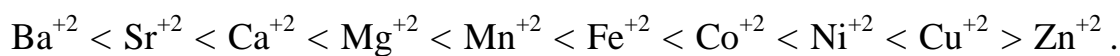


(1-1) Interaction of Ligand with metal ion:

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

Of the most important theories in this respect is the hard and soft acids and bases theory (HSAB) of Pearson, which shows the tendency of metal ions to coordinate with certain groups. Depending on the nature of the donating atom in these groups⁽¹⁾. Also to know the factors affecting the stability of the resulting complexes.

One of the earliest correlations was the Irving-Williams series of stability. For a given ligand, the stability of complexes with dipositive metal ions follows the order:



This order arises in part from a decrease in size across the series and in part from ligand field effects. A second observation is that certain ligands form their most stable complexes with metal ions such as Ag^+ , Hg^{+2} and Pt^{+2} , but other ligands seem to prefer ions such as Al^{+3} , Ti^{+4} and Co^{+3} (2).

Ligands and metal ions are classified as either to type (a) or type (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:

Table (1-1) some ligands and their preferential bonding with metals
(a) and (b)

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

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

One of the most important phenomena that control the stability of the oxidation states of a certain element and the stabilization of one state among another states is known as (symbiosis)⁽⁴⁾.

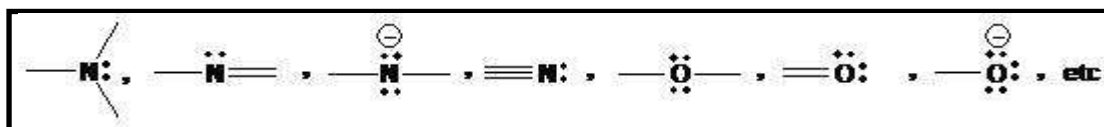
Often metal complexes expand their coordination number by interaction with a Lewis base. This may take place by interaction association or by adduct formation with solvent or other available ligands. The physical properties of the resulting complex often are significantly different from those of the complex not having the expanded coordination number⁽⁵⁾.

(1-2)Metal Complexes of Polydentate Ligand:

Since complex formation or ligand substitution is stepwise even with polydentate ligand, we may expect that polydentate ligands, particularly those with nonequivalent coordination atoms, will exhibit varying dentate natures. Thus, the normally bidentate ethylenediamine can be monodentate⁽⁶⁾ as $NH_2CH_2CH_2NH_3^+$ in the Cr (III) complex

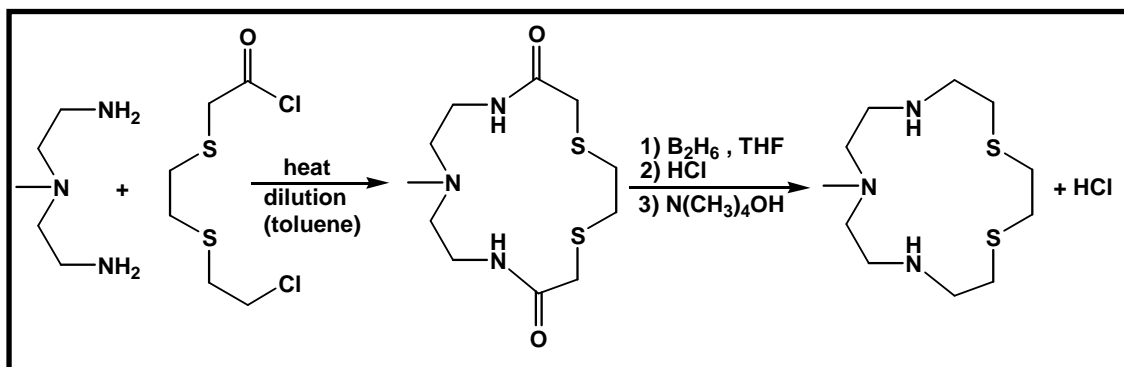
$[\text{Cr}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_3)(\text{H}_2\text{O})_5]^{+4}$, and ethylenediaminetetraacetic acid may coordinate as a bi-to hexa-dentate ligand.

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



It may further be expected that the most important factors affecting the dentate nature of a polydentate ligand will be pH, solvent, the coordinated groups, the relative metal to ligand concentration and any factors that may affect the mechanism of ligand substitution. There have been a number of investigations⁽⁷⁾ on the nature of the complexes formed with multidentate ligands containing the N-hydroxyethyl group.

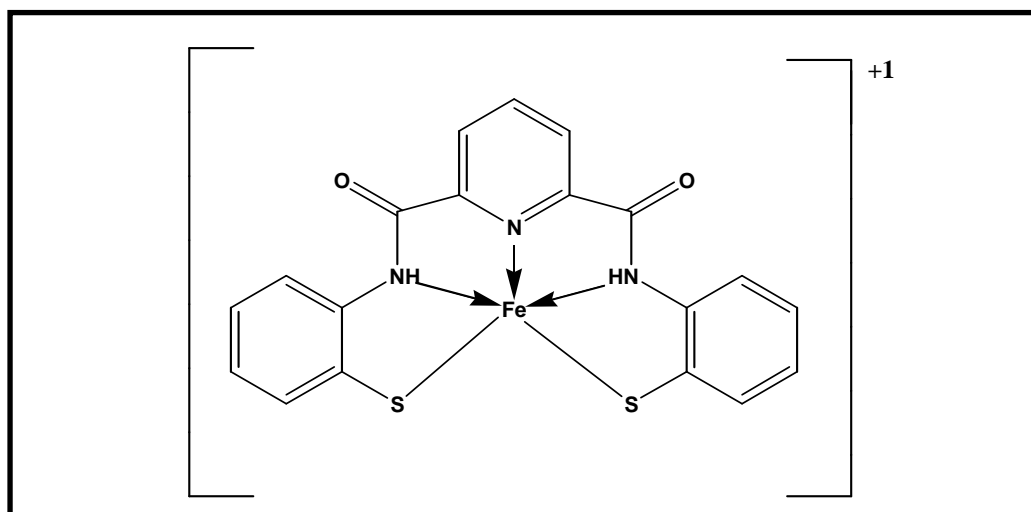
In 1972, (N_3S_2) macrocyclic⁽⁸⁾ type ligand was synthesized according to the following scheme:



Scheme (1-1)

In 2000 Maschark and Marlin⁽⁹⁾ reported the synthesis of the Ligand $[\text{N},\text{N}-\text{bis}-(2\text{-mercaptophenyl})\text{pyridine}-2,6\text{-dicarboxyimide}]$. It's complex with Fe(III) was also prepared, spectroscopic studies showed

that the geometry around Fe(III) is a distorted trigonal bipyramidal, as shown in the following scheme:



Scheme (1-2)

(1-3) Schiff bases

1-3-1 Synthesis of Schiff bases

The term “Schiff base” is used to define those organic compounds which contain the functional group $\text{—C}=\text{N—}$. Schiff bases were firstly prepared by Schiff in 1864^(10,11), from condensation reaction of aldehydes or ketones with primary amines.

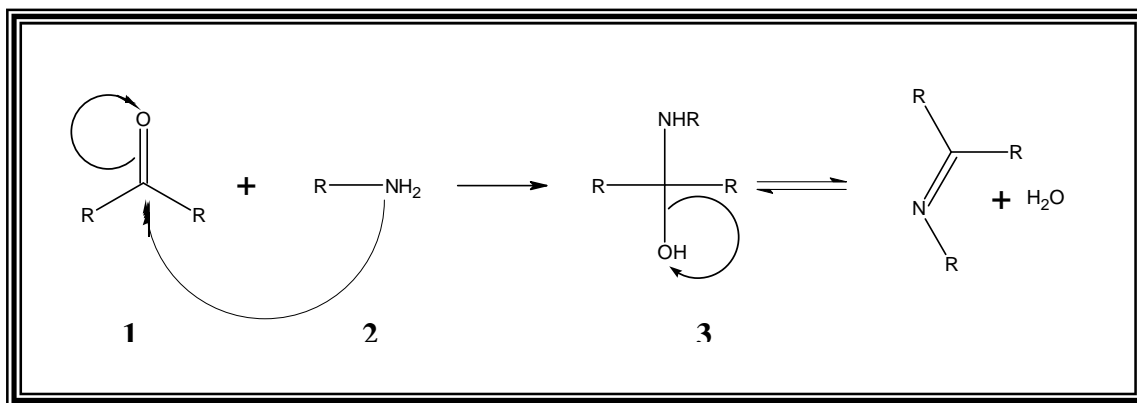
Schiff bases have several nomenclature such as Anils, Imines, Azomethines, Benzanils and Benzyldeneaniline⁽¹²⁾.

Imines, Schiff bases and other C=N compound can be reduced with LiAlH_4 , NaBH_4 , Na-EtOH , hydrogen and a catalyst, as well as with other reducing agents⁽¹³⁾.

Schiff base rapidly decomposed in aqueous acidic media, but they are very stable in basic solutions⁽¹⁴⁾.

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.



Scheme(1-3)Preparation of Schiff base

These bases can also be prepared by refluxing of equimolar quantities of aldehydes 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^(12,15).

Staab⁽¹⁶⁾ prepared Schiff bases by removing water which is formed by condensation of aldehydes with amine by reflexing 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 as N,N-donor Schiff bases, N,O-donor Schiff bases and N,S-donor Schiff bases depending on their structure.

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^(17,18).

(1-4) Thiazole compounds and their derivatives :-

Thiazole is considered to be of a great biological importance, in which activity and potency of many enzyme depend on behavior of thiazole group when coordination with transition metal ions especially having double equivalence occurs⁽¹⁹⁾. This group is a heterogeneous ring (structure II), fig(1-1), having two donating atom of sigma bonds for the metal (nitrogen, sulfur) which was derivated from imidazol (structure I), fig (1-1), in which NH group is replaced by with one sulfur atom in position 1.

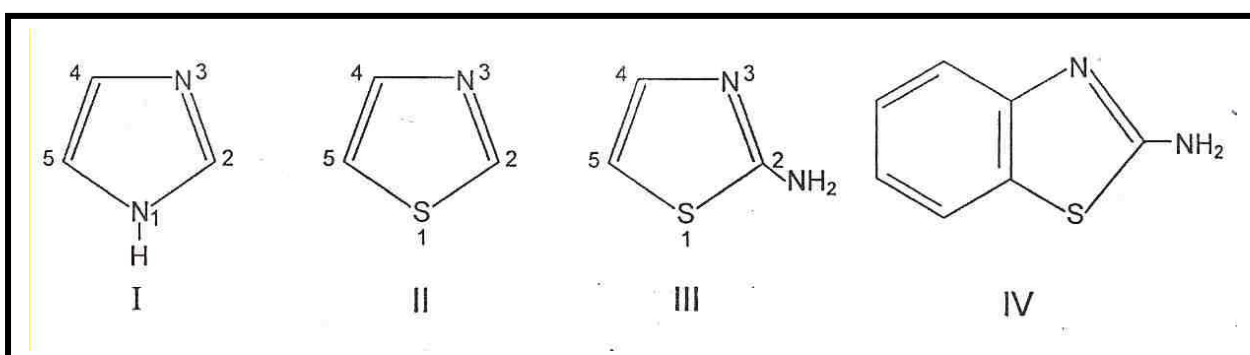


Fig (1-1) Thiazole derivatives.

This makes thiazole group accepts (π) bond better than imidazole as a result of the existence of one empty(d) orbital on sulfur atom. Researches found that the overlapping of this group with metals showed a connection between metal ion and ligand was taking place through the nitrogen atom which is most possible than the connection by the sulfur atom, while the restoring of the hydrogen in position 2 with NH₂ group (structure III), fig(1-1), provides a third position for donating the band to the metal ion⁽²⁰⁾.

One of the other derivative of the thiazole ring is 2-aminobenzothiazole which was prepared by Lane⁽²¹⁾ from the reaction of thiocyanogen with o-aminothiophenol, consisting of a double ring system in which one benzene ring cohere with one thiazole ring in two position 4,5 (structure IV) fig(1-1).

1-4-1 Benzothiazols

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

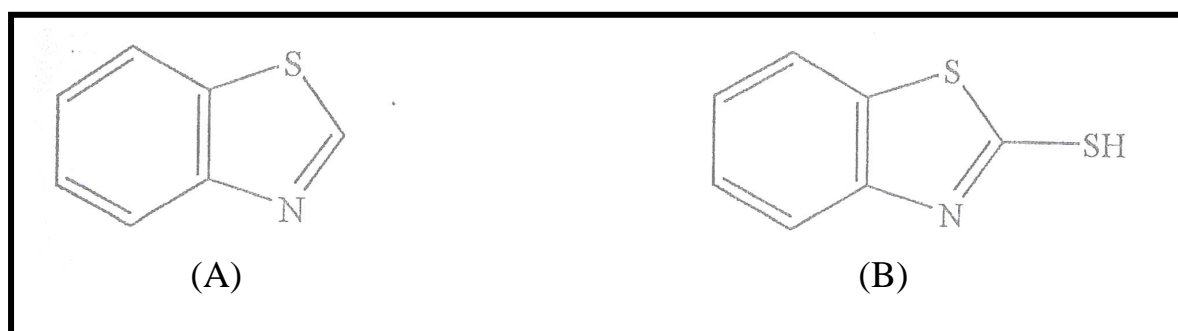


Fig (1-2) Benzothiazoles and its derivatives

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

The benzothiazoles are aromatic because they are cyclic, planer molecules, and has six pairs of delocalized (π) electrons, four of the pairs are shown as (π) bonds, and one pair is shown as a pair of nonbonding electrons on the sulfur atom and the other pair is shown as a pair of nonbonding electrons on the nitrogen atom⁽²²⁾.

In 1922, 2-mercaptobenzothiazol was developed as a rubber vulcanization accelerators, thus the early impetus to the study of thiazole chemistry came from the practical importance of the benzothiazole⁽²³⁾.

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

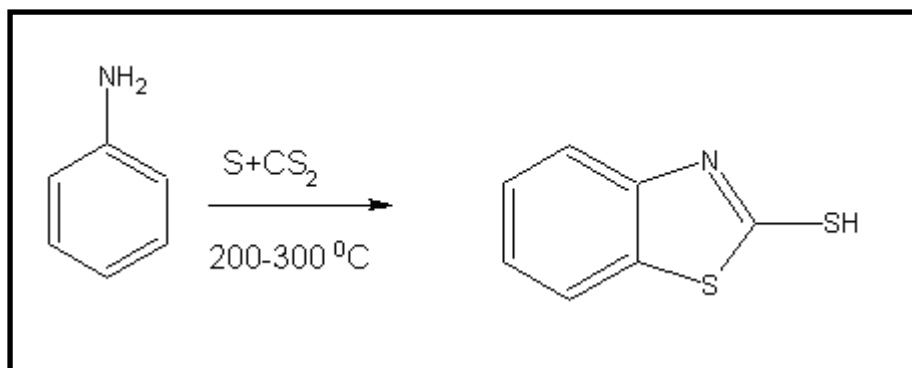
The biological importance of benzothiazole derivative was further emphasized during the period 1941-1945. The work on the structure of the antibiotic, penicillin, which has showed the presence of a thiazolidine ring in this important therapeutic agent⁽²⁴⁾.

1-4-2 Synthesis of 2-Mercaptobenzothiazoles :

The 2-mercaptobenzothiazole and their derivatives are available through a variety of ring closure routes. In the following sections the most important methods for the preparation of 2-mercaptobenzothiazole derivatives are listed, here in :

Reaction of aryl amine with carbon disulfide and sulfur :

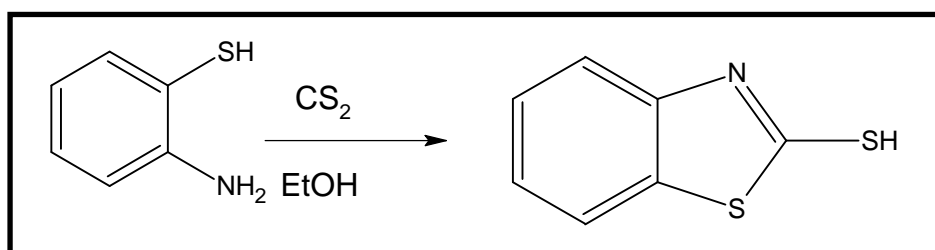
2-Mercaptobenzothiazole is prepared in good yields by treatment of aniline with carbon disulfide and sulfur under pressure at temperatures up to 300°C.



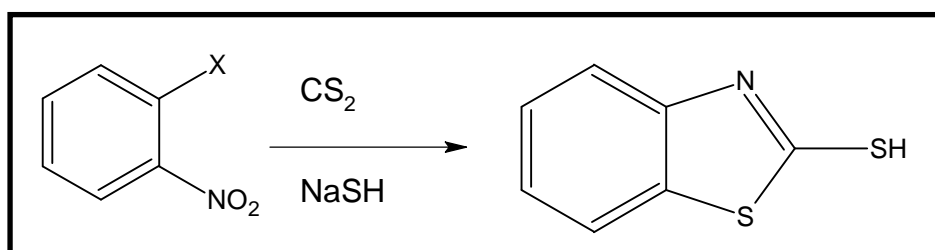
This method can be used with certain substituted aryl amines in place of aniline to yield mercaptobenzothiazol substituted in the benzenoid ring⁽²⁵⁾.

Reaction of o-amino thiophenol with carbon disulfide :

A more versatile process and one that is more readily applicable in the laboratory involve the treatment of o-aminothiophenole with carbon disulfide⁽²⁶⁾.



A very useful modification of this procedure takes advantage of the reaction of an o-nitroaryl halide with a mixture of sodium hydrogen sulfide and carbon disulfide⁽²⁷⁾.

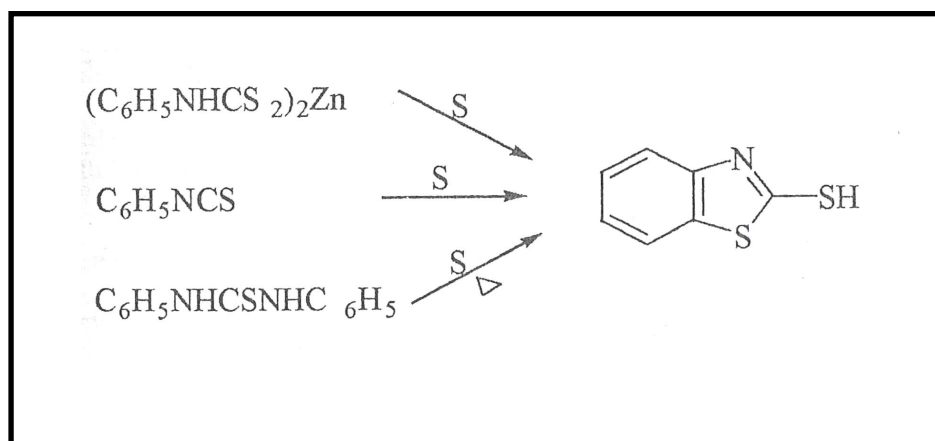


Reaction of o-amino thiophenol with thiophosgen:

The synthesis of 2-Mercaptobenzothiazole by reaction of thiophosgen with o-aminophenol is of interest in connection with the independent existence of the two tautomeric form of the 2-Mercaptobenzothiazoles⁽²⁶⁾.

Miscellaneous methods:

2-Mercaptobenzothiazoles are produced from N-aryldithiocarbamates, arylisothiocyanate and N,N-diphenylthioureas when these compounds heated with sulfur⁽²⁸⁾.



Scheme(1-4) Type of 2-Mercaptobenzothiazole produced

1-4-3 Thiazole metal complexes:-

Many scientists studied the coordination behavior of thiazole and its derivatives with a number of transition metal ions^(29,30).

Thiazole group contains two possible bonding locations (nitrogen, sulfur).

After locating amine group at carbon 2 another bonding location appears because of the similarity between the nitrogen base and substituted nitrogen amine.

It has been found that most of metal ions bound with nitrogen atom^(31,32), and when using soft atom like Au, Cu it will tend to bound with sulfur rather than nitrogen with bidentate and this behavior with hard soft acid base (HSAB)^(31,33). Formation of number of metal complexes for ligand 2-aminothiazol has been studied with transition metal ion in aqueous solution and those metals are Cu(II), Cd(II), Mn(II), Co(II), Ni(II) and has been suggested the connection with ions will depend on the nitrogen atom in thiazole ring except Copper ion which it may connect with sulfur atom⁽²⁷⁾.

It has also been found that 2-aminothiazol suffer from rearrangement within the ring depending on pH-solution when it coordinates with Pt(II) and Pd(II) ⁽³⁴⁾.

For the important of thiazole complexes and in order to know if this ring is working as a monodentate or bidentate ligand when adding NH₂ group in position 2 for benzothiazole molecule. A study has been made on the Fe (III) complex with 2-aminobenzothiazole using different spectral methods, and it has been noted that the ligand behave as a monodentate and also as a bridge group in polymer composition through the two sulfur and nitrogen ring atoms⁽³⁵⁾.

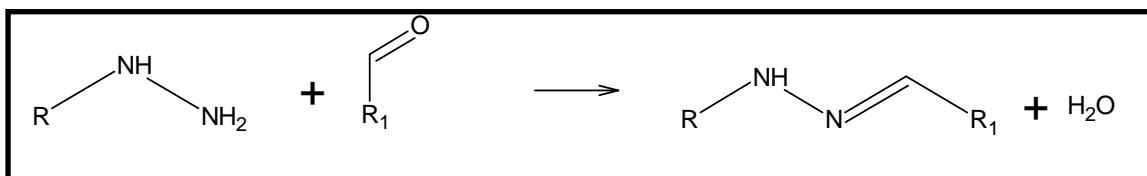
A study and preparation has also been made for this ligand with other transition elements included Zn(II), Cd(II), Hg(II)⁽³⁶⁾, Sb(IV) and Sn(II)⁽³⁷⁾, Cu(I), Ag(I)⁽³⁸⁾.

Fitting the connection of ligand with center ion by nitrogen ring . In a study made at the year 1980 which included the preparation of radium (I) complex with benzothiazole, It has been noted that the radium ion bond with benzothiazole through the

(π) bond of the NCS group or the one distributed on the overall molecules. It has also been found that the prepared complexes own a catalyze properties in speeding up the polymerization of acetone to alcohldiacetone and Mesityl oxide and benzaldehyde polymerization⁽³³⁾.

(1-5) Hydrazones:

Hydrazones are compounds derived from the condensation of Hydrazine or its derivatives with carbonyl compounds, namely aldehydes or ketones (scheme(1-5))



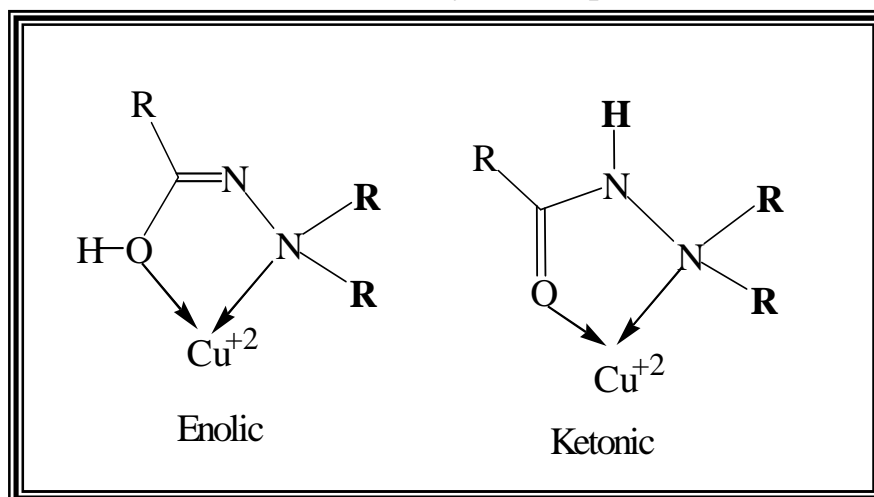
R=aliphatic , aromatic or heterocyclic unit , etc

scheme(1-5) Preparation of Hydrazones

Hydrazone compounds obtained by the reaction of aromatic and heterocyclic hydrazides with mono and di aldehydes or ketones have revealed very versatile behavior in the coordination with the metal ions⁽³⁹⁾. Many researches have synthesized a number of new hydrazones because of their easy of synthesis⁽⁴⁰⁾. Hydrazones are known to function as chelating agents .

These compounds can display antitubercular effects^(42,41), based on their tendency to form chelates with transition metal ions.

The reaction of arylhydrazones derivatives with transition metal ions can proceed according to the following two path ways attaining the ketonic or enolic structure for the hydrazone part of the molecule.



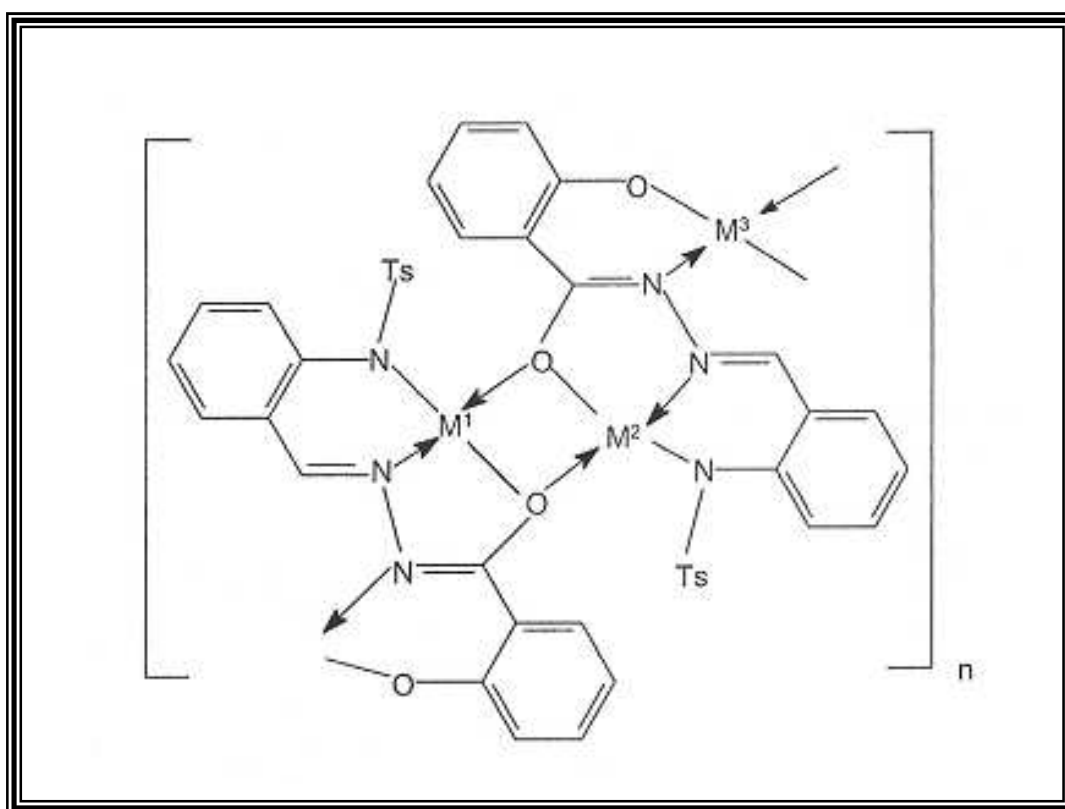
Fig(1-3) Ketonic or enolic structures of hydrazides

The mode of bonding depends on the nature of both the ligand and metal ions, the anion of the metal salt and the solvent used⁽³⁸⁾. Furthermore, some hydrazones are used as quantitative analytical

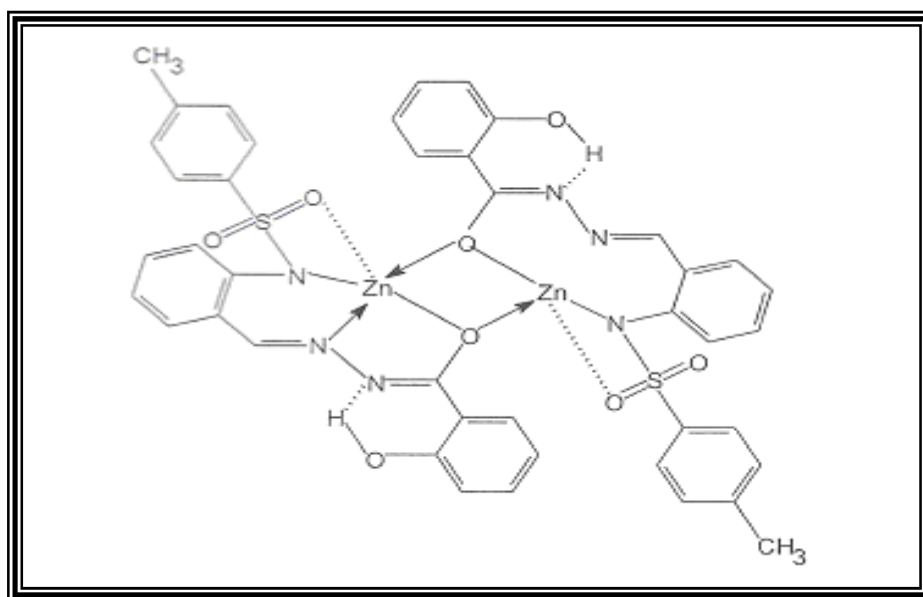
reagents, especially in colorimetric and fluorimetric determination of metal ions.

The coordination chemistry of hydrazones is an intensive area of study and numerous transition metal complex of these ligands have been investigated.

L.M. Balanco and B.I. Kharisov^(41,42) synthesized a new ligand system, salicylhydrazone of 2-(N-tosylamino)benzaldehyde, and they explain that the interaction of this ligand with elemental cobalt, copper and zinc leads to the chelates $[M_3L_2]_n$ (M=Co,Cu) or $[Zn(LH)]_2$. The structures of these complexes were deduced from spectroscopic analysis and magneto chemical data.

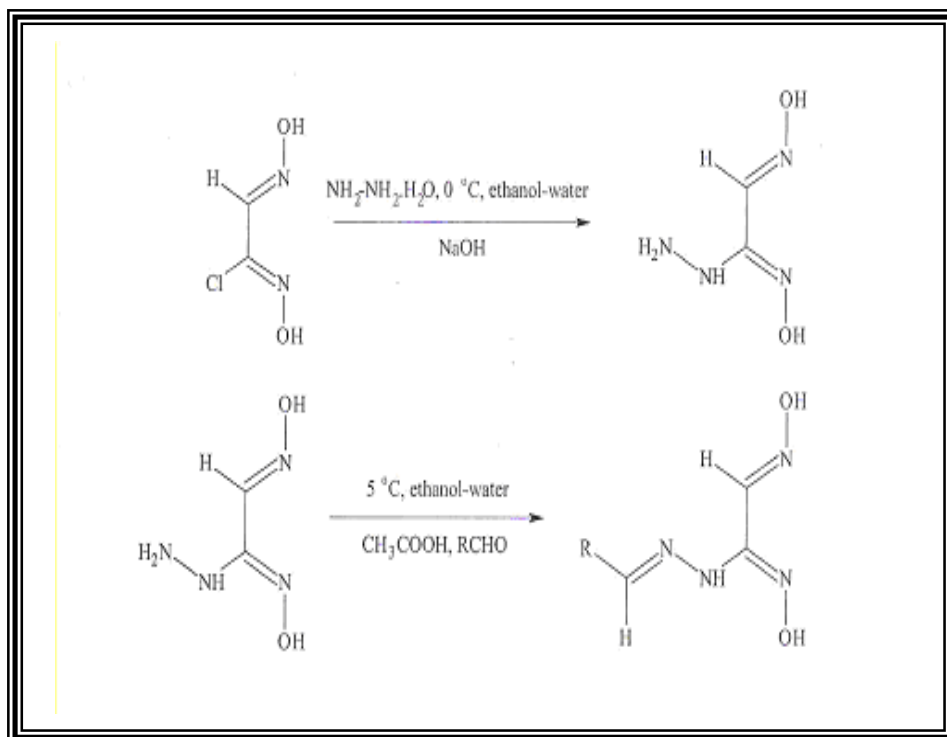


M1,M2,M3= Co or Cu

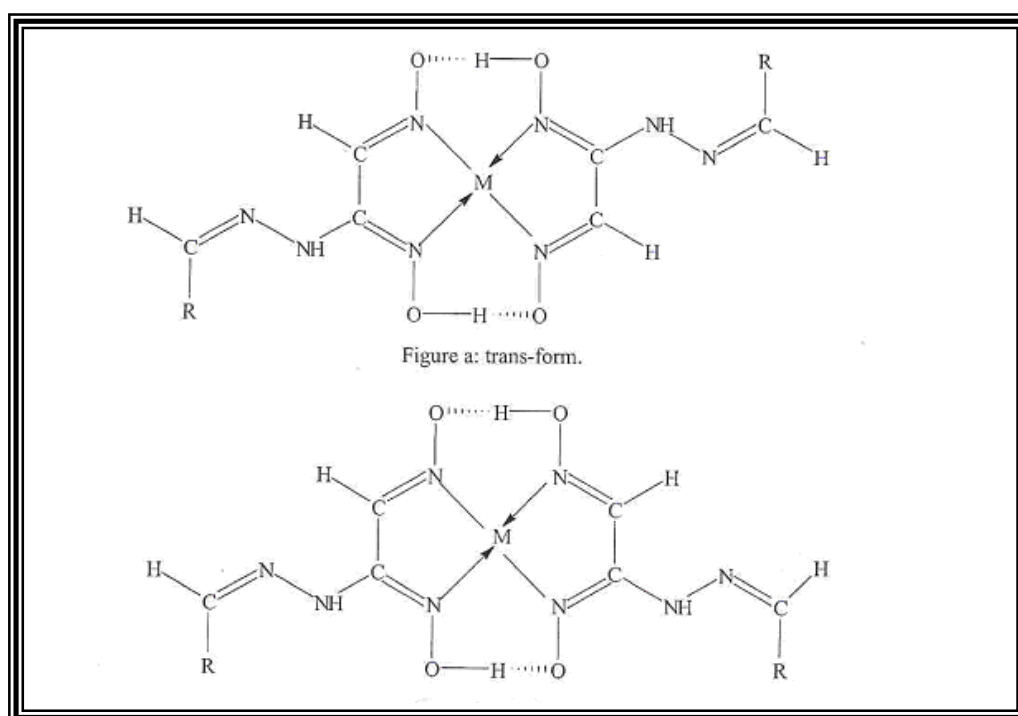


Fig(1-4) Complexes of ligand 2-(N-tosylamino)benzaldehyde

Other researcher⁽⁴³⁻⁴⁴⁾ have synthesized three novel vic-dioxim compounds and their transition metal complexes, these ligands are antiglyoxim ethyl hydrazin (GH₂), anti-2-pyridine aldehyde glyoxime hydrazone (PYGH₂) and anti 2-furancarboxaldehydyoxim hydrazone (FGH₂). Mononuclear complexes of these ligands with a metal ligands ration of 1:2 they prepared with Ni(II), Co(II) ions, and they determined the structure of the ligands and complexes by H-NMR, I.R spectroscopy and elemental analytical techniques.



Scheme (1-6) Preparation of vic-dioxim compounds

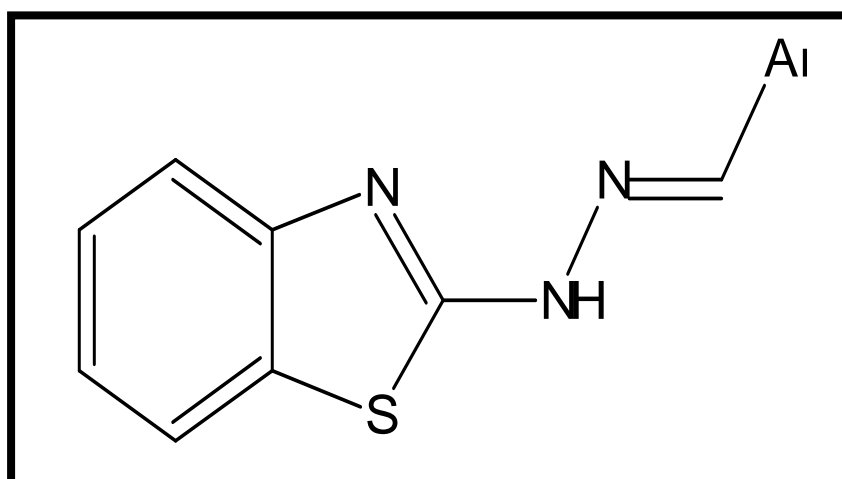


Scheme (1-7) Complexes of dioxim compounds

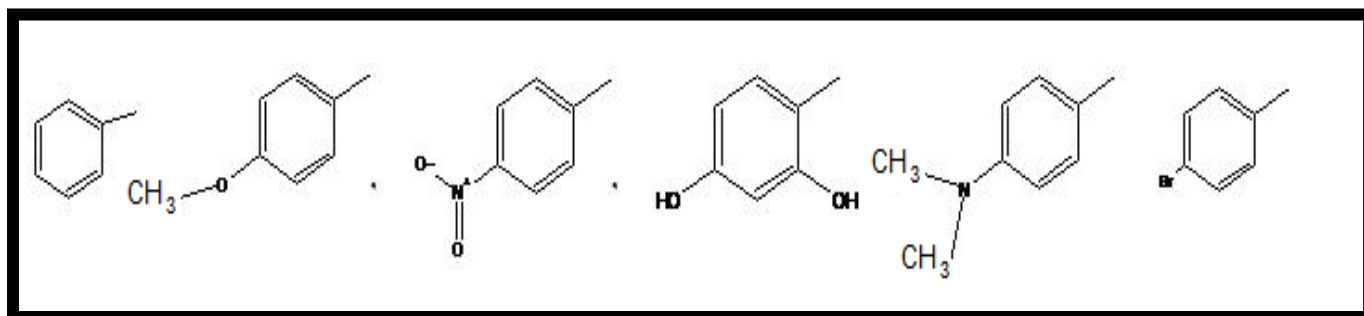
(1-6) Aim of the work:-

The coordination chemistry of hydrazones is an intensive area of study and numerous transition metal complexes of these ligands have been investigated, which stemmed from the interest in the biological and pharmacological properties of these hydrazones.

It is also known that mono and bis-hydrazones find wide applications in medicine as active physiological preparations, due to their antibacterial, tuberculostatic, fungicidal properties as well as activities against certain types of cancers and microorganisms. Furthermore benzothiazole and its derivatives constitute an important class of compounds having a wide spectrum of biological activity. In view of the above facts. It was planned to synthesize 2-(aryl hydrazones) benzothiazole having the following structural formula and to carry out available analyses such as IR, UV Visible , Atomic absorption and conductivity to suggest possible structure for the metal complexes of hydrazones with Iron(III), Cobalt(II) and Manganese(II).



Where Ar=



[Lig1]

[Lig2]

[Lig3]

[Lig4]

[Lig5]

[Lig6]

(2-1) Chemicals and techniques:**1- Chemicals:**

All the chemicals used in this work were of highest purity available and supplied without further purification. The following Table (2-1) shows the reagents and the companies which supply them.

Table (2-1) chemicals used in experimental part

| Compounds | Structure | M.wt. | Purity | Supplied company |
|--|---|-------|--------|------------------|
| Acetone | CH_3COCH_3 | 58 | 99% | Fluka |
| Cobalt Nitrate Tetrahydrate tetrahydrate | $\text{Co}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ | 255 | 99% | Fluka |
| Ferric sulfate dihydrate dihydrate | $\text{Fe}_2(\text{SO}_4)_3 \cdot 2\text{H}_2\text{O}$ | 436 | 99% | Fluka |
| Manganese Acetate Tetrahydrate tetrahydrate | $\text{Mn}(\text{CH}_3\text{COOH})_2 \cdot 4\text{H}_2\text{O}$ | 183 | 98% | BHD |
| Absolute Ethanol | $\text{CH}_3\text{CH}_2\text{OH}$ | 46 | 99% | Fluka |
| Hydrazine hydrate | $\text{N}_2\text{H}_4 \cdot 2\text{H}_2\text{O}$ | 68 | 95% | Fluka |
| 2-Mercaptobenzothiazole | $\text{C}_7\text{H}_5\text{NS}_2$ | 167 | 98% | Fluka |
| 4-Dimethyl aminobenzaldehyde | $\text{N}(\text{CH}_3)\text{C}_6\text{H}_4\text{COH}$ | 149 | 98% | Fluka |
| 3-Nitrobenzaldehyde | $\text{NO}_2\text{C}_6\text{H}_4\text{COH}$ | 151 | 99% | Fluka |
| Anisaldehyde | $\text{CH}_3\text{OC}_6\text{H}_4\text{COH}$ | 136 | 99% | Fluka |
| Benzaldehyde | $\text{C}_6\text{H}_5\text{COH}$ | 106 | 99% | BDH |
| P-Bromobenzaldehyde | $\text{BrC}_6\text{H}_4\text{COH}$ | 212 | 98% | Fluka |
| 2,4-Dihydroxybenzaldehyde | $\text{C}_6\text{H}_3(\text{OH})_2\text{COH}$ | 138 | 98% | BDH |

2- Techniques:

A) Infrared spectrophotometer:

Infrared spectra were recorded on F.T.IR-8300 Fourier Transform Infrared Spectrophotometer (*SHIMADZU*) as potassium bromide disc in the (4000-400) cm^{-1} spectral range, In the Central Agency for Metrology and Quality Control.

B) Electronic absorption spectra:

The electronic spectra of the complexes were obtained using *SHIMADZU* UV-Vis 1650A Ultra-Violet Spectrophotometer at room temperature using quartz cells of 1.0 cm length and using ethanol or DMSO as solvent, in the range of wave length (200-1100) nm.

C) Magnetic susceptibility measurement:

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

D) Metal analysis:

The metals content of the complexes was measured using atomic absorption technique by PERKIN-ELMER-5000 Atomic Absorption Spectrophotometer for the determination of (Fe, Co, Mn).

E) Conductivity measurements:

The molar conductivity measurements were obtained using corning conductivity 220.

F) Melting point instrument:

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

(2-2) Methods of Preparation

1- Preparation of Ligands

A- Preparation of 2-hydrazino benzothiazole [2] from 2-mercaptobenzothiazole [1]

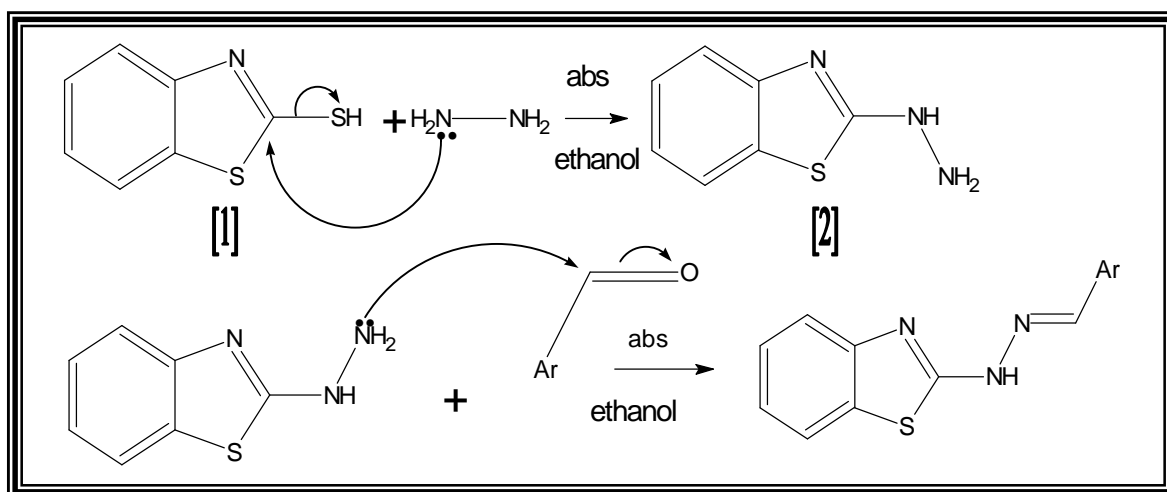
To solution of (0.1mol,16.7gm) 2-mercaptobenzothiazole in ethanol (99%), hydrazin hydrate (99%, 0.1 mole) was added and the mixture was refluxed for (6-hours).

The excess of solvent and hydrazin hydrate was then distilled off , the resulting solid separated out on cooling, filtered and recrystallized from ethanol .

B- Preparation of 2-(aryl hydrazone)benzothiazole [Lig1-Lig6] [2]

Solution of 2-hydrazinobenzothiazole (0.01mol,1.65gm) in ethanol (99%)(15-20) ml and appropriate aldehyde (0.01 mole) was added and the mixture was refluxed on –water bath for (5 hour) .

The solid was isolated and recrystallize from ethanol to give the corresponding product .



Scheme (2-1) Preparation of 2-(arylhydrazone) benzothiazole

Ar is the aldehyde that used in last addition, their structures are as follow:

| | |
|------------------------------------|----------------------|
| Lig1: Benzaldehyde | C_6H_5COH |
| Lig2: Anisaldehyde | $CH_3OC_6H_4COH$ |
| Lig3: 3-Nitrobenzaldehyde | $NO_2C_6H_4COH$ |
| Lig4: 2,4-Dihydroxybenzaldehyde | $(OH)_2C_6H_3COH$ |
| Lig5: 4-Dimethyl aminobenzaldehyde | $(CH_3)_2NC_6H_4COH$ |
| Lig6: P-Bromobenzaldehyde | BrC_6H_4COH |

2-Preparation of the new complexes:

1. Complexes of Lig1:

A) Fe (III) complex (Lig1Fe):

(0.51g, 2mmol) of (Lig1) was dissolved in (15 ml) absolute ethanol and mixed with (0.436g, 1mmol) of the (Ferric sulfate dihydrate) that dissolved in (5 ml) absolute ethanol, the mixture then was refluxed for (1 hour), the resulting precipitate was filtered and washed with absolute ethanol and dried under reduced pressure, the prepared complex was soluble in (DMSO) and partially soluble in warm absolute ethanol, melting point, colour and yield (%) are given in Table (3-3).

B) Co (II) complex (Lig1Co):

(0.51g, 2mmol) of (Lig1) was dissolved in (15 ml) absolute ethanol and mixed with (0.255g, 1mmol) of the (Cobalt Nitrate Tetrahydrate) that dissolved in (5 ml) absolute ethanol, the mixture then was refluxed for (1 hour), the resulting precipitate was filtered and washed with absolute ethanol and dried under reduced pressure, the prepared complex was

soluble in (DMSO) and partially soluble in warm absolute ethanol, melting point, colour and yield (%) are given in Table (3-4).

C) Mn (II) complex (Lig1Mn):

(0.51g, 2mmol) of (Lig1) was dissolved in (15 ml) absolute ethanol and mixed with (0.184g, 1mmol) of the (Manganese Acetate Tetrahydrate) that dissolved in (5 ml) absolute ethanol, the mixture then was refluxed for (1 hour), the resulting precipitate was filtered and washed with absolute ethanol and dried under reduced pressure, the prepared complex was soluble in (DMSO) and partially soluble in warm absolute ethanol, melting point, colour and yield (%) are given in Table (3-5).

2. Complexes of Lig2:

A) Fe (III) complex (Lig2Fe):

(0.57g, 2mmol) of (Lig2) was dissolved in (15 ml) absolute ethanol and mixed with (0.436g, 1mmol) of the (Ferric sulfate dihydrate) that dissolved in (5 ml) absolute ethanol, the mixture then was refluxed for (1hour), the resulting precipitate was filtered and washed with absolute ethanol and dried under reduced pressure, the prepared complex was soluble in (DMSO) and partially soluble in warm absolute ethanol, melting point, colour and yield (%) are given in Table (3-3).

B) Co (II) complex (Lig2Co):

(0.57g, 2mmol) of (Lig2) was dissolved in (15 ml) absolute ethanol and mixed with (0.255g, 1mmol) of the (Cobalt Nitrate Tetrahydrate) that dissolved in (5 ml) absolute ethanol, the mixture then was refluxed for (1 hour), the resulting precipitate was filtered and washed with absolute ethanol and dried under reduced pressure, the prepared complex was soluble in (DMSO) and partially soluble in warm absolute ethanol, melting point, colour and yield (%) are given in Table (3-4).

C) Mn (II) complex (Lig2Mn):

(0.57g, 2mmol) of (Lig2) was dissolved in (15 ml) absolute ethanol and mixed with (0.183g, 1mmol) of the (Manganese Acetate Tetrahydrate) that dissolved in (5 ml) absolute ethanol, the mixture then was refluxed for (1 hour), the resulting precipitate was filtered and washed with absolute ethanol and dried under reduced pressure, the prepared complex was soluble in (DMSO) and partially soluble in warm absolute ethanol, melting point, colour and yield (%) are given in Table (3-5).

3. Complexes of Lig3:**A) Fe (III) complex (Lig3Fe):**

(0.60g, 2mmol) of (Lig3) was dissolved in (15 ml) absolute ethanol and mixed with (0.436g, 1mmol) of the (Ferric sulfate dihydrate) that dissolved in (5 ml) absolute ethanol, the mixture then was refluxed for (1hour), the resulting precipitate was filtered and washed with absolute ethanol and dried under reduced pressure, the prepared complex was soluble in (DMSO) and partially soluble in warm absolute ethanol, melting point, colour and yield (%) are given in Table (3-3).

B) Co (II) complex (Lig3Co):

(0.60g, 2mmol) of (Lig3) was dissolved in (15 ml) absolute ethanol and mixed with (0.255g, 1mmol) of the (Cobalt Nitrate Tetrahydrate) that dissolved in (5 ml) absolute ethanol, the mixture then was refluxed for (1 hour), the resulting precipitate was filtered and washed with absolute ethanol and dried under reduced pressure, the prepared complex was soluble in (DMSO) and partially soluble in warm absolute ethanol, melting point, colour and yield (%) are given in Table (3-4).

C) Mn (II) complex (Lig3Mn):

(0.60g, 2mmol) of (Lig3) was dissolved in (15 ml) absolute ethanol and mixed with (0.183g, 1mmol) of the (Manganese Acetate Tetrahydrate) that dissolved in (5 ml) absolute ethanol, the mixture then was refluxed for (1 hour), the resulting precipitate was filtered and washed with absolute ethanol and dried under reduced pressure, the prepared complex was soluble in (DMSO) and partially soluble in warm absolute ethanol, melting point, colour and yield (%) are given in Table (3-5).

4. Complexes of Lig4:**A) Fe (III) complex (Lig4Fe):**

(0.57g, 2mmol) of (Lig4) was dissolved in (15 ml) absolute ethanol and mixed with (0.436g, 1mmol) of the (Ferric sulfate dihydrate) that dissolved in (5 ml) absolute ethanol, the mixture then was refluxed for (1hour), the resulting precipitate was filtered and washed with absolute ethanol and dried under reduced pressure, the prepared complex was soluble in (DMSO) and partially soluble in warm absolute ethanol, melting point, colour and yield (%) are given in Table (3-3).

B) Co (II) complex (Lig4Co):

(0.57g, 2mmol) of (Lig4) was dissolved in (15 ml) absolute ethanol and mixed with (0.255g, 1mmol) of the (Cobalt Nitrate Tetrahydrate) that dissolved in (5 ml) absolute ethanol, the mixture then was refluxed for (1 hour), the resulting precipitate was filtered and washed with absolute ethanol and dried under reduced pressure, the prepared complex was soluble in (DMSO) and partially soluble in warm absolute ethanol, melting point, colour and yield (%) are given in Table (3-4).

C) Mn (II) complex (Lig4Mn):

(0.57g, mmol) of (Lig4) was dissolved in (15 ml) absolute ethanol and mixed with (0.183g, 1mmol) of the (Manganese Acetate Tetrahydrate) that dissolved in (5 ml) absolute ethanol, the mixture then was refluxed for (1 hour), the resulting precipitate was filtered and washed with absolute ethanol and dried under reduced pressure, the prepared complex was soluble in (DMSO) and partially soluble in warm absolute ethanol, melting point, colour and yield (%) are given in Table (3-5).

5. Complexes of Lig5:**A) Fe (III) complex (Lig5Fe):**

(0.592g, 2mmol) of (Lig5) was dissolved in (15 ml) absolute ethanol and mixed with (0.436g, 1mmol) of the (Ferric sulfate dihydrate) that dissolved in (5 ml) absolute ethanol, the mixture then was refluxed for (1hour), the resulting precipitate was filtered and washed with absolute ethanol and dried under reduced pressure, the prepared complex was soluble in (DMSO) and partially soluble in warm absolute ethanol, melting point, colour and yield (%) are given in Table (3-3).

B) Co (II) complex (Lig5Co):

(0.592g, 2mmol) of (Lig5) was dissolved in (15 ml) absolute ethanol and mixed with (0.255g, 1mmol) of the (Cobalt Nitrate Tetrahydrate) that dissolved in (5 ml) absolute ethanol, the mixture then was refluxed for (1 hour), the resulting precipitate was filtered and washed with absolute ethanol and dried under reduced pressure, the prepared complex was soluble in (DMSO) and partially soluble in warm absolute ethanol, melting point, colour and yield (%) are given in Table (3-4).

6. Complexes of Lig6:

A) Fe (III) complex (Lig6Fe):

(0.719g, 2mmol) of (Lig6) was dissolved in (15 ml) absolute ethanol and mixed with (0.436g, 1mmol) of the (Ferric sulfate dihydrate) that dissolved in (5 ml) absolute ethanol, the mixture then was refluxed for (1hour), the resulting precipitate was filtered and washed with absolute ethanol and dried under reduced pressure, the prepared complex was soluble in (DMSO) and partially soluble in warm absolute ethanol, melting point, colour and yield (%) are given in Table (3-3).

B) Co (II) complex (Lig6Co):


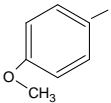
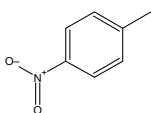
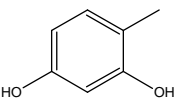
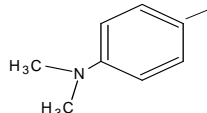
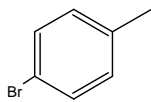
(0.719g, 2mmol) of (Lig6) was dissolved in (15 ml) absolute ethanol and mixed with (0.255g, 1mmol) of the (Cobalt Nitrate Tetrahydrate) that dissolved in (5 ml) absolute ethanol, the mixture then was refluxed for (1 hour), the resulting precipitate was filtered and washed with absolute ethanol and dried under reduced pressure, the prepared complex was soluble in (DMSO) and partially soluble in warm absolute ethanol, melting point, colour and yield (%) are given in Table (3-4).

(3-1) Synthesis and characterization of 2-(aryl hydrazone)-benzothiazole ligand [Lig1-Lig6]:

2-hydrazinobenzothiazole (compound[2], scheme(2-1)) was synthesized from the reaction of 2-Mercaptobenzothiazole (compound[1], scheme(2-1), fig(3-1)) with excess of hydrazine hydrate as it was stated in the experimental part, the authenticity of the product was confirmed by its melting point (210°C), the IR-spectrum of this compound, Fig(3-2), showed stretching bands at (3452, 3315 and 3126) which assigned to the asymmetrical and symmetrical stretching bands of (NH₂) and (NH) groups, more over this compound exhibited significant bands in the regions at (3057, 1647 and 754) which belong to γ C-H aromatic, C=N and C-S bending of o-substituted benzene ring, respectively. That clearly indicated the presence of benzothiazole nucleus.

Reaction of 2-hydrazinobenzothiazole with appropriate aromatic aldehydes afforded the addition – dehydration hydrazones [Lig1-Lig6] ligands normally, 2-(arylhydrazone) benzothiazole show on Scheme (2-1). Their melting points and FT-IR spectral analysis were carried out.

Table (3-1): The melting point and yield percentage % of compounds [Lig1...Lig6]

| Comp.no | Colour | Ar | M.P, °C | Yield% |
|---------|------------------|---|---------|--------|
| [Lig1] | Faint-Yellow |  | 232-235 | 84% |
| [Lig2] | Whitish-Brown |  | 201-205 | 92% |
| [Lig3] | Greenish-Yellow |  | 260-265 | 97% |
| [Lig4] | Yellowish- Brown |  | 263-267 | 91% |
| [Lig5] | Yellow |  | 243-248 | 90% |
| [Lig6] | White |  | 273-276 | 95% |


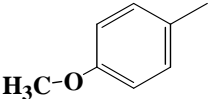
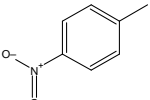
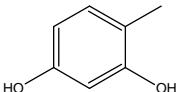
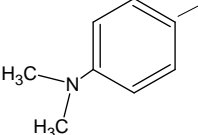
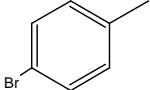
The FT-IR spectra of (Lig1.....Lig6), Figs(3-3)...(3-8) displayed the disappearance of the bands at (3452 and 3315) cm^{-1} due to (NH_2) stretching in the compound [2], while a strong band appeared at about (1620 cm^{-1}) assigned to azomethine linkage $\text{C}=\text{N}$. Beside the typical IR-bands, each of the examined ligands showed other bands characteristic of its own structure.

The colours of the ligands might be related to their UV-Visible absorptions as indicated in Fig. (3-44) to Fig. (3-45). The absorption of the ligands are at 350nm and 300nm where a strong and medium spectra were recorded.

The faint yellow color of these ligands may be related to absorption of the blue end of the visible region by the tail of the ultra bands of the ligands that showed a maximum at 350nm. The transition of their band could be related to a transition from nonbonding orbitals to π^* -orbitals of the unsaturated organic compounds.

In addition there bands were also observed when complexed with the transition metals (Fe^{3+} , Co^{2+} and Mn^{2+}) as shown in Fig (3-) to Fig (3-). However their energies where found to be effected indicating an interaction of these ligands with transition metals cation.

Table (3-2) : FT-IR spectral data (in cm^{-1} , KBr disc) of the ligands [Lig1-Lig6] :-

| Comp.no | Arom. | C-H stretch. Arom. | C=N stretch. | Other bands cm^{-1} |
|---------|---|--------------------|--------------|--|
| [Lig1] |  | 3080 | 1627 | - |
| [Lig2] |  | 3075 | 1620 | C-H stretch. of CH_3 at 2953 and C-O-C stretch. at 1251 cm^{-1} |
| [Lig3] |  | 3083 | 1623 | The NO_2 group appears at 1350 cm^{-1} |
| [Lig4] |  | 3097 | 1620 | O-H stretch. at 3347 cm^{-1} being broad due to hydrogen bond |
| [Lig5] |  | 3076 | 1621 | C-H stretch. at 2931, 2885 cm^{-1} |
| [Lig6] |  | 3081 | 1625 | C-Br at (783 cm^{-1}) |

(3-2) Physical properties of the prepared complexes:-

Tables (3-3), (3-4) and (3-5) show the physical data, yield percentage and metal content of the prepared complexes, which show different melting points, all of them have melting point higher than the parent ligands, the colors which are shown in tables were useful in structural determination.

All reactions were carried out under heating conditions and the solvent was absolute ethanol. The recrystallization solvent was ethanol/water mixture ratio (1:1) for all reactions. Identification and study of these complexes were carried out by metal analysis [the results are shown in table (3-3), (3-4) and (3-5)]. Infrared and Ultra-Visible spectrophotometer, magnetic susceptibility and electric conductivity measurements.

According to these measurements the chemical formula of the prepared complexes has been suggested as given in table (3-10).

Table(3-3)physical properties, yield % metal content of the Fe complexes

| symbol | Colors | Melting point, °C | Yield% | Metal analysis % | |
|--------|-----------------|----------------------|--------|-------------------|-------|
| | | | | Calc [*] | Found |
| FeLig1 | Pale -Yellow | 280-283 | 83 | 5.76 | 5.54 |
| FeLig2 | Brown | 260-263 | 86 | 9.9 | 10.31 |
| FeLig3 | Greenish-Yellow | 291-293 | 78 | 6.17 | 6.14 |
| FeLig4 | Blackish- Brown | 270-275 | 92 | 5.0 | 5.0 |
| FeLig5 | Brownish-Yellow | 297-301 | 76 | 10.03 | 9.72 |
| FeLig6 | Yellowish-White | 340-343 | 84 | 5.03 | 5.07 |

*Been relying on the proportion of metal inside the complex and assuming the form of complex molecular weight is commensurate with

the molecular weight of which got it through a measurement by Atomic Absorption Spectrophotometer.

Table(3-4)physical properties, yield % metal content of the Co complexes

| symbol | Colors | Melting point, °C | Yield% | Metal analysis % | |
|--------|-----------------|----------------------|--------|-------------------|-------|
| | | | | Calc [*] | found |
| CoLig1 | Pale -yellow | 290-293 | 73 | 10.7 | 10.8 |
| CoLig2 | Pale - Brown | 250-252 | 80 | 10.45 | 10.9 |
| CoLig3 | Greenish-Yellow | 310-313 | 82 | 9.0 | 8.9 |
| CoLig4 | Greenish-Brown | 260-263 | 98 | 6.93 | 6.9 |
| CoLig5 | Brownish-Yellow | 298-300 | 70 | 4.66 | 4.6 |
| CoLig6 | Yellowish-White | > 350 | 85 | 9.0 | 9.1 |

*Been relying on the proportion of metal inside the complex and assuming the form of complex molecular weight is commensurate with the molecular weight of which got it through a measurement by Atomic Absorption Spectrophotometer.

Table(3-5)physical properties, yield % metal content of the Mn complexes

| symbol | Colors | Melting point, °C | Yield% | Metal analysis % | |
|--------|-----------------|----------------------|--------|-------------------|-------|
| | | | | Calc [*] | found |
| MnLig1 | Pale -yellow | 287-291 | 78 | 4.00 | 3.6 |
| MnLig2 | Pale - Brown | 245-249 | 84 | 5.22 | 5.24 |
| MnLig3 | Greenish-Yellow | 311-315 | 92 | 4.52 | 4.5 |
| MnLig4 | Deep-Brown | 266-270 | 85 | 6.3 | 6.15 |

*Been relying on the proportion of metal inside the complex and assuming the form of complex molecular weight is commensurate with the molecular weight of which got it through a measurement by Atomic Absorption Spectrophotometer

(3-3) Infra-red spectra of the prepared complexes:

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

3-3-1 The FT.IR spectra of Lig1 and its complexes:-

The ligand Lig1 has the azomethine group. In general azomethine group (-C=N-) absorption occur at (1690, 1470) cm^{-1} depending on the nature of groups linked to it ^(12,45).

The compound containing azomethine group shows basic behavior towards metal ion and coordinated via the nitrogen atom, this coordination shifts the stretching frequency of (-C=N-) group either toward higher frequency in some complexes^(46,47,1), or toward lower frequency in others^(48,49).

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⁽⁴⁶⁾. The decrease in frequency indicates a decrease in 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^(50, 51).

The FT.IR. spectrum of the ligand Lig1, Fig (3-3), Table(3-2), show the absence of the band at $\sim 1735\text{ cm}^{-1}$ ν (N-H) stretching vibration⁽⁵²⁾, and a strong new band appeared at 1627 cm^{-1} assigned to azomethine ν (HC=N) linkage, showing that the amino and aldehyde moieties of the starting material are absent and have been converted in to the azomethine group⁽⁵³⁾.

The bands appeared at 1577 and 1489 cm^{-1} refer to ν (C=C) of aromatic ring, and the band at 2886 and 2829 cm^{-1} refer to ν (C-H) of aliphatic⁽⁵⁴⁾.

A- Iron (III) Complex Lig1 Fe

The spectrum of $[\text{Fe}_2(\text{Lig1})_2(\text{OH})_2(\text{H}_2\text{O})_4](\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$ complex, Fig (3-9), Table (3-6) which shows the shifting of the azomethine band to a lower frequency by $(10)\text{cm}^{-1}$ indicating the participation of azomethine nitrogen in the interaction with ferric ion.

Further conclusive evidence for the coordination of the ligand with the studied metal ion was shown by the appearance of new weak low frequency band at $(594)\text{ cm}^{-1}$ was assigned to ν (Fe-N)⁽⁵⁵⁾.

The broad band found at $(3380)\text{ cm}^{-1}$ refers to the presence of water molecules out of the coordination sphere⁽⁵⁴⁾.

B- cobalt (II) Complex Lig1 Co

The spectrum of $[\text{Co}(\text{Lig1})(\text{NO}_3)(\text{H}_2\text{O})_2] \text{NO}_3 \cdot 4\text{H}_2\text{O}$ complex, Fig(3-10), Table (3-6) showed that the stretching frequency of (C=N) group

was shifted to lower frequency by $(12) \text{ cm}^{-1}$ and appeared at $(1615) \text{ cm}^{-1}$.

The stretching frequency of (C-H) aliphatic group was shifted to lower frequency and appeared at $(2966-2898) \text{ cm}^{-1}$.

The new band which was only observable in the spectrum of the complex, appeared at $(590) \text{ cm}^{-1}$ and refers to the ν (Co-N)⁽⁵⁶⁾.

These observations indicate the coordination of Co(II) ion with the azomethine nitrogen's.

C- Manganese (II) Complex Lig1 Mn

The spectrum of $[\text{Mn}_2(\text{Lig1})_2(\text{OH})_2(\text{H}_2\text{O})_4](\text{OH})_2 \cdot 10\text{EtOH}$ complex, Fig(3-11), Table (3-6) showed that the stretching frequency of (C=N) group was shifted to lower frequency by $(8) \text{ cm}^{-1}$ and appeared at $(1619) \text{ cm}^{-1}$.

The stretching frequency of (C-H) aliphatic group was shifted to higher frequency and appeared at $(2966-2889) \text{ cm}^{-1}$.

The new band which was only observable in the spectrum of the complex, appeared at $(597) \text{ cm}^{-1}$ and refers to the ν (Mn-N)⁽⁵⁶⁾.

3-3-2 FT.IR. Spectra of Lig2 and their metal complexes

The FT.IR. spectrum of Lig2 show the same behavior as those of L^1 , L^2 Fig (3-4), which contain the same group (azomethine group) which interact the metal through azomethine –nitrogen. The azomethine group band appeared at $(1620) \text{ cm}^{-1}$, the band at $(1251) \text{ cm}^{-1}$ refer to the ν (C-O) stretching vibration^(53,57). The band appeared at $(2953, 2833) \text{ cm}^{-1}$ refers to the ν (C-H) band for aliphatic⁽⁵⁴⁾.

The bands which appeared at (1577,1512,1429) cm^{-1} refer to the ν (C=C) of the aromatic ring, and the band at (745) cm^{-1} refer to the ν (C-S)^(26,37,56,58).

The interact with metal ion through both (nitrogen of the ring and azomethine –nitrogen), thus this ligand act chelating ligand (bidentate).

A- Iron (III) Complex Lig2 Fe

On comparison of the Iron (III) complex $[\text{Fe}(\text{Lig2})(\text{H}_2\text{O})(\text{SO}_4)]_2\text{SO}_4$ spectrum, Fig (3-12), Table(3-6), with that of the free ligand, the following changes were observed, first, a shifting of ν (C=N) band to higher frequency by (17) cm^{-1} and appeared at (1637) cm^{-1} , which indicate the participation of nitrogen in the coordination of the complex⁽⁵⁵⁾.

Also the bands at (2933,2854) cm^{-1} which corresponding to ν (C-H) of the aliphatic was shifted to a higher frequency by (19) cm^{-1} . A weak band appeared at (593) cm^{-1} refers to the ν (Fe-N)⁽⁵⁶⁾.

A broad band appeared at (3529) cm^{-1} in the spectrum of complex indicating the presence of water molecules in complex.

B- Cobalt (II) Complex Lig2 Co

The FT.IR. spectrum of $[\text{Co}(\text{Lig2})(\text{NO}_3)(\text{H}_2\text{O})_2](\text{NO}_3).2\text{H}_2\text{O}$ complex, .Fig (3-13), shows the shifting of azomethine band to lower frequency and appeared at (1610) cm^{-1} which indicate the participation of azomethine –nitrogen with Co(II) atom since the ν (C-O) band in the spectrum of complex show difference and appeared at (1253) cm^{-1} , which indicates that it is not participate in coordination with cobalt ion.

The band of ν (C-H) aliphatic was shifted to appeared at (2921,2835) cm^{-1} .The band at (586) cm^{-1} can be assigned ν (Co-N)⁽⁵⁶⁾.

C- Manganese (II) Complex Lig2 Mn

The FT.IR. spectrum of $[\text{Mn}(\text{Lig2})_2(\text{H}_2\text{O})_2](\text{OH})_2 \cdot 6\text{EtOH}$ complex, Fig (3-14), showed that the stretching frequency of (C=N) group was shifted to higher frequency by $(16) \text{ cm}^{-1}$ and appeared at $(1636) \text{ cm}^{-1}$. Which indicate the participation of azomethine –nitrogen with Mn(II) atom since the ν (C-O) band in the spectrum of complex show difference and appeared at $(1298) \text{ cm}^{-1}$, which indicates that its not participate in coordination with manganese ion .

The band of $\nu(\text{C-H})$ aliphatic was shifted to appeared at $(2900,2835) \text{ cm}^{-1}$. The band at $(553) \text{ cm}^{-1}$ can be assigned ν (Mn-N) ⁽⁵⁶⁾.

3-3-3 The FT.IR spectra of Lig3 and its metal complexes

The FT.IR spectrum of Lig4 is in Fig(3-5), Tables (3-6), (3-2), The comparison of FT.IR spectra of Lig3 and its metal complexes indicated that the ligand is principally coordinated to the metal ion through both, the azomethine-nitrogen and the nitrogen of the ring, thus acting as a bidentate ligand.

The azomethine absorption band appeared at $(1623) \text{ cm}^{-1}$, the band appeared at $(1531) \text{ cm}^{-1}$ refer to the ν (C=C) of the aromatic ring stretching vibration ^(53,57). The band at $(3083) \text{ cm}^{-1}$ refers to the ν (C-H) aromatic, the bands appeared at $(2933,2861) \text{ cm}^{-1}$ refer to the ν (C-H) of aliphatic ⁽⁵⁴⁾. The band appeared at $(1350) \text{ cm}^{-1}$ refer to the ν (NO_2) group ⁽⁵⁹⁾.

Finally, the band appeared in $(734) \text{ cm}^{-1}$ refer to the (C-S) ^(26,37,56,58) band.

A- Iron (III) Complex Lig3 Fe

The FT.IR spectrum of $[\text{Fe}(\text{Lig3})_2(\text{H}_2\text{O})_2]_2 (\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ complex is shown in Fig(3-15), the frequency of (C=N) absorption was shifted to higher frequency by $(10) \text{Cm}^{-1}$ and appeared at $(1633) \text{cm}^{-1}$. The band for the ν (C-H) aliphatic was shifted to lower frequency by $(11) \text{cm}^{-1}$ and appeared at $(2922) \text{Cm}^{-1}$. The band appeared at $(595) \text{cm}^{-1}$ can be assigned to ν (Fe-N)⁽⁵⁵⁾. The bands referring to the (NO₂) group were appeared at $(1350) \text{cm}^{-1}$. A broad band appeared at 3440cm^{-1} and another one at 675cm^{-1} refer to the lattice water molecules respectively^(60,61).

B- Cobalt (II) Complex Lig3 Co

The FT.IR spectrum of, $[\text{Co}(\text{Lig3})(\text{NO}_3)(\text{H}_2\text{O})_2](\text{NO}_3)$ complex is shown in Fig (3-16). The frequency of (C=N) is appeared at $(1629) \text{cm}^{-1}$. The ν (C-H) aliphatic band was shifted to higher frequency and appeared at $(2964-2879) \text{cm}^{-1}$. The (NO₂) band appeared at $(1350, 1272) \text{cm}^{-1}$ (26,37,56,58).

Further contusive evidence of the coordination of the ligand was the band of metal ion which appeared at $(558) \text{cm}^{-1}$ assigned to ν (Co-N) vibration⁽⁵⁶⁾.

C- Manganese (II) Complex Lig3 Mn

The FT.IR spectrum of $[\text{Mn}_2(\text{lig3})_2(\text{OH})_2(\text{H}_2\text{O})_4](\text{OH})_2 \cdot 3\text{EtOH}$ complex is shown in Fig (3-17). The frequency of (C=N) is appeared at $(1631) \text{cm}^{-1}$. The (NO₂) band appeared at $(,1350,1272) \text{cm}^{-1}$ (24,35,63,71).

The bands which appeared at $(1577,1527,1427) \text{cm}^{-1}$ refer to the ν (C=C) of the aromatic ring, The ν (C-H) aliphatic band was appeared at $(2902) \text{cm}^{-1}$. The band appeared at $(551) \text{cm}^{-1}$ can be assigned to ν (Mn-N)⁽⁵⁵⁾.

3-3-4 The FT-IR spectra of Lig4 and their metal complexes

The FT-IR spectrum of Lig4 shown in Fig (3-6). This ligand contain azomethine group, stretching appeared at frequency $(1620) \text{ cm}^{-1}$. This ligand act as a bidentate ligand, (the ligand coordinated to metal ion through both nitrogen).

The broad band at $(3347) \text{ cm}^{-1}$ was assigned to the $\nu (\text{O-H})^{(54)}$, which was appeared at the same position in ligand and complex mean that no coordination with the metal ion $(^{55})$. The band which appeared at $(1552) \text{ cm}^{-1}$ refers to $\nu (\text{C=N})$ of the aromatic ring, and the band at $(3097) \text{ cm}^{-1}$ refers to the $\nu (\text{C-H})$ of benzene and the band at $(2963-2817) \text{ cm}^{-1}$ refer to the $\nu (\text{C-H})$ aliphatic $(^{56})$.

The band at $(738) \text{ cm}^{-1}$ refer to the (C-S) vibration band and the band at $(1367) \text{ cm}^{-1}$ refers to the (C-O) band vibration.

A- Iron (III) Complex Lig4 Fe

The spectrum of complex $[\text{Fe}(\text{Lig4})_2(\text{H}_2\text{O})_2]_2(\text{SO}_4)_3 \cdot 6\text{EtOH}$, Fig(3-18), Table (3-6), show that the azomethine stretching band was shifted to lower frequency and appeared at $(1615) \text{ cm}^{-1}$, and the $\nu (\text{C-O})$ vibration was shifted to lower frequency and appeared at $(1254) \text{ cm}^{-1}$.

The broad band at $(3346) \text{ cm}^{-1}$ was assigned to the $\nu (\text{O-H})^{(54)}$, The weak band which appeared at $(583) \text{ cm}^{-1}$ refers to the $\nu (\text{Fe-N})$ band $(^{55})$. The $\nu(\text{C-H})$ aliphatic was shifted to lower frequency which appeared at $(2936) \text{ cm}^{-1}$.

Another bands were appeared at $(3476) \text{ cm}^{-1}$ and $(632) \text{ cm}^{-1}$ referring to the presence of both coordination and lattice H_2O molecules respectively

B- Cobalt (II) Complex Lig4 Co

On comparison of the cobalt (II) complex $[\text{Co}(\text{Lig4})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2 \cdot \text{EtOH}$ spectrum Fig (3-19), Table (3-6), with that of the free ligand, the following changes was observed: first, the $\nu(\text{C}=\text{N})$ band was shifted to a lower frequency by $(6) \text{ cm}^{-1}$ and appeared at $(1614) \text{ cm}^{-1}$, and second the shifting of the $\nu(\text{C}-\text{H})$ to a higher frequency.

The $\nu(\text{C}-\text{O})$ band was also shifted to a higher frequency by $(13) \text{ cm}^{-1}$ and appeared at $(1380) \text{ cm}^{-1}$, the $\nu(\text{O}-\text{H})$ band was appeared at $(3349) \text{ cm}^{-1}$.

A new weak band was appeared at $(539) \text{ cm}^{-1}$ referring to the $\nu(\text{Co}-\text{N})$ vibration ⁽⁵⁵⁾.

Finally a new band appeared at $(3754) \text{ cm}^{-1}$ indicating the presence of ethanol molecules in the structure of the complex.

C- Manganese (II) Complex Lig4 Mn

On comparison of the manganese(II) complex $[\text{Mn}(\text{Lig4})_2(\text{H}_2\text{O})_2](\text{OH})_2 \cdot 3\text{EtOH}$ spectrum Fig(3-20), Table (3-6), with that of the free ligand, the following changes were observed: first, the $\nu(\text{C}=\text{N})$ band was shifted to a lower frequency by $(12) \text{ cm}^{-1}$.

The $\nu(\text{C}-\text{O})$ band was also shifted to a lower frequency by $(9) \text{ cm}^{-1}$, the $\nu(\text{O}-\text{H})$ band was appeared at $(3347) \text{ cm}^{-1}$.

A new weak band was appeared at $(578) \text{ cm}^{-1}$ referring to the $\nu(\text{Mn}-\text{N})$ vibration ⁽⁵⁵⁾.

3-3-5 The FT-IR spectra of Lig5 and their metal complexes

The FT-IR spectrum of Lig5 shows the same behavior of L_1 , Fig (3-7), which contain the same group (azomethine group) that is used to characterize the spectra of the complexes.

This ligand act as a bidentate, through both nitrogen (azomethine – nitrogen and ring nitrogen). The nitrogen ring band appeared of (1621)^(53, 57).

The band which appeared at (1575,1521) cm^{-1} refers to ν (C=C) of the aromatic ring⁽⁵⁴⁾, and the band at (3076) cm^{-1} refers to the ν (C-H) of aromatic, the band at (2931,2885) cm^{-1} refers to the ν (C-H) aliphatic and the band at (748) cm^{-1} refers to the ν (C-S) and the band at (1232) cm^{-1} refers to ν (C-N)^(26,37,58).

A- Iron (III) Complex Lig5 Fe

The spectrum of [Fe (Lig5)(H₂O)₂(SO₄)₂ (SO₄) complex, Fig (3-21), Table (3-6), shows the shifting of azomethine band to lower frequency by (11) cm^{-1} indicating the participation of azomethine nitrogen in the interaction with iron(III) ion.

Another difference appeared which was the shifting of the ν (C-H) aliphatic band to lower frequency and appeared at (2916-2866) cm^{-1} regions.

A new band appeared at (594) cm^{-1} referring to the ν (Fe-N) band⁽⁵⁵⁾. A broad band appeared at (3455) cm^{-1} indicating the presence of water molecules out of the coordination sphere.

B- Cobalt (II) Complex Lig5 Co

The molecular formula of Co (II) complex [Co₂(Lig5)₂(NO₃)₂ (H₂O)₄](NO₃)₂.9H₂O includes nine water molecules, two of them may be coordinated to metal ion and the other six were considered to be lattice water.

The presence of this large number of water molecules is expected due to high tendency of Co(II) to bind to water through a strong bond

which effected the FT.IR spectrum of the complex, so the band at (3095 and 651) cm^{-1} refer to the presence of both coordination and lattice H_2O molecules respectively.

The spectrum of Co(II) ion, Fig(3-22), shows the ν (C=N) band to be shifted to lower frequency by (11) cm^{-1} indicating the interaction of metal ion with the azomethine nitrogen ^(53,57).

The weak band appeared at (565) cm^{-1} refer to the (Co-N) band frequency ^(56,61).

3-3-6 The FT-IR spectra of Lig6 and their metal complexes

The FT.IR spectrum of Lig6, fig(3-8), show the same behavior as the other ligand, which contain the same group (azomethine group) that used to characterize the spectra of this complexes.

The azomethine group (C=N-) absorption was at (1625) cm^{-1} . The bands appearing at (1577, 1458, 1396) cm^{-1} refers to the ν (C=C) aromatic ring, and the band at (3081) cm^{-1} refers to the ν (C-H) of benzene, the band (2927-2893) cm^{-1} refers to the ν (C-H) of aliphatic ring ⁽⁵⁴⁾.

The band appeared at (748) cm^{-1} refers to the ν (C-S) ^(63, 65, 66). The band of ν (C-Br) appeared at (783) cm^{-1} ⁽⁵⁹⁾.

In comparison, the IR spectra of Lig6 and its metal complexes indicated that the ligand is principally coordinated to the metal ion, through both (azomethine –nitrogen, and the ring nitrogen), thus acting as a bidentate.

A- Iron (III) Complex Lig6 Fe

The spectrum of the iron complex $[\text{Fe}_2(\text{Lig6})(\text{OH})_2(\text{H}_2\text{O})_4](\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$, Fig (3-23), showed similar behavior with no much difference compared to the ligand.

The FT.IR spectrum of azomethine band was shifted by $(6) \text{ cm}^{-1}$. The ν (C-H) band was shifted to $(2907-2866) \text{ cm}^{-1}$. A new low band was appeared in low frequency region at $(592) \text{ cm}^{-1}$ this was assigned to (Fe-N) vibration ^(62,63).

The broad band found at $(3434) \text{ cm}^{-1}$ refers to the presence of water molecules out of the coordination sphere for complex ⁽⁵⁴⁾.

Finally the band at $(3434 \text{ and } 633) \text{ cm}^{-1}$ refer to the presence both coordination and lattice H_2O molecules respectively.

b- Cobalt (II) Complex Lig6 Co

The spectrum of this complex $[\text{Co}(\text{Lig6})(\text{NO}_3)(\text{H}_2\text{O})_2](\text{NO}_3) \cdot 2\text{H}_2\text{O}$, Fig (3-24), Table (3-6), show the shifting of ν (C=N) band to lower frequency by $(7) \text{ cm}^{-1}$ indicating the participation of azomethine nitrogen in the interaction with cobalt(II) ion.

The band of ν (C-H) of the aliphatic group shifted to lower frequency and appeared at $(2917-2879) \text{ cm}^{-1}$.

The presence of new weak band observed at $(595) \text{ cm}^{-1}$ was assigned to ν (Co-N)⁽⁶⁷⁾, the band found at $(3321) \text{ cm}^{-1}$ refers to the presence of water molecules out of the coordination sphere for H_2O ⁽⁵⁴⁾.

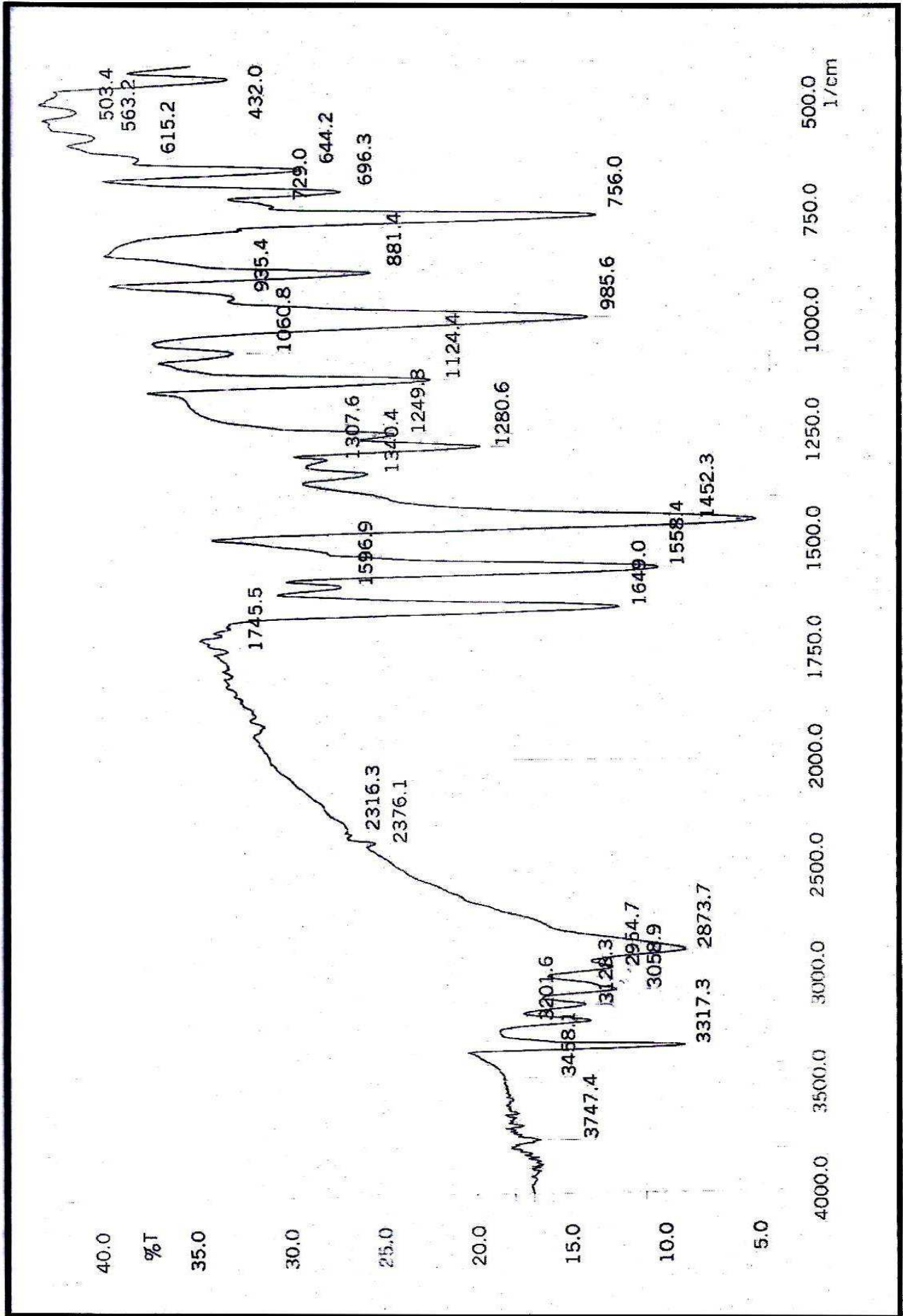


Figure (3-1): FT-IR spectrum of 2-MBT

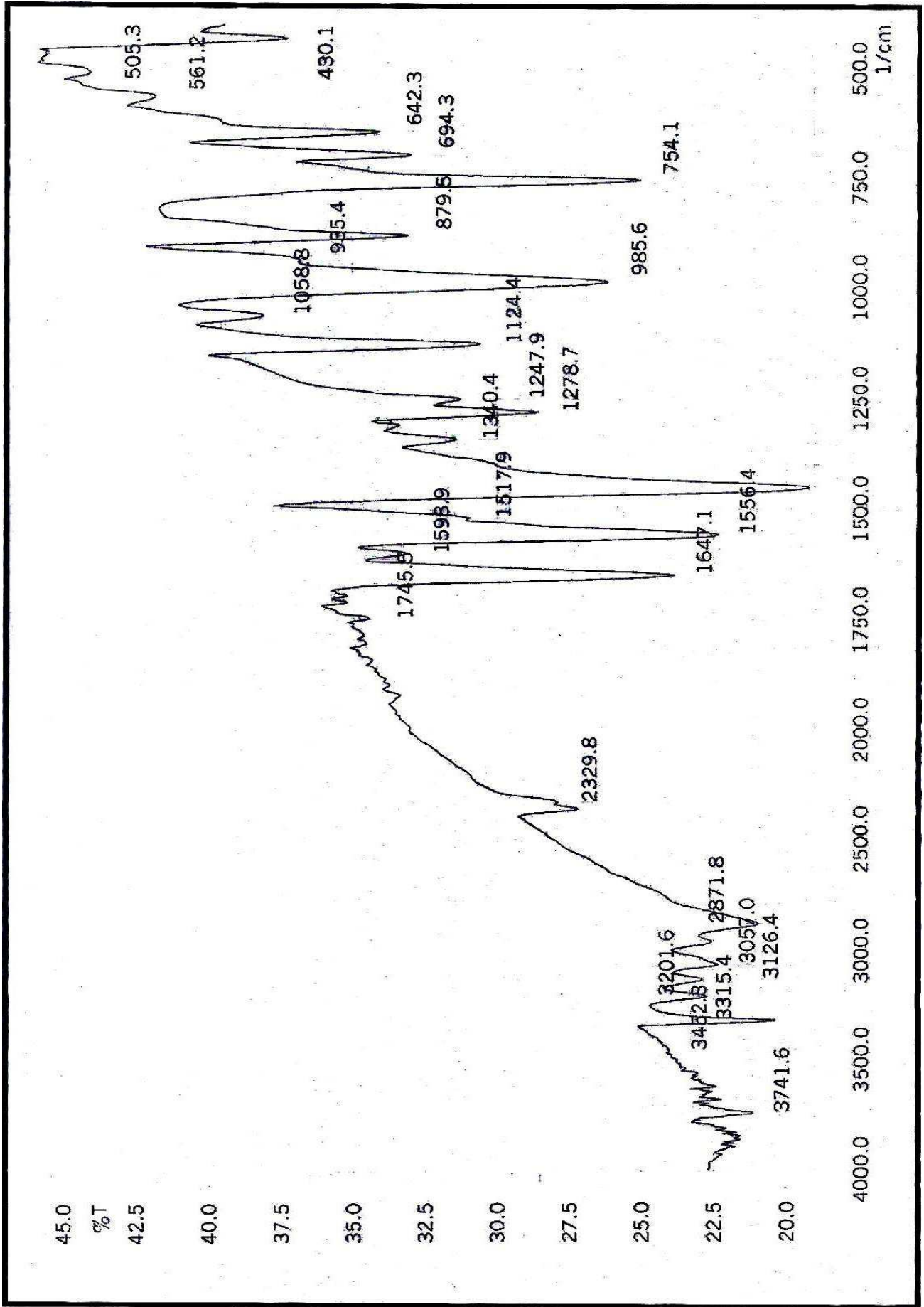
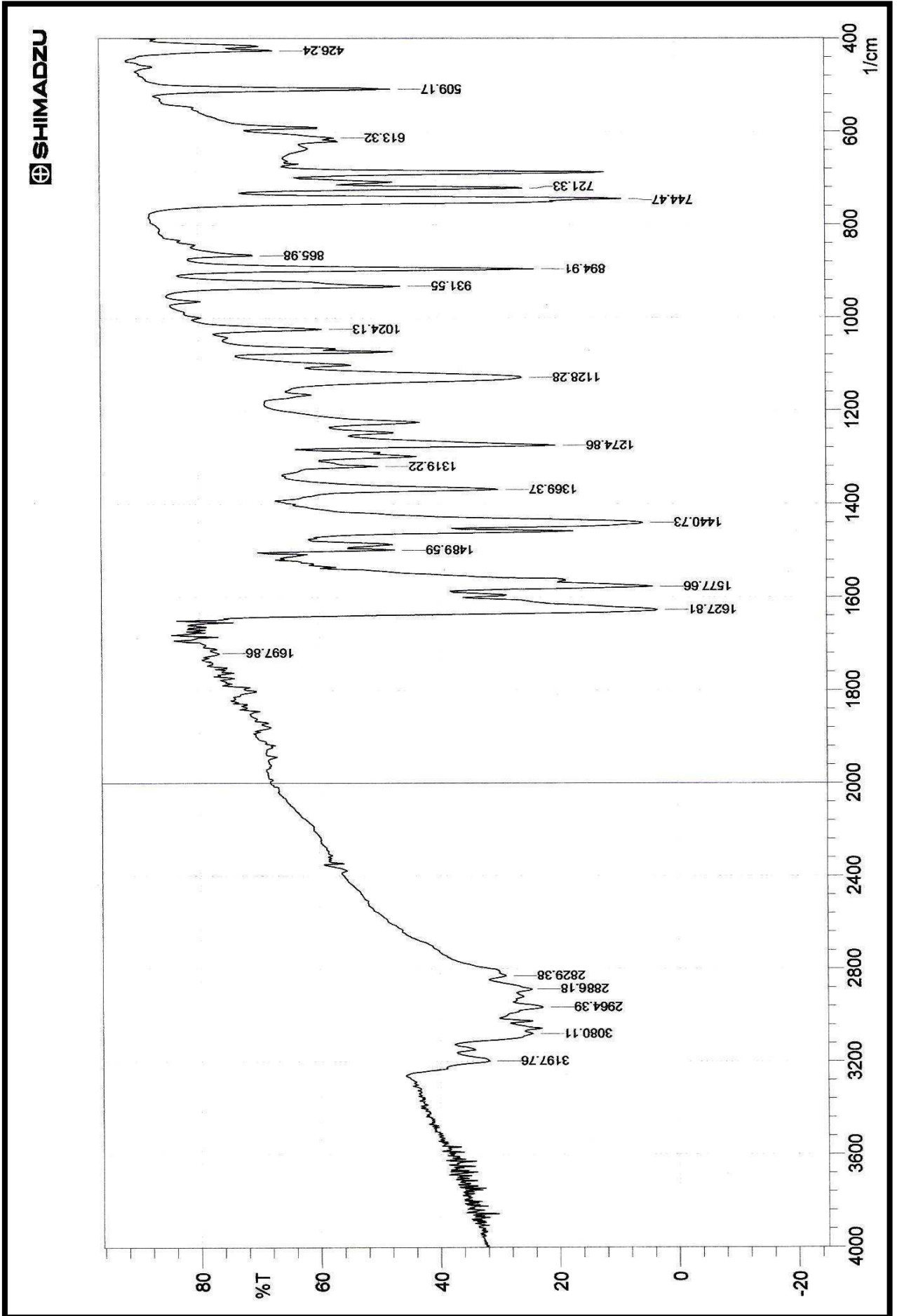
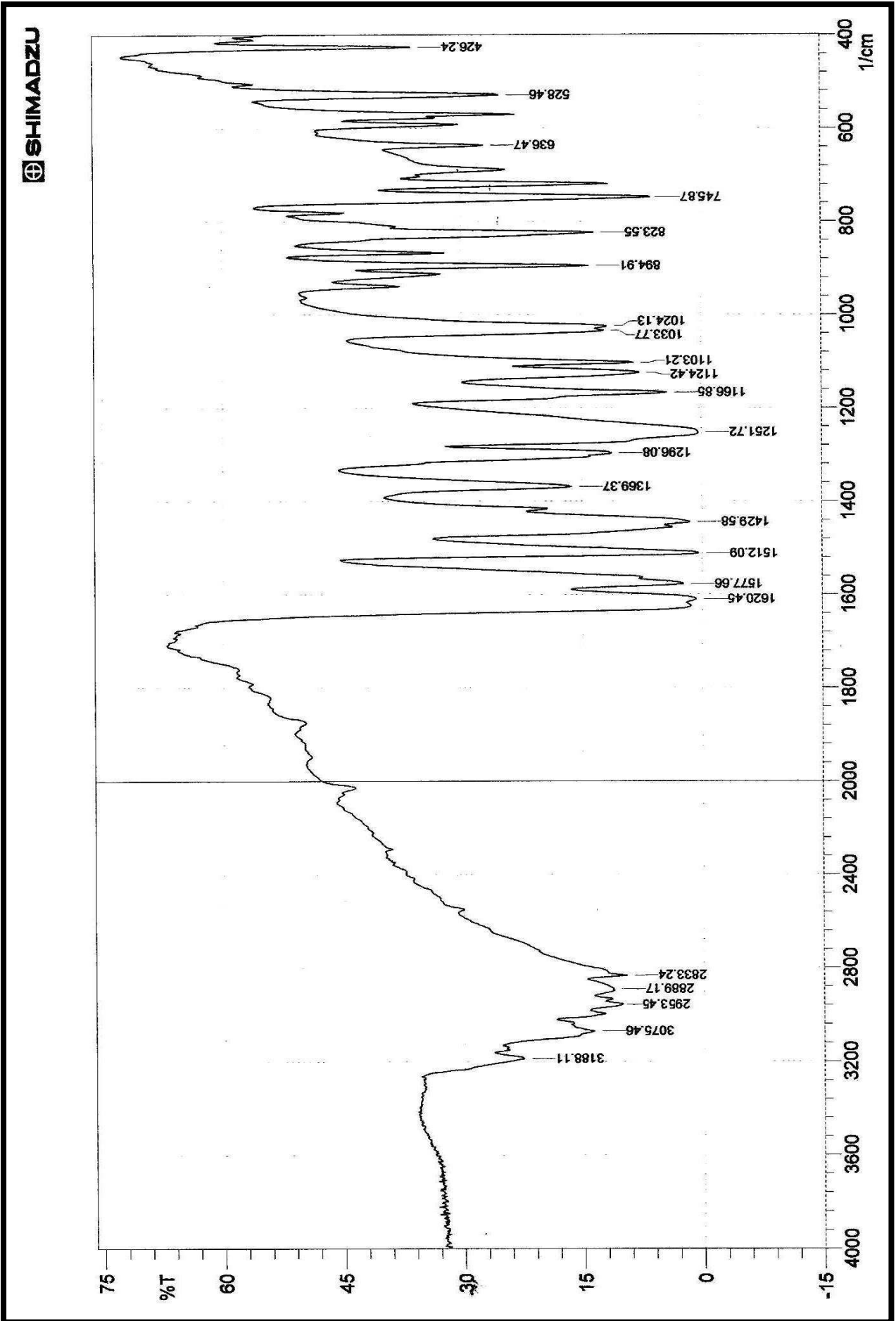


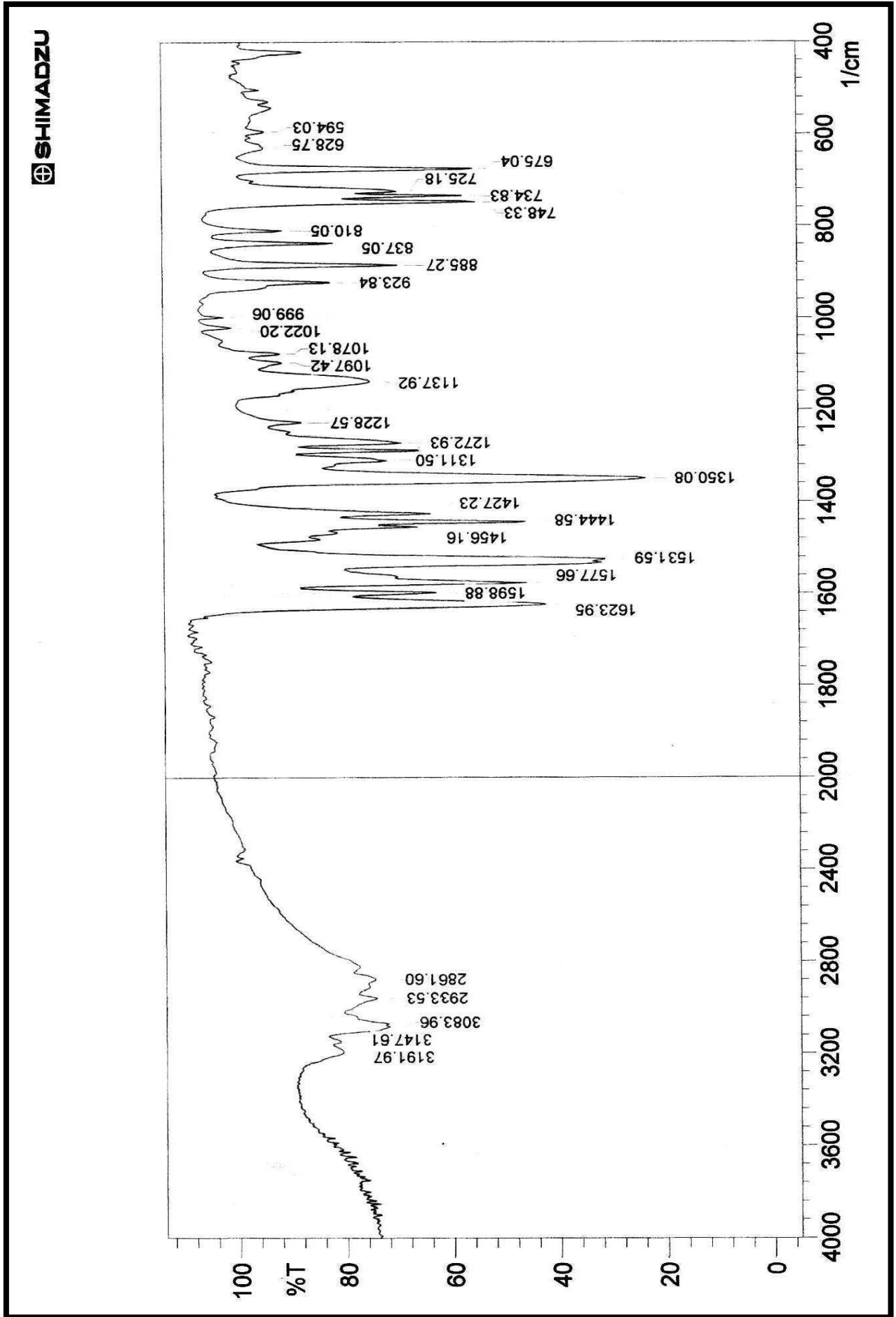
Figure (3-2): FT-IR spectrum of hydrazone



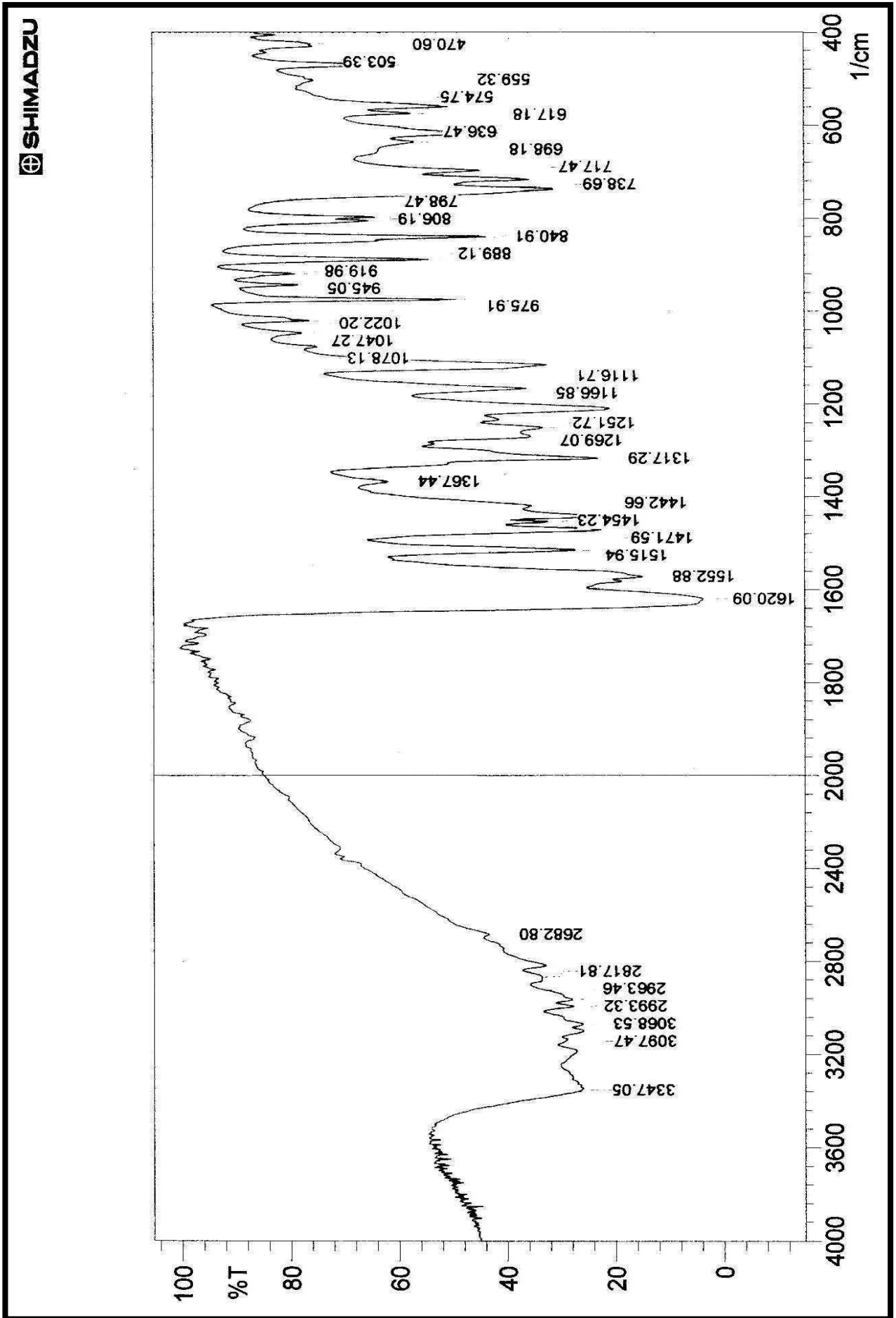
Fig(3-3) FT-IR Spectra of Lig1



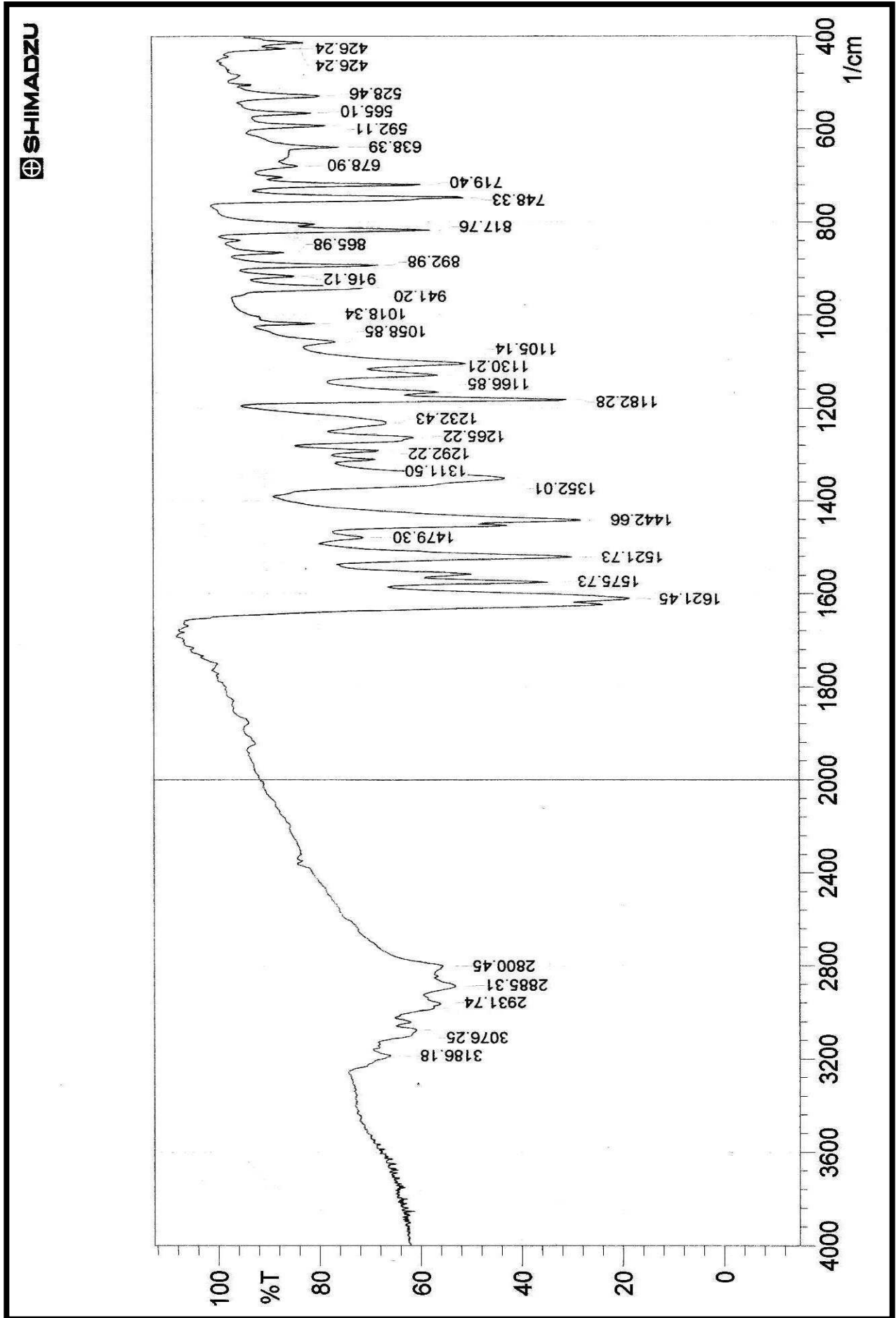
Fig(3-4) FT-IR Spectra of Lig2



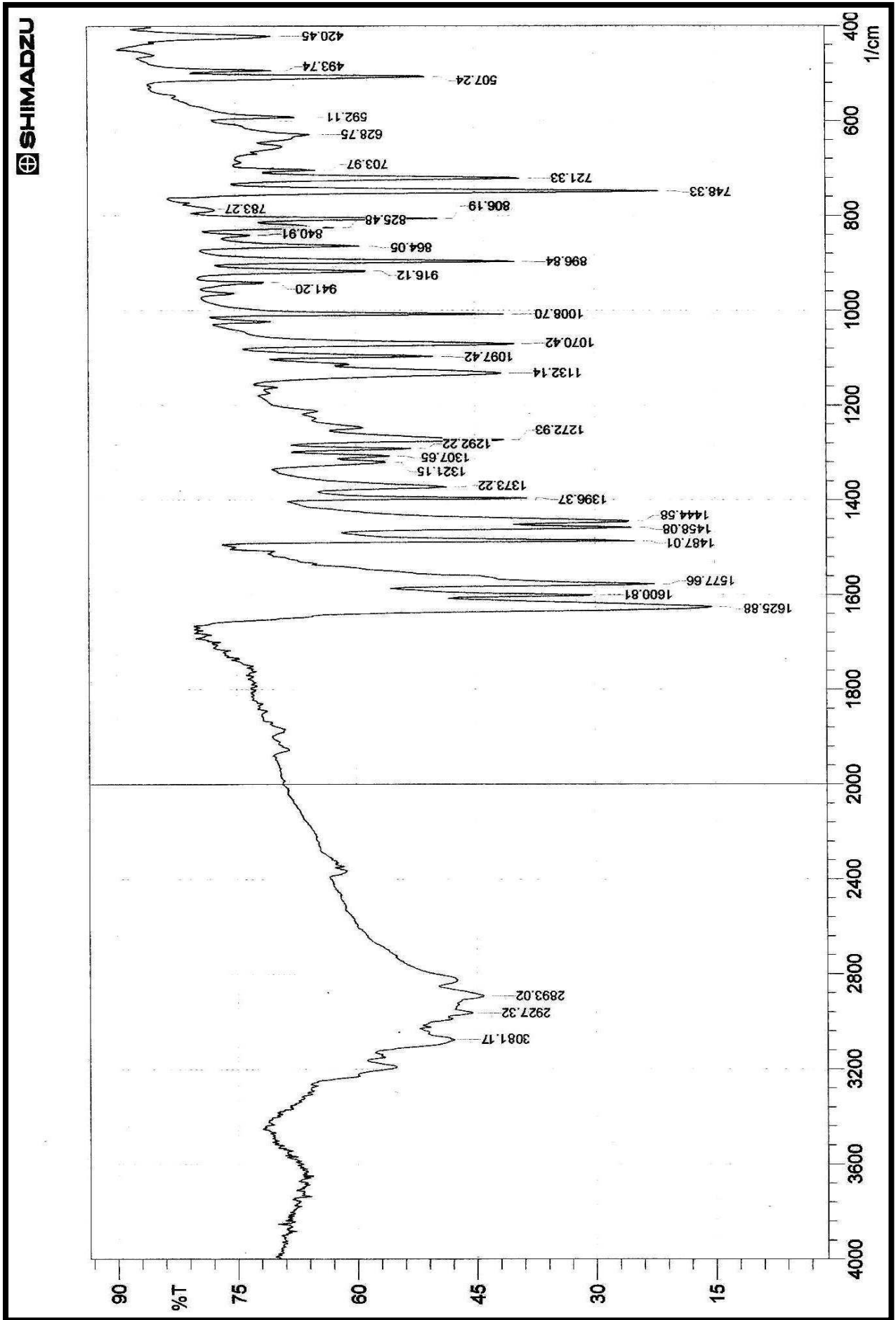
Fig(3-5) FT-IR Spectra of Lig3



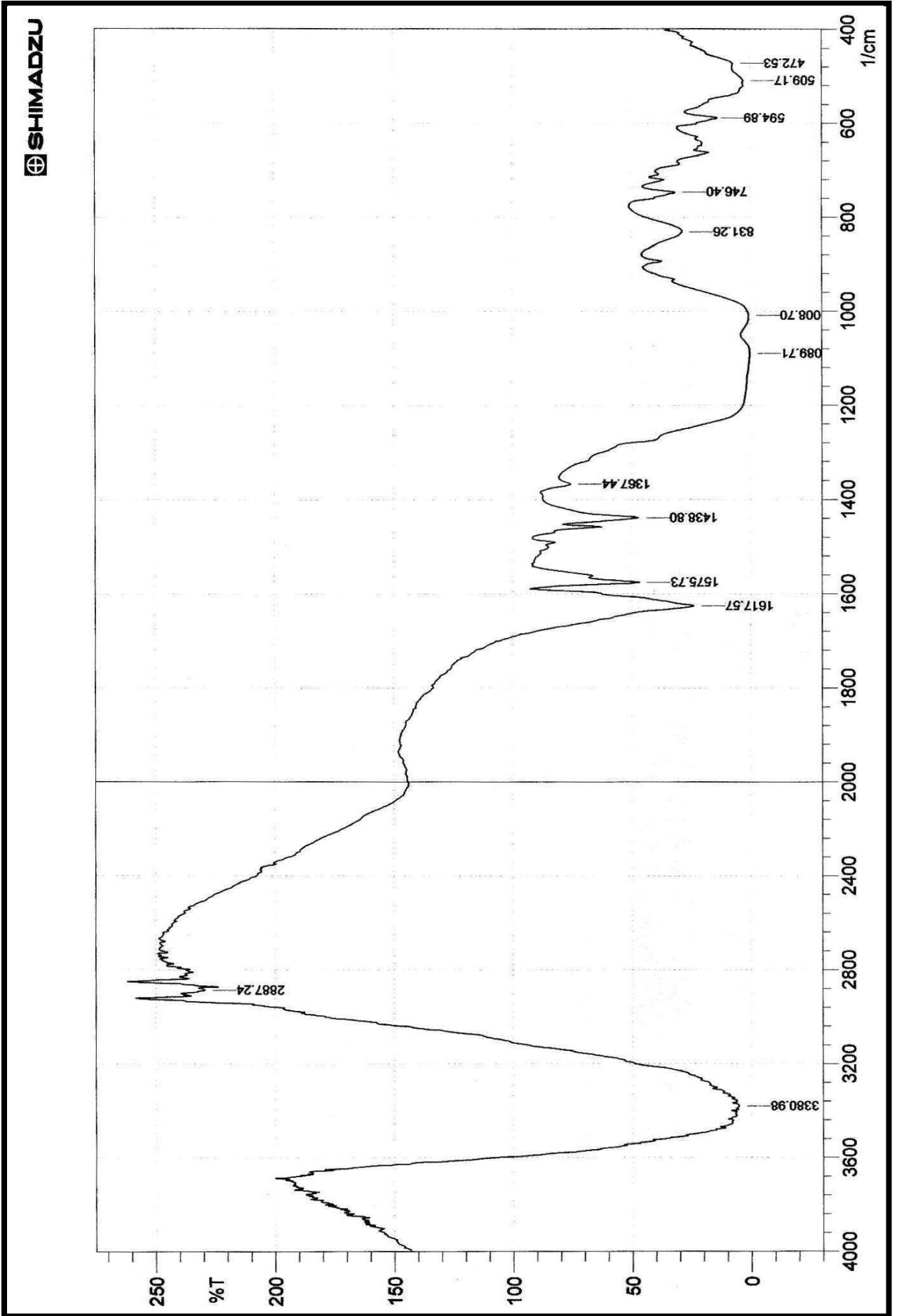
Fig(3-6) FT-IR Spectra of Lig4



Fig(3-7) FT-IR Spectra of Lig5

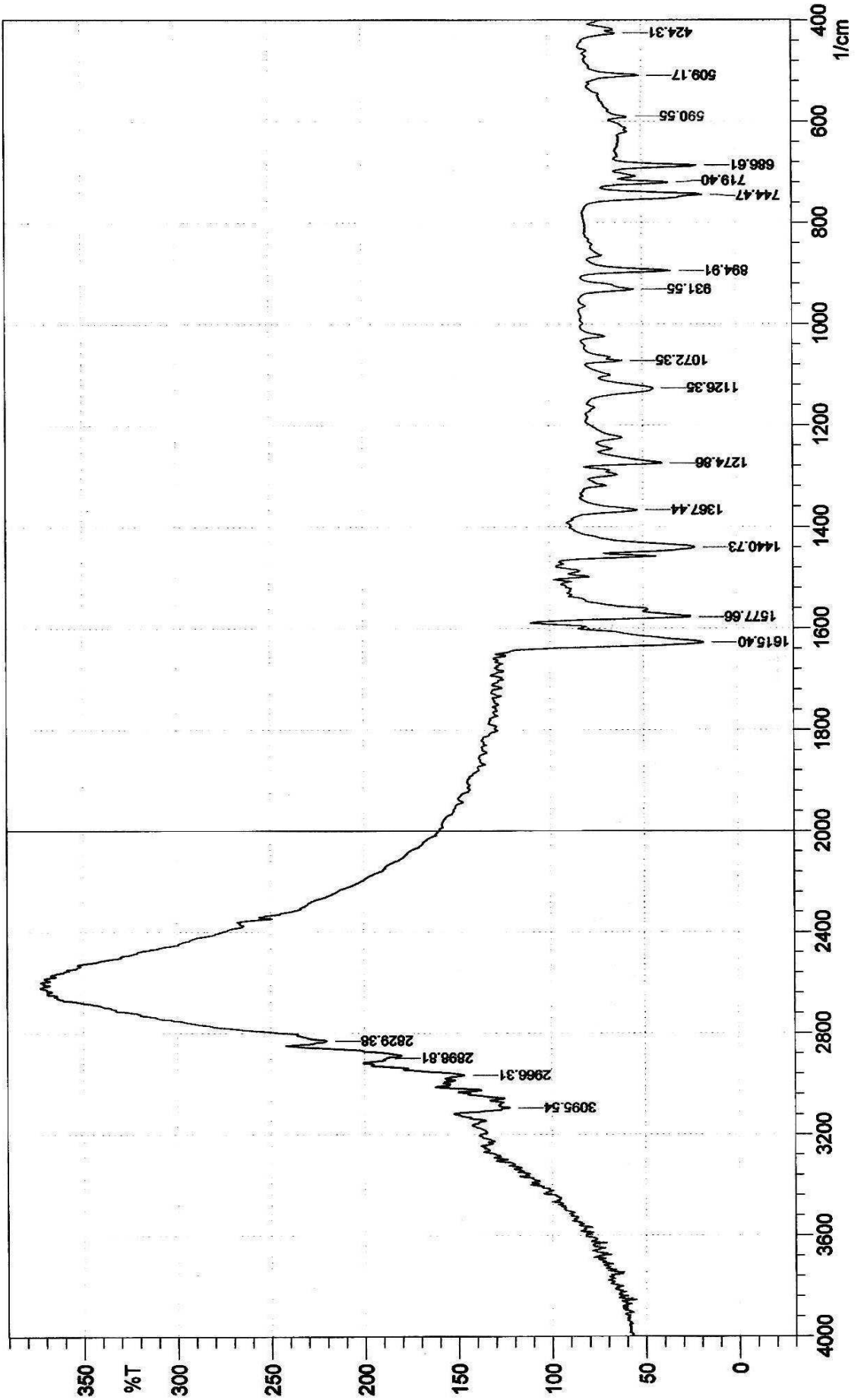


Fig(3-8) FT-IR Spectra of Lig6

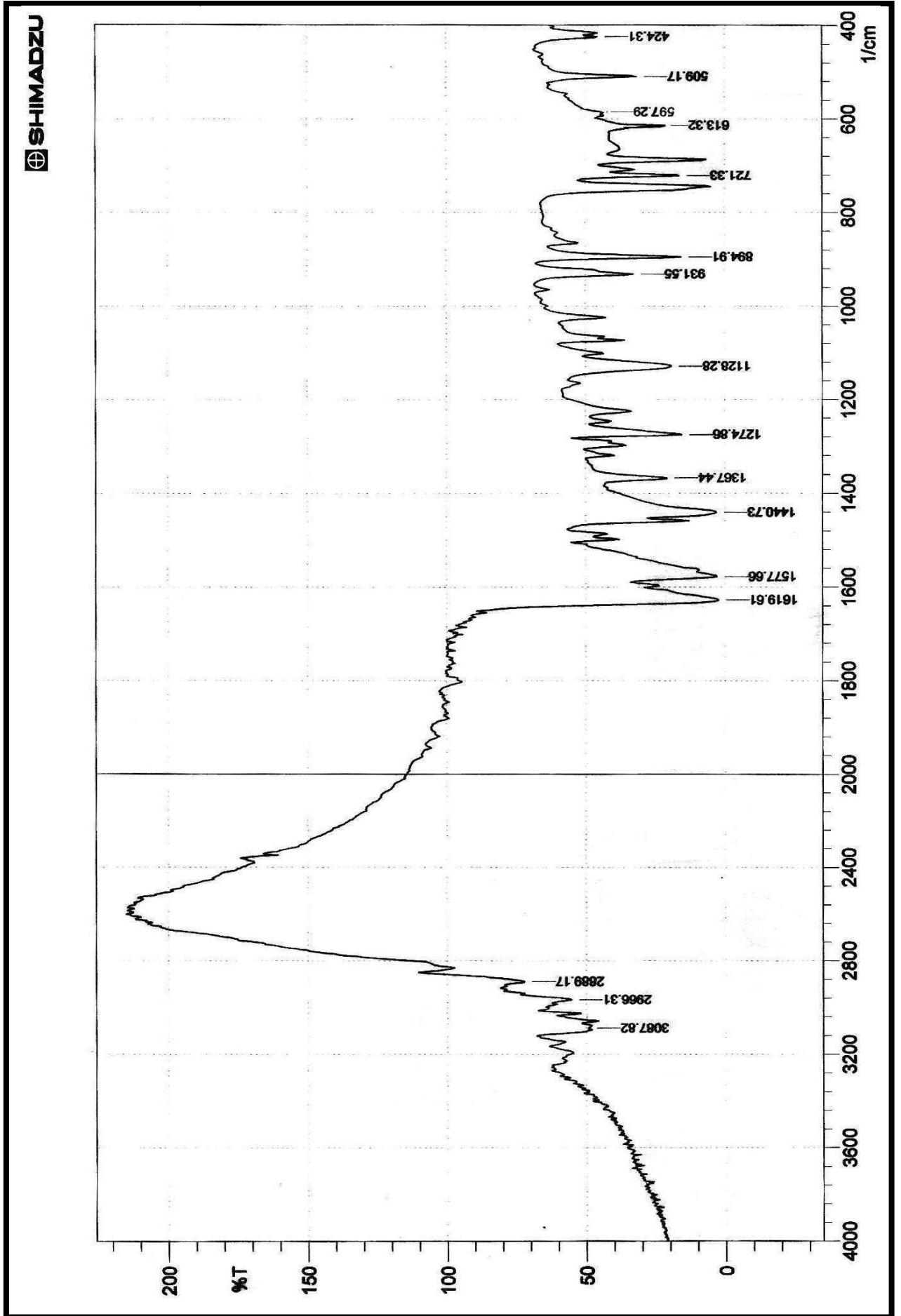


Fig(3-9) FT-IR Spectra of Lig1 Fe

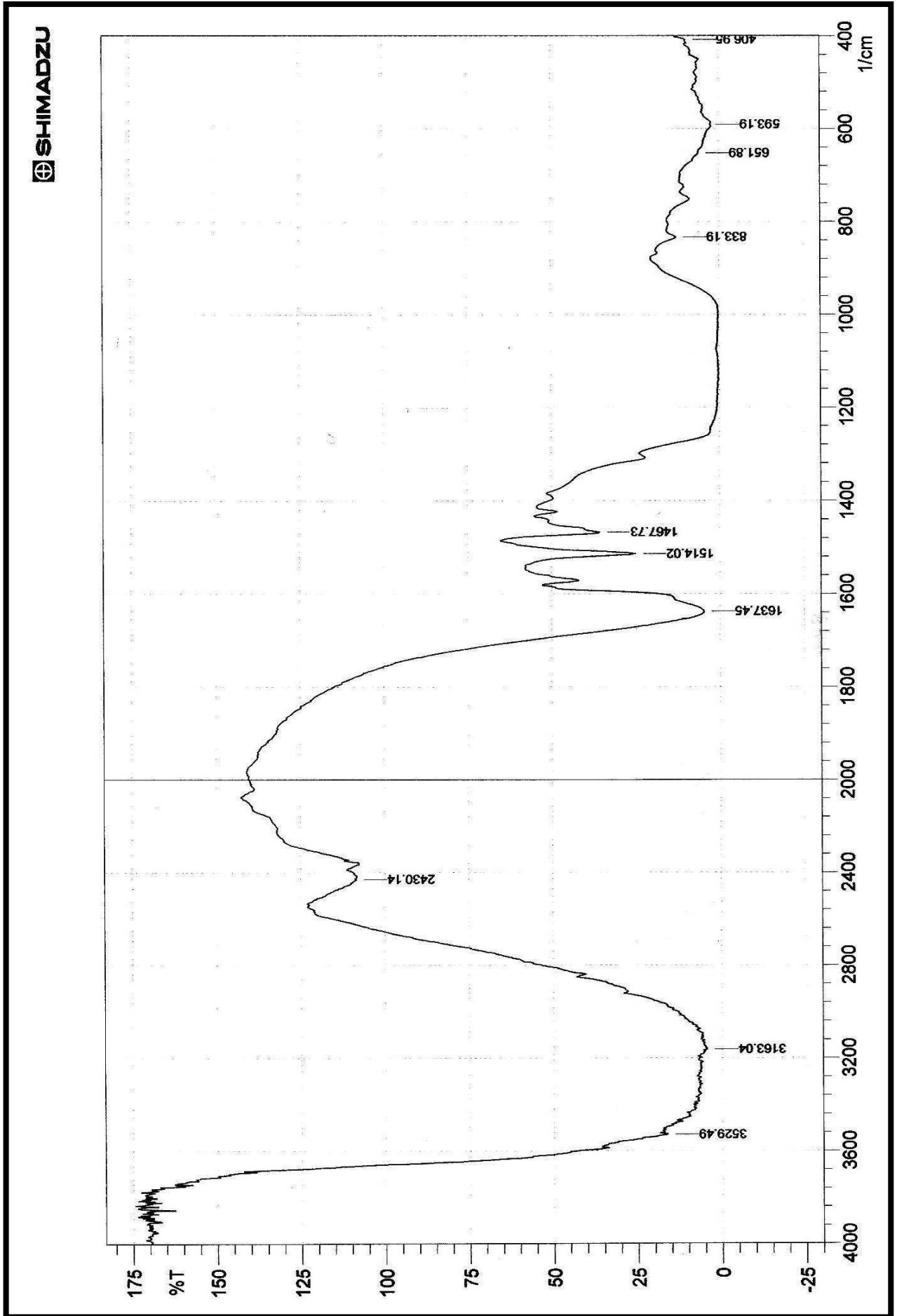
SHIMADZU



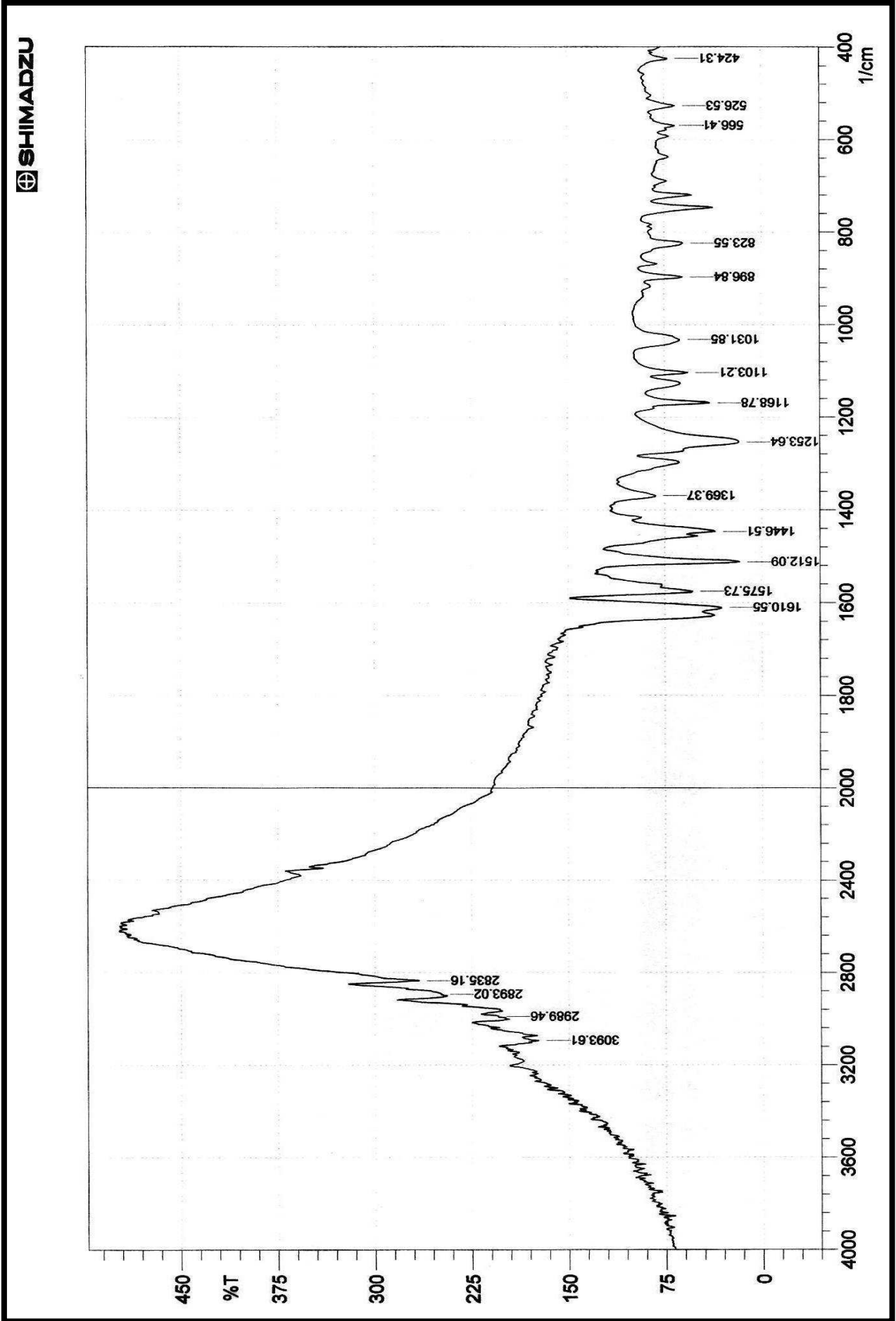
Fig(3-10) FT-IR Spectra of Lig1 Co



Fig(3-11) FT-IR Spectra of Lig1 Mn

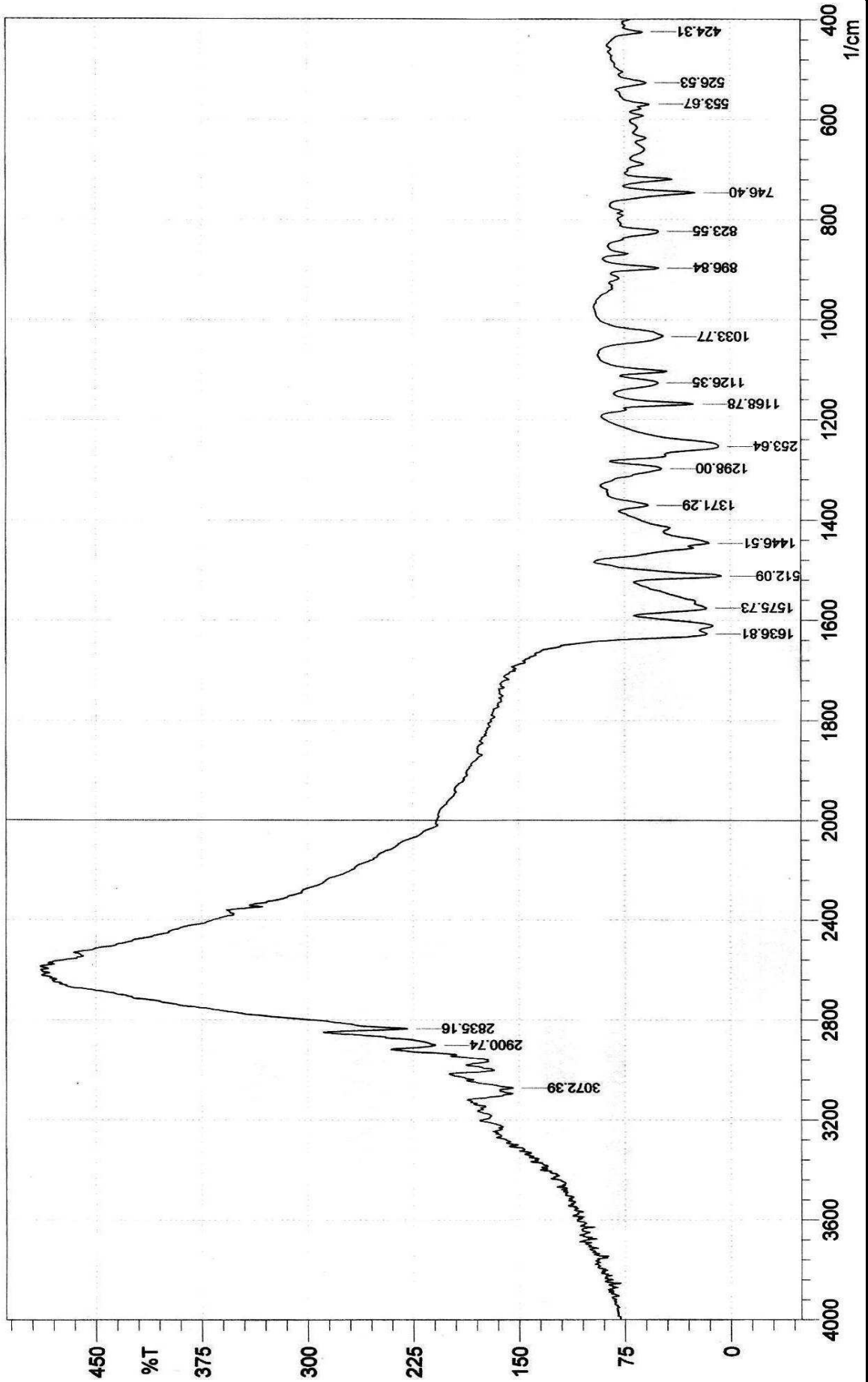


Fig(3-12) FT-IR Spectra of Lig2 Fe

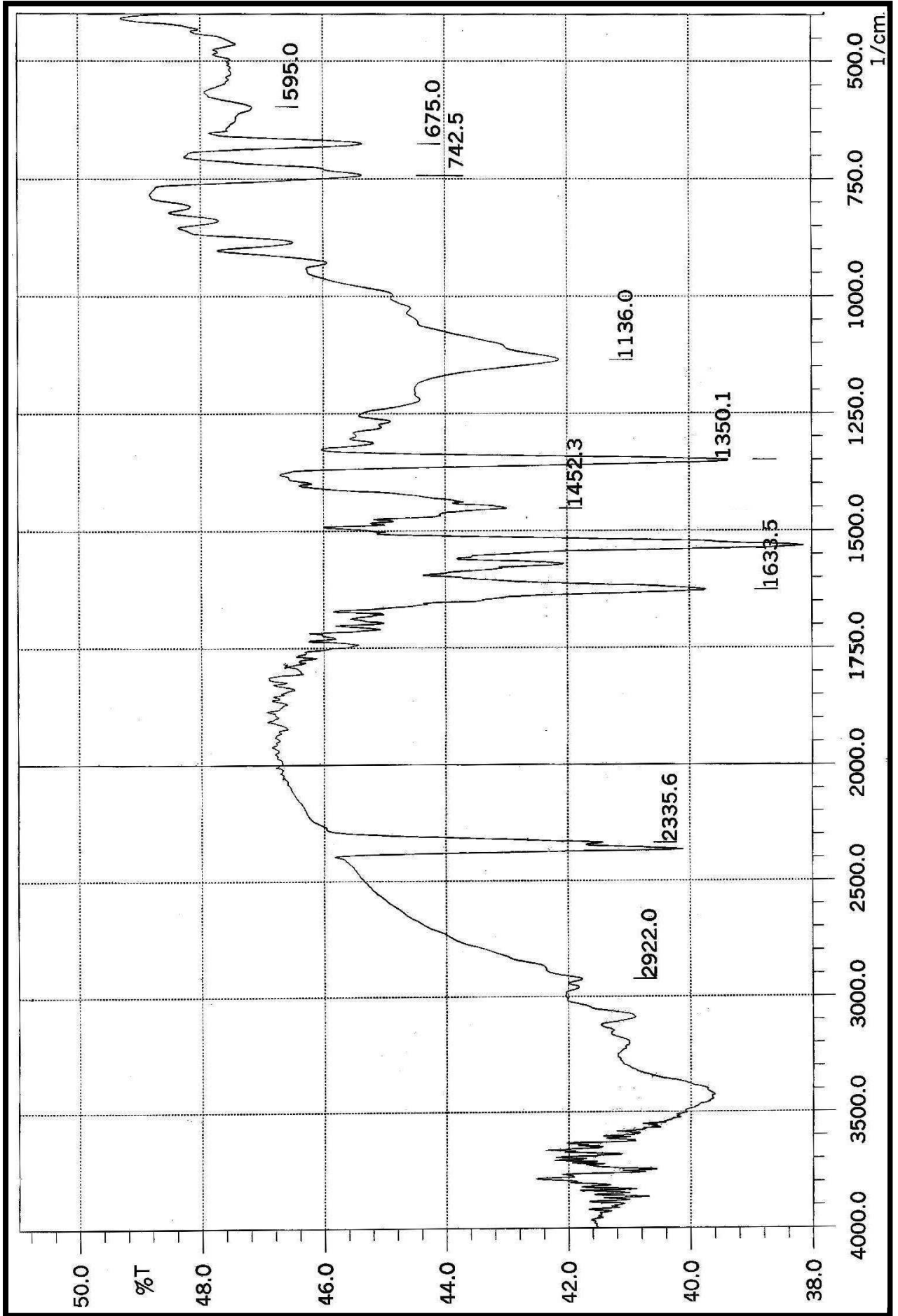


Fig(3-13) FT-IR Spectra of Lig2 Co

SHIMADZU

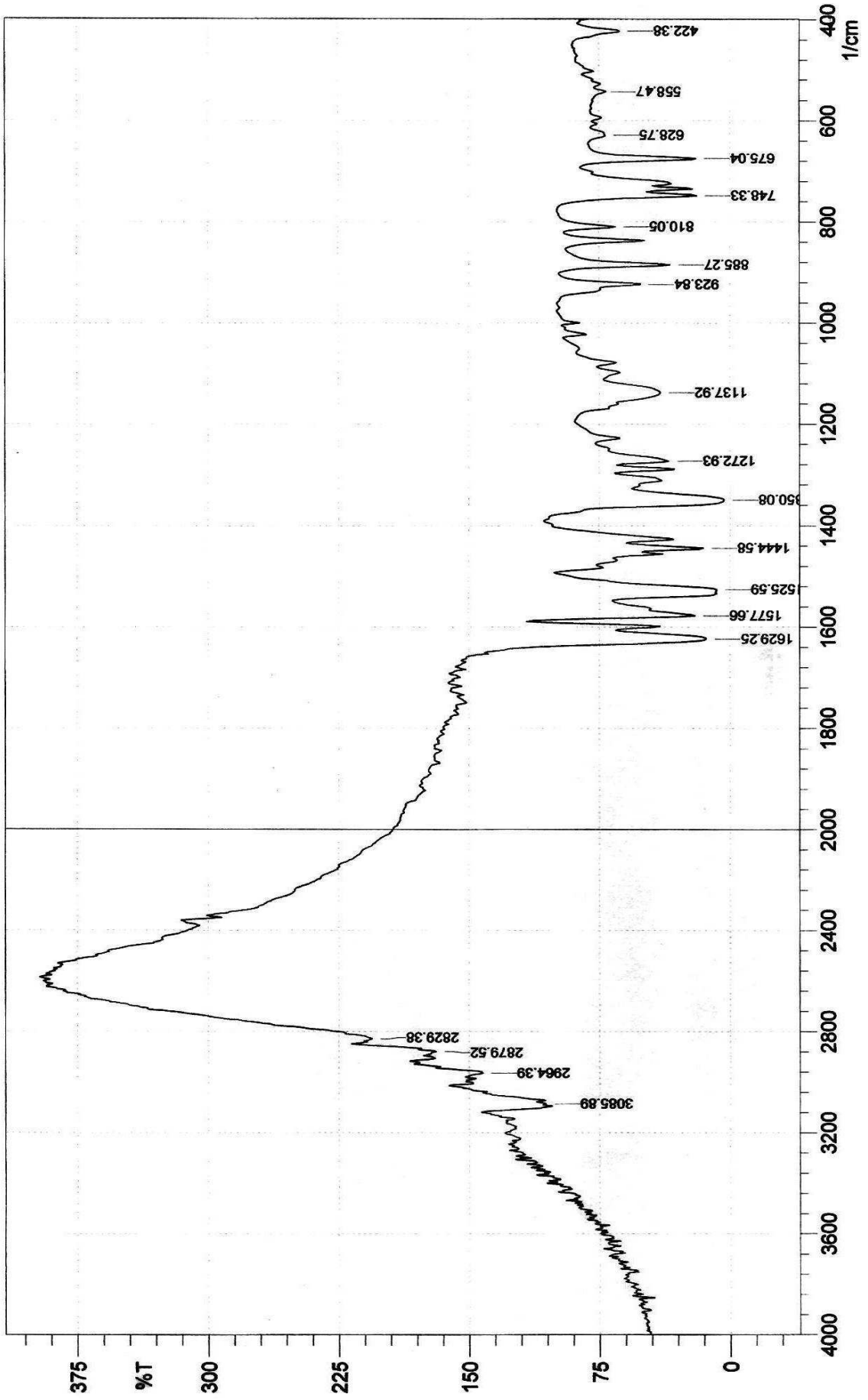


Fig(3-14) FT-IR Spectra of Lig2 Mn

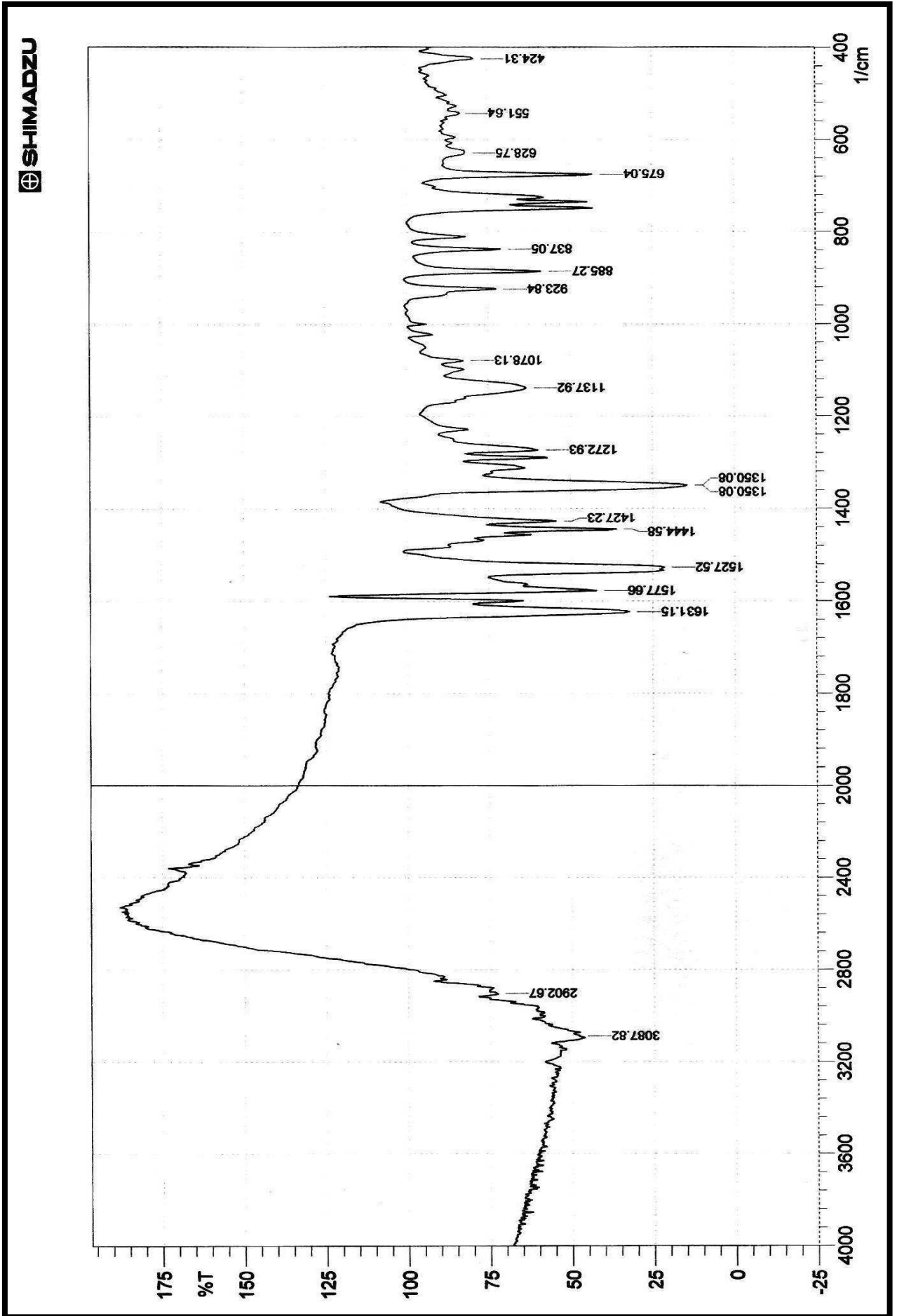


Fig(3-15) FT-IR Spectra of Lig3 Fe

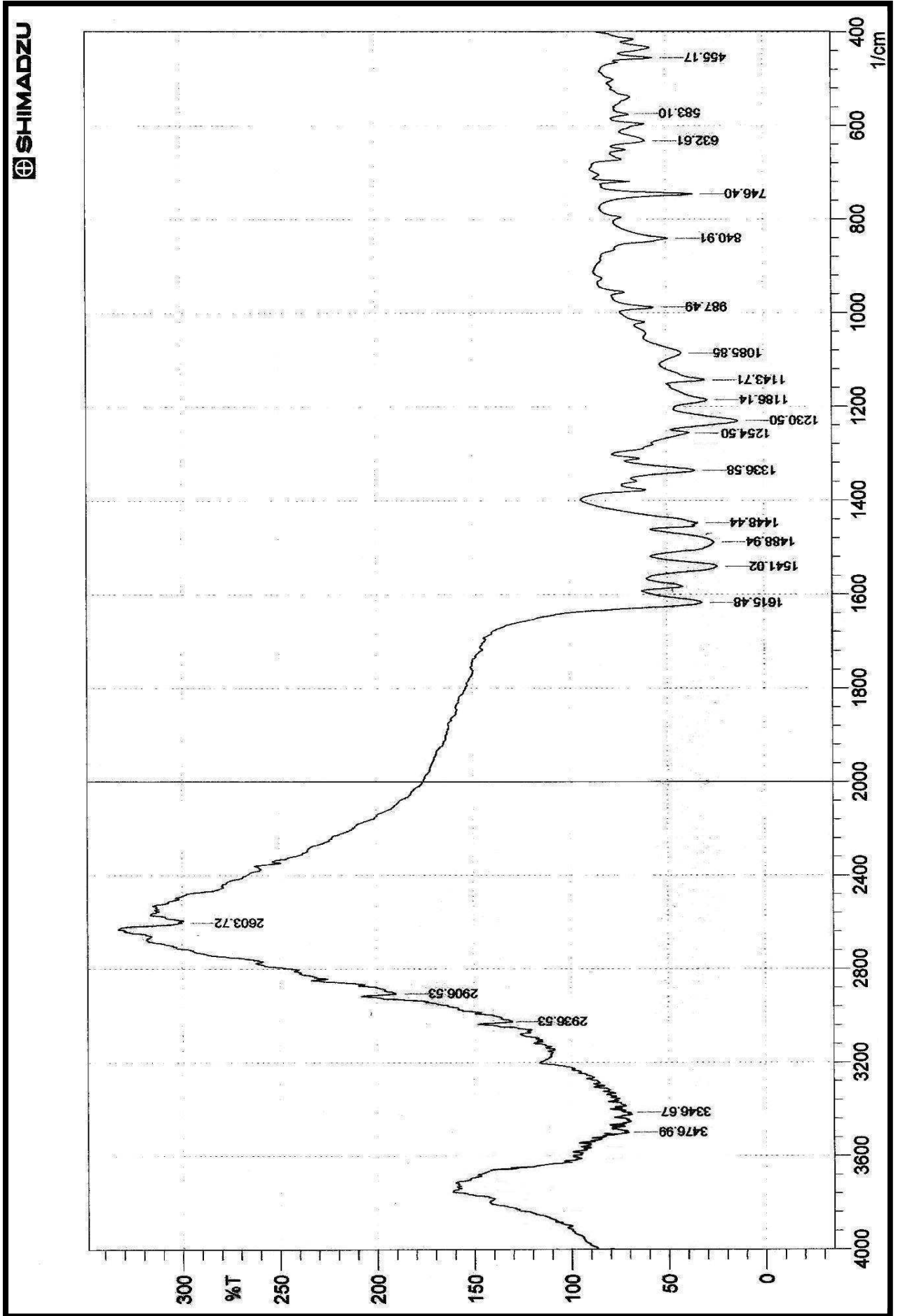
SHIMADZU



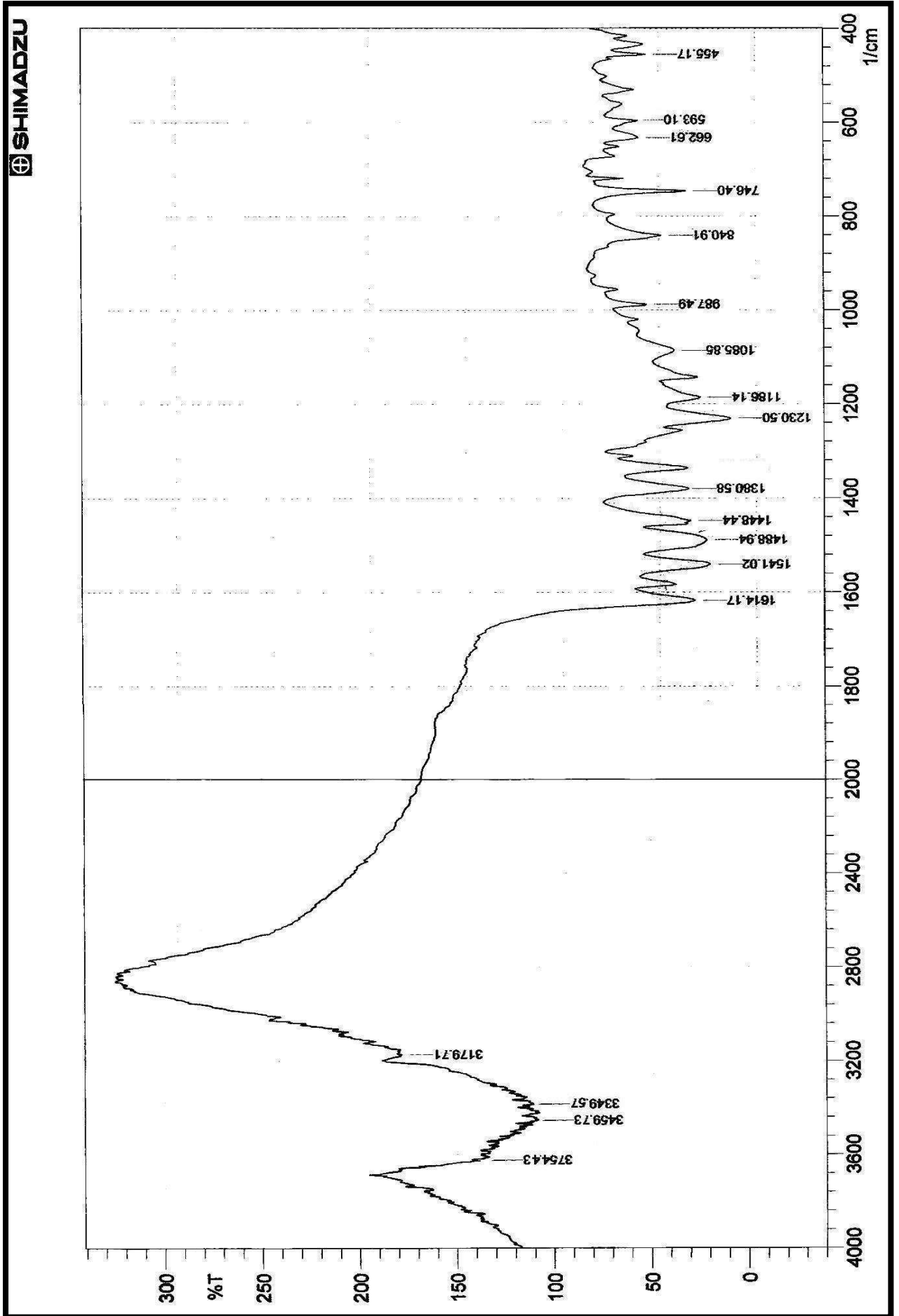
Fig(3-16) FT-IR Spectra of Lig3 Co



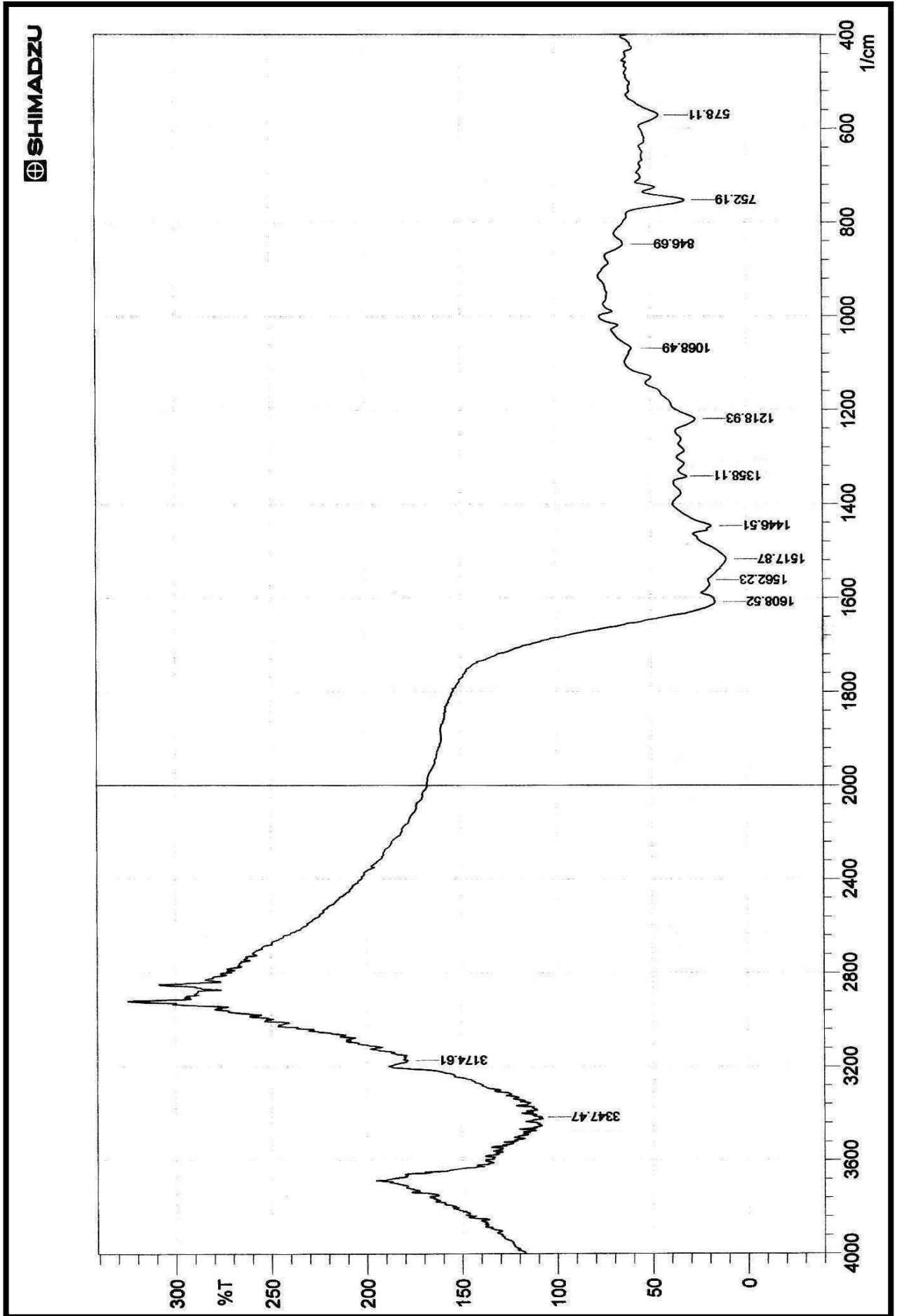
Fig(3-17) FT-IR Spectra of Lig3 Mn



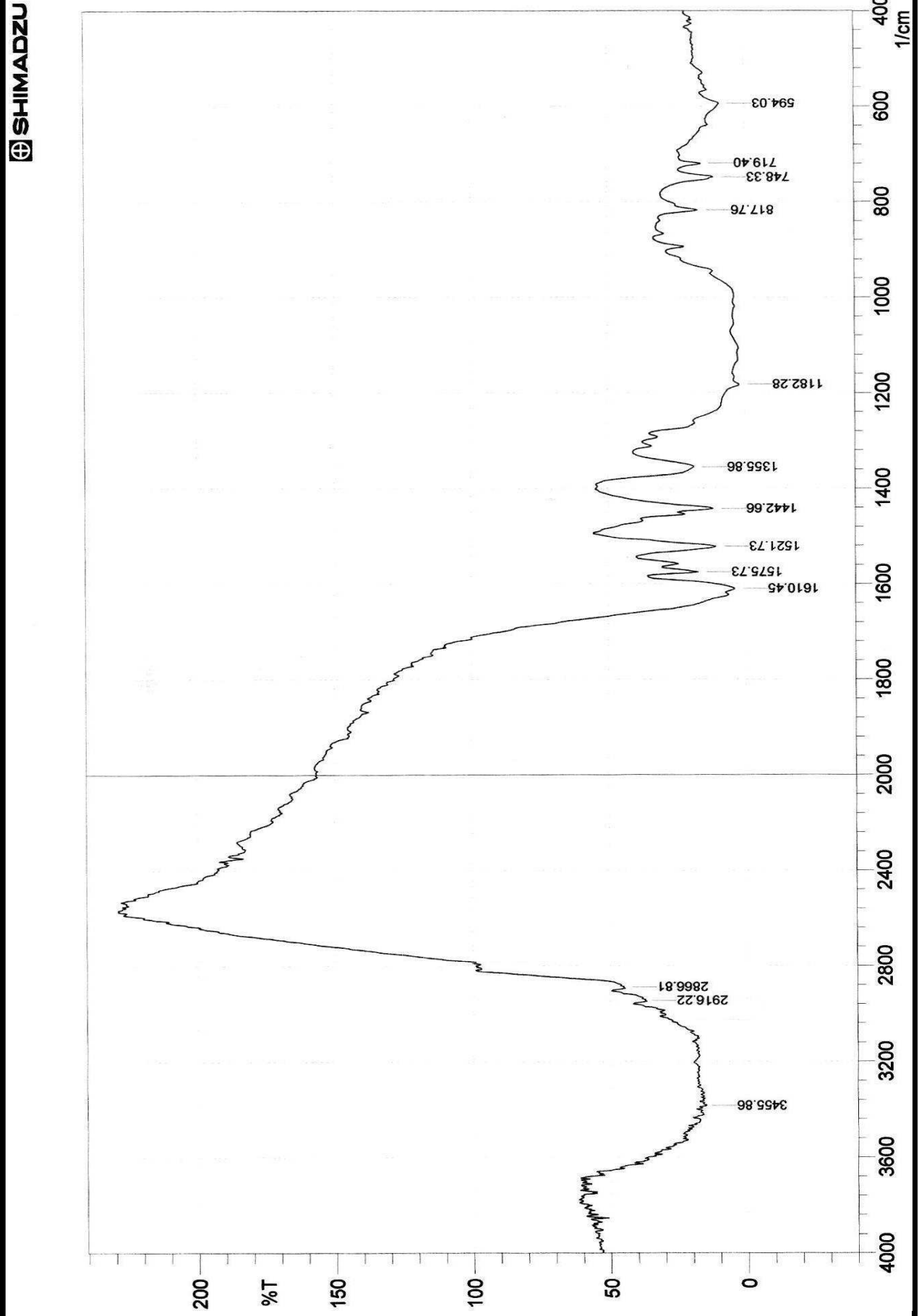
Fig(3-18) FT-IR Spectra of Lig4 Fe



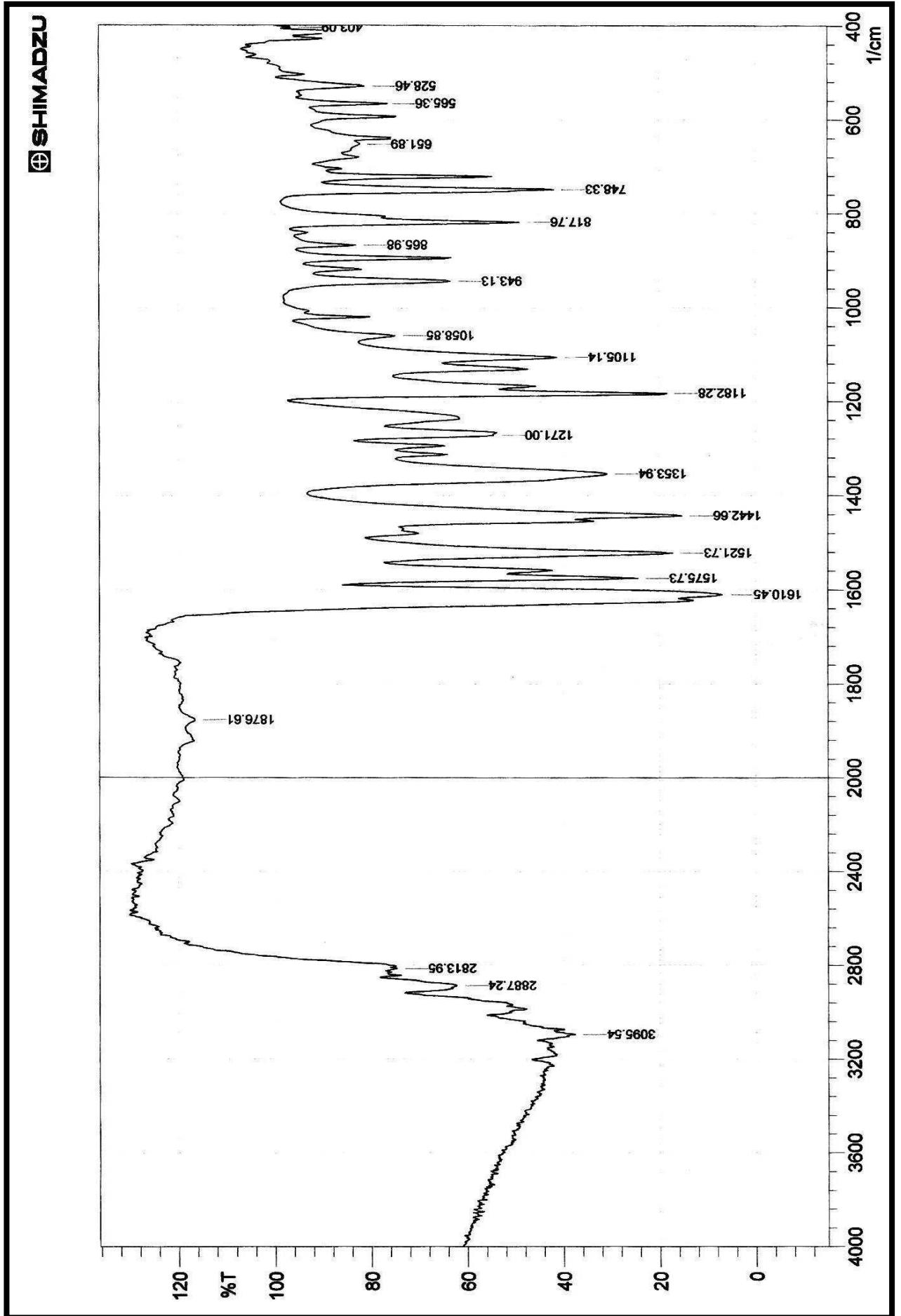
Fig(3-19) FT-IR Spectra of Lig4 Co



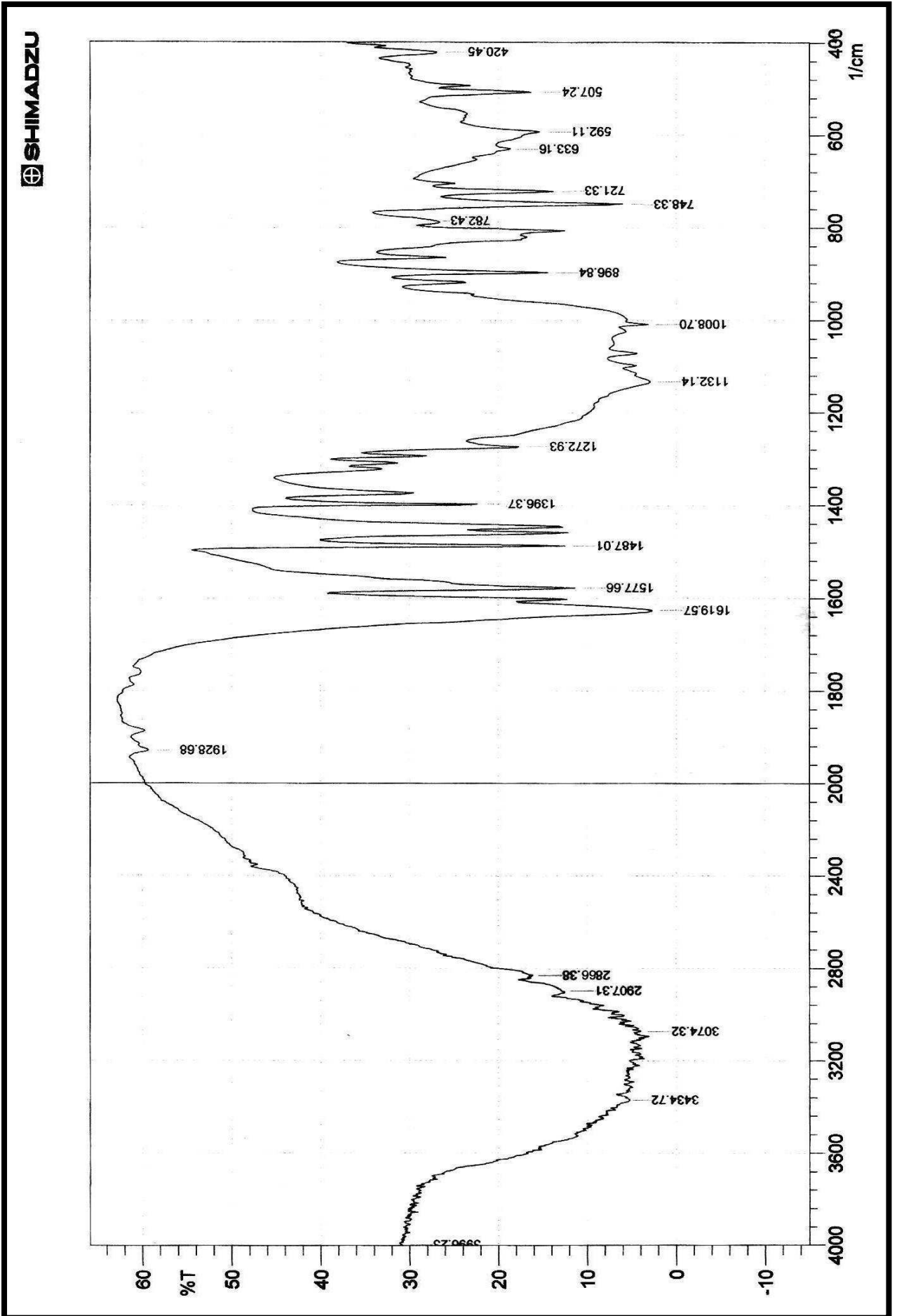
Fig(3-20) FT-IR Spectra of Lig4 Mn



Fig(3-21) FT-IR Spectra of Lig5 Fe

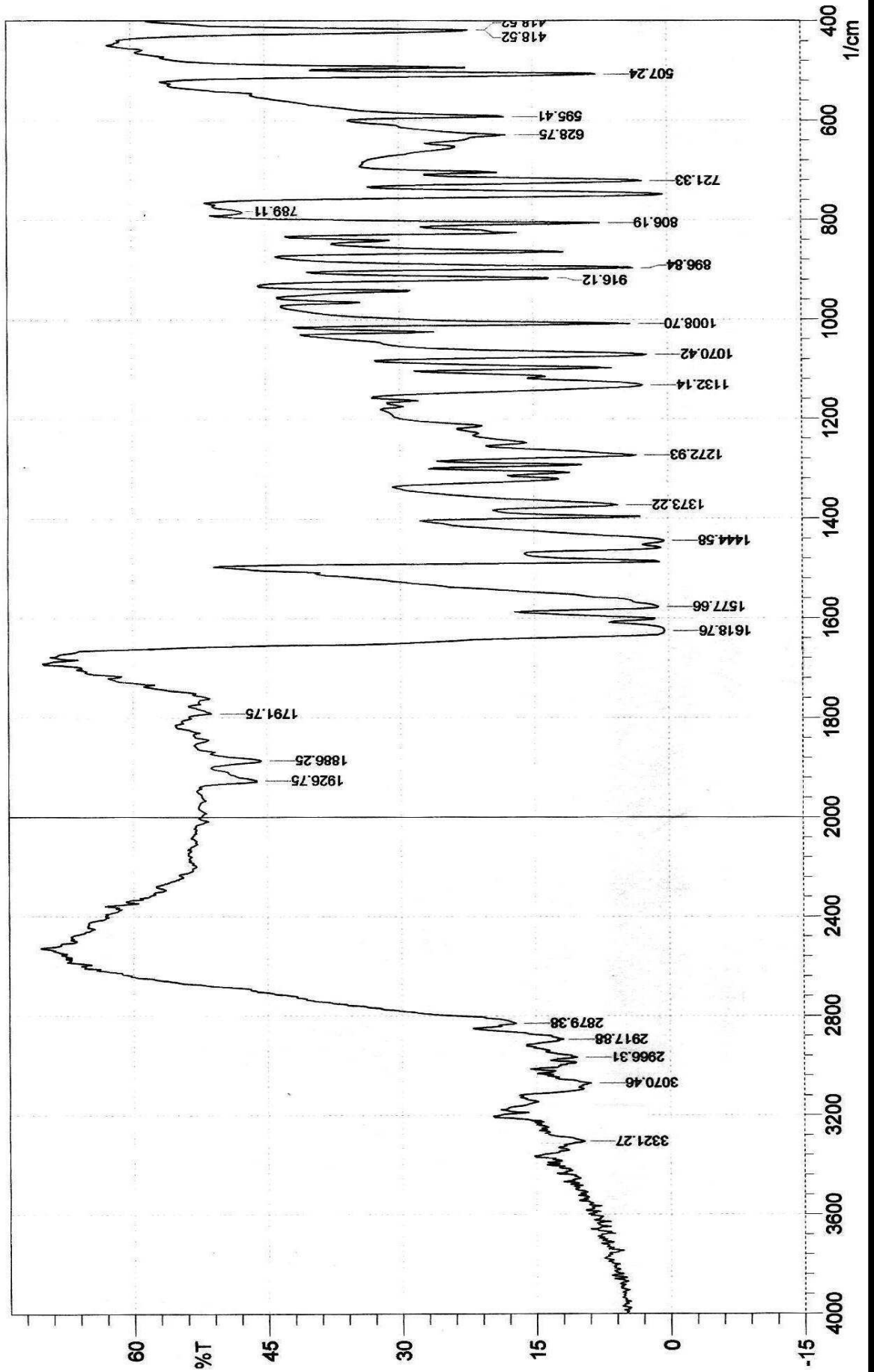


Fig(3-22) FT-IR Spectra of Lig5 Co



Fig(3-23) FT-IR Spectra of Lig6 Fe

SHIMADZU



Fig(3-24) FT-IR Spectra of Lig6 Co

Table (3-6) The most significant FT-IR bands of [Lig1...Lig6] and their metal complexes

| Symbol | $\nu(\text{C}=\text{N})$ | $\nu(\text{C}-\text{H})$ aliphatic | $\nu(\text{OH})$ | $\nu(\text{M}-\text{N})$ | (NO_2^-) bands | $(\text{C}-\text{O})$ | $\delta(\text{OH})$ |
|---------|--------------------------|---------------------------------------|------------------|--------------------------|----------------------------|-----------------------|---------------------|
| Lig1 | 1627 | 2886 2829 | - | - | - | - | - |
| Lig1 Fe | 1617 | 2887 2831 | - | 594 | - | - | - |
| Lig1 Co | 1615 | 2966 2898 | - | 590 | - | - | - |
| Lig1 Mn | 1619 | 2966 2889 | - | 597 | - | - | - |
| Lig2 | 1620 | 2953 2833 | - | - | - | 1251 | - |
| Lig2 Fe | 1637 | 2933 2854 | - | 593 | - | - | - |
| Lig2 Co | 1610 | 2921 2835 | - | 586 | - | 1253 | - |
| Lig2 Mn | 1636 | 2900 2835 | - | 553 | - | 1249 | - |
| Lig3 | 1623 | 2933 2861 | - | - | 1272 1350 1444 | - | - |
| Lig3 Fe | 1633 | 2922 | - | 595 | 1350 | - | - |
| Lig3 Co | 1629 | 2964 2879 | - | 558 | 1272 1350 1444 | - | - |
| Lig3 Mn | 1631 | 2902 2846 | - | 551 | 1272 1350 1444 | - | - |

Continue table (3-6) The most significant FT-IR bands of [Lig1...Lig6]
and their metal complexes

| Symbol | $\nu(\text{C}=\text{N})$ | $\nu(\text{C}-\text{H})$ aliphatic | $\nu(\text{OH})$ | $\nu(\text{M}-\text{N})$ | (NO_2^-) bands | $(\text{C}-\text{O})$ | $\delta(\text{OH})$ |
|---------|--------------------------|---------------------------------------|------------------|--------------------------|----------------------------|-----------------------|---------------------|
| Lig4 | 1620 | 2963 2817 | 3347 | - | - | 1367 | 975 |
| Lig4 Fe | 1615 | 2936 | 3346 | 583 | - | 1254 | 987 |
| Lig4 Co | 1614 | 2955 | 3349 | 539 | - | 1380 | 987 |
| Lig4 Mn | 1608 | 2966 | 3347 | 578 | - | 1358 | 990 |
| Lig5 | 1621 | 2931 2885 | - | - | - | - | - |
| Lig5 Fe | 1610 | 2916 2866 | - | 594 | - | - | - |
| Lig5 Co | 1610 | 2887 | - | 565 | - | - | - |
| Lig6 | 1625 | 2927 2893 | - | - | - | - | - |
| Lig6 Fe | 1619 | 2907 2866 | - | 592 | - | - | - |
| Lig6 Co | 1618 | 2917 2879 | - | 595 | - | - | - |

(3-4) Magnetic Susceptibility Measurements:

Magnetic measurements are widely used in studying transition metal complexes. The paramagnetism are due to the presence of unpaired electrons in the partially filled d-orbital in the outer shell of these elements. These magnetic measurements give an idea about the electronic state of the metal ion in the complex.

Measuring the magnetic susceptibility contributes to the determination of the structure of the complex, in furthermore, these measurements provide information about the type of bonding and strength of ligand field of complexes by giving information about the number of unpaired electrons⁽⁶⁴⁾.

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

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

Where $s = n/2$ ($n = \text{no. of unpaired electrons}$).

In this work the results obtained from this equation were compared to the actual values obtained through magnetic measurements, Table (3-7).

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

$$\mu_{\text{eff}} = 2.828 \sqrt{X_A \cdot T}$$

$$X_A = X_M - D$$

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

Where:

T = absolute temperature 298K

X_A = Atomic susceptibility

X_M = molar susceptibility

X_g = Gram susceptibility

D = Correction factor.

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

Table (3-7): The magnetic moments of (Fe, Co, Mn) metal complexes of Lig1, Lig2, Lig3, Lig4, Lig5 and Lig6.

| Complex | Magnetic moment (B.M) |
|----------------|------------------------------|
| Lig1 Fe | 5.90 |
| Lig1 Co | 3.58 |
| Lig1 Mn | 5.19 |
| Lig2 Fe | 5.17 |
| Lig2 Co | 3.26 |
| Lig2 Mn | 5.92 |
| Lig3 Fe | 5.97 |
| Lig3 Co | 3.94 |
| Lig3 Mn | 5.67 |
| Lig4 Fe | 5.94 |
| Lig4 Co | 3.41 |
| Lig4 Mn | 5.02 |
| Lig5 Fe | 5.39 |
| Lig5 Co | 3.70 |
| Lig6 Fe | 5.77 |
| Lig6 Co | 3.25 |

(3-5) The electronic spectral study and conductivity measurements of the prepared compounds:

Electronic absorption spectra of transition metal complexes are usually attributed to the partially filled d-orbital of the metal, the energy required for such transitions is that of the near UV and visible region and near IR. Charge transfer spectra are due to transitions between metal and ligand. Study of electronic spectra of complexes help in the determination of structure of the complexes through the electronic interaction of the metal d-orbital and ligand orbital. In our work, the spectra were recorded in the range (200-1100) nm, using dimethyl sulphoxide (DMSO) as a solvent.

Conductivity measurements of the prepared complexes in the appropriate solvent are used to decide whether a complex is electrolyte or neutral^(65,66). Table (3-8) shows the positions of the electronic absorption bands and their transitions and also include the calculated values of Racah parameter (B'), $10 Dq$ and nephelauxetic factor (β), Table (3-9) show the conductivity data for the prepared complexes at room temperature and the suggested structure for each complex, the structures were suggested for the prepared complexes according to the band positions of the infra-red spectra, electronic absorption bands, atomic absorption, magnetic properties and electronic conductivity measured for these complexes.

3-5-1 Complexes of Lig1:

A) Fe(III) complex [Lig1 Fe]:

Mishra and Said⁽⁶⁷⁾ studied the electronic spectra of $[\text{Fe}(\text{L})\text{py}(\text{OH})_2]_2$, where L = 2-mercapto-5-phenyl-1,3,4-oxadiazole and found that the spectrum could not be recorded due to its poor solubility, while the spectra of the solid complexes showed bands in the range of $(19,230-18,182)\text{cm}^{-1}$ in addition to a shoulder observed at $(15,625-15,151)\text{cm}^{-1}$. 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 $24,390\text{cm}^{-1}$. These assignments are comparable to the other earlier report made for Fe (III) complexes⁽⁶⁸⁾. The shoulder observed at $15,384\text{cm}^{-1}$ in the solid state spectra disappeared in the solution spectra and a new band at $(18,050-17,094)\text{cm}^{-1}$ appeared. This shift, observed in the solution⁽⁶⁹⁾ 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 was 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 one band in the d-d transition region at $26,809\text{cm}^{-1}$ which could be assigned to ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}$, also showed a shift in the energy of $n-\pi^*$ of the ligand 1 (Lig1) and appeared at $(32,787\text{cm}^{-1})$, which $\pi-\pi^*$ band which supposed to shift to higher energy was not observed due to limitation of the UV-Visible instrument, Figure (3-46).

The above complex and came in accordance to other available data so an octahedral geometry was suggested to the (Lig1 Fe) complex ⁽⁷⁰⁾. The value of the measured magnetic moment for (Lig1 Fe) is (5.90 B.M..) in accordance with the presumption of high-spin d^5 ferric ion in octahedral geometry ⁽⁷¹⁾.

Therefore, there results suggested the coordination of the Lig1Fe complex in an octahedral geometry, restricting the excitation of the $n-\pi^*$ and $\pi-\pi^*$ of the ligand to high energy while maintaining the high spin conformation of the d^5 iron cation as also spin forbidden spectra was observed at high energy. From Tanabe-Sugano diagram for d^5 octahedral field Fig (3-26), the value of $10Dq$ equal to $26,607 \text{ cm}^{-1}$.

Lig1Fe complex was considered have an ionic characterization as indicated by the high conductivity value measured by conductivity measurement as stated in table (3-8), table (3-9), therefore the following structure is suggested for the (Lig1 Fe) complex :

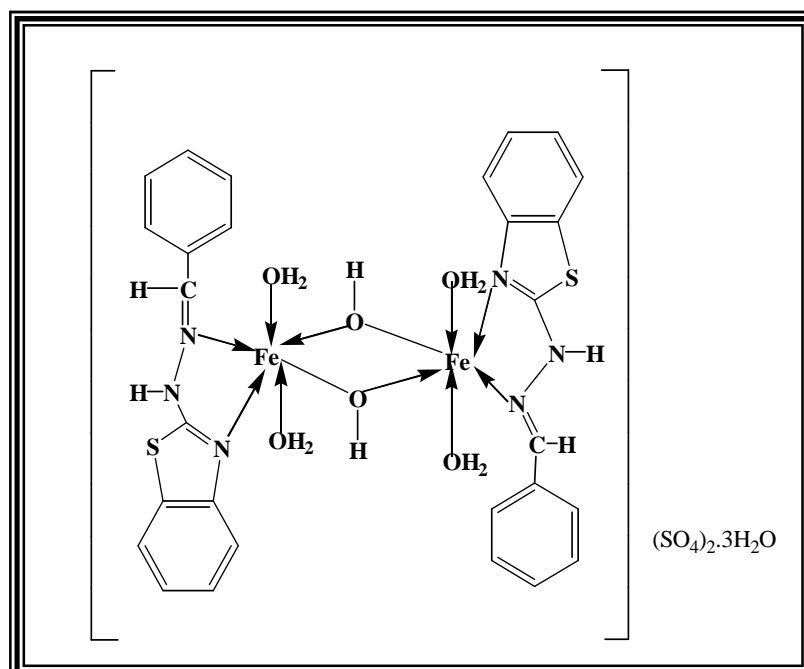


Figure (3-25) Structure of Lig1 Fe complex

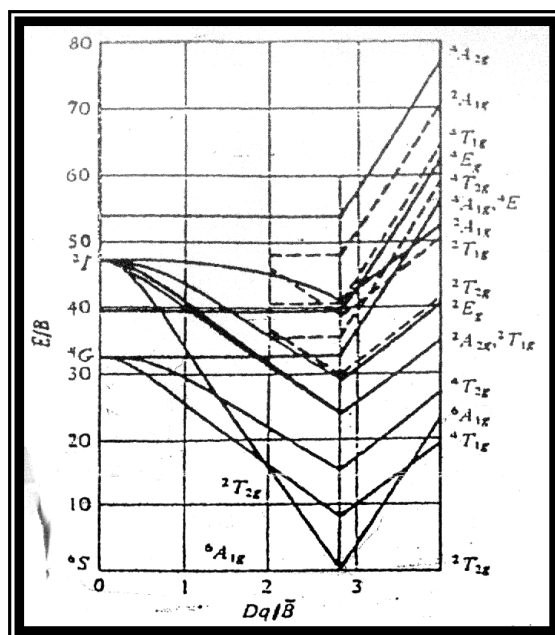
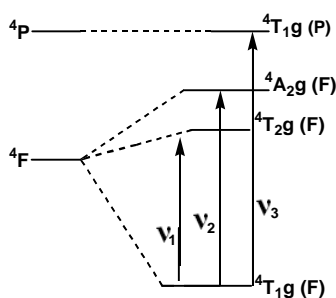


Fig. (3-26) Tanabe-Sugano diagram for d^5 system for Fe (III)⁽²⁾

B) Co(II) complex [Lig1 Co]:

Electronic spectrum of cobalt (II) complex usually show three transitions, but these transitions can not be assigned easily because of the greater overlapping of them^(72,73,75). Octahedral complexes of Co(II) are reported to show of two bands one in the 15,400-15,500 cm^{-1} and the other in the 20,000-20,800 cm^{-1} regions⁽⁷⁴⁾.

The term symbol for the ground state of Co(II) ion is $4F$ which can split in octahedral crystal field as follow⁽⁷⁵⁾.



In the present work the two bands; appeared at 16,750 cm^{-1} and the other at 31,847 cm^{-1} figure (3-28) which were assigned to the transitions ν_2 and ν_3 respectively.

The value of ν_1 was calculated using Tanabe-Sugano diagram for d^7 system, Figure (3-28), and found to be 8,364 cm^{-1} which refers to $4T_{1g}$

(F) \rightarrow ${}^4T_{2g}$ (F) transition, 10 Dq value was also calculated from diagram and found to be $8,364 \text{ cm}^{-1}$ referring to a weak field state. The different ligand field parameters have been calculated using the same diagram, the results are found in Table (3-8).

Octahedral cobalt (II) complex however, maintain a large contribution due to 4T_g ground term and exhibits μ_{eff} . in the range (4.8-5.6 B.M.)⁽⁷⁶⁾, the magnetic measurement of the (Lig1 Co) complex is 5.42 B.M. shows the complex is paramagnetic and have three unpaired electrons indicating a high-spin octahedral configuration.

Therefore, there results suggested the coordination of the Lig1Co complex in an octahedral geometry, restricting the excitation of the $n-\pi^*$ and $\pi-\pi^*$ of the ligand to high energy while maintaining the high spin conformation of the d^7 cobalt cation as also spin forbidden spectra was observed at high energy.

Lig1Co complex was considered have an ionic characterization as indicated by the high conductivity value measured by conductivity measurement as stated in table (3-8), table (3-9), From these results an octahedral geometry around Co(II) ion can be suggested as illustrated in the following structure:

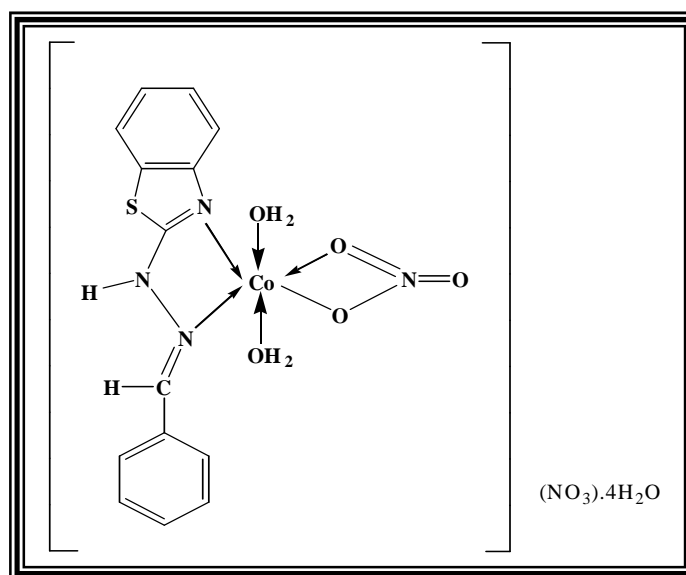


Figure (3-27) Structure of Lig1 Co complex

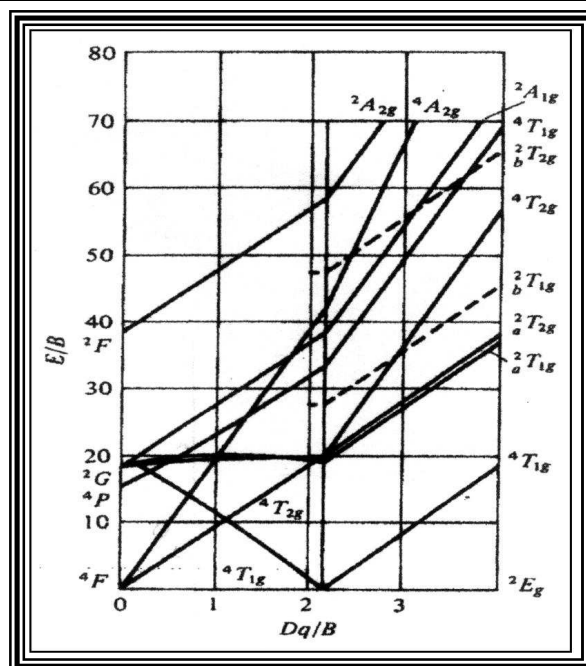


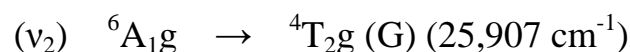
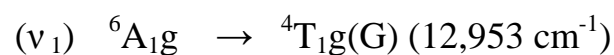
Fig (3-28): Tanabe-Sugano diagram of d^7 system for $\text{Co(II)}^{(2)}$

C) Mn(II) complex [Lig1 Mn]:

Mn(II) considers to be a stable oxidation state because it is half filled ($3d^5$) and consequently more stable. The (d^5) system give one essential symbol in the free ion, (6S), as well as many doublet and four folded symbols, as shown in Figure (3-29), If any transition between the crystal field to being spin-forbidden, 6S term give one symbol, ${}^6A_{1g}$, in the octahedral field therefore the electronic spectra and the colors of (d^5) ions were very weak (which unoccupied from charge transfer observations).

In the (d^5) system the octahedral splitting equal to tetrahedral yellow and green colors but the O.h geometry are characterize by the pale pink or without color^(77,75).

The UV-Vis spectrum, fig. (3-47), of the present complex showed three bands in the d-d transition region at $12,953 \text{ cm}^{-1}$, $25,907 \text{ cm}^{-1}$ and $32,573 \text{ cm}^{-1}$ and can be assigned to the following transitions:



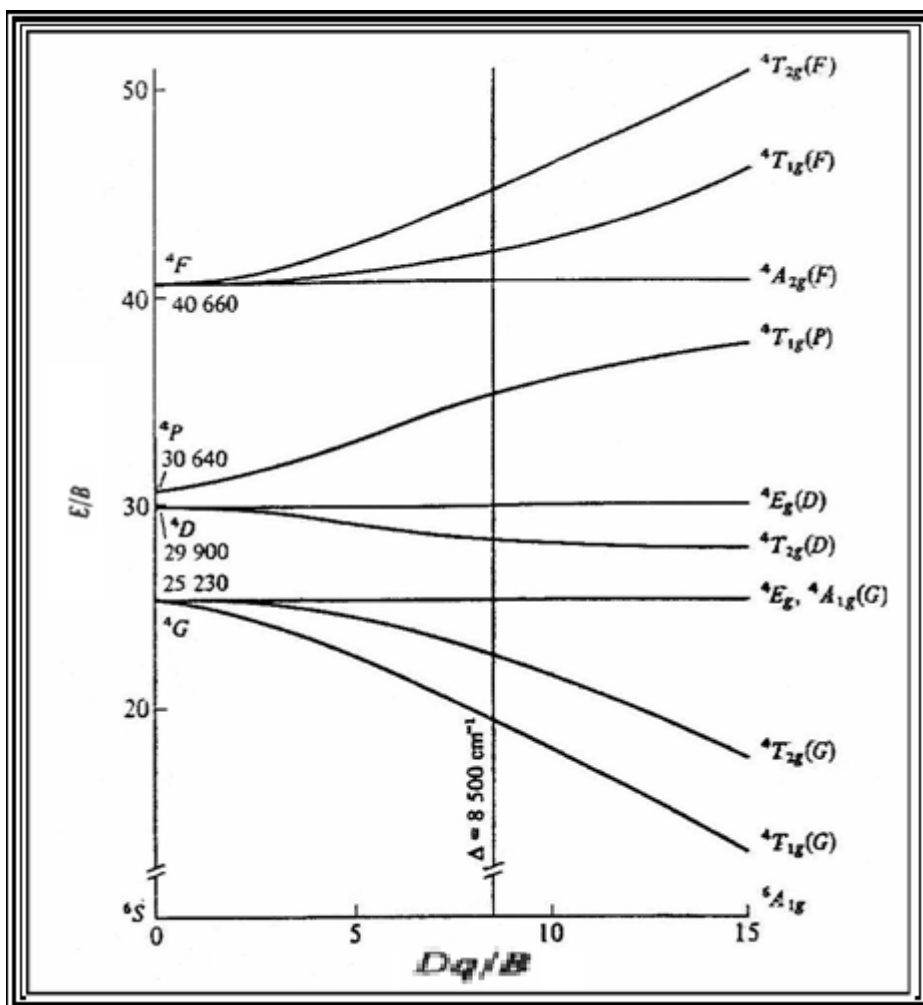
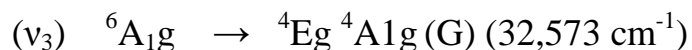


Figure (3-29): Tanabe-Sugano diagram for d^5 system for Mn(II)⁽²⁾

To above complex and came accordance to the other available data so an octahedral geometry was suggested to [Lig1 Mn] complex⁽⁷⁸⁾.

The value of the measured magnetic moment for [Lig1 Mn] is (5,19 B.M.) in accordance with the presumption of high-spin d^5 Mn(II) ion in octahedral geometry⁽⁷¹⁾, table (3-7).

Therefore, there results suggested the coordination of the Lig1Mn complex in an octahedral geometry, restricting the excitation of the $n-\pi^*$ and $\pi-\pi^*$ of the ligand to high energy while maintaining the high spin conformation of the d^5 Manganese cation as also spin forbidden spectra was observed at high energy.

Lig1Mn complex was considered have an ionic characterization as indicated by the high conductivity value measured by conductivity measurement as stated in table (3-8), table (3-9).

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

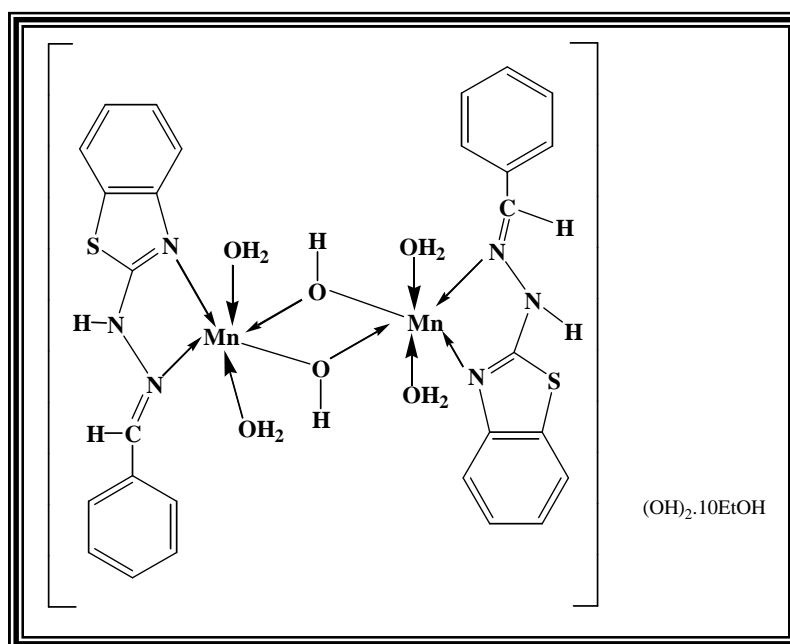


Figure (3-30) Structure of Lig1 Mn complex

3-5-2 Complexes of Lig2:

A) Fe(III) complex [Lig2 Fe]:

The electronic spectrum of [Li2 Fe], figure (3-47), table (3-8) shows a shift in the energy of $n-\pi^*$ of the (Lig2) and appeared at ($30,101 \text{ cm}^{-1}$), which $\pi-\pi^*$ band which supposed to shift to higher energy was not observed due to limitation of the UV-Visible instrument, Figure (3-47).

The value of the measured magnetic moment for [lig2 Fe] complex is (5.17 B.M.), which could be related to high-spin d^5 ferric ion in octahedral geometry.

Therefore, there results suggested the coordination of the Lig2Fe complex in an octahedral geometry, restricting the excitation of the $n-\pi^*$ and $\pi-\pi^*$ of the ligand to high energy while maintaining the high spin

conformation of the d^5 iron cation as also spin forbidden spectra was observed at high energy

Lig2Fe complex was considered have an ionic characterization as indicated by the high conductivity value measured by conductivity measurement as stated in table (3-8), table (3-9), therefore the following structure is suggested for the [Lig2 Fe] complex:

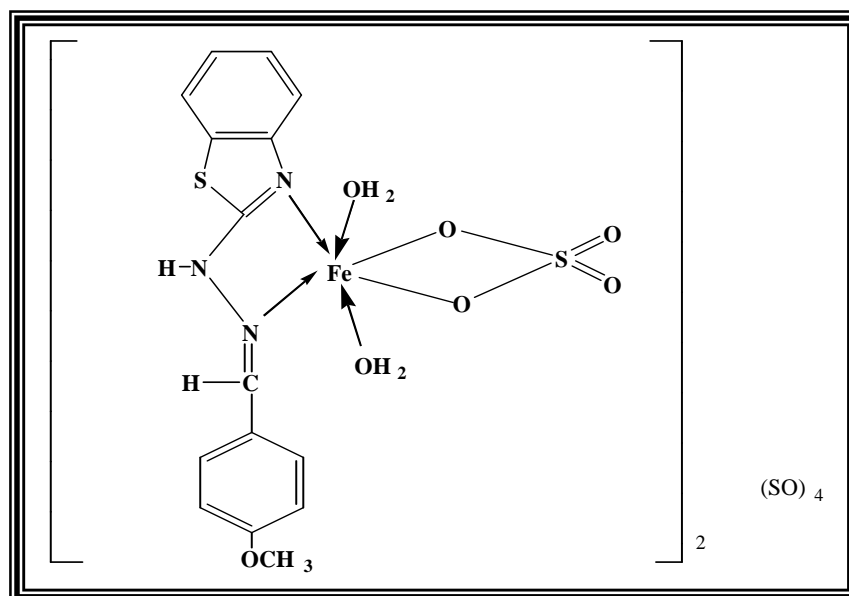


Figure (3-31) Structure of Lig2 Fe complex

B) Co(II) complex [Lig2 Co]:

The spectral behavior of this complex, Figure (3-48) was identical with that of (Lig1 Co), which appeared two bands at $25,907\text{ cm}^{-1}$ and at $28,986\text{ cm}^{-1}$ which was assigned to the transitions ν_2 and ν_3 respectively, ν_1 was calculated using Tanabe-Sugano diagram figure (3-28) for d^7 system and found to be $20,725\text{ cm}^{-1}$ which belong to the transition ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$.

The magnetic susceptibility and molar conductivity show the complex to be octahedral and to be conducting, table (3-9).

The magnetic moment of [Lig2 Co] complex was (5.26 B.M.), which show the complex to be paramagnetic.

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

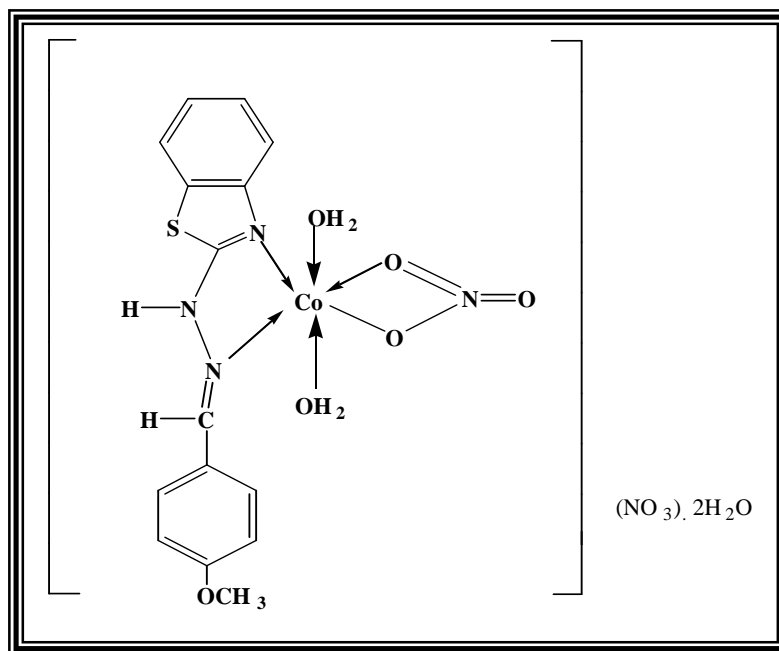


Figure (3-32) Structure of Lig2 Co complex

C) Mn(II) complex [Lig2 Mn]:

The electronic spectrum of [Lig1 Mn] complex, Figure (3-48), Table (3-8) showed a shift in the energy of $n-\pi^*$ of the (Lig2) and appeared at ($33,113 \text{ cm}^{-1}$), which $\pi-\pi^*$ band which supposed to shift to higher energy was not observed due to limitation of the UV-Visible instrument.

These were similar to that shown by [Lig1 Mn] complex so an octahedral geometry was suggested to the [Lig2 Mn] complex⁽⁷⁸⁾.

The value of the measured magnetic moment for [Lig2 Mn] complex was (4.92 B.M.) which could be related to high-spin d^5 Mn ion in octahedral geometry.

Therefore, there results suggested the coordination of the Lig2Mn complex in an octahedral geometry, restricting the excitation of the $n-\pi^*$ and $\pi-\pi^*$ of the ligand to high energy while maintaining the high spin

conformation of the d^5 manganese cation as also spin forbidden spectra was observed at high energy.

Lig2Mn complex was considered have an ionic characterization as indicated by the high conductivity value measured by conductivity measurement as stated in table (3-8), table (3-9), the following structure is suggested for the [Lig2 Mn] complex:

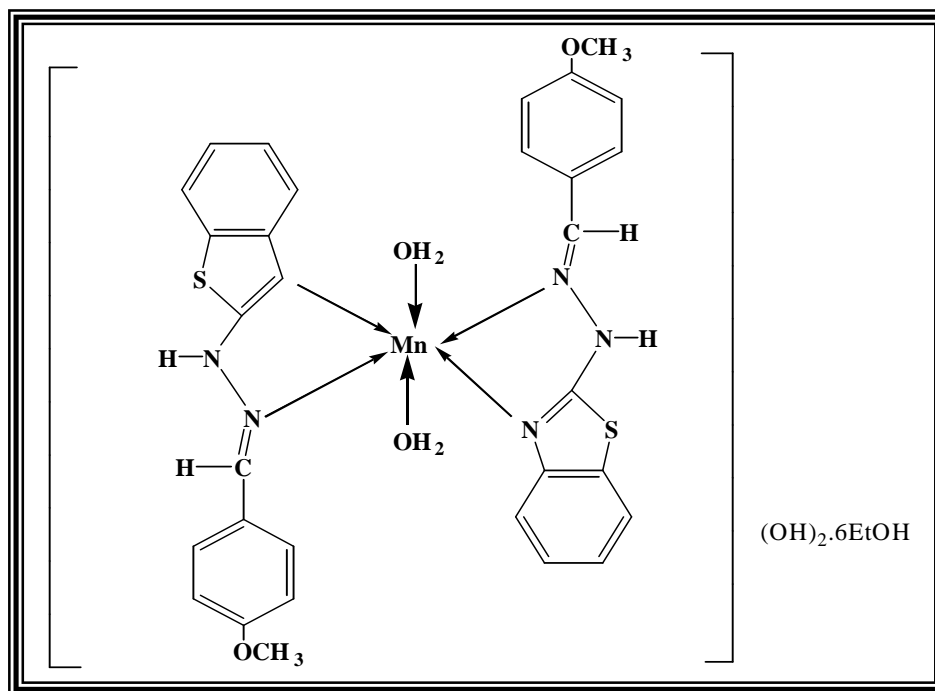


Figure (3-33) Structure of Lig2 Mn complex

3-5-3 Complexes of Lig3:

A) Fe(III) complex [Lig3 Fe]:

The electronic spectrum of [Lig3 Fe], figure (3-49), table (3-8) shows a shift in the energy of $n-\pi^*$ of the (Lig3) and appeared at ($31,446 \text{ cm}^{-1}$), which $\pi-\pi^*$ band which supposed to shift to observed at ($34,014 \text{ cm}^{-1}$).

These are similar to that shown by [Lig2 Fe] complex so an octahedral geometry was suggested to the [Lig3 Fe] complex⁽⁷⁰⁾.

The value of the measured magnetic moment for [Lig3 Fe] complex was (4.97 B.M.) which could be related to high-spin d^5 ferric ion in octahedral geometry.

Therefore, there results suggested the coordination of the Lig3Fe complex in an octahedral geometry, restricting the excitation of the $n-\pi^*$ and $\pi-\pi^*$ of the ligand to high energy while maintaining the high spin conformation of the d^5 iron cation as also spin forbidden spectra was observed at high energy

Lig3Fe complex was considered have an ionic characterization as indicated by the high conductivity value measured by conductivity measurement as stated in table (3-8), table (3-9), therefore the following structure was suggested for the [Lig3 Fe] complex:

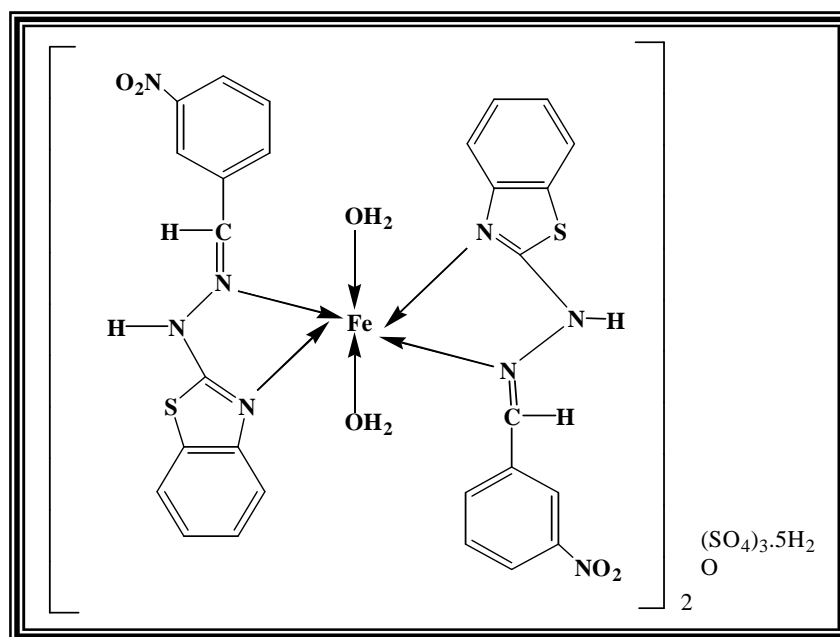


Figure (3-34) Structure of Lig3 Fe complex

B) Co(II) complex [Lig3 Co]:

Electronic spectrum of (Lig3 Co), Figure (3-49), show one band at $26,178 \text{ cm}^{-1}$ which are assigned to the transitions ${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{2g}(\text{F})$, the value of $10Dq$ equal to $26,178 \text{ cm}^{-1}$.

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

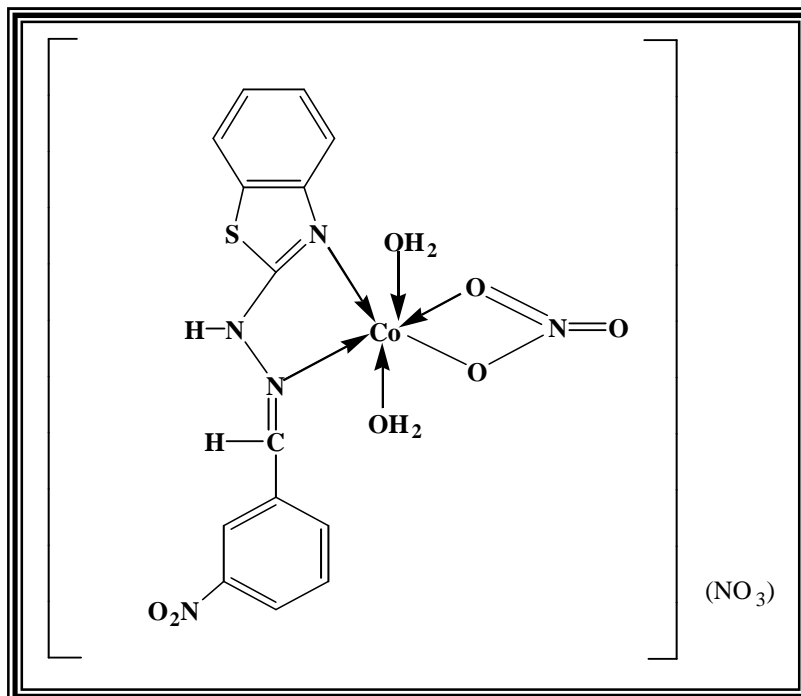


Figure (3-35) Structure of Lig3 Co complex

C) Mn(II) complex [Lig3 Mn]:

The electronic spectrum of [Lig3 Mn] complex, Figure (3-50), Table (3-8), show one band at $(33,113 \text{ cm}^{-1})$ which were assigned to the transition $(v_1) {}^6A_{1g} \rightarrow {}^4T_{1g} (G)$.

These were similar to that shown by [Lig1 Mn] complex, so an octahedral geometry was suggested to the [Lig3 Mn] complex⁽⁷⁸⁾.

The value of the measured magnetic moment for [Lig3 Mn] complex was (5.67 B.M.), which could be related to high-spin d^5 manganese (II) ion in octahedral geometry.

Conductivity measurements show the [Lig3 Mn] complex to be ionic; Table (3-9). The following binuclear octahedral structure can be suggested:

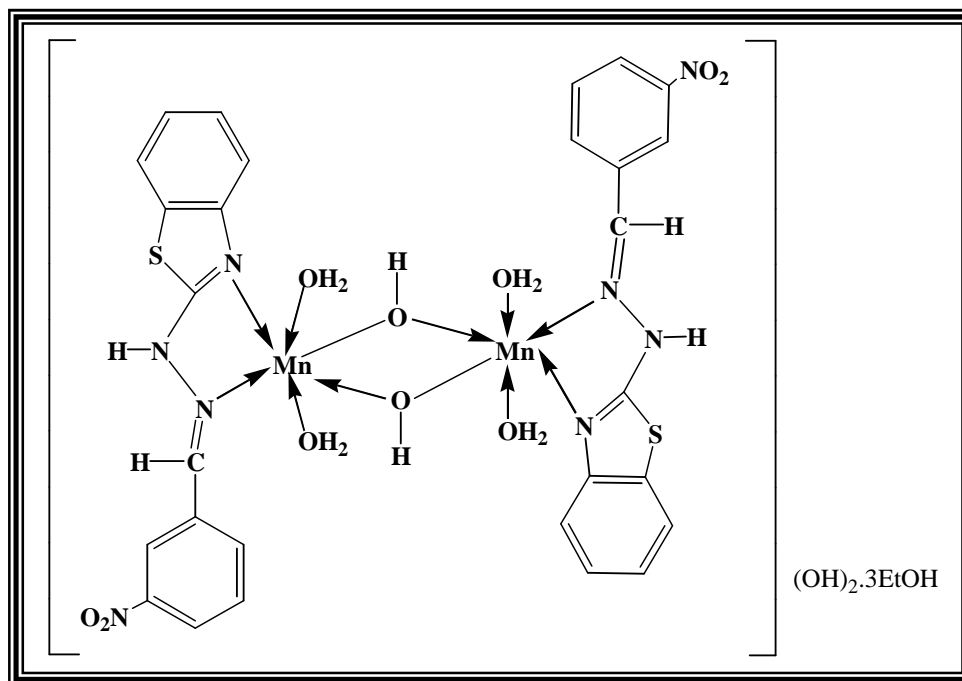


Figure (3-36) Structure of Lig3 Mn complex

3-5-4 Complexes of Lig4:**A) Fe(III) complex [Lig4 Fe]:**

The electronic spectrum of (Lig4 Fe) complex, Fig (3-50) table(3-8) . Show one band at $(16,667 \text{ cm}^{-1})$ which is assigned to the transitions ${}^6A_{1g} \rightarrow {}^4T_{1g}$.

These are similar to that shown by (Lig1 Fe) complex so an octahedral geometry was suggested to the (Lig4 Fe) complex⁽⁷⁰⁾.

The value of the measured magnetic moment for (Lig4 Fe) complex is (4.94 B.M.), which could be related to high-spin d^5 ferric ion in octahedral geometry, the value of $10Dq$ equal to $(16,667 \text{ cm}^{-1})$. Lig4Fe complex was considered have an ionic characterization as indicated by the high conductivity value measured by conductivity measurement as stated in table (3-8), table (3-9), therefore the following structure is suggested for the (Lig4 Fe) complex:-

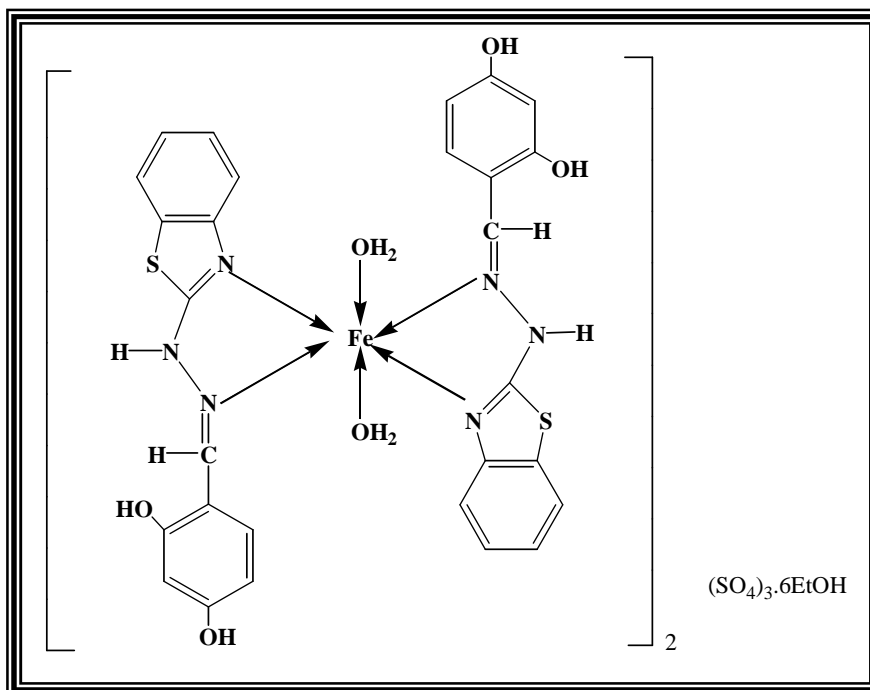


Figure (3-37) Structure of Lig4 Fe complex

B) Co(II) complex [Lig4 Co]:

Electronic spectra of cobalt (II) complex generally show three transitions, but these transitions can not be assigned because of the greater overlapping of them^(2,3,73,75).

Octahedral spectra of Co(II) consist of two bands one in the regions (15,400-15,500 cm^{-1}) and the other in the (20,000-20,830) cm^{-1} regions⁽⁷⁴⁾.

The term symbol for the ground state of Co(II) ion is 4F , which can split in octahedral crystal field⁽⁷⁵⁾.

Electronic spectra of cobalt (II) complex generally show one band appeared at (29,674 cm^{-1}), Fig (3-51) which were assigned to the transitions $^4T_{1g}(F) \rightarrow ^4T_{2g}(F)$.

Therefore, there results suggested the coordination of the Lig14Co complex in an octahedral geometry, restricting the excitation of the $n-\pi^*$ and $\pi-\pi^*$ of the ligand to high energy while maintaining the high spin conformation of the d^7 cobalt cation as also spin forbidden spectra was observed at high energy.

Lig1Co complex was considered have an ionic characterization as indicated by the high conductivity value measured by conductivity measurement as stated in table (3-8), table (3-9).

Octahedral cobalt (II) complex however maintain a large contribution due to 4T_g ground term and exhibits μ_{eff} in the range (4.85-5.6B.M.)⁽⁷⁶⁾.

The magnetic measurement of the [Lig4 Co] complex is (5.23B.M.) shows the complex to be paramagnetic and have three unpaired electrons indicating a high –spin octahedral configuration.

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

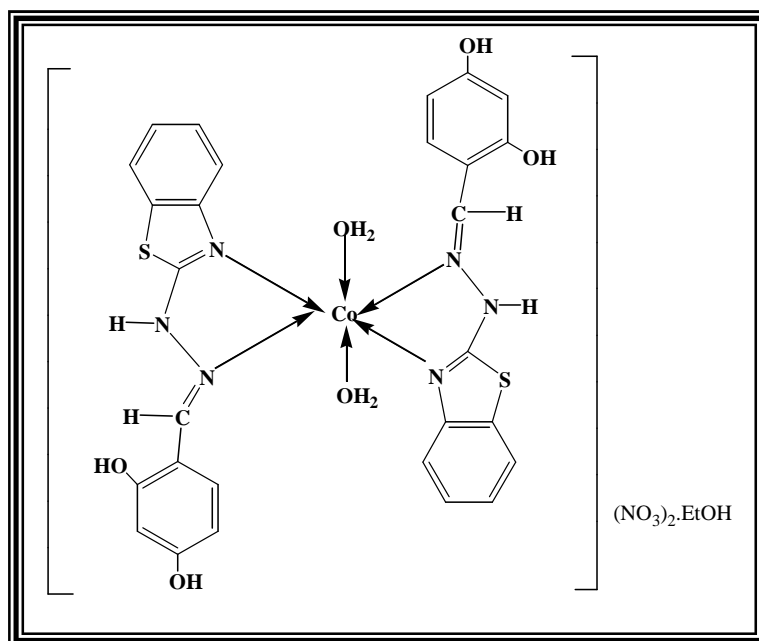


Figure (3-38) Structure of Lig4 Co complex

C) Mn(II) complex [Lig4 Mn]:

The electronic spectrum of [Lig4 Mn] complex, figure (3-51), table (3-8), show a shift in the energy of $n-\pi^*$ of the (Lig1) and appeared at ($32,258 \text{ cm}^{-1}$), which $\pi-\pi^*$ band which supposed to shift to higher energy was not observed due to limitation of the UV-Visible instrument.

These were shown by [Lig1 Mn], [Lig2 Mn] and [Lig3 Mn] complexes, so an octahedral geometry was suggested to the [Lig4 Mn] complex⁽⁷⁸⁾.

The value of the measured magnetic moment for [Lig4 Mn] complex was (5.02 B.M.), which could be related to high-spin d^5 manganese (II) ion in octahedral geometry.

Conductivity measurements show the [Lig4 Mn] complex to be ionic; Table (3-9). The following octahedral structure can be suggested:

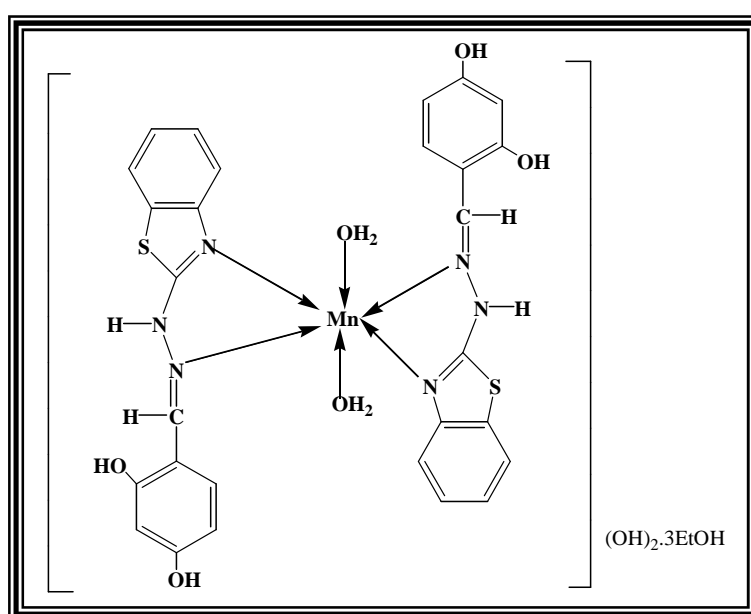


Figure (3-39) Structure of Lig4 Mn complex

3-5-5 Complexes of Lig5:

A) Fe(III) complex [Lig5 Fe]:

The electronic spectrum of (Lig5 Fe) complex, fig(3-52) table(3-8) . Showed a shift in the energy of $n-\pi^*$ of the (Lig5) and appeared at ($31,294 \text{ cm}^{-1}$), which $\pi-\pi^*$ band which supposed to shift to higher energy was not observed due to limitation of the UV-Visible instrument

These are similar to that shown by (Lig1 Fe) complex so an octahedral geometry was suggested to the (Lig5 Fe)complex⁽⁷⁰⁾.

The value of the measured magnetic moment for (Lig5 Fe) complex is (5.39 B.M.), which could be related to high-spin d^5 ferric ion in octahedral geometry.

Therefore, there results suggested the coordination of the Lig5Fe complex in an octahedral geometry, restricting the excitation of the $n-\pi^*$ and $\pi-\pi^*$ of the ligand to high energy while maintaining the high spin conformation of the d^5 iron cation as also spin forbidden spectra was observed at high energy.

Lig5Fe complex was considered have an ionic characterization as indicated by the high conductivity value measured by conductivity measurement as stated in table (3-8), table (3-9), therefore the following structure is suggested for the (Lig5 Fe) complex:-

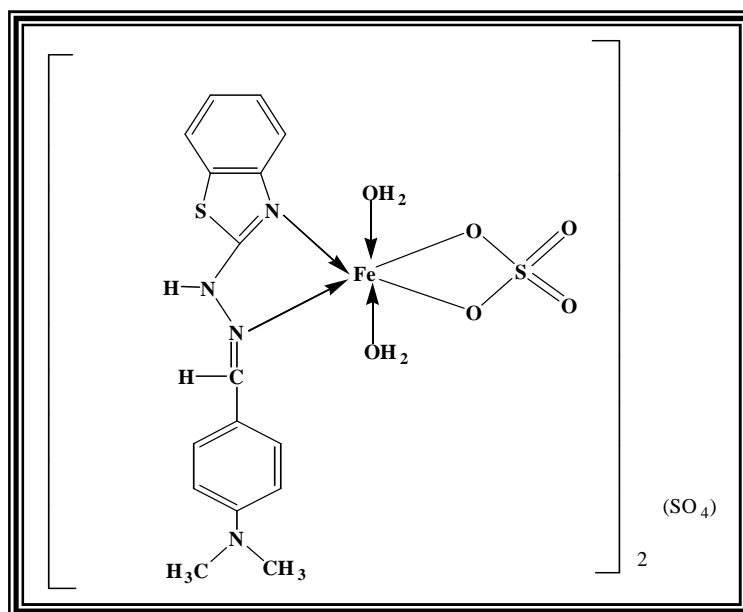


Figure (3-40) Structure of Lig5 Fe complex

B) Co(II) complex [Lig5 Co]:

The spectral behavior of this complex, figure (3-52) was identical with that of (Lig5 Co), which also shows one band at $31,056 \text{ cm}^{-1}$ which was assigned to the transition ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$.

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

The magnetic moment of [Lig5 Co] complex was (4.86 B.M.), which show the complex to be paramagnetic.

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

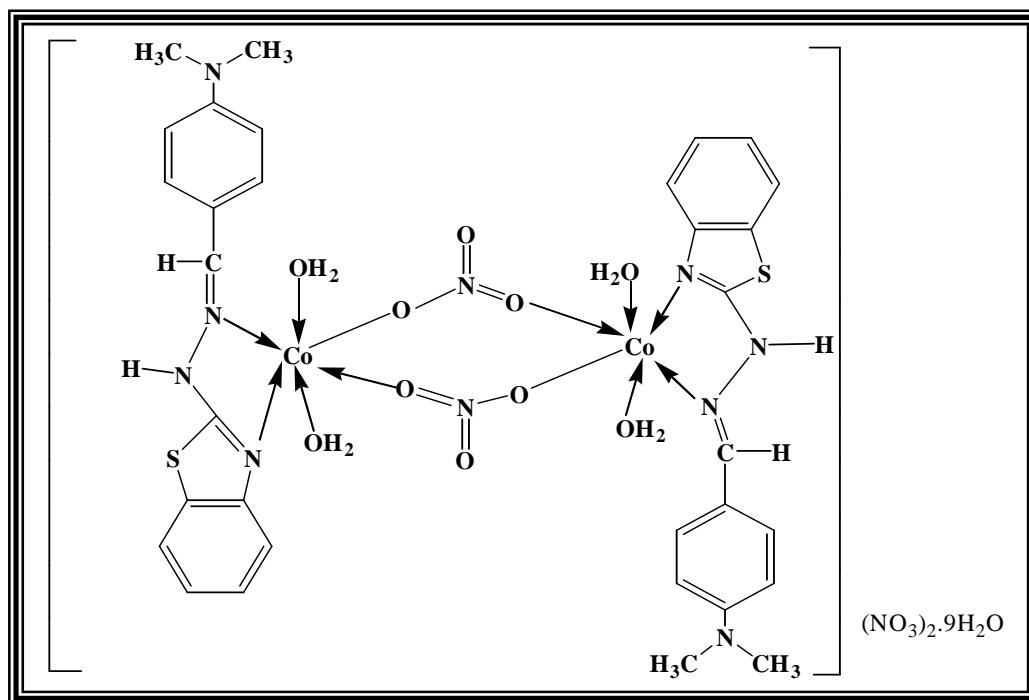


Figure (3-41) Structure of Lig5 Co complex

3-5-6 Complexes of Lig6:

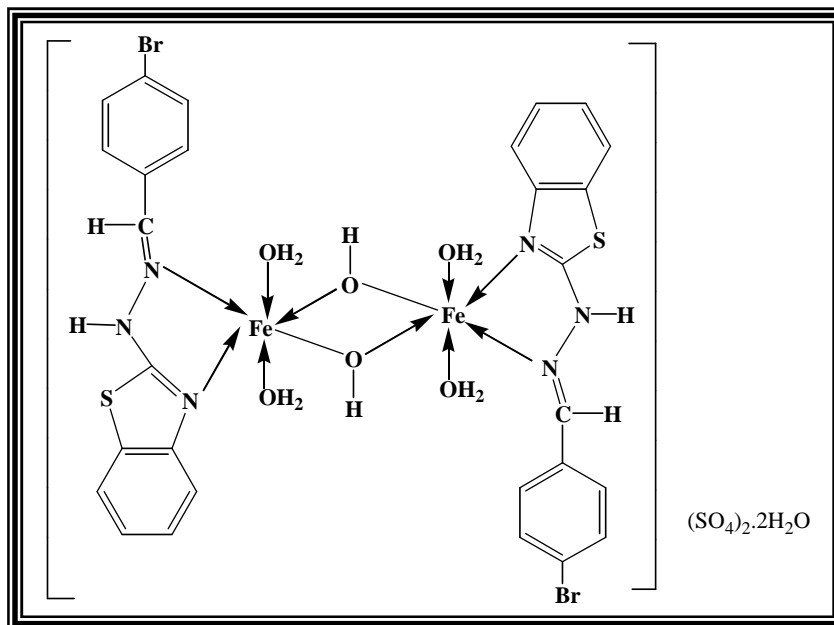
A) Fe(III) complex [Lig6 Fe]:

The electronic spectrum of (Lig6 Fe) complex, fig(3-53) table(3-8) . Showed a shift in the energy of $n-\pi^*$ of the ligand 1 (Lig1) and appeared at $(31,467 \text{ cm}^{-1})$, which $\pi-\pi^*$ band which supposed to shift to higher energy was not observed due to limitation of the UV-Visible instrument,

These are similar to that shown by (Lig1 Fe) complex so an octahedral geometry was suggested to the (Lig6 Fe) complex ⁽⁷⁰⁾.

The value of the measured magnetic moment for (Lig6 Fe) complex is (5.77 B.M.), which could be related to high-spin d^5 ferric ion in

octahedral geometry therefore the following structure is suggested for the (Lig6 Fe) complex:-



B) Co(II) complex [Lig6 Co]:

The spectral behavior of this complex, Figure (3-53) was identical with that of (Lig1 Co), which also shows one band one at $31,546 \text{ cm}^{-1}$ which was assigned to the transition ${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{2g}(\text{F})$.

The magnetic susceptibility and molar conductivity show the complex to be octahedral and to be conducting, Table (3-9).

The magnetic moment of [Lig6 Co] complex was (5.29 B.M.), which show the complex to be paramagnetic.

Therefore, there results suggested the coordination of the Lig6Co complex in an octahedral geometry, restricting the excitation of the $n-\pi^*$ and $\pi-\pi^*$ of the ligand to high energy while maintaining the high spin conformation of the d^7 cobalt cation as also spin forbidden spectra was observed at high energy.

Lig6Co complex was considered have an ionic characterization as indicated by the high conductivity value measured by conductivity

measurement as stated in table (3-8), table (3-9), from these results and that of FTIR study the suggested structure is follows:

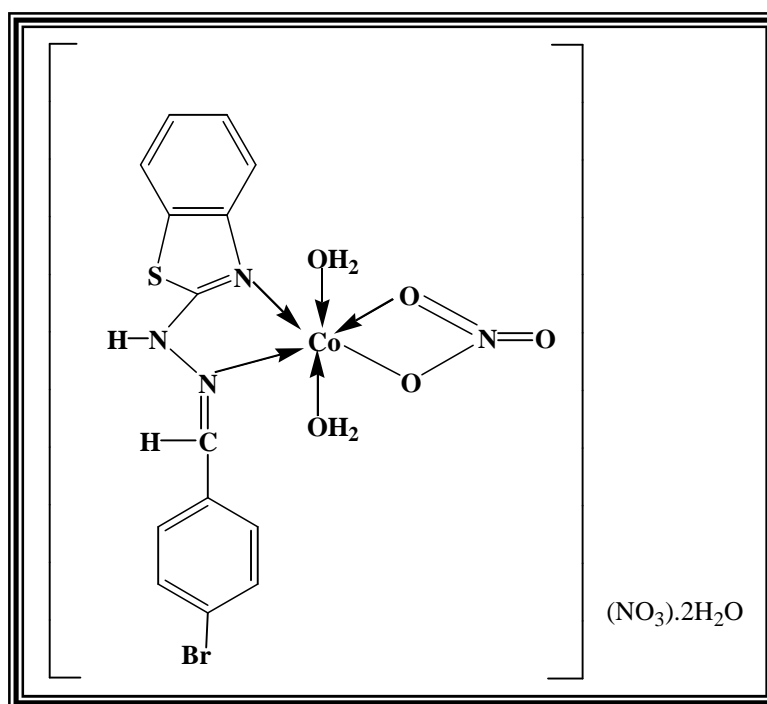


Figure (3-43) Structure of Lig6 Co complex

Table (3-8): Electronic spectral data for complexes of Lig1, Lig2, Lig3, Lig4, Lig5 and Lig6 in 10^{-3} M DMSO solvent (cm^{-1}).

| Symbol | Absorption Band (cm^{-1}) | Transitions | B | B' | β | 10Dq | 15 B' |
|---------|--------------------------------------|---|------|------|---------|--------|--------|
| Lig1 Fe | 26,809 | $(\nu_1) {}^6A_{1g} \rightarrow {}^4T_{1g}$ | 1300 | - | - | 26,809 | - |
| Lig1 Co | 8,753 cal 16,750 31,847 | $(\nu_1) {}^4T_{1g} (F) \rightarrow {}^4T_{2g} (F)$ $(\nu_2) {}^4T_{1g} (F) \rightarrow {}^4A_{2g} (F)$ $(\nu_3) {}^4T_{1g} (F) \rightarrow {}^4T_{2g} (P)$ | 971 | 1196 | 0.66 | 8,753 | 22,338 |
| Lig1 Mn | 12,953 25,907 32,573 | $(\nu_1) {}^6A_{1g} \rightarrow {}^4T_{1g} (G)$ $(\nu_2) {}^6A_{1g} \rightarrow {}^4E_{1g} {}^4A_{1g} (G)$ $(\nu_3) {}^6A_{1g} \rightarrow {}^4T_{2g} (G)$ | 960 | 1295 | 0.74 | 12,953 | 21,576 |
| Lig2 Fe | 17,730 | $(\nu_1) {}^6A_{1g} \rightarrow {}^4T_{1g}$ | 1300 | - | - | 17,730 | - |
| Lig2 Co | 33,113 | $(\nu_1) {}^4T_{1g} (F) \rightarrow {}^4T_{2g} (F)$ | 971 | - | - | 33,113 | - |
| Lig2 Mn | - | - | 960 | - | - | - | - |
| Lig3 Fe | - | - | 1300 | - | - | - | - |
| Lig3 Co | 26,178 | $(\nu_1) {}^4T_{1g} (F) \rightarrow {}^4T_{2g} (F)$ | - | - | - | 26,178 | - |
| Lig3 Mn | 9,268 11,947 22,421 | $(\nu_1) {}^6A_{1g} \rightarrow {}^4T_{1g} (G)$ $(\nu_2) {}^6A_{1g} \rightarrow {}^4E_{1g} {}^4A_{1g} (G)$ $(\nu_3) {}^6A_{1g} \rightarrow {}^4T_{2g} (G)$ | 960 | 438 | 0.46 | 9,273 | 6,564 |
| Lig4 Fe | 16,667 | $(\nu_1) {}^6A_{1g} \rightarrow {}^4T_{1g}$ | 1300 | - | - | 16,667 | - |
| Lig4 Co | 29,674 | $(\nu_1) {}^4T_{1g} (F) \rightarrow {}^4T_{2g} (F)$ | 971 | - | - | 29,674 | - |
| Lig4 Mn | - | - | 960 | - | - | - | - |

Table (3-8): Electronic spectral data for complexes of Lig1, Lig2, Lig3, Lig4, Lig5 and Lig6 in 10^{-3} M DMSO solvent (cm^{-1}).

| Symbol | Absorption Band (cm^{-1}) | Transitions | B | B' | β | 10Dq | 15 B' |
|---------|--------------------------------------|---|------|----|---------|--------|-------|
| Lig5 Fe | - | - | 1300 | - | - | - | - |
| Lig5 Co | 31,056 | $(v_1) {}^4T_{1g} (F) \rightarrow {}^4T_{2g} (F)$ | 971 | - | - | 31,056 | - |
| Lig6 Fe | 17,953 | $(v_1) {}^6A_{1g} \rightarrow {}^4T_{1g}$ | 1300 | - | - | 17,953 | - |
| Lig6 Co | 31,546 | $(v_1) {}^4T_{1g} (F) \rightarrow {}^4T_{2g} (F)$ | 971 | - | - | 31,546 | - |

Table (3-9): Magnetic moments, Conductivity and Suggested Structures for complexes of Lig1, Lig2, Lig3, Lig4, Lig5 and Lig6 in 10^{-3} M DMSO ⁽⁷⁹⁾.

| Complex | Magnetic moment (B.M) | Conductivity $\mu\text{S.cm}^{-1}$ | Suggested structure |
|---------|-----------------------|------------------------------------|---------------------|
| Lig1 Fe | 5.90 | 43 | Octahedral |
| Lig1 Co | 3.58 | 32 | Octahedral |
| Lig1 Mn | 5.19 | 33 | Octahedral |
| Lig2 Fe | 5.17 | 45 | Octahedral |
| Lig2 Co | 3.26 | 31 | Octahedral |
| Lig2 Mn | 5.92 | 36 | Octahedral |
| Lig3 Fe | 5.97 | 37 | Octahedral |
| Lig3 Co | 3.94 | 34 | Octahedral |
| Lig3 Mn | 5.67 | 33 | Octahedral |
| Lig4 Fe | 5.94 | 32 | Octahedral |
| Lig4 Co | 3.41 | 38 | Octahedral |
| Lig4 Mn | 5.02 | 34 | Octahedral |
| Lig5 Fe | 5.39 | 37 | Octahedral |
| Lig5 Co | 3.70 | 33 | Octahedral |
| Lig6 Fe | 5.77 | 63 | Octahedral |
| Lig6 Co | 3.25 | 35 | Octahedral |

Table (3-10) The chemical formula and the name of the ligands and complexes

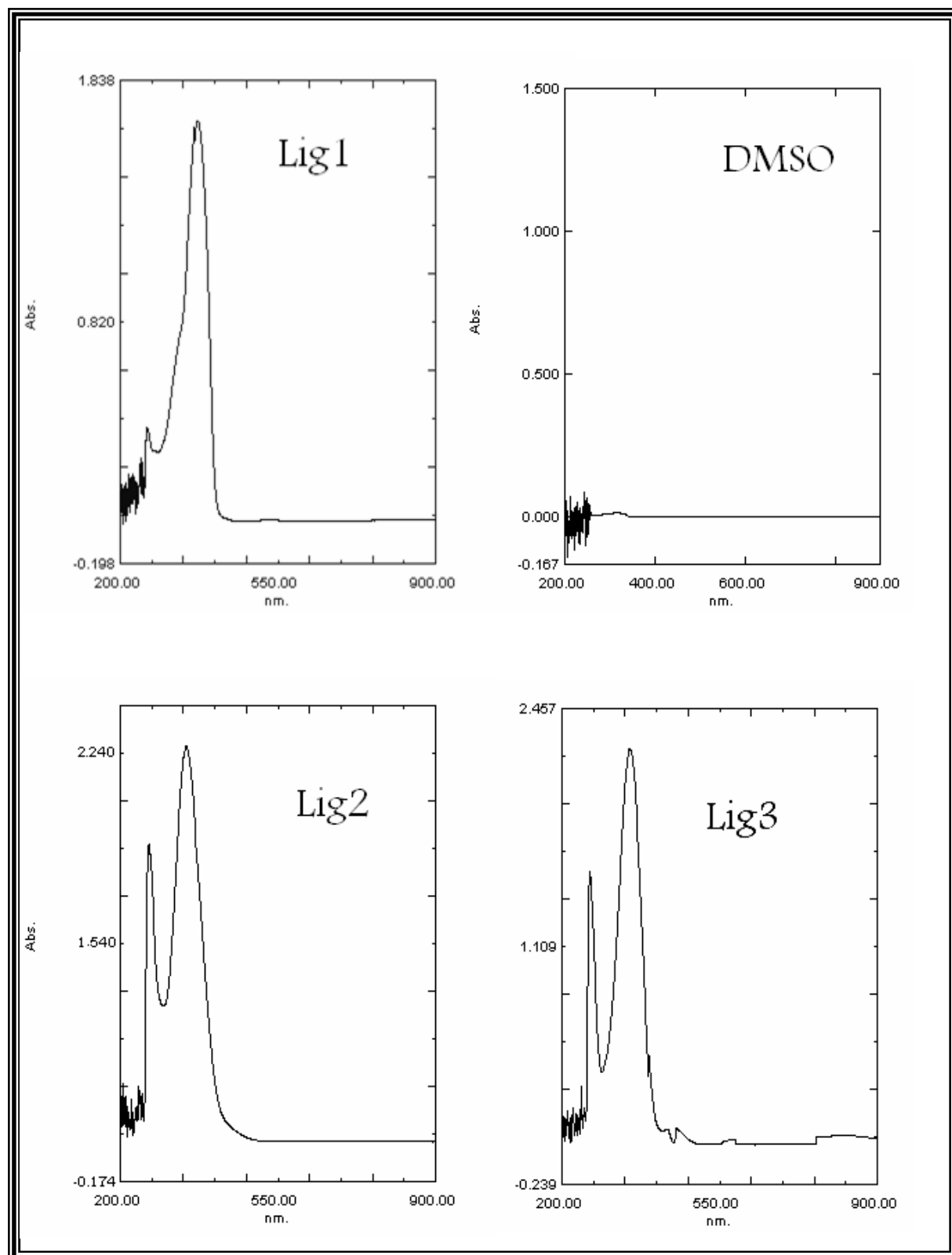
| Symbol | Chemical formula | Name of the compounds |
|--------|--|--|
| Lig1 | $C_{14}H_{11}N_3S$ | Benzylidene-1-benzothiazolhydrazone |
| Lig1Fe | $[Fe_2(Lig1)_2(OH)_2(H_2O)_4] 2SO_4 \cdot 3H_2O$ | Dihydroxy tetraaqua bis-[benzylidene-1-benzothiazolhydrazone] Iron (III). disulphate trihydrate |
| Lig1Co | $[Co (Lig1) (NO_3) (H_2O)_2] NO_3 \cdot 2H_2O$ | Nitrato diaqua [benzylidene-1-benzothiazolhydrazone] cobalt(II) nitrate dihydrate |
| Lig1Mn | $[Mn_2(Lig1)_2(OH)_2(H_2O)_4]2(OH) \cdot 10EtOH$ | Dihydroxy tetraaqua bis-[benzylidene-1-benzothiazol hydrazone] Manganese(II) dihydroxy decaethanol |
| Lig2 | $C_{15}H_{13}N_3SO$ | p-methoxy benzylidene-1-benzothiazolhydrazone |
| Lig2Fe | $[Fe (Lig2) (SO_4) (H_2O)]_2 (SO_4)$ | Sulfato diaqua [p-methoxy benzylidene-1-benzothiazolhydrazone] Iron(III) sulfate |
| Lig2Co | $[Co (Lig2) (NO_3) (H_2O)_2] NO_3 \cdot 2H_2O$ | Diaqua nitrato [p-methoxy benzylidene-1-benzothiazolhydrazone] cobalt(II) nitrate |
| Lig2Mn | $[Mn(Lig2)_2(H_2O)_2] 2(OH) \cdot 6EtOH$ | Diaqua bis-[p-methoxy benzylidene-1-benzothiazol hydrazone] Manganese(II) dihydroxy hexaethanol |

Continue table (3-10) The chemical formula and the name of the ligands and complexes

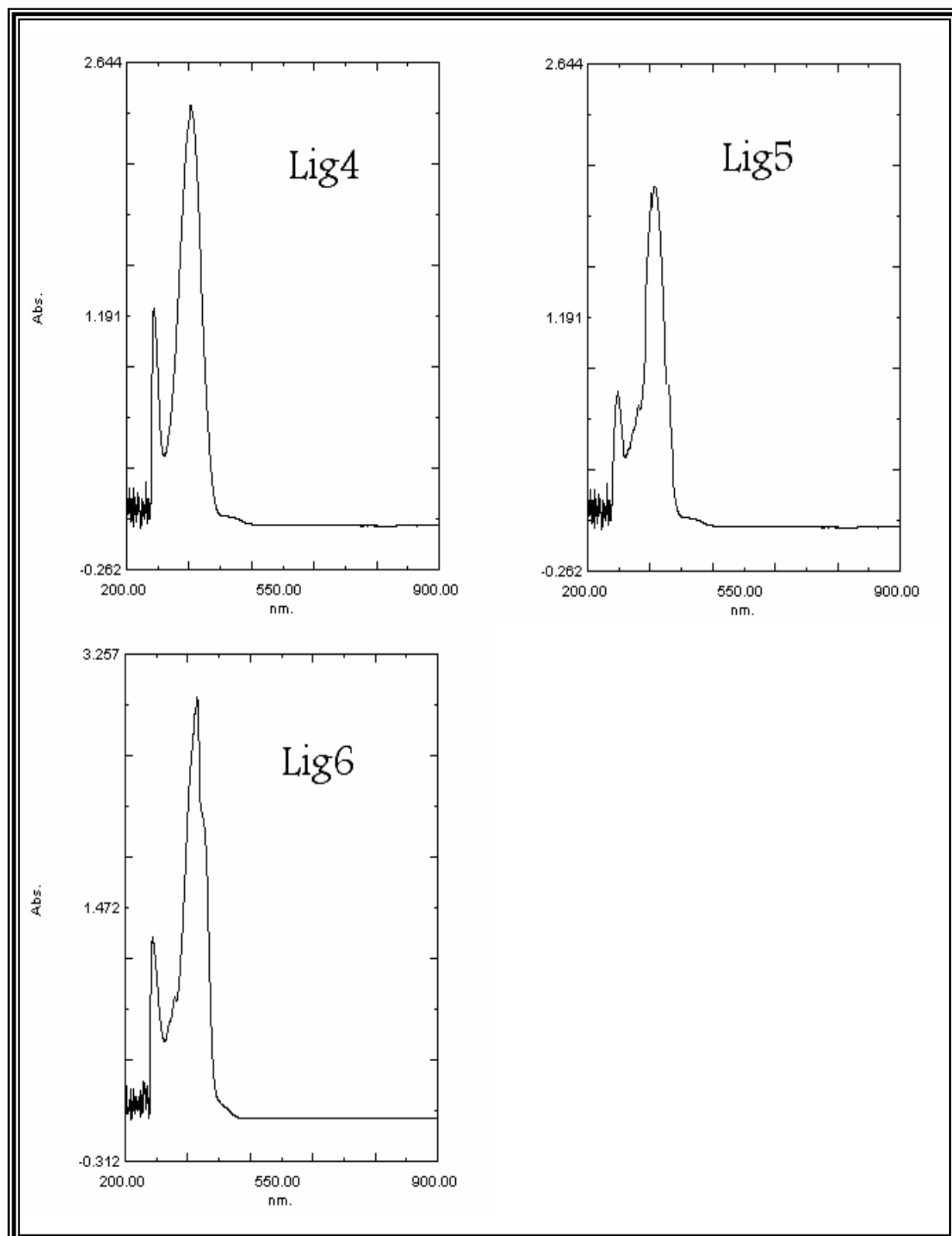
| Symbol | Chemical formula | Name of the compounds |
|--------|--|--|
| Lig3 | $C_{14}H_{10}N_4SO_2$ | <i>m</i> -nitro benzylidene-1-benzothiazolhydrazone |
| Lig3Fe | $[Fe(Lig3)_2(H_2O)_2]_2 \cdot 3SO_4 \cdot 5H_2O$ | Diaqua bis-[<i>m</i> -nitro benzylidene-1-benzothiazolhydrazone] Iron (III) sulfate pentahydrate |
| Lig3Co | $[Co(Lig3)(NO_3)(H_2O)_2] NO_3$ | Nitrato diaqua [<i>m</i> -nitro benzylidene-1-benzothiazolhydrazone] cobalt(II) nitrate |
| Lig3Mn | $[Mn_2(lig3)_2(OH)_2(H_2O)_4]2(OH) \cdot 3EtOH$ | Dihydroxy tetraqua bis-[<i>m</i> -nitro benzylidene-1-benzothiazolhydrazone] Manganese(II) dihydroxy triethanol |
| Lig4 | $C_{14}H_{11}N_3SO_2$ | 2,4-dihydroxy benzylidene-1-benzothiazolhydrazone |
| Lig4Fe | $[Fe(Lig4)_2(H_2O)_2]_2 \cdot 3SO_4 \cdot 6EtOH$ | Diaqua bis-[2,4-dihydroxy benzylidene-1-benzothiazolhydrazone] Iron(III) sulfate hexaethanol |
| Lig4Co | $[Co(Lig4)_2(H_2O)_2] \cdot 2NO_3 \cdot EtOH$ | Diaqua bis-[2,4-dihydroxy benzylidene-1-benzothiazolhydrazone] cobalt(II) nitrate ethanol |
| Lig4Mn | $[Mn(Lig4)_2(H_2O)_2]2(OH) \cdot 3EtOH$ | Diaqua bis-[2,4-dihydroxy benzylidene-1-benzothiazolhydrazone] Manganese(II) dihydroxy triethanol |

Table (3-10) The chemical formula and the name of the ligands and complexes

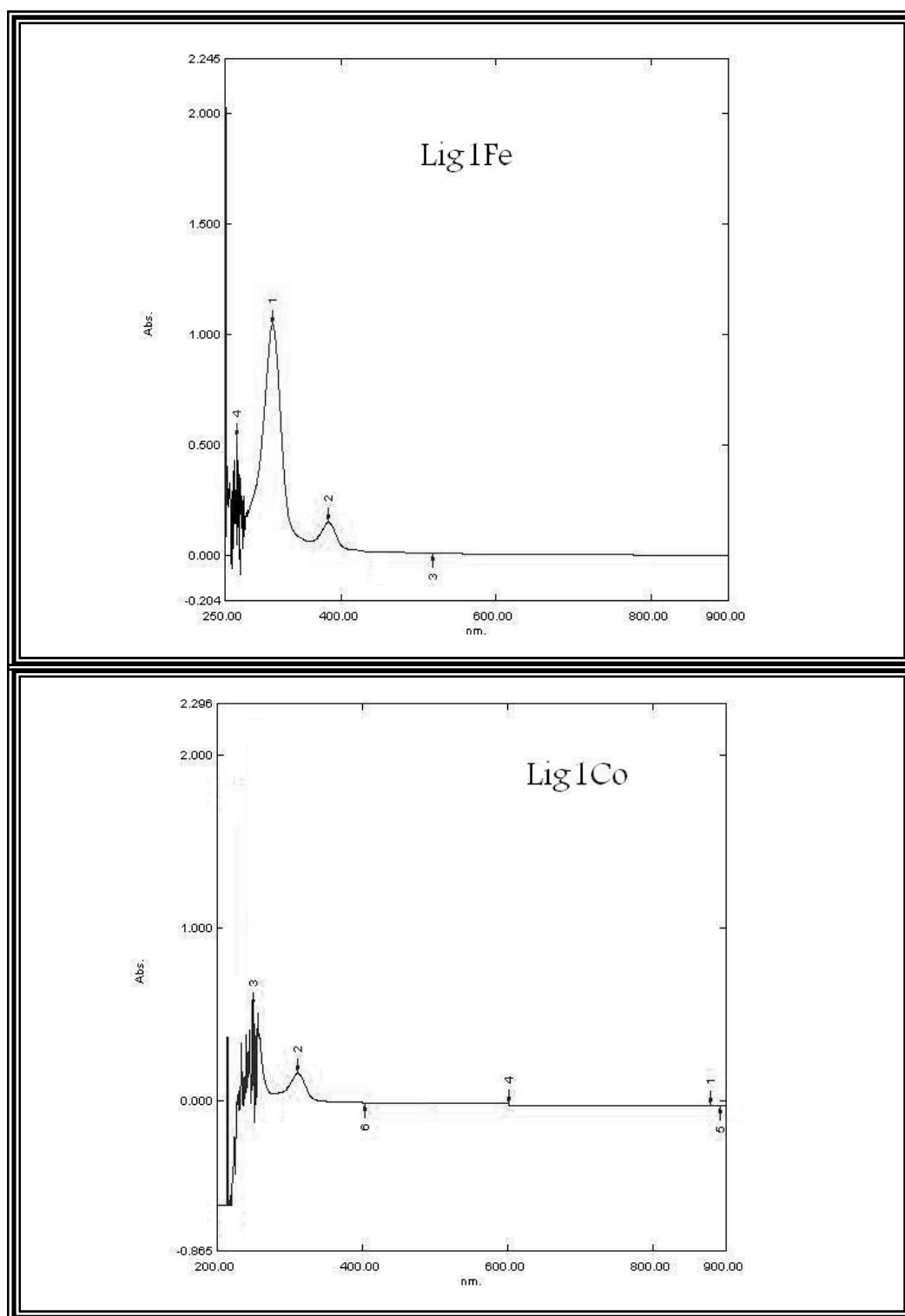
| Symbol | Chemical formula | Name of the compounds |
|--------|---|--|
| Lig5 | $C_{16}H_{16}N_4S$ | ρ -(N,N-dimethyl amine) benzylidene-1-benzothiazolhydrazone |
| Lig5Fe | $[Fe (Lig5)(H_2O)_2(SO_4)]_2 SO_4$ | Sulfato diaqua [ρ -(N,N-dimethyl amine) benzylidene-1-benzothiazolhydrazone]Iron(III) sulfate |
| Lig5Co | $[Co_2 (Lig5)_2(NO_3)_2(H_2O)_4] 2NO_3.9H_2O$ | Tetraaqua dinitrato bis-[ρ -(N,N-dimethyl amine) benzylidene-1-benzothiazolhydrazone] cobalt(II). nitrate heptehydrate |
| Lig6 | $C_{14}H_{10}N_3SBr$ | ρ -bromo benzylidene-1- benzothiazolhydrazone |
| Lig6Fe | $[Fe_2(Lig6)(OH)_2(H_2O)_4] 2SO_4.2H_2O$ | Dihydroxy tetraaqua bis-[ρ -bromo benzylidene-1- benzothiazolhydrazone] Iron(III) sulfate dihydrate |
| Lig6Co | $[Co (Lig6)(NO_3)(H_2O)_2] 2 NO_3.2H_2O$ | Nitrato diaqua [ρ -bromo benzylidene-1-benzothiazolhydrazone] cobalt(II) nitrate dihydrate |



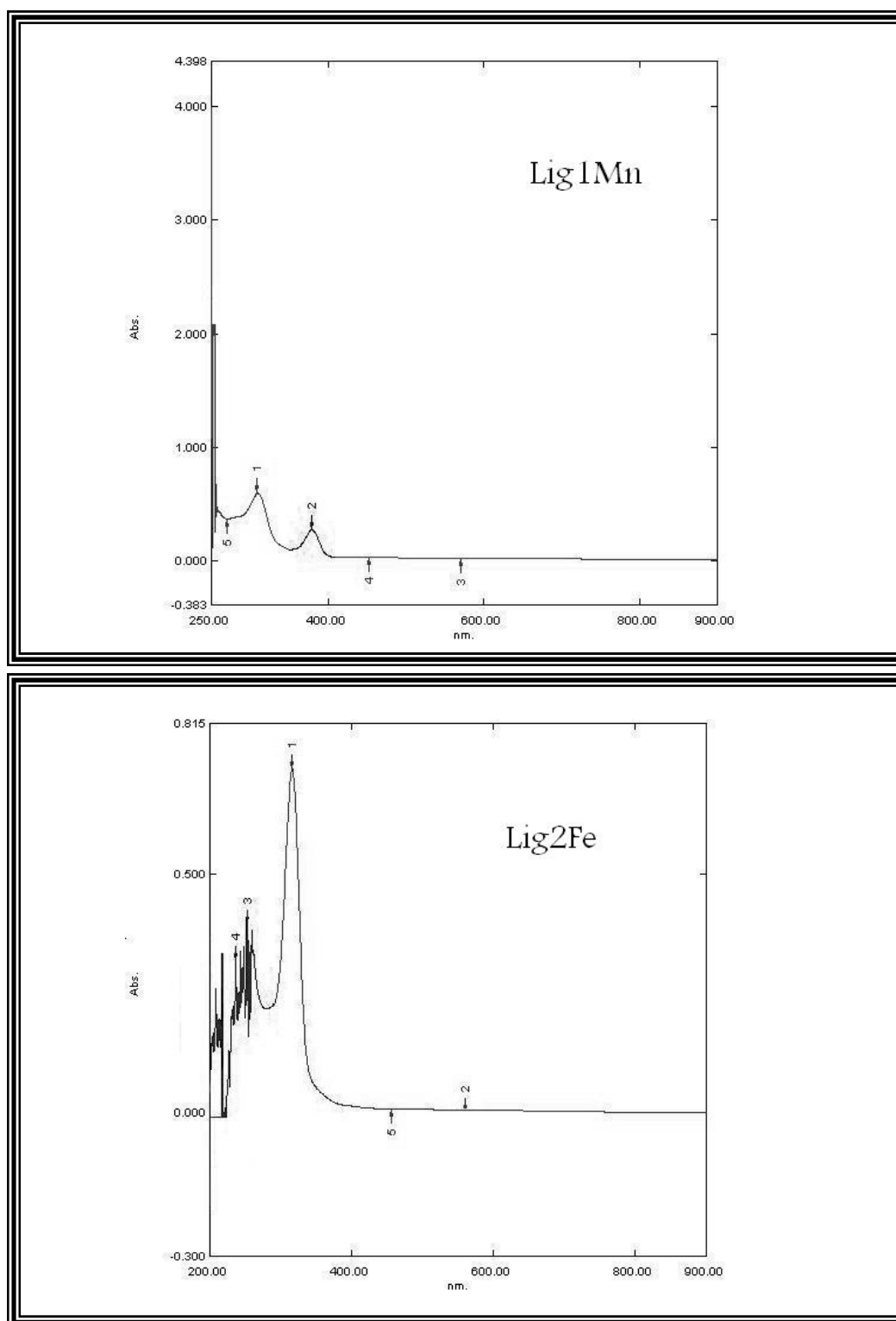
Fig(3-44) Electronic spectra of DMSO, Lig1, Lig2 and Lig3



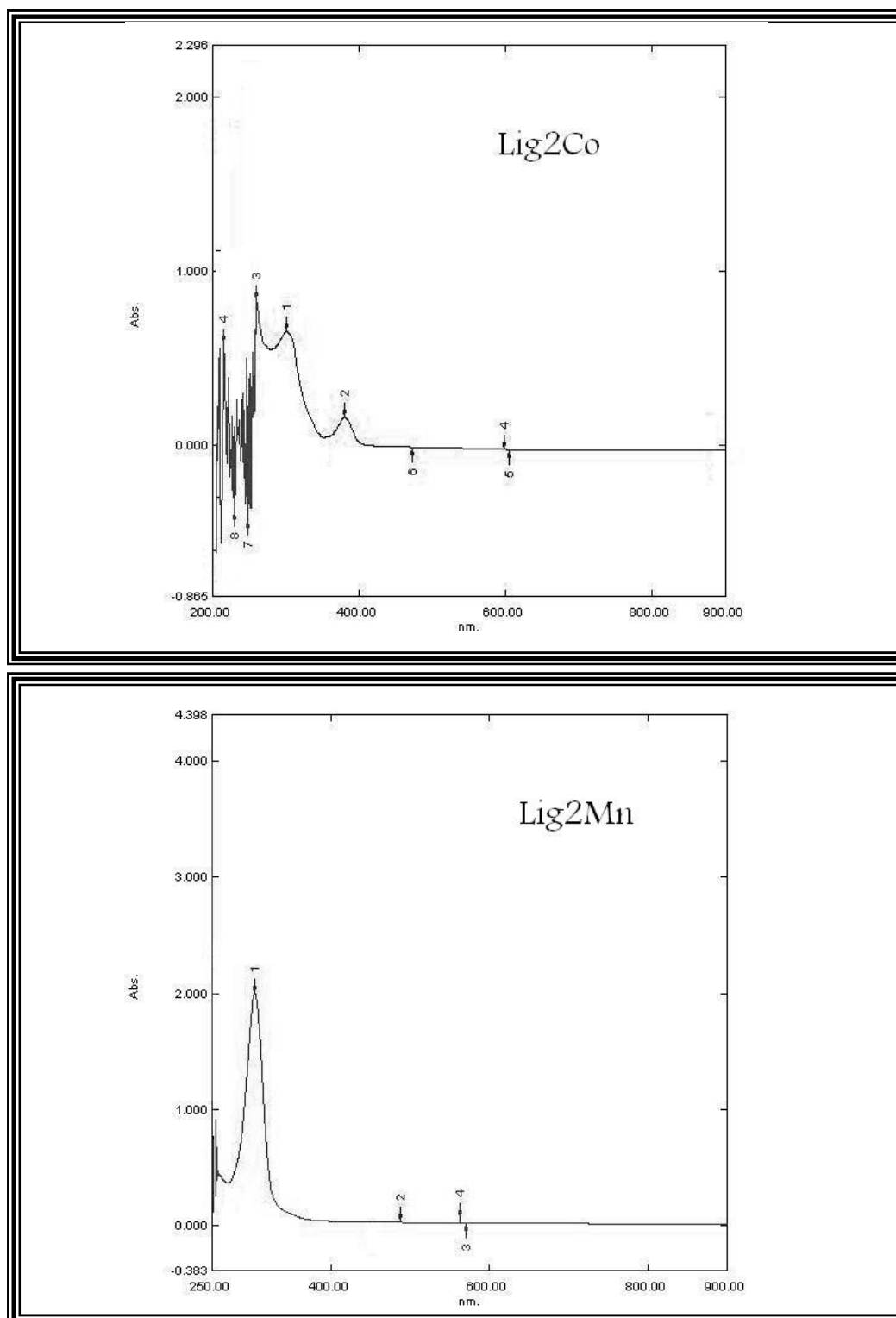
Fig(3-45) Electronic spectra of Lig4, Lig5 and Lig6



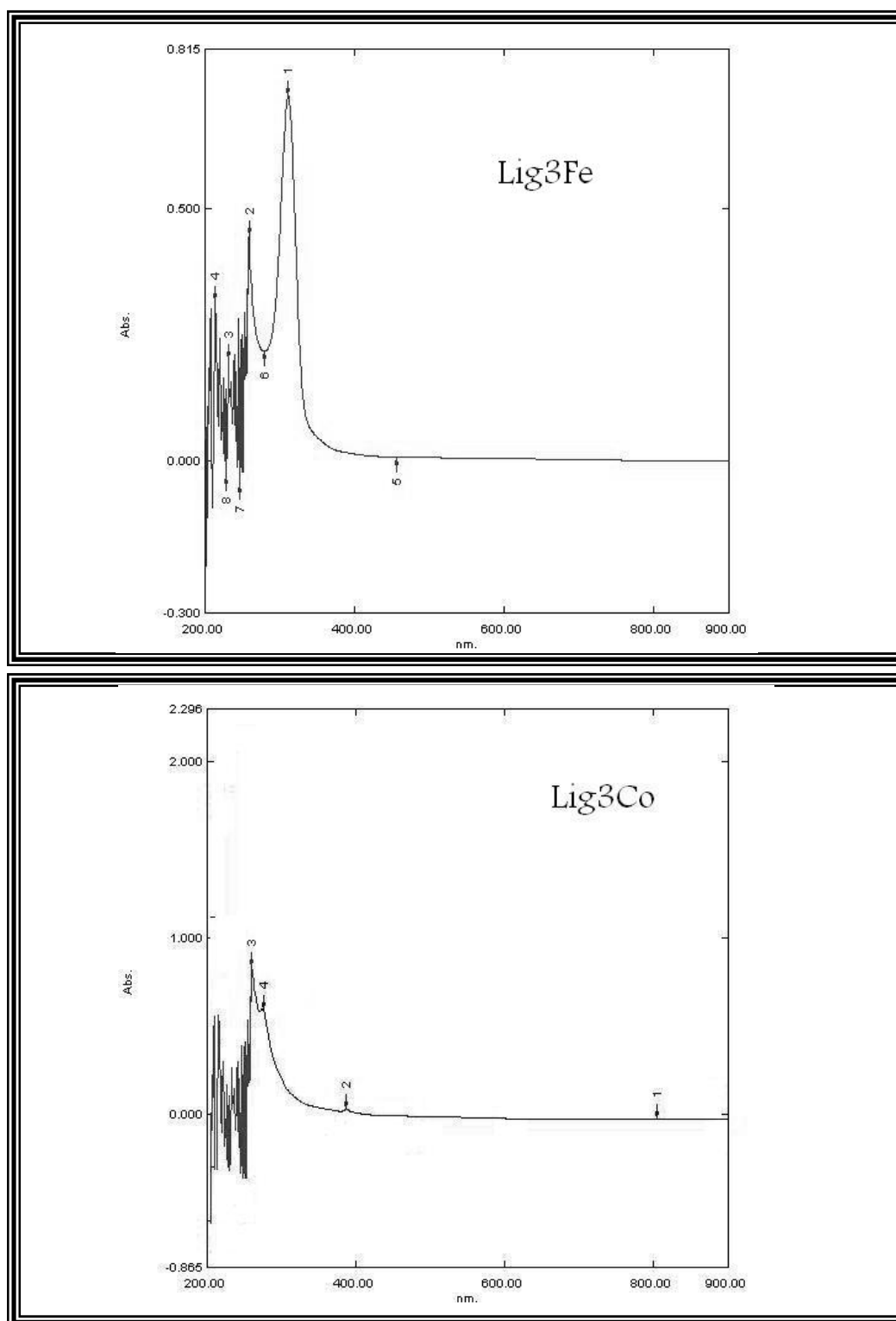
Fig(3-46) Electronic spectra of Lig1Fe and Lig1Co



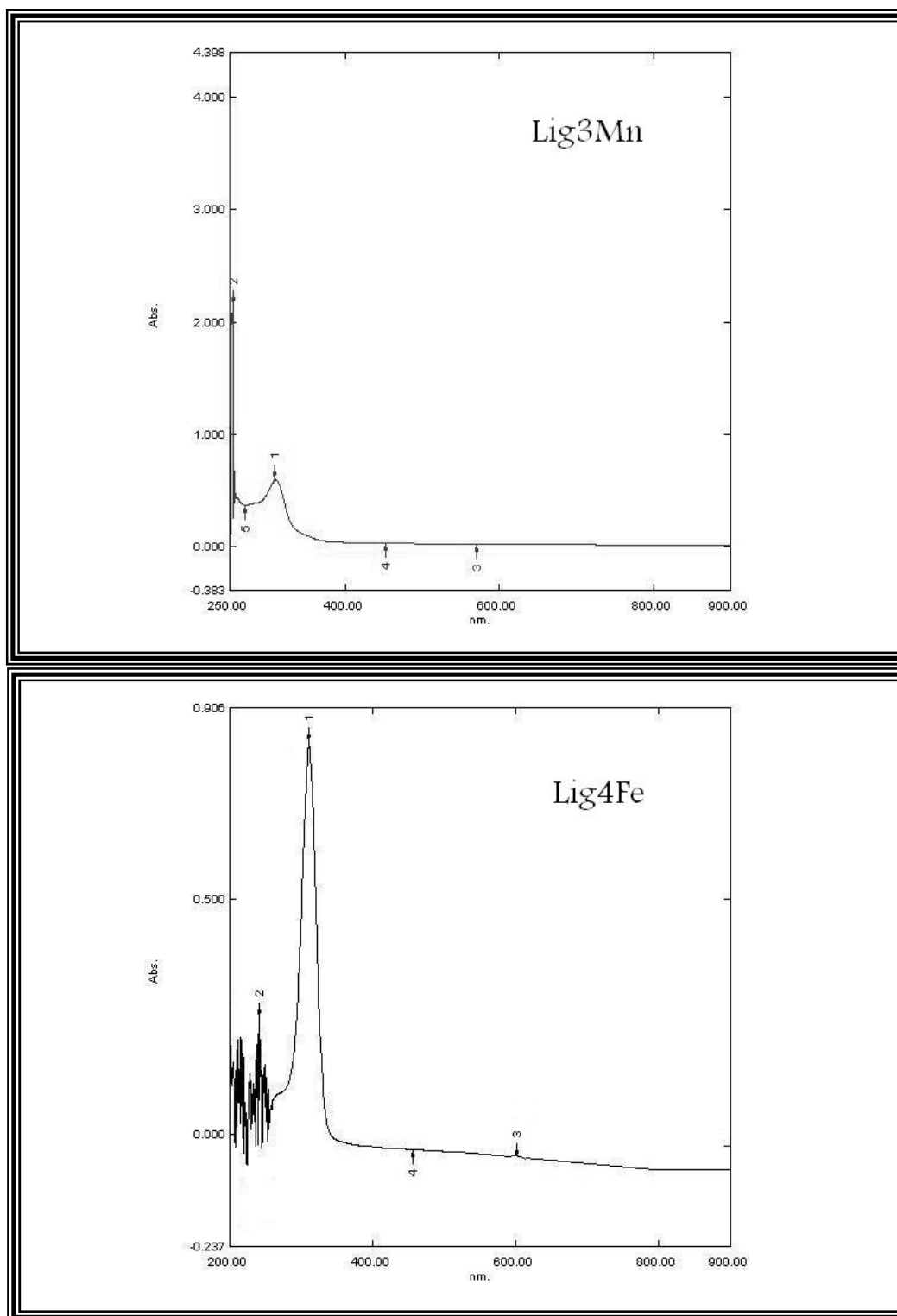
Fig(3-47) Electronic spectra of lig1Mn and Lig2Fe



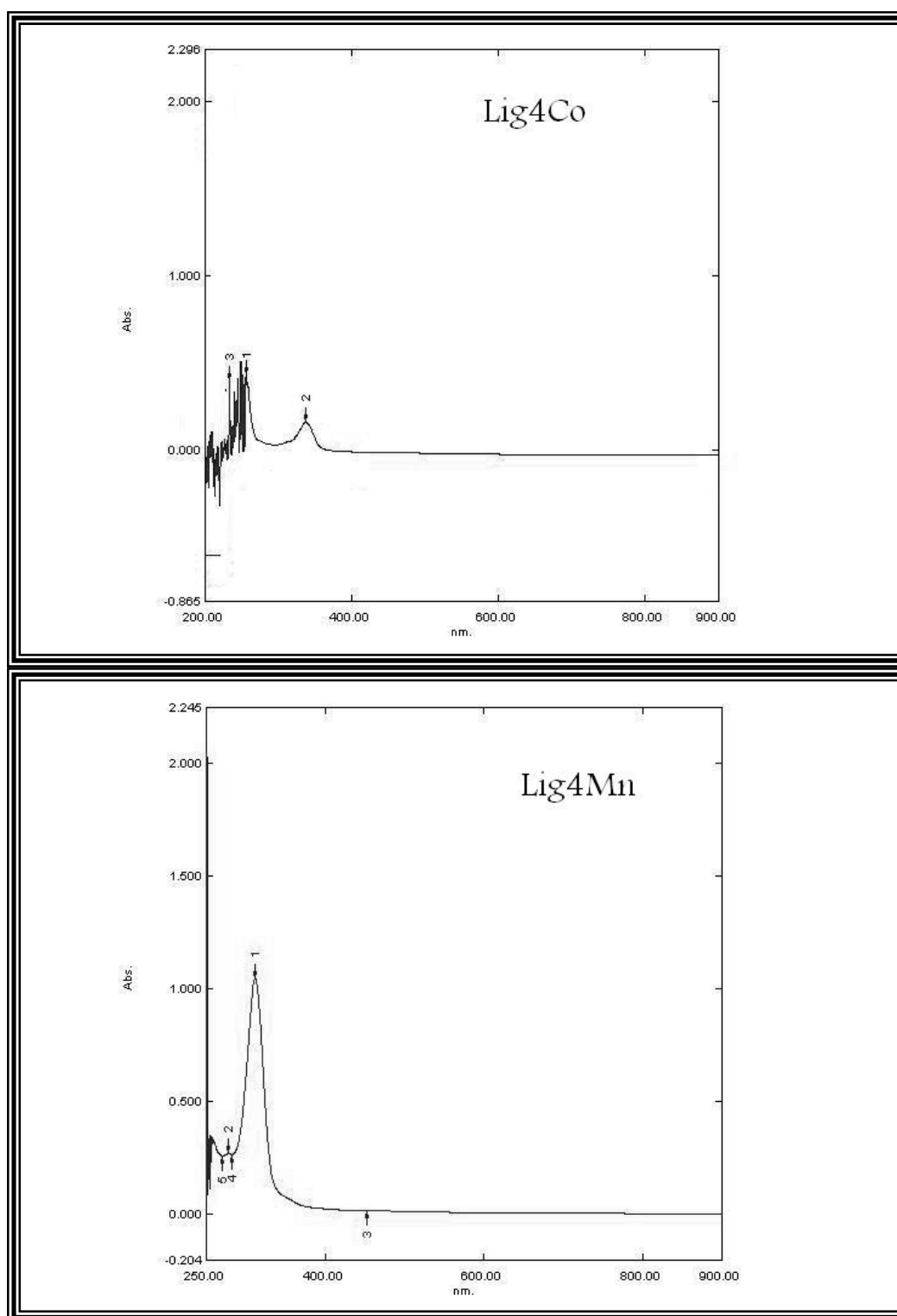
Fig(3-48) Electronic spectra of Lig2Co and Lig2Mn



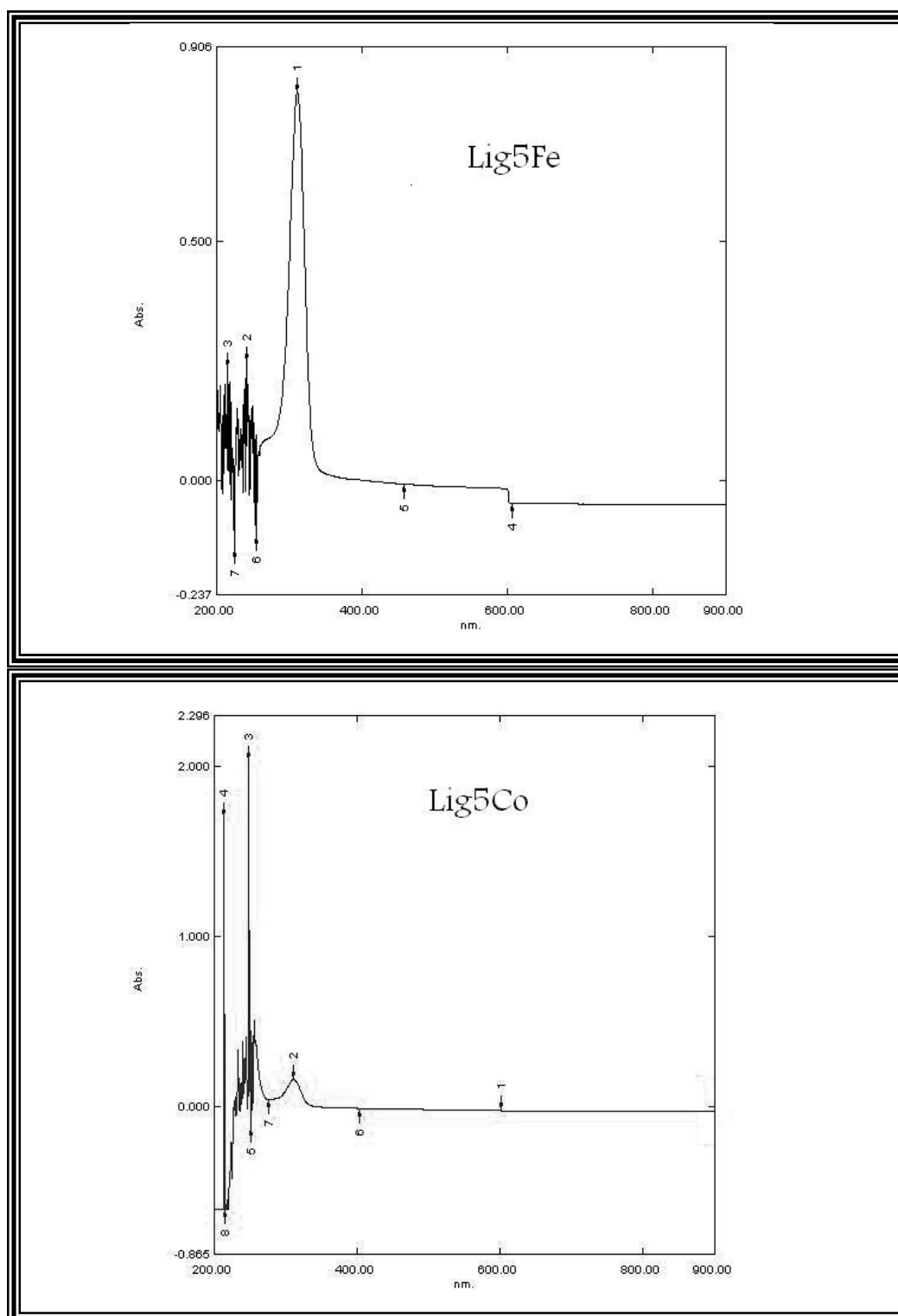
Fig(3-49) Electronic spectra of Lig3Fe and Lig3Co



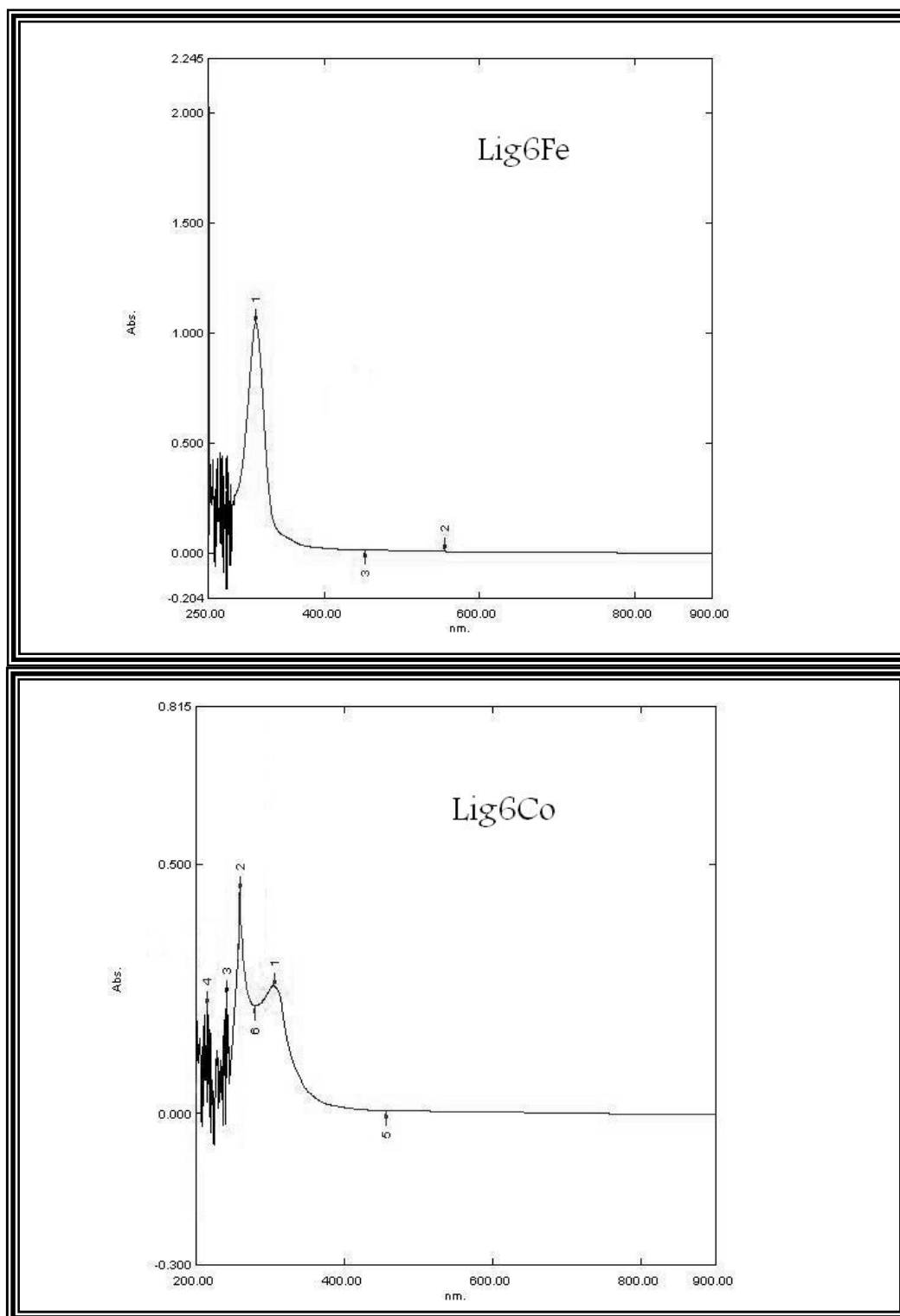
Fig(3-50) Electronic spectra of lig3Mn and Lig4Fe



Fig(3-51) Electronic spectra of Lig4Co and Lig4Mn



Fig(3-52) Electronic spectra of Lig5Fe and Lig5Co



Fig(3-53) Electronic spectra of Lig6Fe and Lig6Co

(3-6) Conclusions:

1. The different Schiff bases which have been prepared showed different physical properties, where the Schiff bases derivatives show different melting point.
2. The reaction of ligands (Lig1, Lig2, lig3, Lig4, Lig5 and Lig6) with the selected transition metal ions gave complexes of monomeric and dimeric structure as follow:

| | Lig1 | Lig2 | Lig3 | Lig4 | Lig5 | Lig6 |
|---------|-----------|-----------|-----------|-----------|-----------|-----------|
| Fe(III) | dimeric | monomeric | monomeric | monomeric | monomeric | dimeric |
| Co(II) | monomeric | monomeric | monomeric | monomeric | dimeric | monomeric |
| Mn(II) | dimeric | monomeric | dimeric | monomeric | --- | --- |

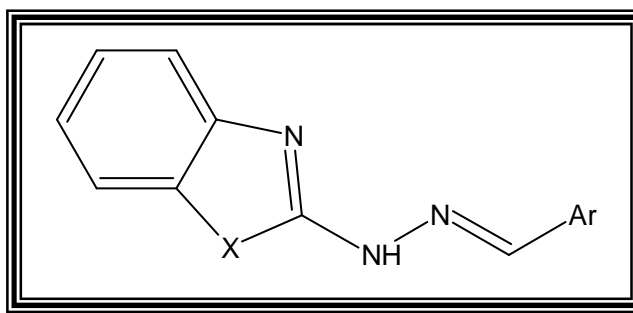
3. All the prepared complexes were ionic.
4. All the prepared complexes were soluble in DMSO.
5. The ligand field calculations showed different field strength (according to the $10Dq$ value) and different electron-repulsion parameter (β) , which refer to different ionic character between the metal and donor atoms of the ligand .

(3-7) Suggestion for future work:

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

- 1) Preparation of another set of transition metal complexes with the other transition metal ions.
- 2) Making a screening antibacterial and antifungal activity of the Schiff base and all the metal complexes, to explore their activity and the synergic effect between the metal and the ligand.
- 3) Synthesizing of some new ligands having the following structure formulae

X=O,NH



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INTRODUCTION

Chapter

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EXPERIMENTAL PART

Chapter

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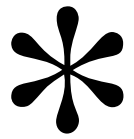
RESULTS AND DISCUSSION

Chapter

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Symbols and Abbreviations

| | |
|------------------|-----------------------------------|
| <i>FT-IR</i> | <i>Fourier transform infrared</i> |
| <i>U.V.-Vis.</i> | <i>Ultraviolet-Visible</i> |
| <i>DMSO</i> | <i>Dimethyl Sulfoxide</i> |
| <i>EtOH</i> | <i>Ethanol</i> |
| <i>Oh</i> | <i>Octahedral</i> |
| <i>B.M.</i> | <i>Bohr magneton</i> |
| ν | <i>Stretching frequency</i> |
| <i>nm</i> | <i>Nanometer</i> |
| λ | <i>Wave length</i> |
| <i>M.P.</i> | <i>Melting point</i> |

Abstract

The present work can be divided into two parts :-

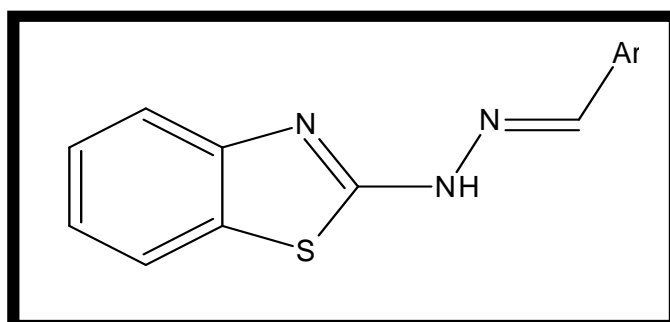
Part one : - Synthesis of six 2-(arylhyazone) benzothiazole ligands and their Fe(III),Co(II) and Mn(II) complexes:

The six ligands were prepared according to the following steps:-

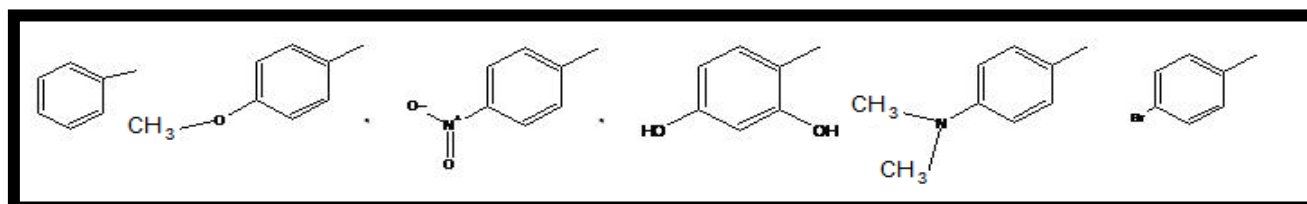
Step-1- :-hydrazinolysis of 2-Mercaptobenzothiazole gave 2-hydrazino benzothiazole .

Step-2- :-The new six ligands [Lig1...Lig6] 2-(arylhyazone)-benzothiazols were synthesized by condensing 2-hydrazino benzothiazole with the appropriate aromatic aldehydes .

The structural formulae of these hydrazones are shown below :-



where Ar =



Step-3- :-Eighteen Fe(III), Co(II) and Mn(II) complexes of the six hydrazones ligands [Lig1...Lig6] were prepared by reaction of the

appropriate metal salt with the corresponding ligand in ethanol under reflux.

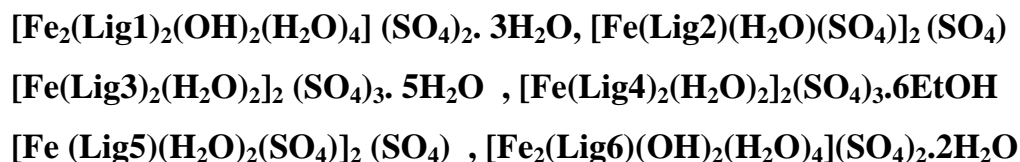
Part two:- Characterization of all the prepared compounds:

The synthesized ligands [Lig1...Lig6] were characterized on the basis of IR spectral analysis and the results were compatible with their assigned structures .

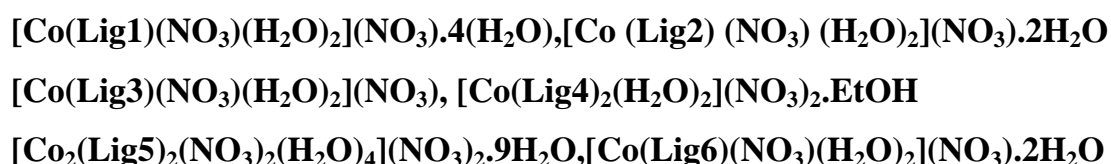
The metal complexes of the hydrazones [Lig1...Lig6] have been characterized by FT-IR, UV-Vis spectra, conductivity, magnetic susceptibility measurements and metal analysis .

On the bases of these techniques the structural and formulae of the complexes have been suggested which were octahedral for all complexes:-

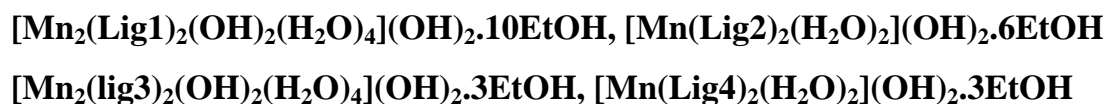
1. The complexes of Fe(III) ion with the ligands [Lig1...Lig6] suggested to have the following molecular formula:-



2. The complexes of Co(II) ion with the ligands [Lig1...Lig6] suggested to have the formula :-



3. The complexes of Mn(II) ion with the ligands [Lig1...Lig6] suggested to have a formula :-



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

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It is a pleasure to express my Sincere thanks and appreciation to my best supervisor Prof. Dr. Ayad Hamza Jassim for suggesting the subject of this thesis and the supervision and encouragement throughout the course of the work without which this work would not been completed.

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At Last, in life you see a lot of people, but a few of them can give you some of help....

Zaid Almaliky
2007

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عنوان الأطروحة: تحضير و دراسة خواص بعض

معقدات العناصر الانتقالية $Co(II), Fe(III)$

$Mn(II)$ مع ٢- ارايل هايدرازون-

بنزو ثيازول.

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الأهداء

الى من نزفه وما زال ينزفه الدهاء

الى وطني الحبيب

الله أكبر

العراق

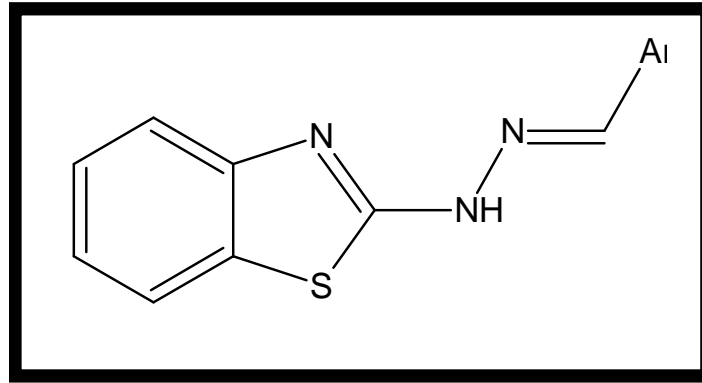
الخلاصة

هذا العمل يمكن تجزئته إلى جزئين :-

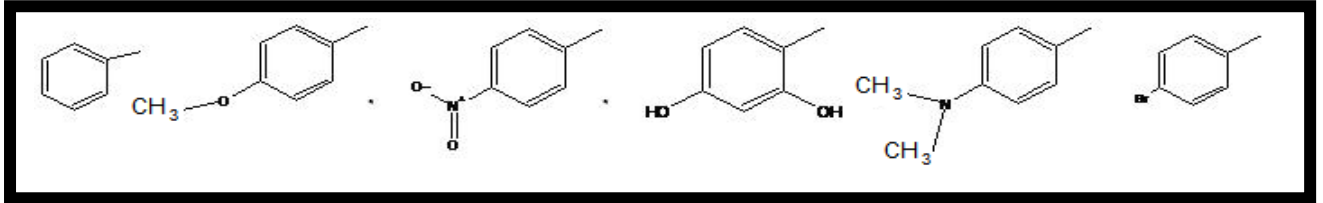
الجزء الأول :- تحضير ستة ليكندات عضوية 2-اراييل هايدروزون – بنزو ثيازول و معقداتها التي حضرت بالتفاعل مع الفلزات الاتية $(Mn (II), Co (II), Fe (III))$ ، التي تم تحضيرها خلال الخطوات التالية :-

(١) - اضافة هايدرازين الى ٢-مركبتو بنزو ثيازول والذي ينتج ٢- هايدرازينو بنزو ثيازول.
(٢) الليكندات الستة و هي ٢- ارايل هايدروزون – بنزو ثيازول [Lig1- Lig6] التي تحضر باضافة الديهايدات الاروماتية الستة [Ar] الى ٢-هايدرازينو بنزو ثيازول.

الصيغة البنائية لهذه الليكندات الستة توضح بالصيغة التالية:-



Ar =

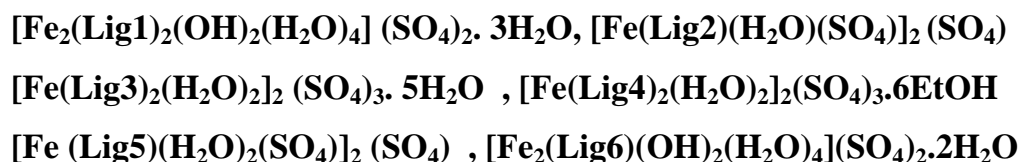


(٣) - المعقدات الستة عشر للاملاح $(Mn (II), Co (II), Fe (III))$ تحضر من تفاعل الليكندات الستة التي هي ٢- ارايل هايدروزون – بنزو ثيازول مع أملاح الفلزات التالية $(Mn (II), Co (II), Fe (III))$ في محلول الايثانول وتحت حرارة معينة .

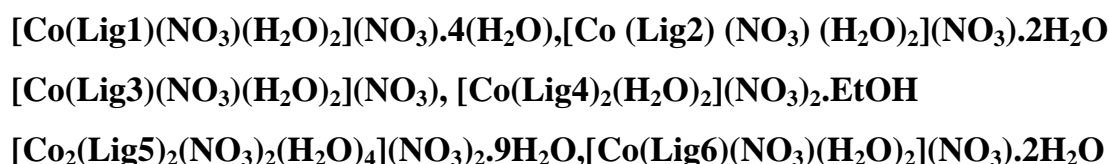
الجزء الثاني :- تم عزل المعقدات الفلزية للكندات في الحالة الصلبة وكانت مستقرة اتجاه الضوء والرطوبة والحرارة . شخضت المعقدات الجديدة بواسطة اطياف الاشعة تحت الحمراء

(FT-IR) ، والأشعة فوق البنفسجية المرئية (UV-VIS) ، والقياسات المغناطيسية والتوصيلية الكهربائية إضافة إلى تحليل العناصر وجد أن كل المعقدات ثمانية السطوح استناداً إلى نتائج القياس أعلاه تم اقتراح الصيغ التركيبية الآتية :-

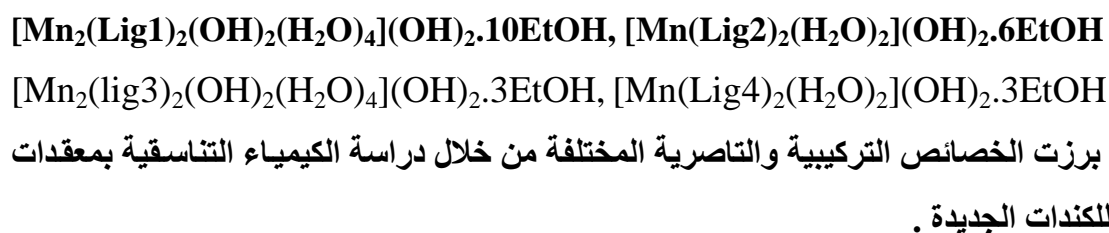
(١) - معقدات أيون الحديد الثلاثي مع اللكندات [Lig1... Lig6] تعطي الصيغ التالية:-



(٢) - معقدات أيون الكوبلت الثنائي مع اللكندات [Lig1... Lig6] تعطي الصيغ التالية:-



(٣) - معقدات أيون المنغنيز الثنائي مع اللكندات [Lig1... Lig6] تعطي الصيغ التالية:-



فسرت طبيعة التأصل بين أيون الفلزات والذرات المانحة في الليكند بمعامل رآكاح ومقياس المجال الليكندي الأخرى التي تم احتسابها بواسطة مخطط (تنابا-سوكانو) لـ أيون الحديد الثلاثي والكوبلت الثنائي والمنغنيز الثنائي .

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



*Synthesis and Characterization of Fe (III),
Co (II) , and Mn (II) with 2- (Arylhydrazone)-
Benzothiazoles Complexes*

A Thesis
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بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

وَفَوِّضْ

صَدَقَ اللَّهُ الْعَظِيمُ

سورة يوسف
الاية (٧٦)

Supervisor Certification

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

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

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We, the examining committee, certify that we read this thesis and have examined the student (**Zaid M. Abbas**), in its contents and that, in our opinion; it is adequate as a thesis for the Degree of Master of Science in Chemistry .

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كلية العلوم
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تحضير و دراسة خواص بعض معقدات
العناصر الانتقالية $Co(II), Fe(III)$
 $Mn(II)$ مع ٢ - ارايل هايدرازون -
بنزو ثيازول

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

من قبل
زيد محمد المالكي
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