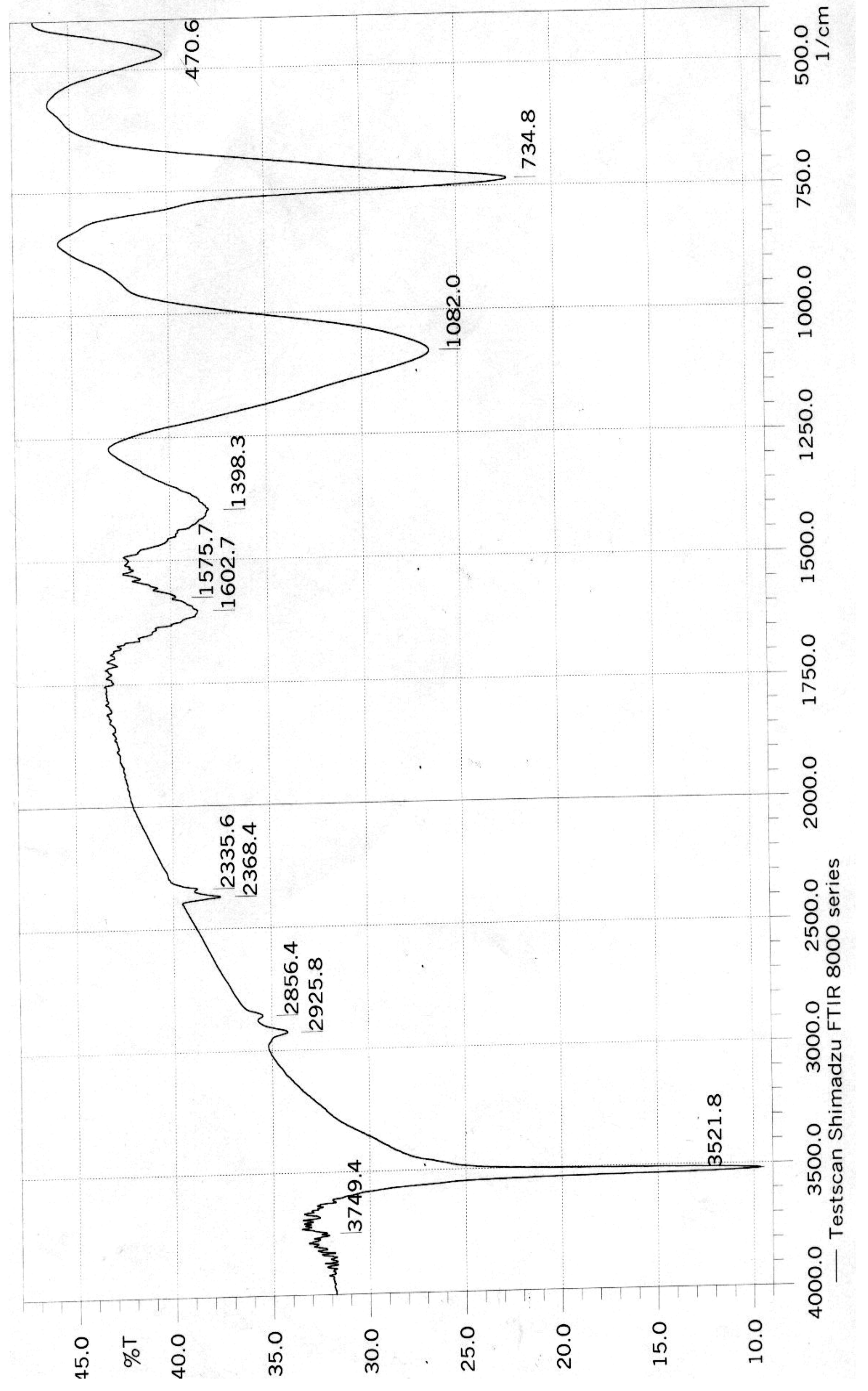


Figure (3-10): F.T.IR spectrum of CSSBHg

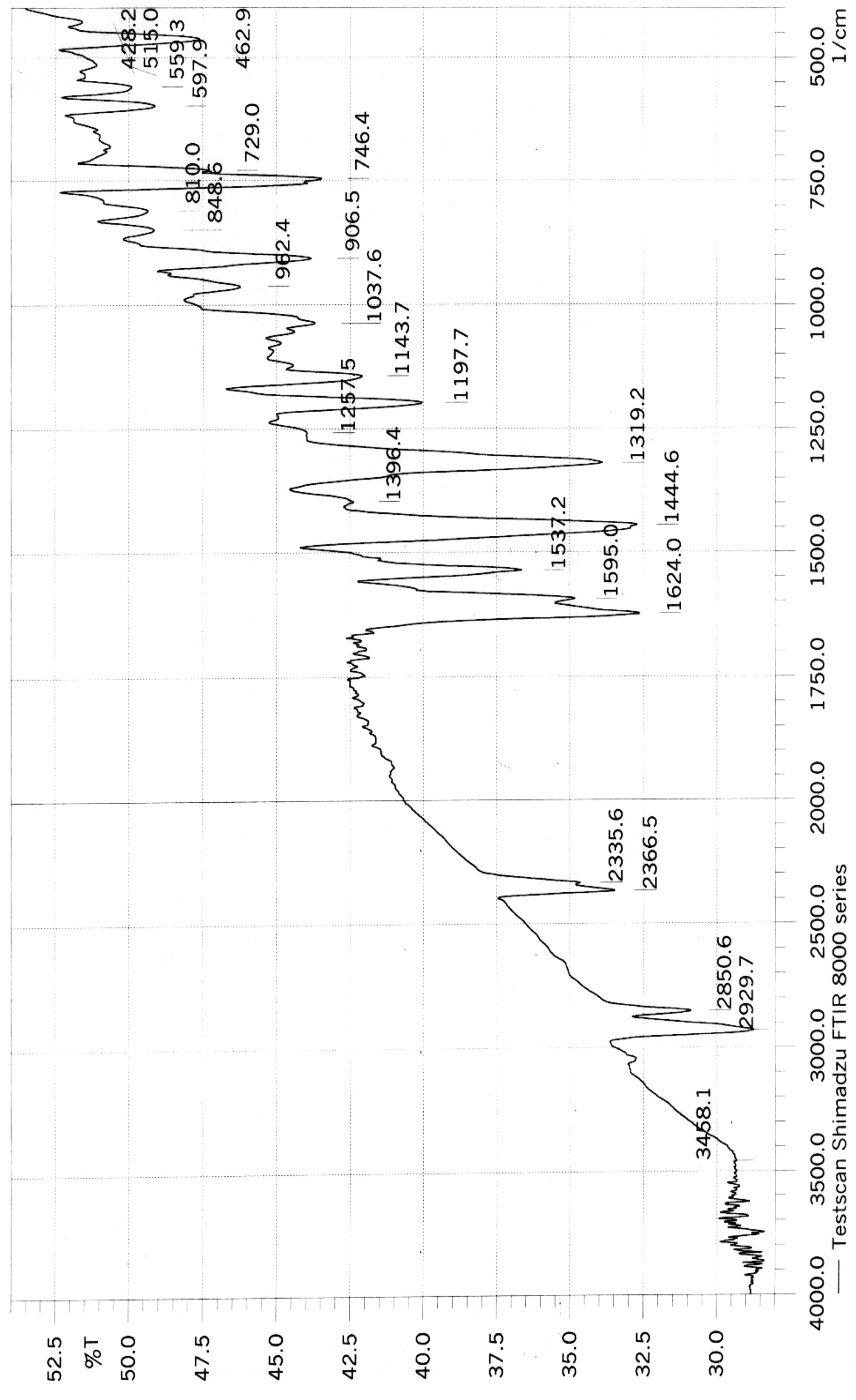


Figure (3-11): F.T.IR spectrum of CSSBPd

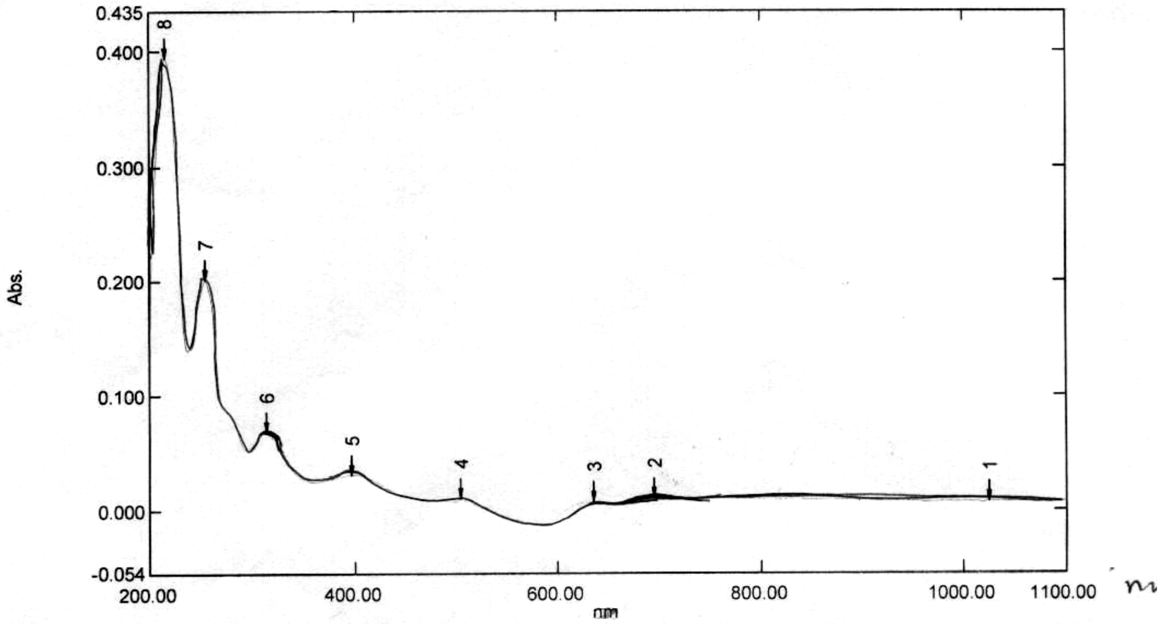


Figure (3-12): UV-Vis. spectrum of CSSBVO

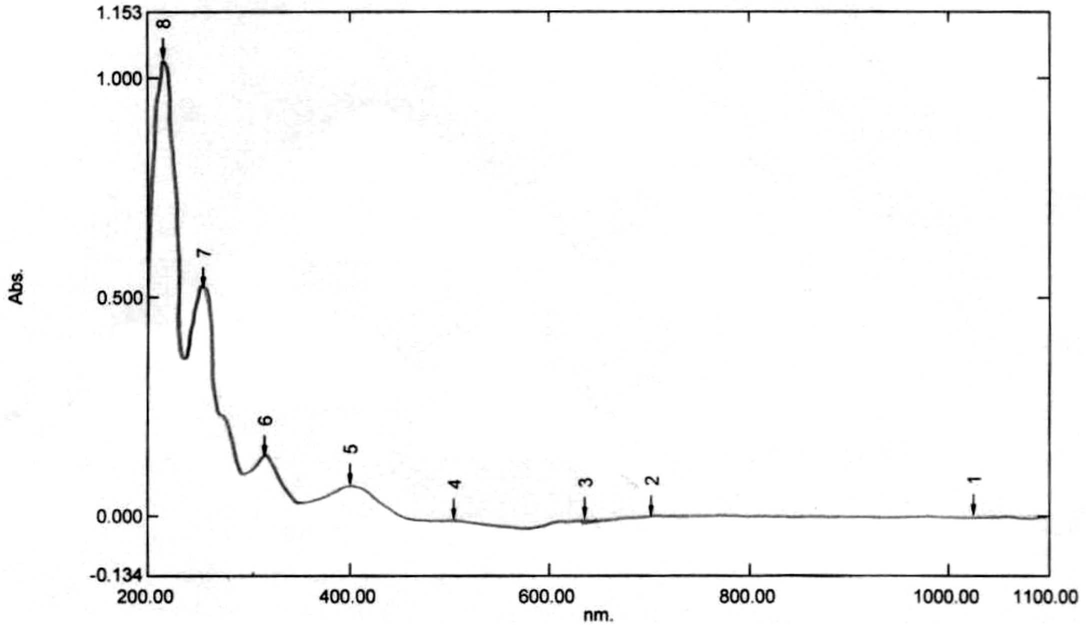


Figure (3-13): UV-Vis. spectrum of CSSBCr

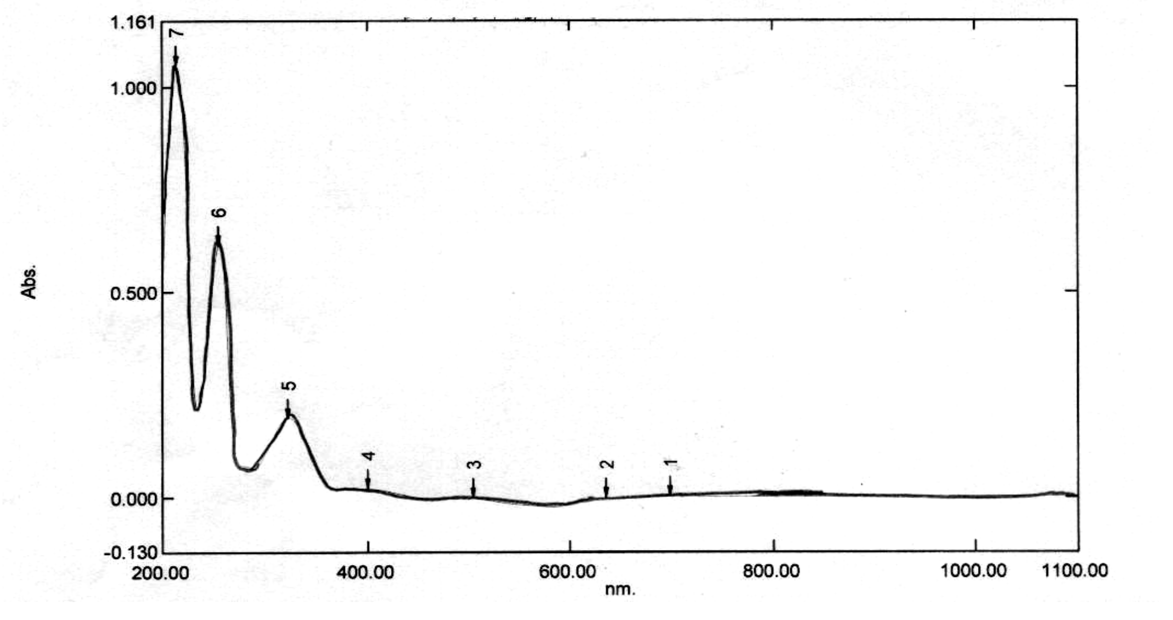


Figure (3-14): UV-Vis. spectrum of CSSBFe

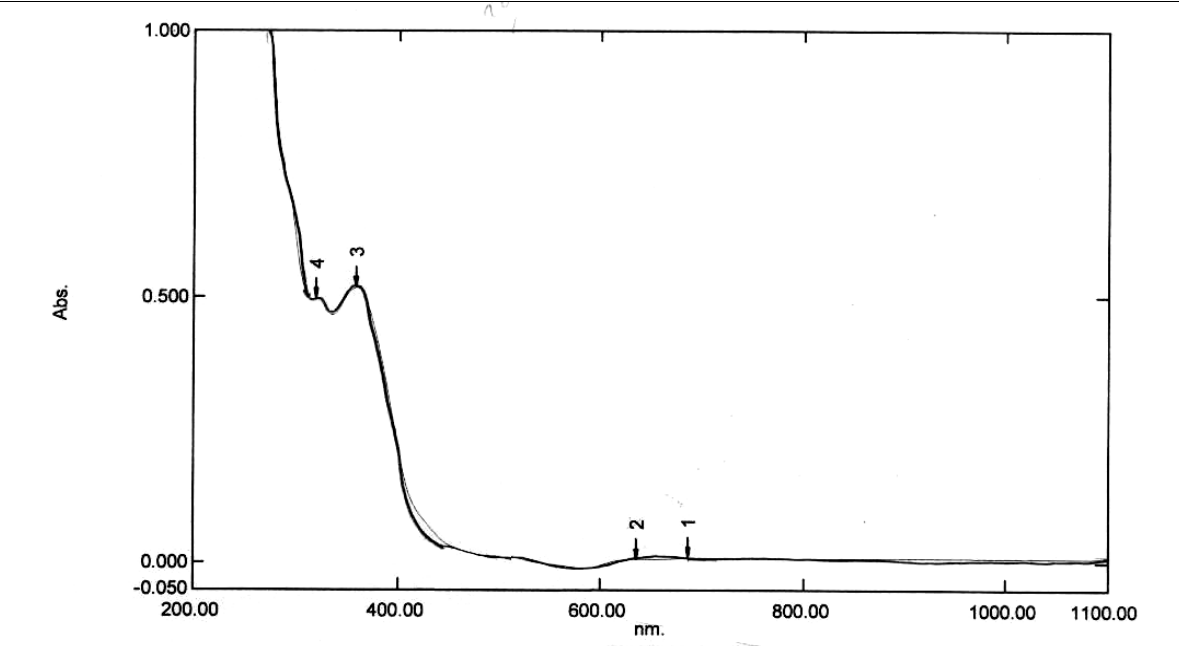


Figure (3-15): UV-Vis. spectrum of CSSBCo

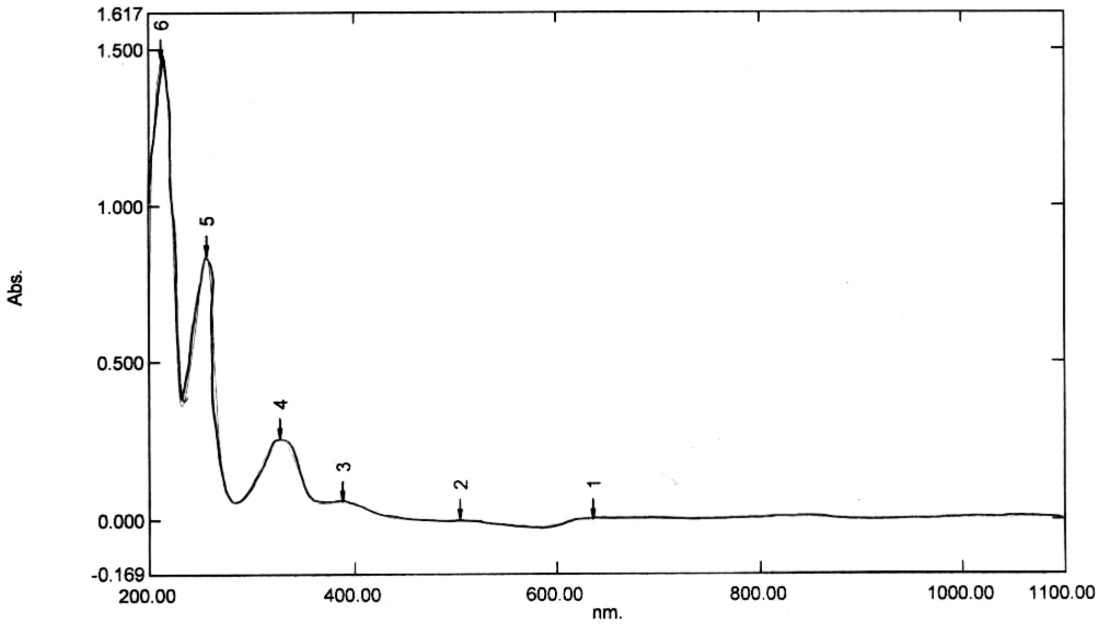


Figure (3-16): UV-Vis. spectrum of CSSBNi

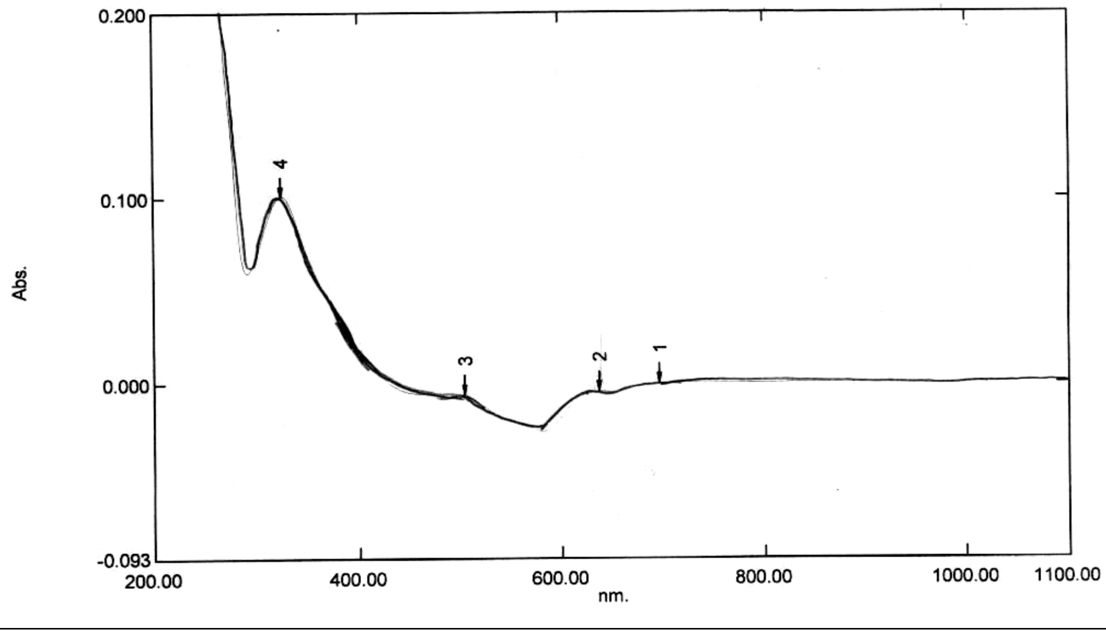


Figure (3-17): UV-Vis. spectrum of CSSBCu

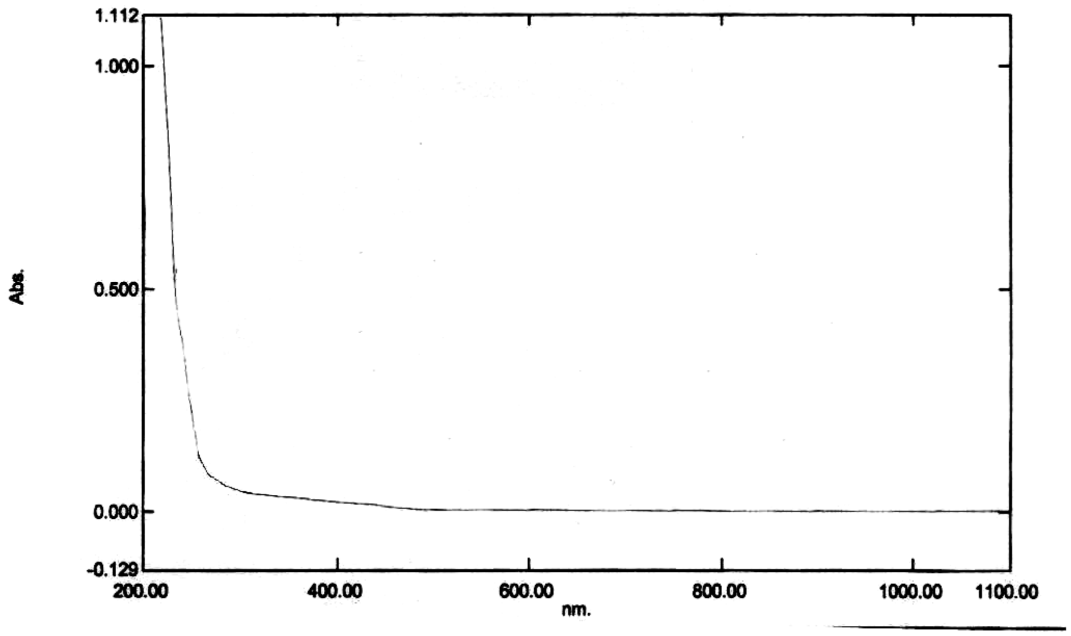


Figure (3-18): UV-Vis. spectrum of CSSBZn

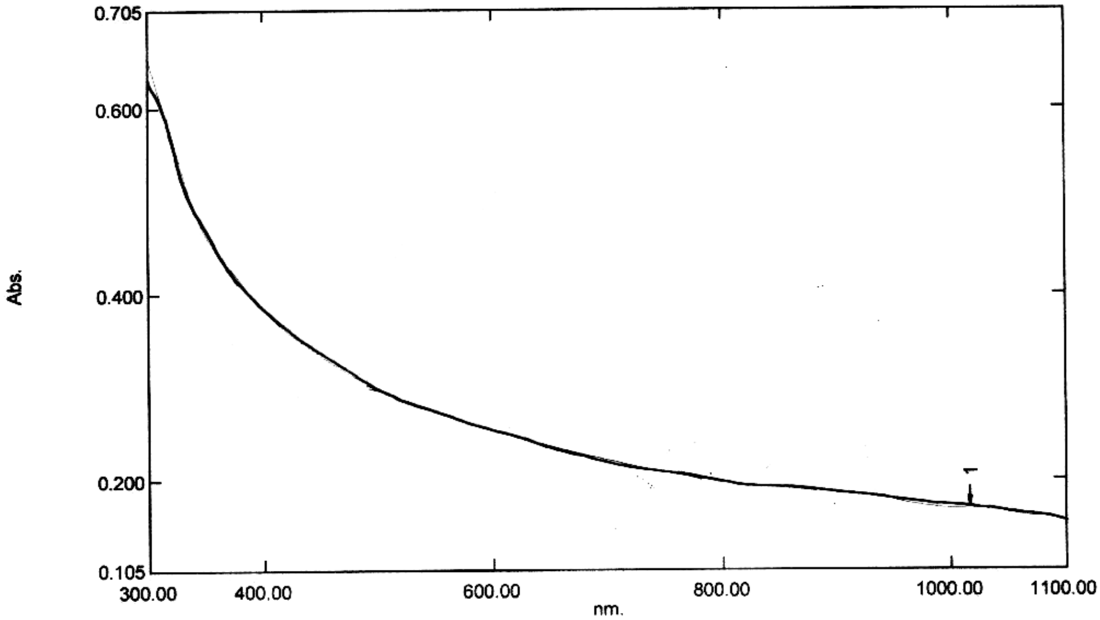


Figure (3-19): UV-Vis. spectrum of CSSBCd

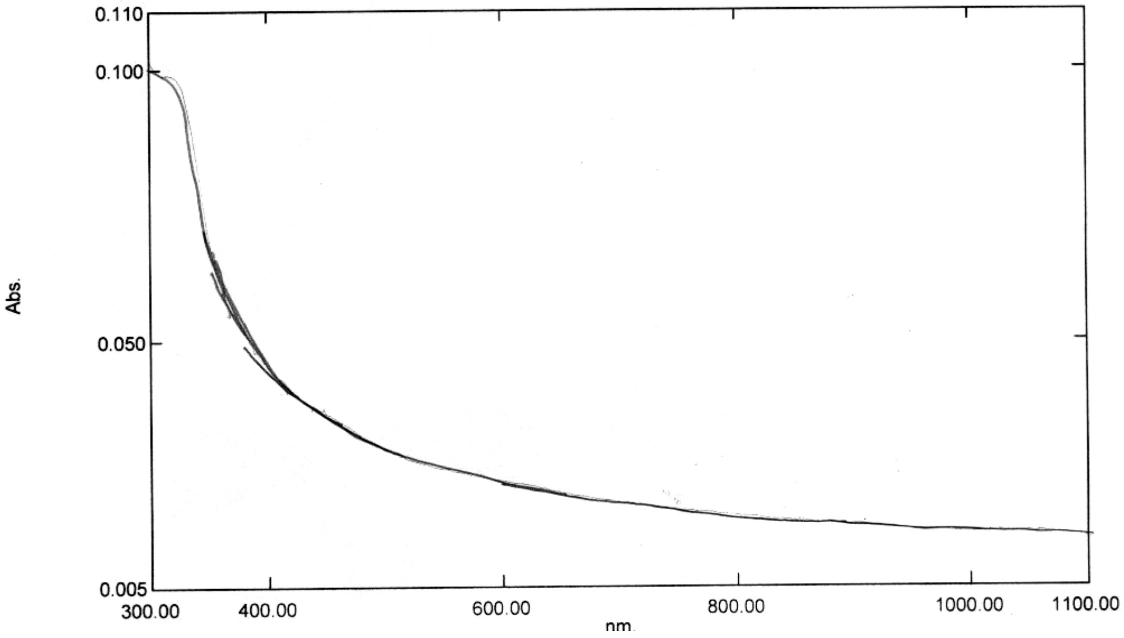


Figure (3-20): UV-Vis. spectrum of CSSBHg

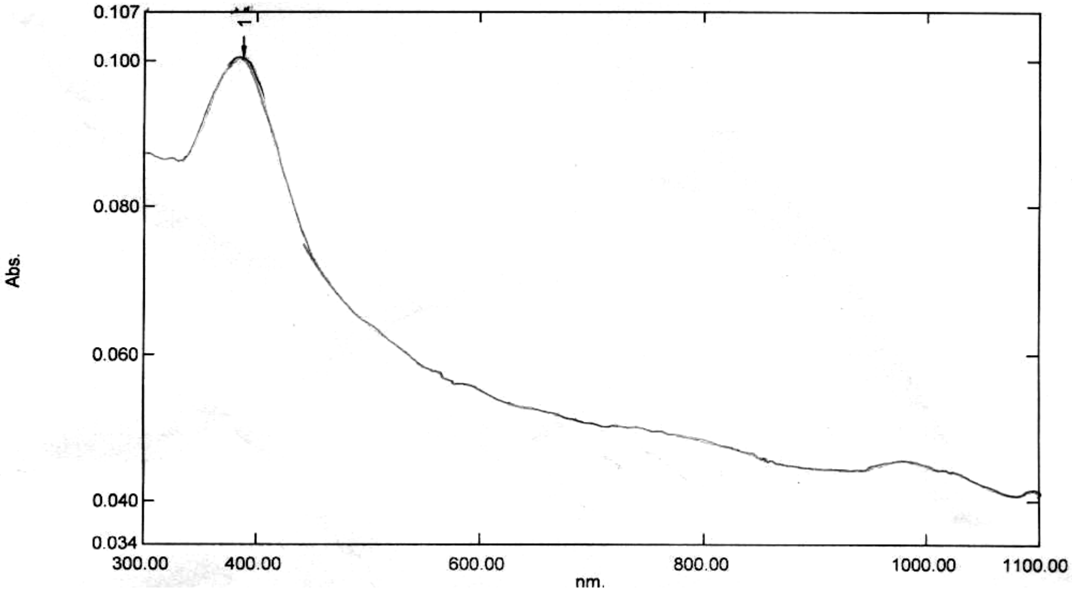


Figure (3-21): UV-Vis. spectrum of CSSBPd

Contents

References:-

1- C.X. Zhang and S.J Lippard, ***Current Opinion in Chemical Biology* , 7,**481-489 (2003).

2- J.E Brady and G.E Humiston ***"General Chemistry,principle and structure"*** 4th Ed,John Wiely and Sons Inc. (1986).

3- H.A.O. Hill , J.M. Patt , and J.P. Williams, Chem. Brit. **5 ,** 156 (1969).

4- R.G. Pearson , J.***Am. Soc*** **85** , 3533 , (1963).

5- F.Basola and R.G Pearson "***Mechanism of Inorganic Reaction***". p.12. (1964).

6- a) G.R. Burubaker , D.W. Johason , ***Coord Chem Rev* , 53 ,** 14 (1984).

b) R.D. Hancock , prog. chem **, 36 ,** 187 (1989).

7- A.A.H. Saeed . ***Journal of chemical and Engineering Data*** , **29(3)**, 359 (1984).

8- A.A.H. Saeed and A.Y Khedar , ***Canadian . J.Appli. Spectroscopy*** , **39(6)**, 173 (1994).

9- U. Casellato , P. Gerriero , S. Tamburini and P.A. Uigato , ***Inorg Chem Acta*** ,**75**, 119 (1986).

10- J.A. Goodiwn , L.J .Wilson , D.M . Stanbury. And R.A . Scott , ***Inory Chem*** , **28,** 42, (1989).

11- A.A.H. Saeed , M.N. Al-Zagoum and M.H .Watton, ***Can .J. Spectroscopy,*** **25,** 137, (1980).

12- Heinz , A.Staab . Ber, **98** (8) 2681, (1965).

13- A.G.Sharp **"Inorganic chemistry,"** John wiley and sons, Inc. ,New york , london , p. 595 (1981) .

14- A.C. Massey , B.F.G. Johnson , , **"The chemistry of copper , silver and gold,"** pergamon press , Oxford , **41,** P.20 (1975).

15- B.N. Figgis **"Introduction to ligand fields,"** Interscience , New york , P. 316 (1966).

16- G. Wilkinson , R.D. Gillard and J.A Mc Cleverty **“Comprehensive coordination chemistry,“** pergamon press , Oxford , England ,**l. 2** (1987).

17- S. Davagi and Y. Degani , 1970 , **“The chemistry of the carbon-nitrogen double bond “**, S. Patai , John wiley and sons , interscience , New york , P.64 .

18- D.Y. Curtin and J.W. Hausser **“Effects of structural changes on the interconversion of steroisomeric imines**. Iso-electronic models for vinyl anions,“ J.Am. Soc. **, 83,** 3474 (1961).

19- Robert W. Layer , ***“The chemistry of imines”, Chem. Review***, **63**, 489 , (1963).

20- P.L. Orioli , M.D. Vaira and L. Socconi , Inorg .Chem. Soc. , 400 (1966).

21- R.M. Countryman , W.T. Robinson and E. Sinn ,***Inorg. Chem*** . **13**, 2013 (1974).

22- T. Ueki, T. Ashida , Y. Sasada and M. Kakudo , ***Acta crystallogr***, sec. B, **25** , 328 (1969).

23- A. Syamal and K.S. Kale , ***Inorg. chem***. , **18** , 992 (1979).

24- R.R. Gange , R.P. Kreh and J.A. Dodge , J.Am. soc., 101, 6917 (1979).

25- V.J. Raju , V. Rana baose , B.B. Kumar and M.C. Ganokar , ***J. Indian Chem. ,*** Soc. **, 8,** 724 (1983).

26- M. Seleborg , S.L. Rolt and B. Post , ***Inorg. Chem***. **, 10 ,** 1501 (1971).

27- P.C. Healy , G.M. Mockier , D.P. Freyberg and G. Sinn , ***J. chem., soc***. Dalton Trans. , **69** (1975).

28- E. Sinn , G. Sim , E.V. Dose , M.F. Tweedle and L.J. Wilson ***, J.Am. chem. soc***., **100** , 3375 (1978).

29- R.H. Holm , G.W. Everett , Jr , and A. Chakravorthy , ***“Progress in inorganic chemistry ,”*** Interscience , New york ,**7** (1966).

30- I.J. Sallomi ***, Dirasat (Jordan) ,*** **24 ,** 1 (1997).

31- I.J. Sallomi and M.S. Al-Fadhel ***, J. Ed Sci*** , **29,** 12 (1998).

32- A.M. Amine , M.sc. Thesis , University of Mosul (1996).

33- A.Z. Mohomad , M.sc.Thesis , University of Mosul (1992).

34- G.L. Echhor , ***“Inorganic Biochemistry”***, Elsevier scientific puplishing company , Amusterdam , P.1137 , (1993).

35- O. Banerjea , ***“Coordination chemistry,”*** Pergaman press Oxford , New york , P.15 . **36** . 141-148 (1980) .

36- H. Shady , F.A. Regab and E.IAly , kim pharmzh 16(12) .1466(1988) , chem. Abst. (10). , 173068w (1989).

37- F. Miliani , Y. Casellato , P.A – Vigato , M.Vidali and D.E. Fenton and M.S. Leal Gonzalez , ***Inorg. chem***. Acta. **103** , 15 (1985).

38- M.D. Temple , P. Recabarren , W.D. Mcfadyen , R.J. Holmes , W.A. Denny and V. Murray , Biochim . Biophys . Acta **, 1574 ,** 223 – 230 , (2002).

39- T. Okado , Im. El. Mehasseb , M. Kodaka , T. Tomohiro , K. Okamato , H. Okunc , ***J. Med. chem***. **44** , 4661 – 4667 , (2001).

40- K. Kselrakumar and S. Van cheeson , proc***, Indian, Acadi. sci* , 107 ,** 179 (1995).

41- P.S.J. Sastry and T.R. Rao , proc. ***, Indian , Aead. sci.*** , **107**. no. 2. 101 (1995).

42- N.M. Aziz , M.sc. Thesis. college of Education for women, Baghdad university , Iraq (1999).

43- F.A. Cotton and G. Wikinson , ***“Advanced Inorganic chemistry”*** , 4th . ed. , wileyinterscience , (1980).

44- K. Dey and K.C , Ray , J. Inorg. Nucl.chem , **37**. 695 (1975).

45- B. Singh , V.A. Banerjie , B.V. Agarwala , and A.K. Dey, J. ***Indian – chem***. soc , Lv 11 . 365 (1980).

46- G.P. Arora , and S.N. Misra. J. ***Indian. chem soc***, LV II , 273, (1980).

47- B. Dash , M. Patra , and S. Praharaj , ***Indian Jon rnal and chemistry***. 19(B). 894 (1980).

48- R.M. Silverstein. G.C. Bassler , and T.C. Morrill , ***“Spectrometric Identification of organic compound”*** 4th Ed. John wiely and sons Inc. (1981).

49- B. Dash , P.K. Mahapatca , D.Pada , and J.M. Pattnaik , ***J. Indian. chem***. soc. ,Lx$_1$, 1061 (1984).

50- V.V. Sarant , J.G. Krishnan and C.G. Patel , ***Inorg chem*** , 9. 718 (1970).

51- D.E. Fenton , and R. Moody , T.chem , soc. Dalton trans , 219 (1987).

52- S. Patai , ***“The chemistry of the Carbon-Nitrogen Double Bond”***, John wiely and sons Inc. , New york , P. 162 (1979).

53- N.M. Abbas , M.Sc thesis , university of Baghdad (1997).

54- R.W. Layer .chem. Rev. **, 63 ,** 489 (1963).

55- A.A.H. Saeed and G.Y Matti , can. J .Spectrosc , 25(2) , 29 (1980).

56- P. Brocklehurst , tetrahedron. **18** , 299 (1962).

57- G. Favini , D. Pitea , and F. Zuccarello. J. chem. Phys. **, 2 ,** 69 (1972).

58- B. Scheuer.Lamalle and G. Durocher , can . J. Spectrose. , 21 (6). 165 (1976).

59- W.F. Smith. Tetrahedron **, 19 ,** 445 (1963).

60- E. Ebra , Bull. chem. soc. , Japan **, 33 ,** 534 (1960).

61- A.A.H. Saeed ,and S.J. Titinchi , Iraq , J. chem. , 15(2) , 110 (1990).

62- R.L. Reeves , J. Am. chem .soc. **, 84 ,** 3332 (1962).

63- D.J. Pasto and C.R. Johnson, ***“Inorganic structure Determination”*** Canada (1969).

64- R.J. Shriner , R.C. Fuson , D.Y. Cnntin , and T.C. Morrill , In ***”the systematic Identification of organic compounds”*** 6th Ed. John wiley and sons (1980).

65- Ahmed. S. M. Al-Ani,M. Sc. thesis , Al-Nahraien university (Previously saddam university) , (1999).

66- Nada M.A. Al-Abidy , M. Sc , Thesis , Baghdad university (1997).

67- N.S , Biradar and V.H. Kukanni , J. Inorg , Nucl chem. **, 33 ,** 3847 (1971).

68- D.H. Bursch and J.C. Bailor , J. Am. chem. soc.**, 78 ,** 1137 , (1656).

69- R.K. Parasher and R.C. Sharma , Inorg. chem. Acta **, 151 ,** 201 , (1988).

70- A.K. Pand and D.C. Dash and P. Mishra , Indian , J. of chemistry. 35A , PP.843. 847 , (1996).

71- Mayada H. Al-Qaissy , Ph.D. thesis , Al-Nahrain university ,(2001).

72- K. Nakamoto , **“Infrared and Raman spectra of Inorganic and coordination compounds”** 5th ed. , wiely and sons , Inc. (1997).

73- M.H.A. Qaissy , PH. D thesis , Al-Nahraien university . 2001.

74- J.V. Quagliano , J. Fujita , G. Finaz , O.J. Phitalips , T. Awalmsley and S.Y. Tyree , J. Amer , chem. soc.**, 81 ,** (1961) 3370 .

75- G. Preti and G. Tosi , ***J. Inory Nucl chem*.*, 42 ,** (1980) 37 . 42.

76- B.N. Figgis and Lewis , ***prog-chem*.*, 6 ,** (1964) 37.

77- N.N. Green wood and A. Earnshow **“Chemistry of element”** Pergamon press (1984).

78- S.V.J. Lakshman , J. Lakshman and A. rao , J. inorg. nocl . chem.**, 37,** 903 – 906 (1975).

79- J. Selbin , chem. Rev., 65 , 153 (1665).

80- R.J.H. Clark, ***“The chemistry of Titanium and vanadium”*** Elserier , Amsterdam (1968).

81- James E. Huheey**“Inorganis chemistry, principle of structure and reactivity”** 3th d eddittion , Harper international SI. Edittion , (1983).

82- C.K. Jorgenson , **“Absorption spectra and chemical bonding in complexes”** , pergamon press , (1964).

83- R. Laspat and R.C. Saxena , J. Indian chem., vol. **IV** 925, 926 (1979).

84- M. Meger , A.A. Gurg , C.O. Dietrich-Buchecker and J.P. Saurage , ***J. Am*. *chem.*,** soc. , 119 , 4599 – 4607 (1977).

85- K. Hussain Reddy , M. Radhakrishna Reddy and Lingappa ***, Indian J of chem.,* 775** , (1996).

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

Preparation and characterization of transition metal complexes of schiff base and nitrides derived from cyclohexyl amine and aromatic aldehyde

A
thesis
submitted to the
College of Sciences
Al-Nahrain University as a partial fulfillment
of the requirements for the Degree of M. Sc in
Chemistry

By:

Rasha Urfi Hammed

(B.SC. 2003)

2006 ١٤٢٧

بسم الله الرحمن الرحيم

إِنِّي تَوَكَّلْتُ عَلَى اللّه رَبِّي وَرَبِّكُمْ
مَا مِنْ دَابَّةٍ إِلا هُوَ آخِذٌ
بِنَاصِيَتِهَا إِنَّ رَبِّي عَلَى صِرَاطٍ
مُسْتَقِيمٍ

صدق الله العظيم
سورة هود(٥٦)

Supervisor Certification

We certify that this thesis was prepared under our supervision at the Department of Chemistry, Collage of Science, AL- Nahrain University as partial requirements for the **Degree of Master of Science in Chemistry.**

Signature:
Supervisor: Prof. Dr. Ayad H. Jassem
Date:

In view of the available recommendations, I forward this thesis for debate by the Examining Committee.

Signature:
Name: Assist. Prof. Dr. Afaf AL-Derzi
Head of Chemistry Department
College of Science
AL-Nahrain University

Examining Committee's Certification

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

Chairman	**Member**
Signature:	Signature:
Name:	Name:
Date:	Date:

Member	**Supervisor**
Signature:	Signature:
Name:	Name:**Prof. Dr. Ayad H. Jassem**
Date:	Date:

Approved for the College Committee of Graduate Studies

Signature:
Name: **Assist. Prof. Dr. LAITH ABDUL AZIZ AL-ANI**
Address: Dean of the College of Science AL-Nahrin University
Date:

الأهداء

الى من شجعني على خوض التجربة وجعلني أُمسك بدفة
المركب و بموج هذه الحياة
أبي

الى سر الحياة و منبع الحب و الدفء و الحنان الى
أروع ما خلق الرحمن
أمي

الى خير ما كان في قدري الذي شدّ من ازري
و هون عليّ امري
زوجي

الى رمز البراءة و منبع الطهر الى من يحلو لعينيه
السهر الى من بذلت له جهدي ليحضى بالفخر
ولدي

الى من رافقوني في طفولتي
اخوتي

Acknowledgment

I wish to express my sincere gratitude and appreciation to my supervisor, Dr. Ayad H. Jassim for their patience, advice and encouragement through my study.

My sincere thanks are to the Dean of the college of Science, head of chemistry department and staff of the chemistry department.

My thanks to all my friends.

Abstruct:

A new schiff base contaning cyclohexyl moiety and phenyl group i.e. p-hydroxy benzyliden phenyl imine (CSSB), have been prepared, and was reacted with a number of transition metal ions, which include: (V^{+4} , Cr^{+3} , Fe^{+2} , Co^{+2} , Ni^{+2} , Cu^{+2} , Zn^{+2} , Cd^{+2} , Hg^{+2} and Pd^{+2})

CSSB was characterized by it's FT-IR spectrum, while it's complexes were characterized by their electronic (uv-vis) spectra and vibrational

(FT-IR) spectra, metal analysis (using atomic absorption technique), conductivity and magnetic susciptibility measurments.

The new colored complexes show to have the following general formula

1-[M L_2 (X) (M)].S

X=M=zero	S=Zero	when M= Vo(II)
X=Cl,M=H_2O	S= Zero	when M= Cr(III)
X=M=H_2O	S=$2H_2O$	when M=Fe(II)
X=NO_3 ,M=H_2O	S=Zero	when M= Co(II)
X=M=H_2O	S=Zero	when M=Ni(II)
X=M=H_2O	S=Zero	when M=Cu(II)
X=M=Zero	S=2Cl	when M= Zn(II)
X=M=Zero	S=$2Cl.C_2H_5OH$	when M= Cd(II)
X=M=Zero	S= $2Cl.C_2H_5OH$	when M= Hg(II)
X=M=Zero	S=2Cl	when M= Pd(II)

The vibrational and elucidation electronic spectral studies and conductivity measurment were very useful in the illusidation of the structural formula of the prepared complexes, which were either octahedral (Vo^{+2} , Cr^{+3} , Cu^{+2} , Co^{+2} , Ni^{+2} , Fe^{+2}), square planar (for Pd^{+2}) or tetrahedral (for Zn^{+2} , Cd^{+2} , Hg^{+2}).

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

تحضير و تشخيص معقدات عناصر إنتقاليه لقواعد شيف ونتريدات مشتقه من سايكلوهكسيل امين والديهايد أروماتيه

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

من قبل

رشا عرفي حميد
بكالوريوس علوم في الكيمياء
(جامعة النهرين) ٢٠٠٣

١٤٢٧ هـ ٢٠٠٦م

بسم الله الرحمن الرحيم

إِنِّي تَوَكَّلْتُ عَلَىِ ّ الله رَبِّي وَرَبِّكُمْ
مَا مِنْ دَابَّةٍ إِلا هُوَ آخِذٌ
بِنَاصِيَتِهَا إِنَّ رَبِّي عَلَى صِرَاطٍ
مُسْتَقِيمٍ

صدق الله العظيم
سورة هود(٥٦)

الخلاصة:-

تم في هذا البحث تحضير قاعدة شيف الجديده، بارار-هيدروكسي بينزلدين فنيل اِمين(CSSB) والتي تمتلك حلقة السايكلوهيكسيل المشبعة وحلقة الفتيل الاروماتيه. تم مفاعلتها مع عدد من ايونات العناصر الانتقاليه، والتي شملت:

(V^{+4} , Cr^{+3} , Fe^{+2} , Co^{+2} , Ni^{+2} , Cu^{+2} , Zn^{+2} , Cd^{+2} , Hg^{+2} and Pd^{+2})

تم تشخيص (CSSB) عن طريق اطيافية الاشعة تحت الحمراء (FT-IR) بينما شخصت معقدات القاعدة عن طريق الاطياف الالكترونيه (الاشعة فوق البنفسجية المرئية) والاطياف الاهتزازيه (FT-IR) وكذلك عن طريق تحليل العناصر بتقنيه الامتصاص الذري اللهبي إضافه الى قياسات توصيلية الكهربائية والحساسية المغناطيسية .

أظهرت نتائج القياسات كون المعقدات الملونه المحضره تمتلك الصيغ الاتيه:

1-[M L_2 (X) (M)].S

X=M=zero	S=Zero	when M= Vo(II)
X=Cl,M=H_2O	S= Zero	when M= Cr(III)
X=M=H_2O	S=2H_2O	when M=Fe(II)
X=NO_3 ,M=H_2O	S=Zero	when M= Co(II)
X=M=H_2O	S=Zero	when M=Ni(II)
X=M=H_2O	S=Zero	when M=Cu(II)
X=M=Zero	S=2Cl	when M= Zn(II)
X=M=Zero	S=2Cl.C_2H_5OH	when M= Cd(II)
X=M=Zero	S= 2Cl.C_2H_5OH	when M= Hg(II)
X=M=Zero	S=2Cl	when M= Pd(II)

كانت نتائج دراسة الأطياف الاهتزازية والالكترونيه وكذلك قياسات التوصيليه الكهربائيه ذات فائدة كبيرة في توضيح الصيغ التركيبية للمعقدات المحضرة، والتي كانت إما ثمانية السطوح (Vo^{+2} , Cr^{+3} , Cu^{+2} , Co^{+2} , Ni^{+2} , Fe^{+2}) او ذات شكل مربع مستوي (لعنصر $Pd^{+٢}$) او رباعية السطوح العناصر Zn^{+2} , Cd^{+2} , Hg^{+2} .