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College of Science

Synthesis and Characterization of some Transition Metal Complexes via Schiff Bases Derived from Dithiooxamide and Selective Aldehydes

A Thesis Submitted to the College of Science

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By

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In the name of Allah

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Abstract

The first part of this work was to optimize the synthesis of a Schiff base *N,N′*-bis (2-hydroxybenzylidene) dithiooxamide (LH1) derived from the reaction between the dithiooxamide with 2-hydroxybenzyaldehyde. Five complexes were synthesized using metal ions Cobalt (II), Nickel (II) , Copper (II), Palladium(II) and Platinum (IV), characterized and the properties of these compounds were studied. CHNS elemental analysis technique was used to identify and determine the amount of elements that are present in a ligand. Infrared spectroscopy (FT-IR), UV- Visible spectroscopy and ^{1}H NMR spectroscopy were used to identify the structures of the compounds. The magnetic susceptibility was measured; magnetic moment of Cobalt (II) complex was 2.82 B.M, magnetic moment of Nickel (II), Copper(II), Palladium(II) and Platinum(IV)complexes were dimagnatic. Conductivity of complexes were measured using DMSO as a solvent where conductivities of complexes as follow, ionic in ratio (1:1) of Co(II) complex while non-ionic of Ni(II) , Cu(II), Pd(II) and Pt(IV) complexes. The atomic absorption of complexes was calculated and we found that the experiment values were approximately equal to theory values. Therefore, the proposed structures of complexes were, octahedral of CoLH1 , square planer of NiLH1,CuLH1 and PdLH1 and octahedral for PtLH1. Lastly, the ligand LH1, CoLH1 and CuLH1 showed greater activity against *Aspergillus niger* while the complexes NiLH1, PdLH1 and PtLH1 not show any activity against this fungi.

The second part of this work was to optimize the synthesis of a Schiff base *N,N'*-bis(3,4,5-trimethoxybenzylidene)dithiooxamide (LH2). derived from the reaction between the dithiooxamide with 3,4,5-trimethoxybenzyaldehyde. The reaction was refluxed for 12 hours at 70 °C. Five complexes were synthesized using metal ions Cobalt (II), Nickel (II) , Copper (II), Palladium (II) and Platinum (IV), characterized and the properties of these compounds were studied. CHNS elemental analysis technique was used to identify and determine the amount of elements that are present in a ligand. Infrared spectroscopy (FT-IR), UV- Visible spectroscopy an ^{1}H NMR spectroscopy were used to identify the structures of the compound. The magnetic susceptibility was measured; magnetic moment of Cobalt (II) complex was 2.6885 B.M, magnetic moment of Nickel (II) was 3.394 B.M, magnetic moment of Copper(II) was 1.65856 While, Palladium(II) and Platinum(IV) complexes were dimagnatic. Conductivity of complexes were measured using DMSO as a solvent where conductivities of complexes were ionic in ratio (1:2) of Co(II), Ni(II), Cu (II), Pd (II) and Pt (IV) complexes. The atomic absorption of complexes was calculated and we found that the experiment values were approximately equal to theory values. Therefore, the proposed structures of complexes were, octahedral of CoLH1, NiLH1,CuLH1, PtLH1 and square planer of PdLH1. Lastly, the ligand LH2, NiLH2 and CuLH2 showed greater activity against *Aspergillus niger*. while the complexes CoLH2, PdLH2 and PtLH2 not show any activity against this fungi.

List of symbols and abbreviations

Symbol	***Meaning***
en	ethylenediamine
gly	glycinate ion
dien	diethylentriamine
Terpy	Terpyridine
Tetriene	Triethylenetetramine
$(EDTA^{-4})$	Ethylenediaminetetraacetato
CO	Carbon oxide
L	Ligand
M	Metal
VBA	Valence Bond Approach
CFA	Crystal Field Approach
LFA	Ligand Field Approach
MOA	Molecular Orbital Approach
Δ G	Activation energy
E	Energy
h	Plank constant frequency
-N=CH-	imine
DTO	Dithiooxamide
PDT	Photodynamic therapy
LH1	*N*,*N*′-bis(2-hydroxybenzylidene) dithiooxamide
LH2	*N*,*N*′-bis(3,4,5-trimethoxybenzylidene) dithiooxamide

%	Percentage
dec.	decomposition
h	hour
mol	mole
M	Molar
℃	Degree Celsius
EMR	Electromagnetic radiation
s	strong
m	medium
w	weak
Coor.	Coordination
o.o.p.	Out of plane
s.	symmetric
as	asymmetric
Vis	Visible
UV	Ultraviolet Spectroscopy
IR	Infrared Spectroscopy
EA	Elemental Analysis
AAS	Atomic Absorption Spectrometry
Λ_m	Molar conductiviyy
NMR	Nuclear Magnetic Resonance
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
nm	nano meter
B	Bohr magnaton
λ_{max}	Wave length

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CHAPTER 1

INTRODUCTION

The first section of this chapter includes a general introduction about coordination chemistry and transition metal complexes of Schiff bases. General methods of preparation of Schiff bases derived from dithiooxamide will be reviewed. Metal complexes will be illustrated in the second part of this chapter.

1.1. Coordination Chemistry

Bonds in introductory chemistry are typically classified according to whether they are ionic or covalent in character[1]. **Coordinate covalent bonds** are a third classification. In this type of bond, a lone pair of electrons from one chemical species is donated to an empty orbital on another chemical species to form the new bond[2]. This type of bond is known variously as a coordination, a dative covalent or a donor-acceptor bond[3]. A compound containing such bonding is known as a coordination compound. Coordination compounds are formed between a metal atom or ion and a molecule with one or more unshared electron pairs, called a **ligand**[4]. Ligands are species (neutral or anionic) bonded to the metal ion[5]. Anions as well as neutral molecules may act as ligands. If one or more neutral molecules coordinate to metal ion, the resulting species retains the charge of the transition metal ion and is called a **complex ion**[6]. A Coordination Complex/Compound is One of a number of complex compounds in which an atom or group of atoms is bound to the central atom by a shared pair of electrons supplied by the coordinated group and not by the central atom[7]. An example for this complex is shown in figure (1-1):

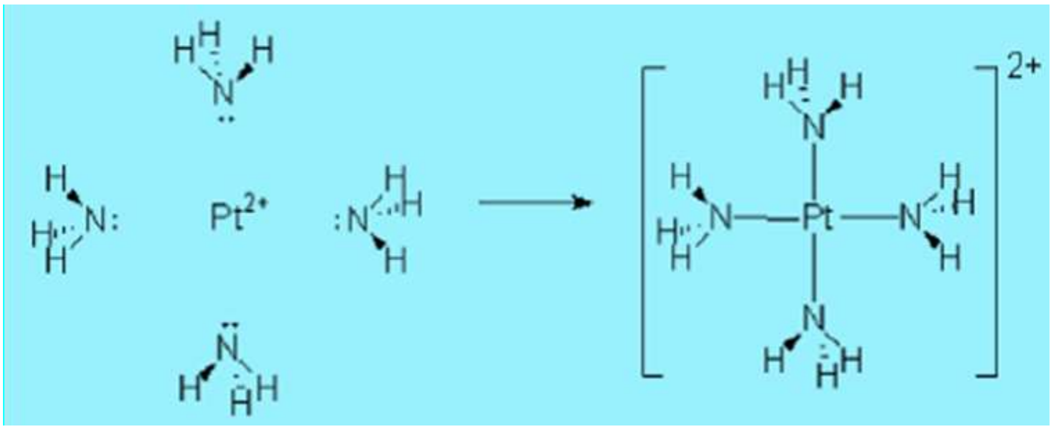


Fig.(1-1):Formation of Coordination Complex

Ligands may be classified according to the number of donor atoms they contain. A **monodentate** ligand donates a single electron pair to the metal or metal ion[8]. There are many examples of monodentate ligands in figure (1-2) :

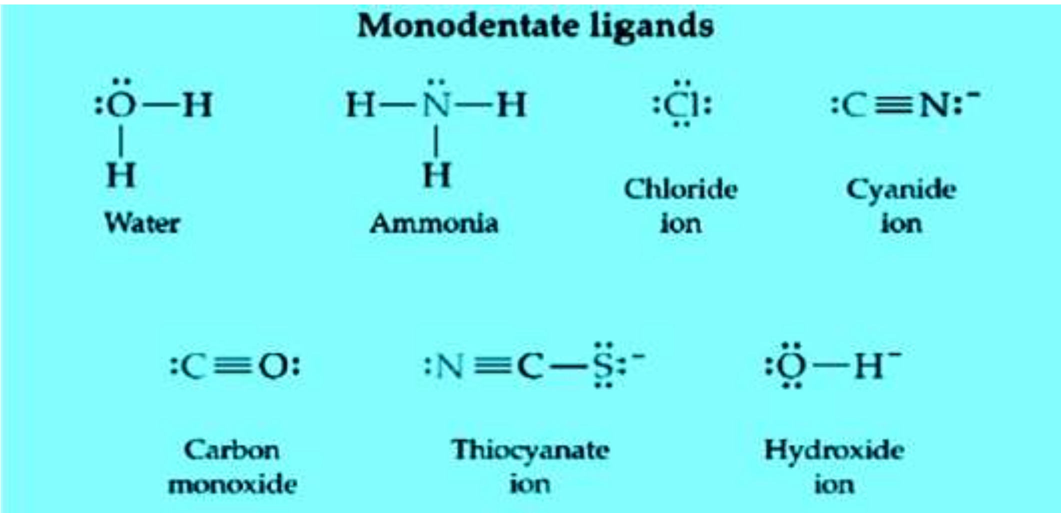


Fig.(1-2): Examples of monodentate Ligands

A **bidentate** ligand, as the name suggests, donates two electron pairs to the metal or metal ion. A good example is ethylenediamine, $NH_2CH_2CH_2NH_2$. There are many example of bidentate ligand such as [9] in figure (1-3):

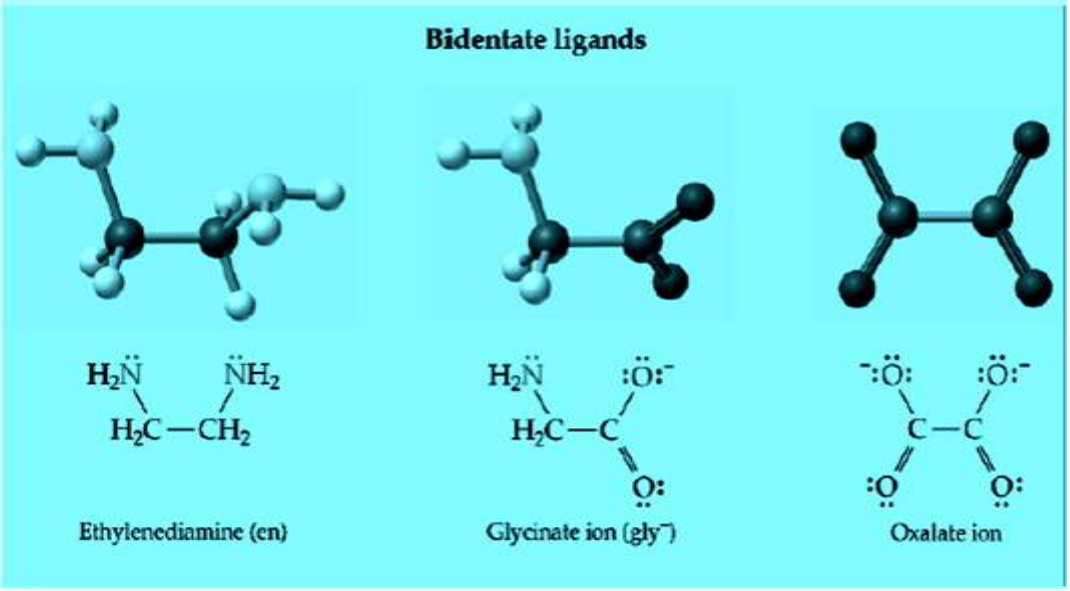


Fig.(1-3): Examples of bidentate Ligands

Bidentate ligands may be classified according to the number of atoms in the ligand which separate the donor atoms and hence the size of the chelate ring formed with the metal ion. Thus 1,1-ligands form a four-membered chelate ring when bound to a metal ion, 1,2-ligands a five membered ring, and 1,3-ligands a six membered ring[10]. These types are shown in figure (1-4):

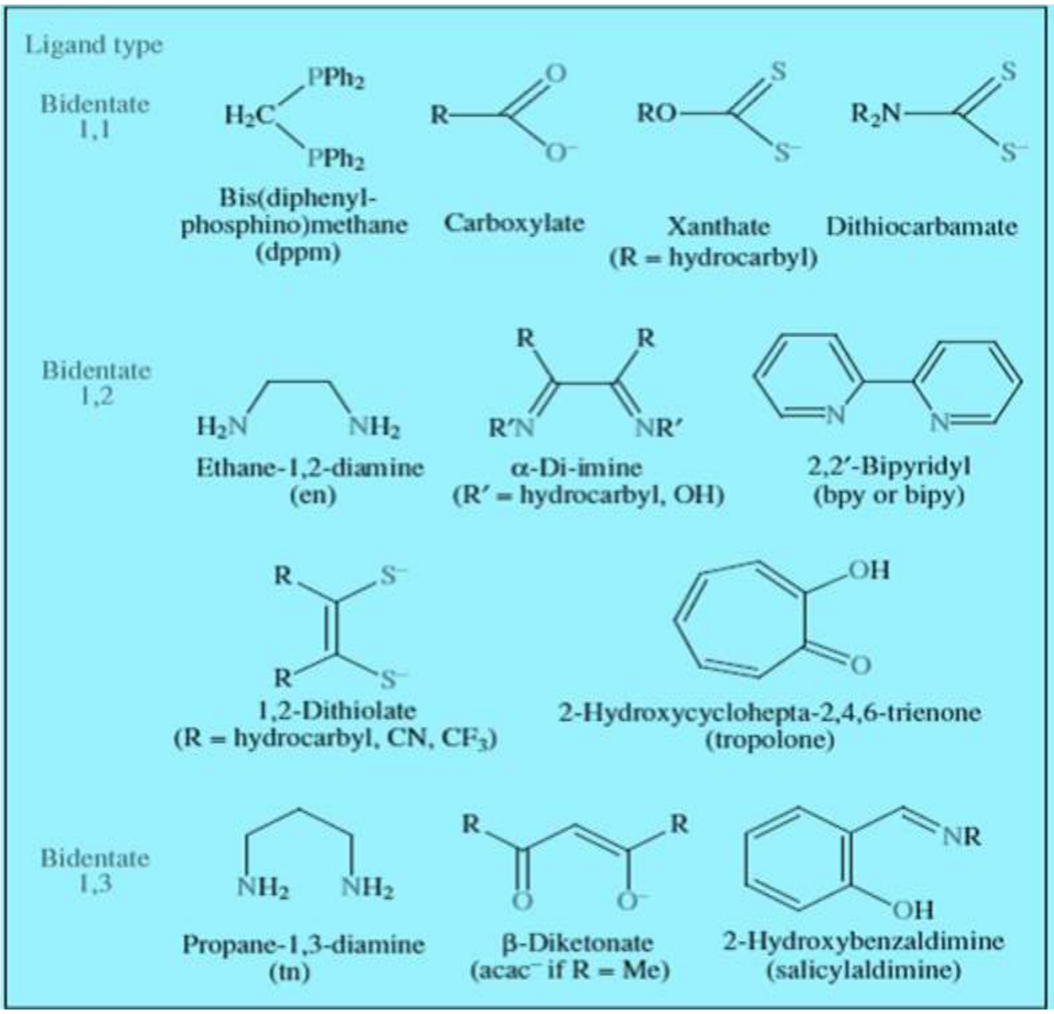


Fig.(1-4):Types of Bidentate Ligands difference in membered chelate ring

Polydentate ligands having more than two donor atoms(tridentate, tetradentate, pentadentate, hexadentate, etc)[11]. Tridentate (denticity of 3), e.g. diethylenetriamine (dien), terpyridine (terpy) etc. Here coordination to the metal atom can take place through the three nitrogen atoms[12].

There are types of tridentate ligand shown in figure (1-5)[13]:

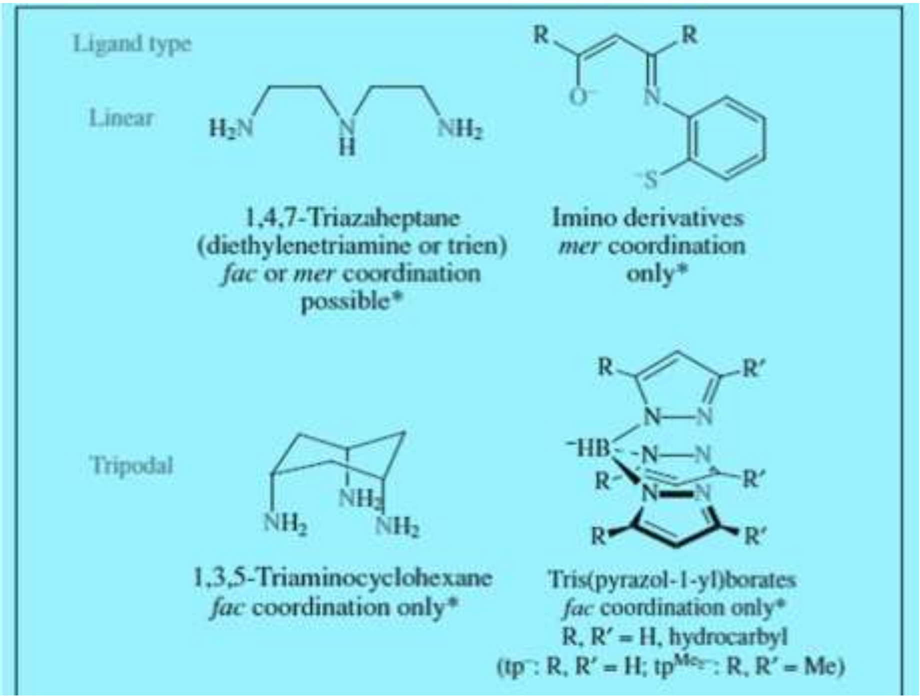


Fig.(1-5):Types of Tridentate ligands

There are types of tetradentate ligand shown in figure (1-6)[14,15]:

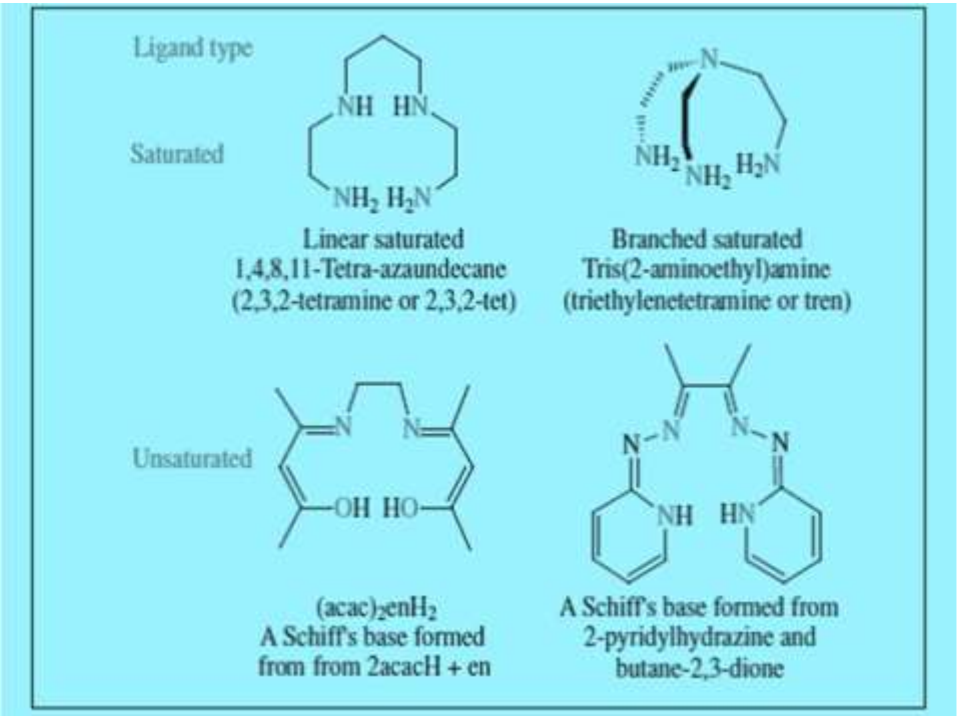
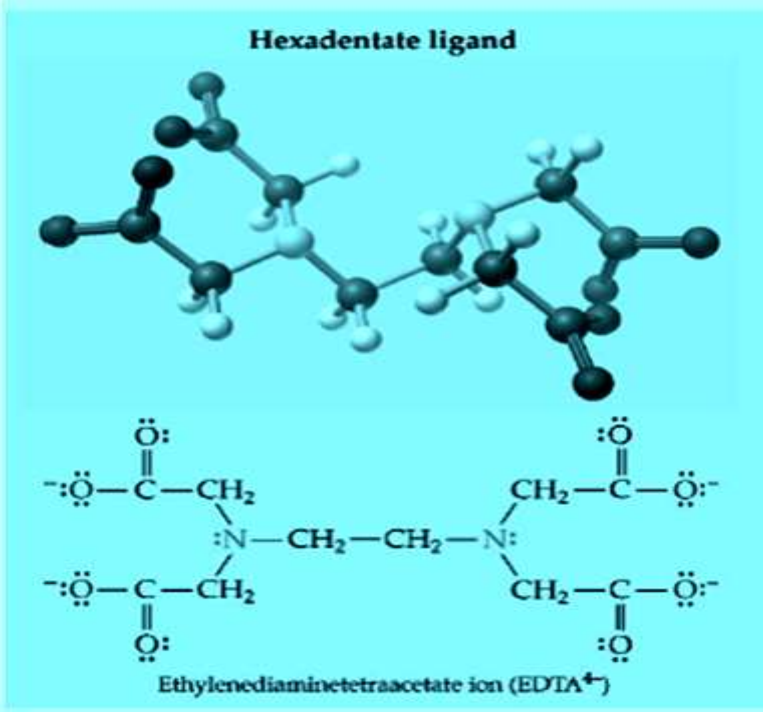


Fig.(1-6):Types of Tetradentate Ligands

pentadentate ligand (denticity of 5), e.g. ethylenediaminetriacetato. Here coordination to the metal atom can take place through the two nitrogen atoms and three oxygen atoms of the acetate group[16].

hexadentate ligand (denticity of 6) , e.g. ethylenediaminetetraacetato ($EDTA^{-4}$). Here coordination to the metal atom can take place through the two nitrogen atoms and four oxygen atoms of the acetate group[17]. Also there are many examples of hexadentate Schiff base. Here coordination to the metal atom can take place through the four nitrogen atoms and two oxygen atoms[18]. figure (1-7) shows examples of hexadentate ligands :



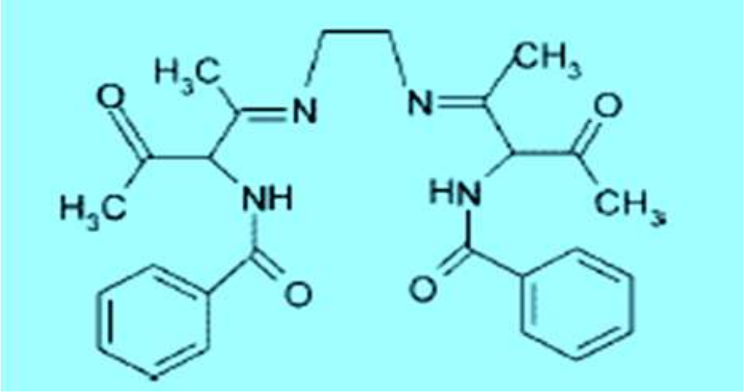


Fig.(1-7):Types of Hexadentate Ligands

In many bidentate to polydentate ligands, the ligand is bonded to the same central metal atom at two or more places due to which a ring structure is formed. Such a ring structure formed by a bidentate (or polydentate) ligand is known as a **chelate**[19]. called a chelate (***Chelating Ligands***) is commonly added to food products such as commercial salad dressings, is often used to treat heavy metal poisoning such as Hg^{2+}, Pb^{2+}, and Cd^{2+}. One very important chelating agent is ethylenediaminetetraacetate EDTA is used to tie up Ca^{2+} in bathroom cleaners, shower sprays to prevent blood clots ,to remove heavy metals from the body when poisoned to

\iron in plant fertilizer and to remove the iron taste from mayonnaise (arising from its preparation in iron vats)[20]. There are many examples of chelating ligand such as in figure (1-8)[21]:

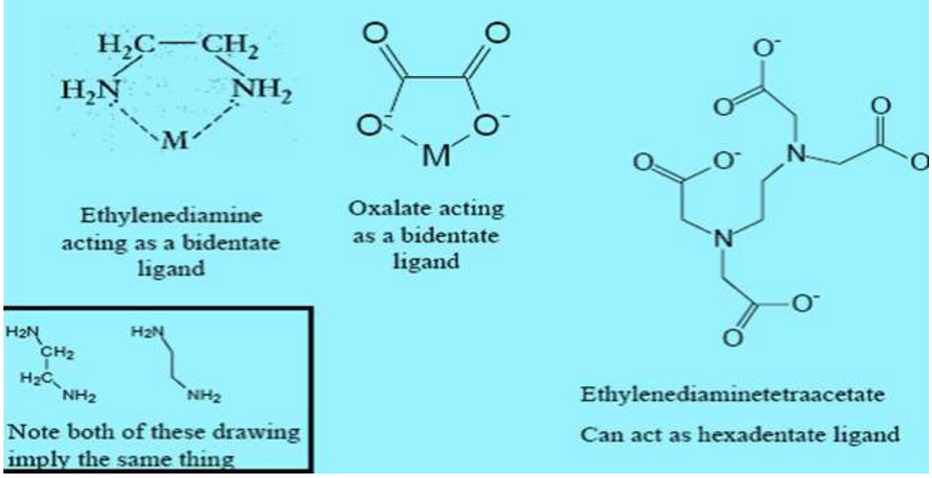


Fig.(1-8):Types of Chelating Ligand

In addition there are macroacyclic and macrocyclic ligands of importance [22]. Macroacyclic ligands derived from β – diketones and alkylamines are commonly known as Schiff bases, e.g. acacen. Macrocyclic ligands, such as porphyrin and its derivatives, phthalocyanine and similar others have important role in biological systems. Macrocyclic ligands classified into macrocyclic tridentate, macrocyclic tetradentate and macrocyclic cryptand. These are shown in figure (1-9) [23]:

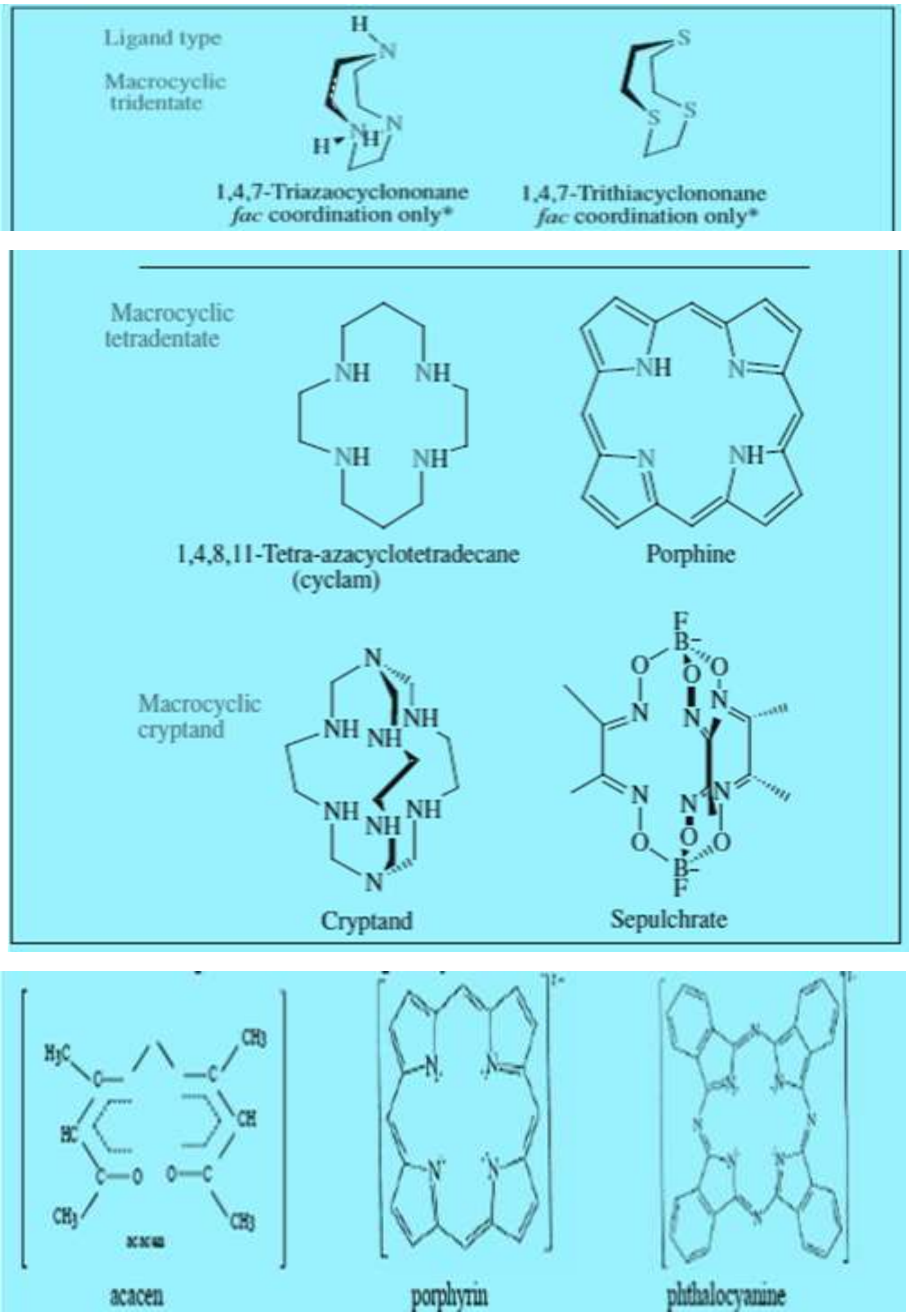


Fig.(1-9): Types of Macrocyclic Ligands

A **macrocyclic ligand** may be defined as a cyclic compound comprising a ring of at least nine atoms including at least three donor atoms oriented so as to bind to a metal ion. In this minimum form a macrocyclic ligand would occupy three adjacent coordination sites on one side of a metal ion. However, larger rings such as cyclam or porphine derivatives may have a central cavity large enough for the metal ion to fit into the plane of the macrocycle[24].

Sometimes ligands can bind to more than one metal ion in a bridging arrangement, for example in $[W_2Cl_9]^{-3}$. Certain polydentate ligands are particularly good at linking together several metal ions and are refered to as **polynucleating ligands**[25]. This illustrated in figure (1-10):

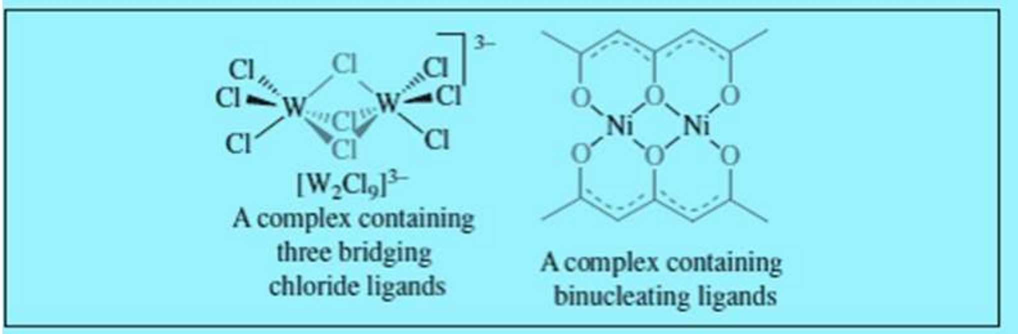


Fig.(1-10): Polynucleating Ligands

Ligands are normally classified into three types according to their interactions: σ-donor ligands, π-acceptor ligands and π-donor ligands [26]. The σ-donor ligands have an electron pair capable of being donated directly to an empty metal orbital. π-donor ligands can donate electrons from a filled p-orbital of a ligand π-donor ligands (e.g. halide) give smaller Δ's because the filled π symmetry ligand orbitals interact with the t_2g symmetry orbitals on the metal. This is why F^-, Br^- OH^- are weak field ligands (give small Δ's)[27]. This is shown in figure (1-11)a:

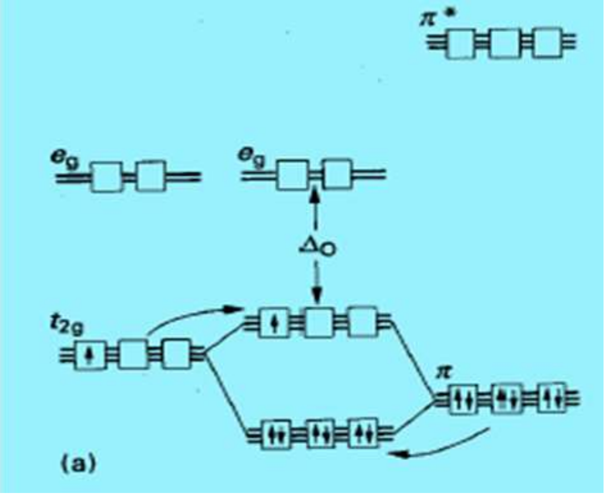


Fig.(1-11)a: π-Donor Ligands

In π-acceptor ligands, σ-donation is complemented by the ability of the ligand to accept electron density from the metal onto suitable acceptor orbitals[28]. Ligands with empty π- symmetry orbitals e.g. CO give large Δ's because the empty orbitals on the ligands interact with the t_2g orbitals on the metal and increase Δ[29]. This is shown in figure (1-11)b:

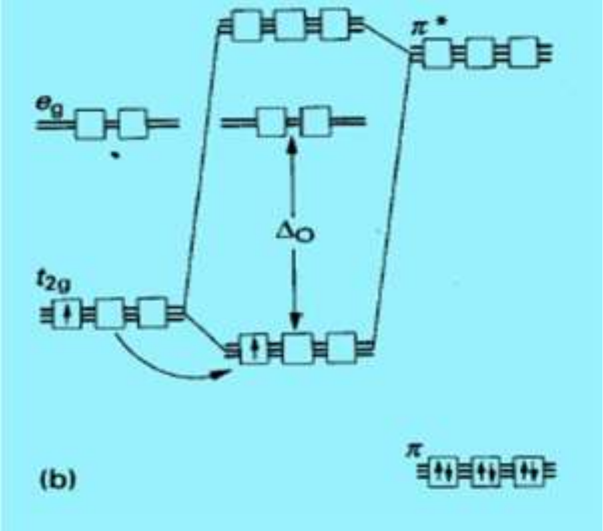


Fig.(1-11)b: π-Acceptor Ligands

In the past the most common ligand known to implement simultaneous σ-donation and π-acceptor properties was the carbonyl ligand CO. Carbonyl ligands are strong π-acceptors– backbonding (the interaction between the filled t_2g orbitals on the metal and the π orbitals on the CO) weakens the C=O bond as seen by vibrational spectroscopy .The CO stretch frequency in a metal complex such as $Ni(CO)_4$ is lower than that for molecular CO[30].

1.2. Transition Metal Complexes

Transition metals differ from main group metals in several key properties. One of the more interesting aspects of transition metals are their ability to form **coordination compounds**[31]. The bonding between the centred atom and the ligand in metal complexes are the result of electron donor and acceptor interactions. The centred metal atom represents a Lewis acid and the ligand a Lewis base [32]. From the negative charged ligand acts a repulsing force on the electron orbitals of the centred atom. On the other hand the positive charge of the centred atom affects an attracting force on the ligand [33]. As well as the repulsing force of the negative charged ligand has no energetic effect on the spherical-symmetrical s-orbital of the centred metal ion, it has an energetic effect on the d-orbitals[34]. Depending on the structure, diameter and charge of the ligand the energy of some d-orbitals is raised and of some others it is abased, means the orbitals are heavier or easier to fill up with electrons[35]. Formation of coordinate covalent bonds between a metal ion and a ligand (L) is through a Lewis acid-base interaction. This interaction is shown in figure (1-12) [36]:

empty metal ion hybrid atomic orbital

Lone pair on the ligand in a hybrid atomic orbital

Fig.(1-12):A Lewis Acid-Base Interaction

Many approaches have been put forth to explain the nature of bonding in complexes. Important ones are: valence bond approach (VBA) ,crystal field approach (CFA), molecular orbital approach (MOA) and ligand field approach (LFA) [37]. Crystal field theory is an electrostatic approach when treat the ligands as point negative charges and the effect of repulsion between these charges and the d-electrons on the metal ions. Explains many of the basic physical properties of transition metal complexes but not all of them. Molecular orbital theory is more complex than crystal field theory, but it allows a more complete explanation of the observed physical properties[38]. Reactions of transition metal complexes typically involve the replacement of one ligand by another (substitution) or oxidation or reduction. The stability of coordination compounds (metal complexes) is given by two different variables[39]:

Thermodynamic stability: refers to the change in energy going from reactants to products. **Kinetic stability:** refers to the reactivity, generally ligand substitution**.** High thermodynamic stability does not imply slow reactivity. The kinetic stability depends on the activation energy ($\Delta G‡$) of the ligand substitution reaction, the thermodynamic stability is given by the free energy change is shown in figure (1-13) [40]**:**

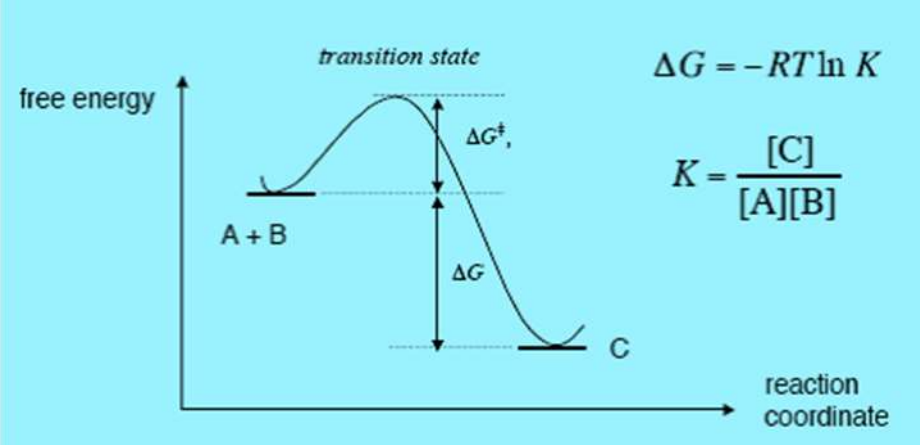


Fig.(1-13): The Activation Energy (Δ G‡) of The Ligand

Complexes may be classified as **inert** or **labile**, depending upon the speed at which substitution reactions occur[41]. Complexes which undergo fast ligand substitution reactions are called kinetically labile, those which undergo only very slow substitution reactions are called kinetically inert. According to the Hunds Rule the orbitals with the lowest energy are filled firstly[42]. If the spin matching energy is higher than the single occupying one for the orbital with the highest energy, all orbitals firstly are filled with a single electron. The resulting complex has high spin. The octahedral and tetrahedral complexes in figure (1-14) are examples for high spin complexes[43]. All orbitals are firstly filled single. If the spin matching energy is lower than the double occupying one for the orbital with the lowest energy, some orbitals will already be filled double while some orbitals are not yet singly occupied and the complex has low spin. The quadratic-planar complex in figure (1-14) is an example for such a low spin complex. The high and low spin model also explains magnetic behavior of metal complexes. The tetrahedral and octahedral complexes in figure (1-14):

both are paramagnetic. This is caused by the homogenous distribution of the electrons over the whole complex. The quadratic-planar complex is diamagnetic[44]. Its electrons are not homogenously distributed over the complex. The double occupancy of some orbitals while others are still unoccupied results in majority of electrons on one side. The complex this way gets a negative charge on one side while the other side appears positively charged. This division of charge gives the complex two poles of different charge what makes him diamagnetic[45].

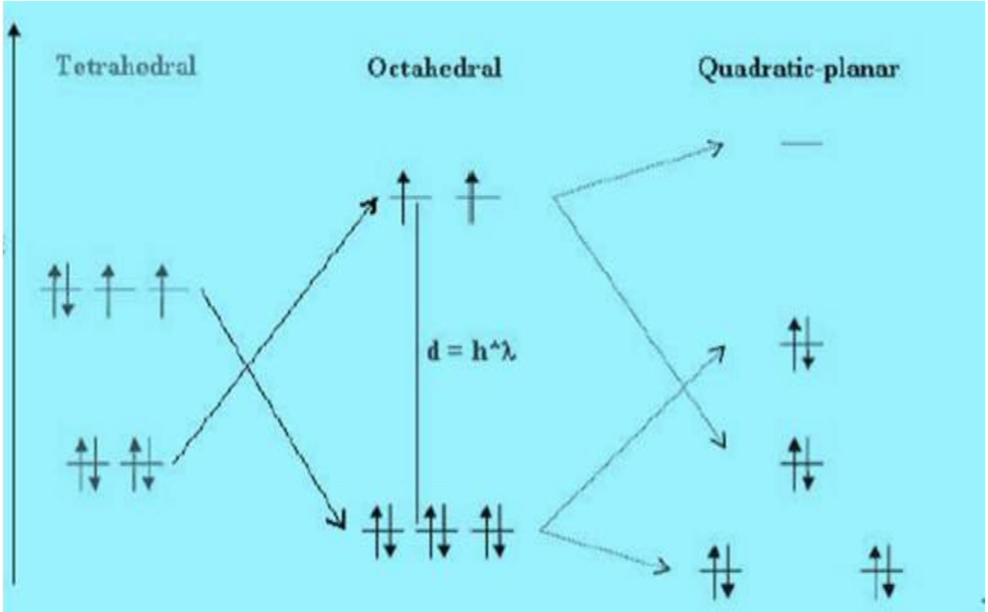


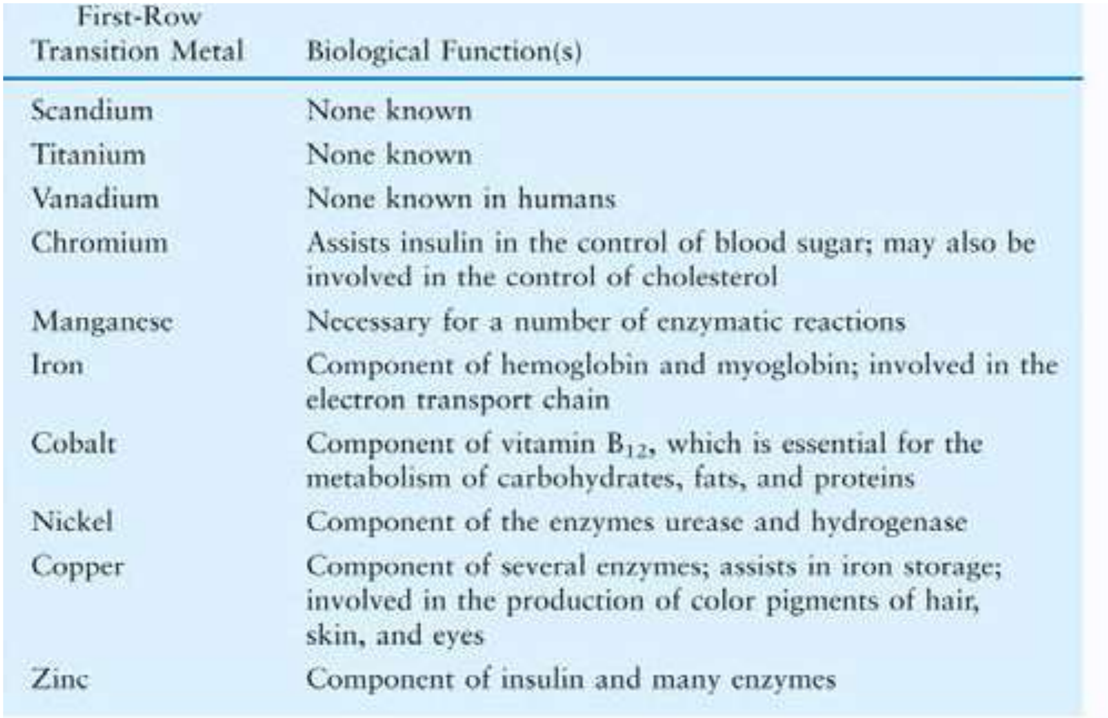
Fig.(1-14): High Spin Complexes

With the ligand field theory also the colour of complexes can be explained. The electrons in a complex can be transferred from a low energy orbital into a higher energetic one[46]. Therefore specific amount of energy is needed. This energy is calculated as $E = \text{h} \times \upsilon$ where h is the Plank constant and υ the frequency of an electromagnetic ray. The energy of E depends on the mass of the ligand field splitting which is dependent on the structure, charge and diameter of the ligand [47].

This means that a strong ligand for example splits the ligand field more than a weak one and the activating energy to move an electron from a lower energy state into a higher is bigger. The energy for transferring an electron into a higher energetic orbital is taken from electromagnetic waves[48]. The reason transitionappear colored is that the magnitude of the orbital splitting often matches the energy of photons of visible light. When this occurs, the light is absorbed by the sample and electrons are promoted from a lower energy state (one of the t_2g orbitals) to a higher energy state (one of the eg orbitals)[49]. The magnitude of the orbital splitting is dependent upon the nature of the ligands attached to the metal center [50] If a complex absorbs a wavelength within the visible spectrum the complex appears coloured. Important is to notice that the observed colour of a complex is the complementary colour to the colour of wavelength by the complex[51]. The NiEDTA complex for example absorbs red light so it appears green.

1.3.The Applications of Transition Metal Complexes

Metal ion complexes find diverse applications: transport and storage of oxygen and other essential elements ,electron transfer agents ,catalysts (enzymes) and drugs[52]. Some biological function of transition metal are shown in figure (1-15):



First-Row Transition Metal	Biological Function(s)
Scandium	None known
Titanium	None known
Vanadium	None known in humans
Chromium	Assists insulin in the control of blood sugar; may also be involved in the control of cholesterol
Manganese	Necessary for a number of enzymatic reactions
Iron	Component of hemoglobin and myoglobin; involved in the electron transport chain
Cobalt	Component of vitamin B_{12}, which is essential for the metabolism of carbohydrates, fats, and proteins
Nickel	Component of the enzymes urease and hydrogenase
Copper	Component of several enzymes; assists in iron storage; involved in the production of color pigments of hair, skin, and eyes
Zinc	Component of insulin and many enzymes

Fig.(1-15): Biological Function of some Transition Metal

Transition metal Schiff base complexes are used in various field, such as medicine, agriculture, industries etc. For example, [Co(acac$_2$-en)] in dimethylformamide, pyridine and substituted pyridines proved to be involved in oxygen metabolism[53]. Transition metal complexes with 1,10-phenanthroline and 2,2-bipyridine are used in petroleum refining [54]. Schiff base formed by the condensation of 1-formyl-2-hydry-3-naphtholic arylamide with o-hydroxyl or o-methoxy aniline complexes of Co(II), Ni(II), Cu(II) and Zr(II) are useful as figment[55].

Oxovanadium complexes have been found strongly active, against some type of leukemia[56]. Transition metal complexes derived from a number of amino acids have been reported to have biological activity [57].

There is antibacterial activity of Ni(II) with salicyaldehyde and 2-amino-benzoic acid complex[58]. However, molecular complexes, organometallic compounds, and solid-state compounds such as oxides, sulfides, and halides of transition metals are used in the most active research areas in modern inorganic chemistry[59]. For examples of the use of coordination complexes/compounds Hemoglobin, contains a molecule of heme, which serves as the active site of oxygen transport (Fe^{+2}/Fe^{+3} couple) from the lungs to the tissues in which it is used to oxidize glucose, this oxidation serving as the source of energy required for cellular metabolic processes[60]. The heme complex in which an Fe^{+2} ion is coordinated to four nitrogen atoms of a planar porphyrin ligand[61]. The heme complex shown in figure (1-16) :

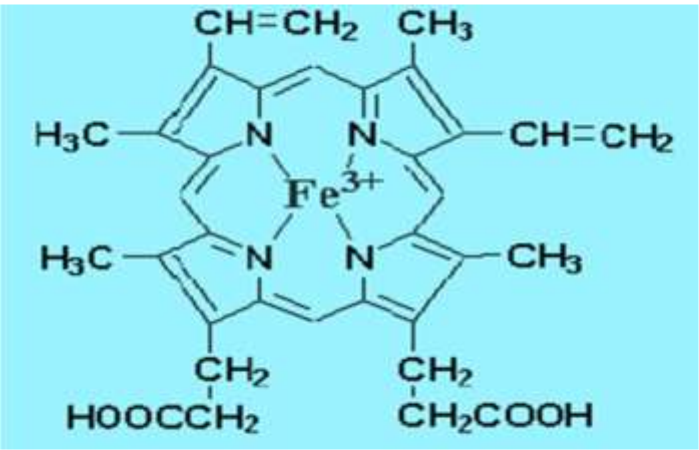


Fig.(1-16): Structure of Heme Complex

1.4. Schiff Bases

Schiff bases named after Hugo Schiff described the condensation between an aldehyde or a ketone and primery amine[62]. The carbonyl group of the aldehyde gives aldimines while that of ketone gives ketimines [63]. The common structural feature of these compounds is the azomethine group with a general formula $RHC=N-R_1$, where R and R_1 are alkyl, aryl, cycloalkyl or heterocyclic groups which may be variously substituted. These compounds are also known as anils, imines or azomethines[64]. Several studies showed that the presence of a lone pair of electrons in an SP^2 hybridized orbital of nitrogen atom of the azomethine group is of considerable chemical and biological importance[65]. The imines produced in figure (1-17) typically decompose or polymerize unless at least one aryl group is bound to the nitrogen or carbon atom [66].

A great number of metal complexes of the Schiff bases (acyclic or cyclic) have been prepared, and they have provided an enormously rich world of chemistry[67].

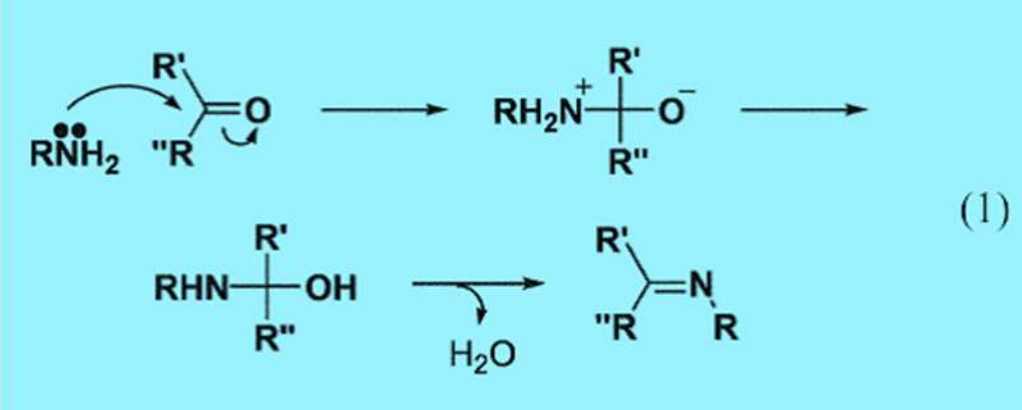


Fig.(1-17): Mechanism of Imine formation

Schiff base ligands containing various donor atoms (like N,O,S etc.) show broad biological activities and are special interest because of the variety of ways in which they are bonded to metal ions[68]. Schiff bases are generally excellent chelating agents, especially when a functional group like –OH or –SH is present close to the azomethine group so as to form a five or six membered ring with the metal ion[69]. In recent years , there has been enhanced interest in the synthesis and characterization of transition metal complexes containing Schiff bases as ligands due to their importance as catalysts in many reactions[70].

Schiff base complexes can be classified in a number of ways as: mononuclear, binuclear and polynuclear on the basis of number of metal ions/atom present and as monodentate, bidentate and polydentate [71]. The use of metal complexes of quinquedentate Schiff base , such as salicylaldimine as bidentate chelating group /agents to form binuclear and trinuclear centers has been wet documented[72]. Schiff bases resulted from aromatic aldehydes *ortho*-substituted with a hydroxy group have initially arouse. This interest because of their ability to act as bidentate ligands for transitional metal ions[73]. Later, in studies concerning quantitative structure-antitumor activity relationship of a series of Schiff bases derived from variously substituted aromatic amines and aldehydes, it has been shown that azomethines from salicylaldehyde gave the best correlation[74]. Aromatic Schiff bases or their metal complexes catalyze reactions on oxygenation, hydrolysis, electro-reduction, and decomposition[75].

Schiff bases of salicylaldehydes have also been reported as plant growth regulators, antimicrobial or antimycotic activity[76]. Schiff bases also show some analytical applications[77]. Schiff bases are the important compound owing to their wide range of biological activities and industrial application[78,79]. They have been found to posses the pharmacological activities such as antimalarial, anticancer, antibacterial, antifungal, antitubercular, antiinflammetery, antimicrobial, and antiviral[80,81].

Schiff bases are characterized by the -N=CH- (imine) group which imports in elucidating the mechanism of transamination and rasemination reactions in biological systems [82]. Schiff bases are active against a wide range of organisms for example; *Candida Albicans, Escherichia coli Staphylococcus aureus, Bacillus polymax, Trychophyton gypseum, Mycobacteria, Erysiphe graminis and plasmopora viticola*[83].

In organic methodology, Schiff base complexes have role in catalysis of a variety of organic reactions such as metathesis process ,reductive carbonization ,polymerization ,decarboxylation and oxidation[84].

Because of new interesting applications found in the field of pesticides and medicine. The metal complexes with tridentate O,N,N types of alternative structures have attracted the attention of chemist various metal complexes with bi-and tridentate[85]. Schiff bases containing nitrogen and oxygen donor atoms play important role in biological systems and represent interesting models for metalloenzymes, which efficiently catalyze the reduction of dinitrogen and dioxygen[86].

1.5. General Methods of Preparation of Schiff Base Metal Complexes

Generally Schiff base metal complexes are prepared by producing a reaction between the Schiff base and available metal salts in ethanolic medium[87]. This approach is clearly simple and suitable. Essentially, five different synthetic routes can be identified for the preparation of Schiff base metal complexes in figure (1-18).

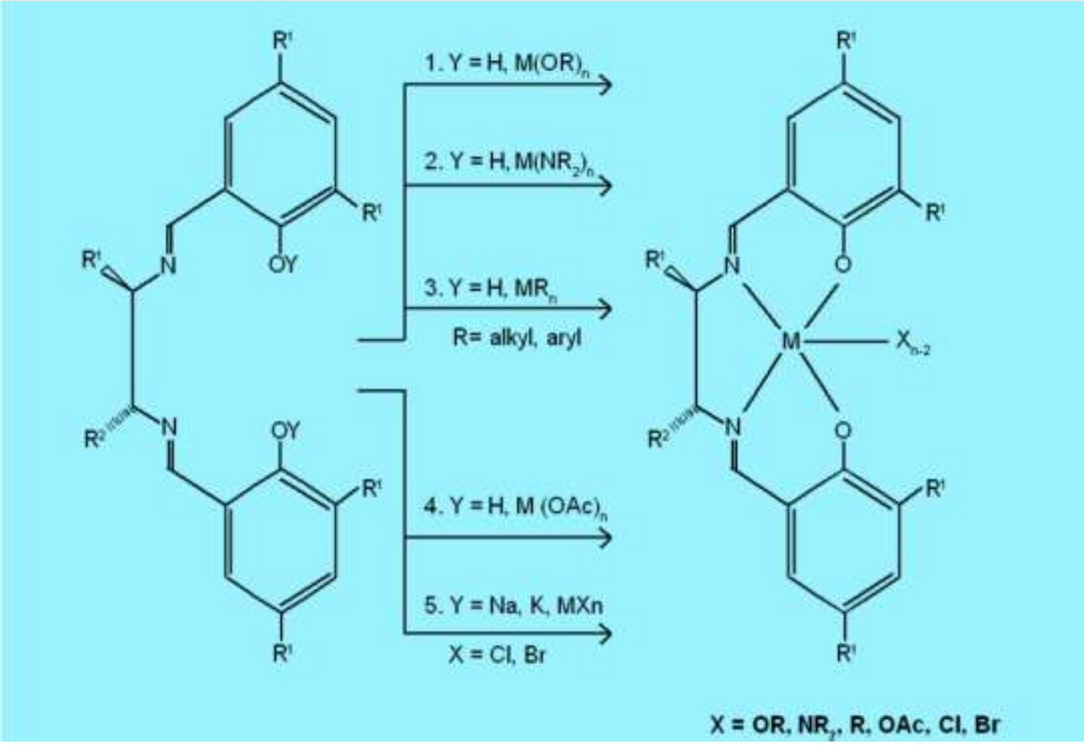


Fig.(1-18): General methods of preparation of Schiff base complexes

1.6 Dithiooxamide

Dithiooxamide (DTO) or rubeanic acid is an organic compound. It is the sulfur analog of oxamide. It acts as a chelating agent, e.g. in the detection or determination of copper. It has also been used as a building block in the synthesis of cyclen[88]. The molecular formula of dithiooxamide is $N_2C_2S_2H_4$ and its red crystals soluble in alcohol; used as a reagent for copper, cobalt, and nickel, and for the determination of osmium [89]. The structural formula of cis and trans- dithiooxamide is shown in figure (1-19) :

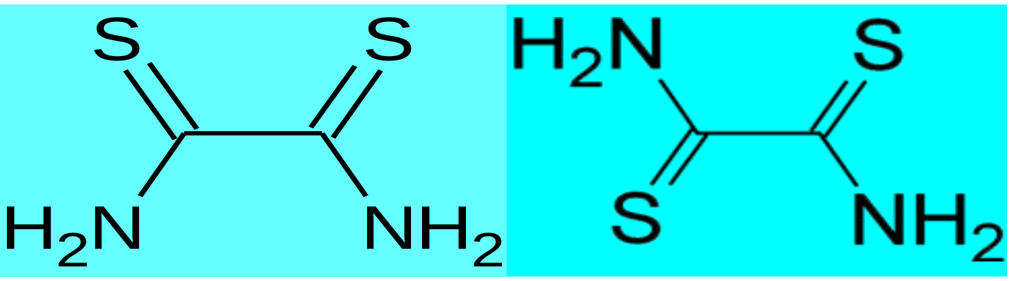


Fig.(1-19):General Formula of Dithiooxamide

Dithiooxamide is also a well-known ligand for complexation or coordination with transition metal cations. In particular, it is known to coordinate with such cations as Ni^{+2}, Zn^{+2}, Pd^{+2}, Pt^{+2}, Fe^{+2}, Cu^{+2} , and Co^{+2} [90]. The monomer complex can be generally represented by the formula $M(DTO)_2$ where in M is a transition metal cation having an oxidation state of +2 and DTO is a dithiooxamide ligand, having an overall charge of -1 due to removal of one thioamide hydrogen therefrom[91]. The polymer complex comprises a one to one coordination between ligand and transition metal cation and can be generally characterized by the formula $(ML)_n$ where in M is a transition metal cation having an oxidation state of +2 and L is a dithiooxamide ligand wherein two thioamide hydrogens (one from each nitrogen) have been removed resulting in an overall charge on the ligand of -2 [92].

The "cationic" complex is represented by the general formula $M(DTO)_2\ X_2$ where in M is a transition metal cation having an oxidation state of +2, DTO is a dithiooxamide ligand and X is an anion having a charge or valence number of -1[93]. (DTO) a metallochromogenic reagent, has been immobilized in a composite biopolymer matrix for the quantitative determination of Cu(II) by an optical fibre method[94]. DTO has utilized it to detect copper concentrations as low as 10^{-9} mg in human skin[95], De spite the fact that DTO has not been employed in sensor applications. Copper sensors use different detection methods such as amperometry, mass spectrometry, fluorimetrty and potentimetry[96].

Dithiooxamide forms a class of compounds which contain the thioamide group, and two soft S- atoms besides two hard N- atoms in one molecule[97]. Infrared and crystallographic studies have shown that *N*,*N*-mono substituted dithiooxamide. And there are compounds of the class of *N*,*N*- di(monocyclic hetrocyclic) dithiooxamide, useful as amebicides[98]. This invention is concerned with novel *N*,*N*-disubstituted dithiooxamides, and to a method for making the same. More particularly, this invention is concerned with those *N*,*N*-dithiooxamides which are represented by the following general formula in figure (1-20)[99]:

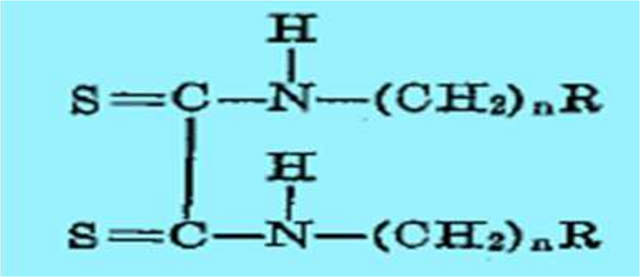
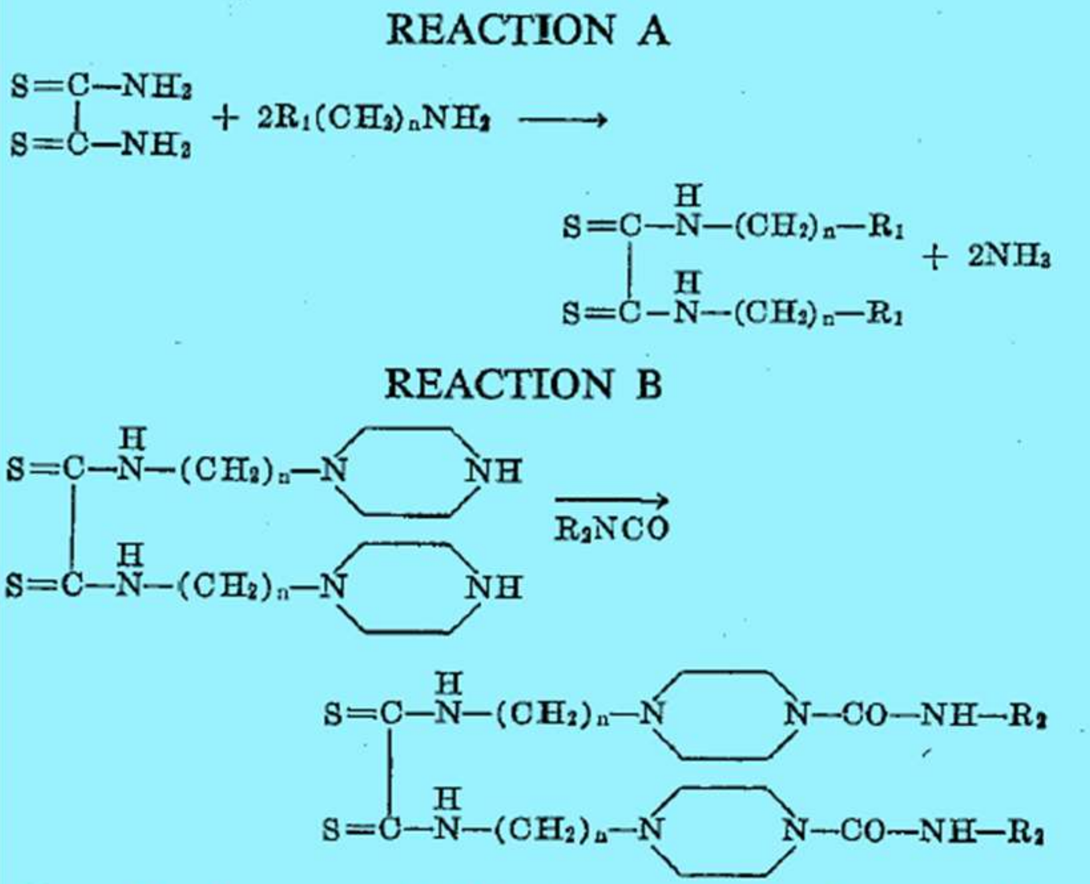


Fig.(1-20):General Formula of N,N-disubstituted dithiooxamide

To obtain those compounds formula where R is a substituted hetrocyclic group as shown in reactions in figure (1-21):



REACTION A

REACTION B

where R_1 is an unsubstituted monocyclic heterocyclic group, R_2 is a halophenyl or nitrophenyl group and *n* is as hereinbefore defined.

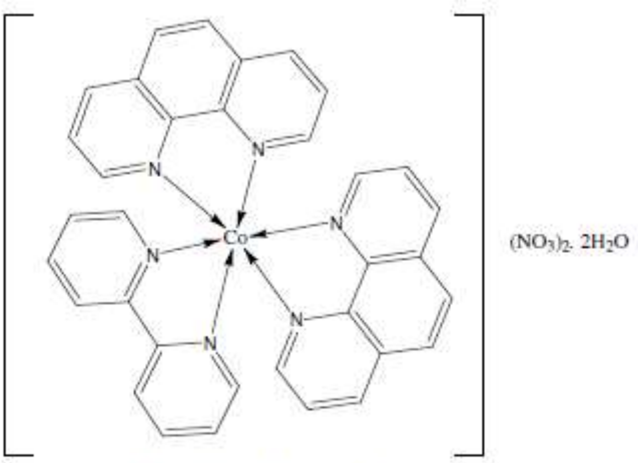
Fig.(1-21): Synthesis of N,N- disubstituted- dithiooxamide

1.7. Cobalt Complexes

Common oxidation states of cobalt include +2 and +3. Compounds of cobalt are classified as coordination complexes, that is molecules or ions that contain cobalt linked to several ligands. Complexes formed from Schiff bases and metals such as cobalt have been studied as "oxygen carriers"[100]. Cobalt is an essential trace element for all animals, as the active center of coenzymes called cobalamins. These include vitamin B_{12} which is essential for mammals. Cobalt is also an active nutrient for bacteria, algae and fungi[101].

The bioactive Co(II) complex with Schiff base derived from the condensation of furane-2-carbaldehyde and 2-aminobenzoic acid has been synthesized and characterized[102]. Coordination takes place through amine N atom, furan ring oxygen and oxygen of carboxyl group forming octahedral geometry[103]. The complex could be applied fairly in the treatment of some common diseases caused by E. coli eg. Septiaemia, Gastroenteritis, urinary tract infections and hospital acquiredinfections. The mixed ligand complexes of Co(II) with Schiff base 2, 6- pyridine di-carbaldehyde bis(p-hydroxyphlamine) and 2-aminopyridine has been studied [104]. The Schiff base coordinated to the metal ion tridentate manner with Pyridine N, two azomethine N, while 2-amino pyridine coordinated to the metal ion via its pyridine N giving octahedral geometry.

A large number of mixed-ligands complexes involving heterocyclic bases has been reported due to their bioinorganic applications and thermal stability. The complex had a variety of applications including biological, clinical, analytical and industrial in addition to their important role in catalysis and organic synthesis[105]. The complex was found to be very active against T-lymphoblastic leukemic cells. 1,10-phenanthroline and 2,2’-bipyridine mixed-ligand complexes of $[Co(bpy)(phen)_2](NO_3)_2.2H_2O$ was synthesized. The complex results indicate that both ligands are coordinated to the respective metal ions giving octahedral complexes. Antimicrobial studies showed that there is increased antimicrobial activity of the metal ions on coordination to the ligands. The water soluble complexes showed antimicrobial activities that are higher than those of the metal salt and 2,2’-bipyridine but lower than those of 1,10-phenanthroline[106]. The proposed structure of the complexe is shown in figure (1-22):



$[Co(bpy)(phen)_2](NO_3)_2.2H_2O$

Fig.(1-22): The proposed structure of the cobalt **complexes containing mixed ligands**

In binuclear Cobalt (II) complexes with aryl Schiff bases the oxygen bridged homo and hetero binuclear and trinuclear complexes have attracted much attention due to their interesting spectral and magnetic properties and their use in biochemical processes and homogeneous catalysis. That is shown in figure (1-23)[107]:

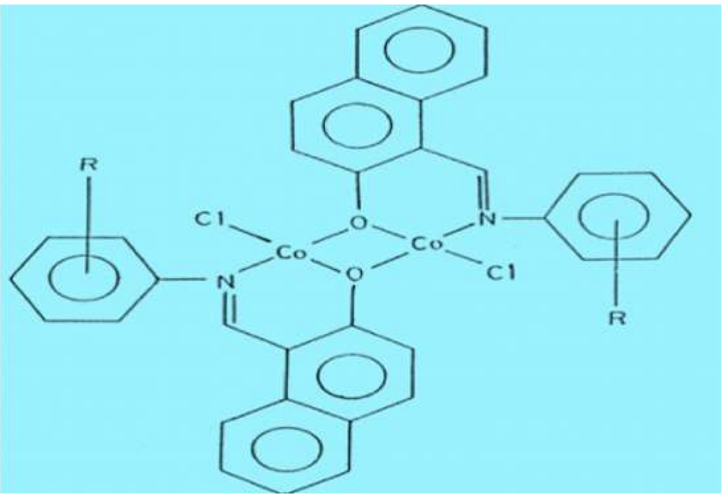


Fig.(1-23): binuclear Cobalt (II) Complex

1.8. Copper Complexes

Copper forms a rich variety of compounds with oxidation states +1 and +2, which are often called cuprous and cupric, respectively [108].Copper, like all metals, forms coordination complexes with ligands, this make it to use in several fields especially in an industry[109]. Copper is an important trace element for plants and animals and is involved in mixed ligand complex formation in a number of biological processes[110]. Copper complexes, Schiff base ligands are of great interest since they exhibit numerous biological activities such as antitumor, anticandida[111] antimicrobial activities, etc. The Cu(II) complex of Schiff base is important in catalysis and acts as model in bioinorganic system because of charge symmetry and the possible fine-tuning of the electronic properties, originating from the different substitutions, can create active sites with potential region selective molecular recognition, as suggested by the head-to-tail arrangements of the molecules found in the crystal structures[112].

Cu(II) complex with Schiff base (salicylaldehyde-amino ethanol) and phenanthroline base has suggested square pyramidal geometry[113].
The Schiff base coordinates in tridentate manner through ONO system, while heterocyclic base in bidentate manner through *N-N* system[114].

Copper exhibits considerable biochemical action either as an essential trace metal or as a constituent of various exogenously administered compounds in humans. In its former role it is bound to ceruloplasmin, albumin, and other protein, while in the its latter it is bound to ligands of various types forming complexes that interact with biomolecules, minly proteins and nucleic acids. Copper is good for liver function, its level in blood and urine has influence in pregnancy disorders, nephritis nepatitis, leprosy, anemia and leukemia in children [115].

It is well known that some drugs have greater activities when administered as metal complexes than as free organic ligands only[116]. The transition metal complexes having oxygen and nitrogen donor Schiff bases possess unusual configuration, structural labiality and are sensitive to molecular environment [117]. Example of this complex 1 and 2 are shown in figure (1-24):

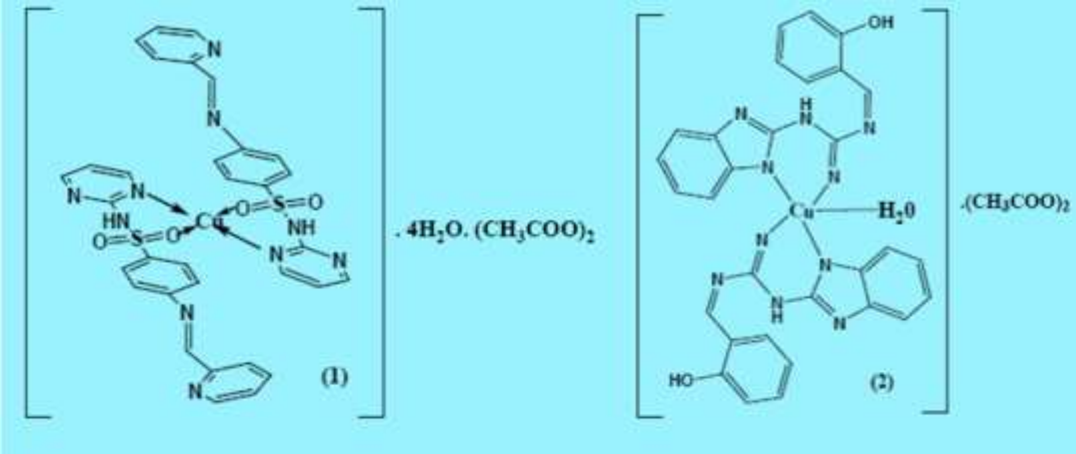


Fig.(1-24):Copper complexes having Oxygen and Nitrogen donor

Cu(II) complexes of Schiff bases have played a central role in the development of coordination chemistry[118]. Schiff bases with metal complexes via benzil monophenylhyrazone and its related compounds have been extensively used as biologically active complexing agents and analytical reagents[119]. Cu(II)complexes of Schiff base derived from the condensation of benzyil-2,4-dinitrophenylhydrazone with aniline. The proposed structure of the complex is shown in figure (1-25) :

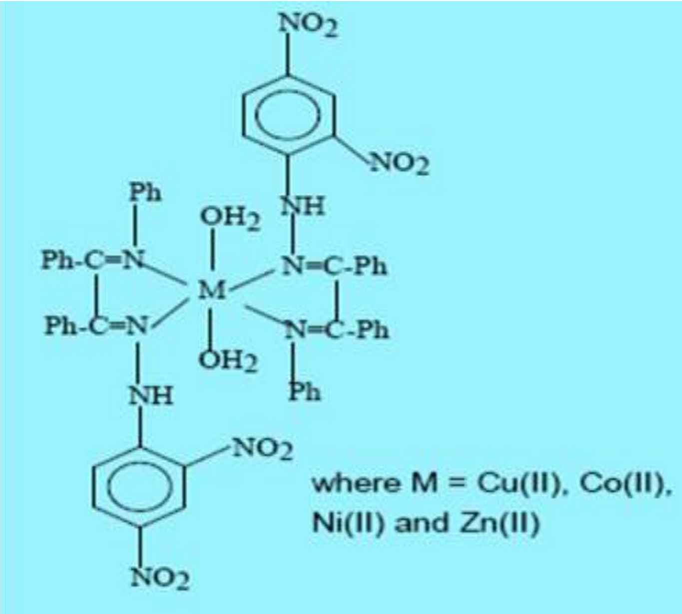


Fig.(1-25): The proposed structure of the complex

examples of copper complexes grouped according to ligand similarity that have been tested for their anti-cancer activity in about the last ten years [120]. It has been established that the copper ion chelation plays a definite role in the biological activity of most of the selected organic ligands, enhancing the anti-tumor activity of the metal-free substances. Example of complexes that have anti-cancer medicinal chemistry such as[121] in figure (1-26) :

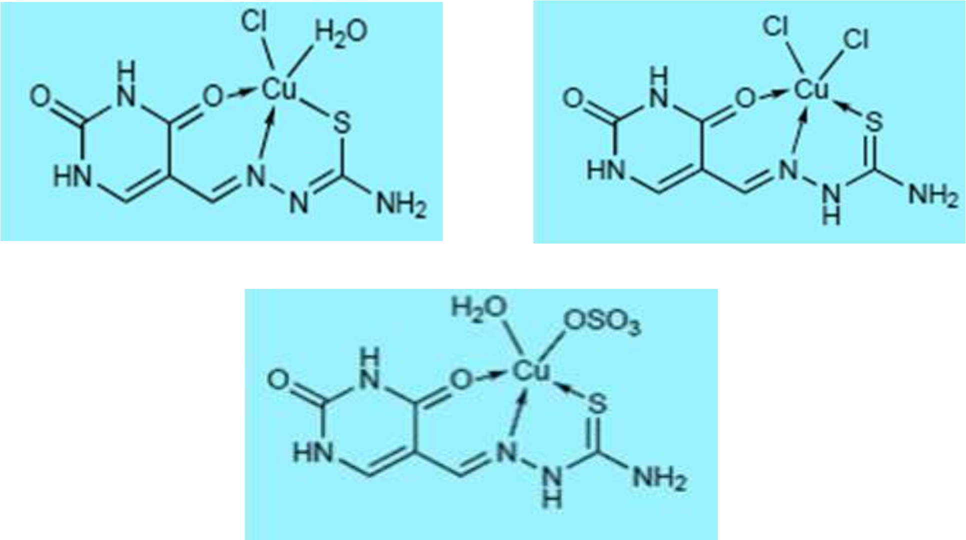


Fig.(1-26): complexes of Cu(II) that have anti-cancer

1.9. Nickel Complexes

The nickel ion in nickel(II)-complexes exists in the coordination number of 4, 5 and 6. Its octahedral, trigonal-bipyramidal, quadratic-pyramidal and tetrahedral complexes are paramagnetic and have in the majority of the cases a green or blue colour[122]. The quadratic-planar nickel complexes are diamagnetic and mostly have a yellow, red or brown colour[123]. Nickel forms compounds in various oxidation states although the most important is +2[124]. Example of this complexes are shown in figure (1-27) :

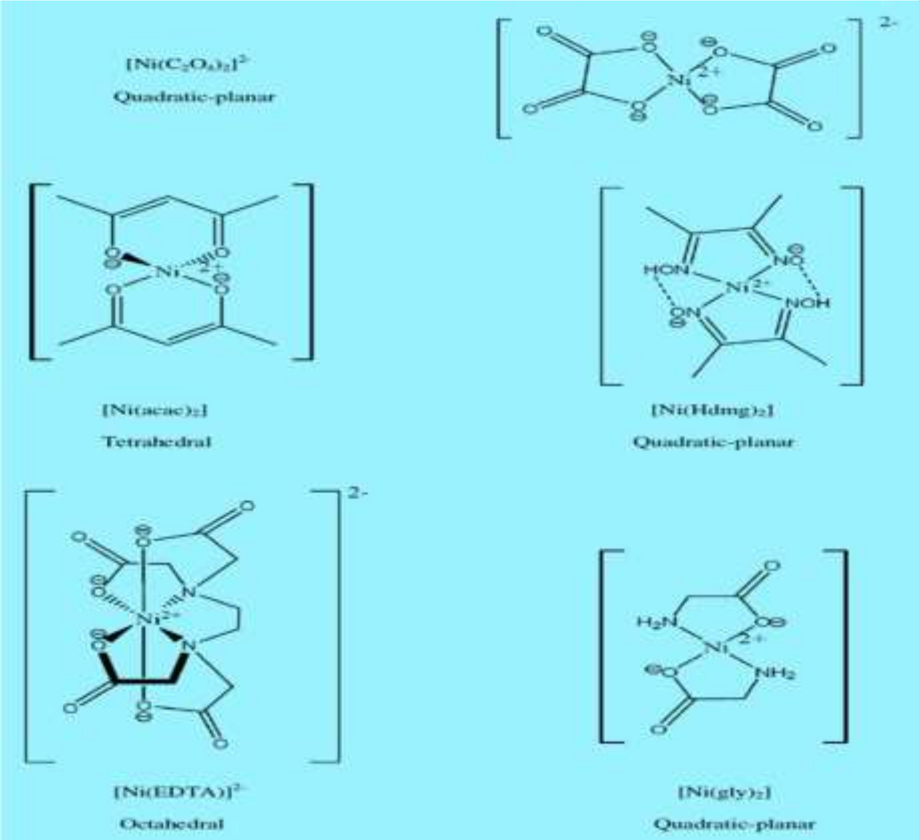


Fig.(1-27):Examples of Nickel(II) Complexes with different ligands

Nickel also forms organometallic complexes including nickel carbonyl [Ni(CO)$_4$], which is a colorless volatile and highly reactive liquid[125]. In general, nickel organometallic compounds are not very stable, often only intermediate complexes in the synthesis of other organic compounds[126]. The synthesis of nickel(II)-complexes passes over ligand substitution reactions where one or several ligands are replaced by other ones. These reactions are equilibrium reactions[127]. Compounds containing carbonyl and thiocarbonyl group occupy an important position among organic reagents as potential donor ligand for transition metal ions[128]. Among these thiourea derivatives are potentially very versatile ligand, able to coordinate to a range of metal centers as neutral ligands, monoanions or dianions[129]. The oxygen, nitrogen and sulfur donor atoms of thiourea derivatives provide a multitude of binding possibilities. Both the ligand and their metal complexes display a wide range of biological activity[130].. Synthesis of these complexes as shown in figure (1-28):

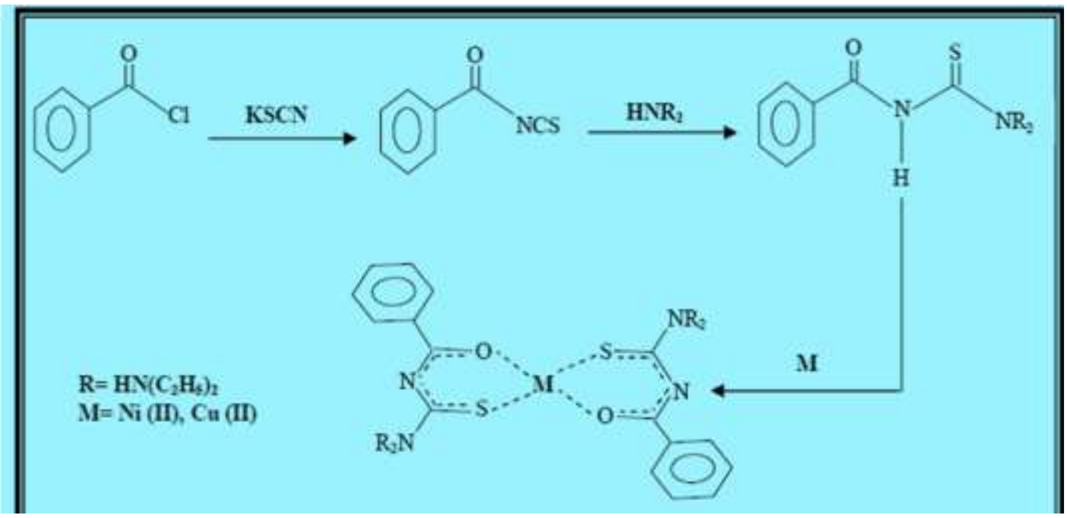


Fig.(1-28): Examples of Nickel and Copper complexes containing thiourea derivatives

Nickel is one of the most toxic among transition metals. It shows the toxicity even in low doses to both plants and animals. Excess nasal and lung cancers are known to be associated with the refining of nickel. Epidemiological data and animal study confirm that crystalline nickel compounds are carcinogenic, while amorphous nickel compounds are weak or non-carcinogenic[131]. Ni(II) complex with tetradentate Schiff base derived from thiosemicarbazide and glyoxal has been studied . The coordination takes place through four azomethine nitrogen atom and the sulphur atom does not involve in the coordination. The complex has many applications in pharmacology as it has anticancer, antibacterial antifungal and other biological properties[132].

There are novel Nickel complexes containing tetrathiafulvalene units are often used as building blocks for conductors either acting as simply as counter-anions[133]. Synthetic route of novel nickel coordination compounds are shown in the figure (1-29) :

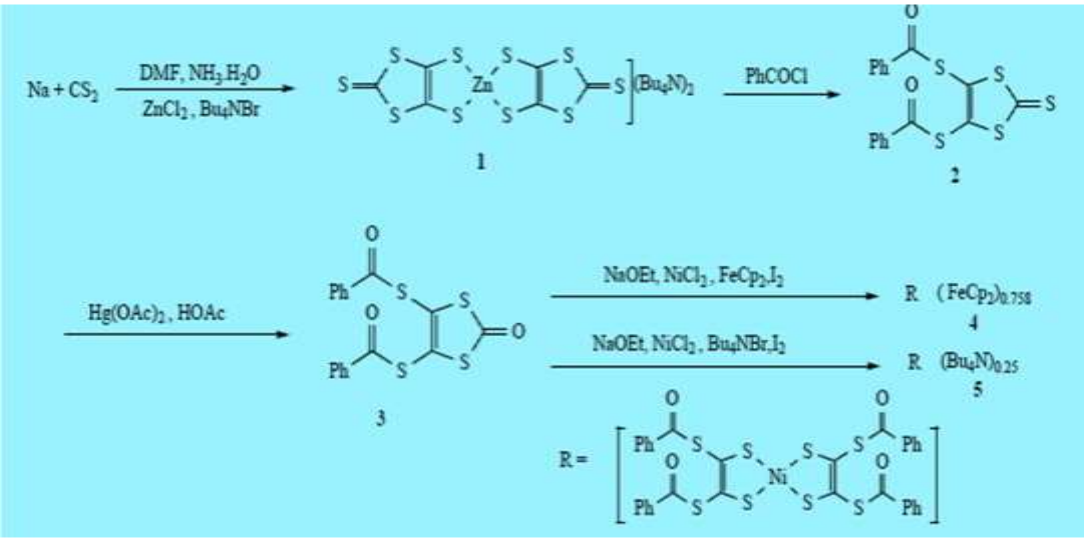


***Fig.(1-29): Synthetic of Novel Nickel Complexes* containing tetrathiafulvalene units**

1.10. Palladium Complexes

Common oxidation states of palladium are 0, +1, +2 and +4 [134]. Although originally +3 was thought of as one of the fundamental oxidation states of palladium, there is no evidence for palladium occurring in the +3 oxidation states; this has been investigated via X-ray diffraction for a number of compounds, indicating a dimer of palladium(II) and palladium(IV) instead[135]. A series of mononuclear and dinuclear palladium complexes has been investigated by different researchers including their cytotoxicity against a number of cancer cell lines. Some of the palladium compounds showed some anticancer activities but so far no promising candidate has emerged[136]. The great many reactions in which palladadium compounds serve as catalysts are collectively known as palladium-catalyzed coupling reaction.

N,N,O,O-tetradentate Schiff base ligands and Palladium(II) metal complexes, as catalyst, have application in agrochemical and radio-pharmaceutical industries for cancer targeting, as model system for biological macromolecule[137]. Transition-metal-catalyzed cross-coupling is currently recognized to be one of the most powerful carbon–carbon bond forming reactions. Palladium-catalyzed carbon-carbon and carbon-nitrogen bond forming reactions are widely used in modern organic chemistry. Such catalytic procedures have numerous applications in the preparation of many natural products, in addition to their uses in materials science and the agrochemical industry[138].

The palladium-catalyzed coupling of aryl halides or their synthetic equivalents are very often used in the synthesis of biaryl molecules, whose skeletons are found in a wide range of important compounds including natural products, organic functional materials and building blocks for medicinal products[139]. Furthermore, these can be applied to other palladium-catalyzed coupling reactions, including those that occur through C-H or C-C cleavage . A general catalyst cycle for the Suzuki coupling reaction is shown in figure (1-30):

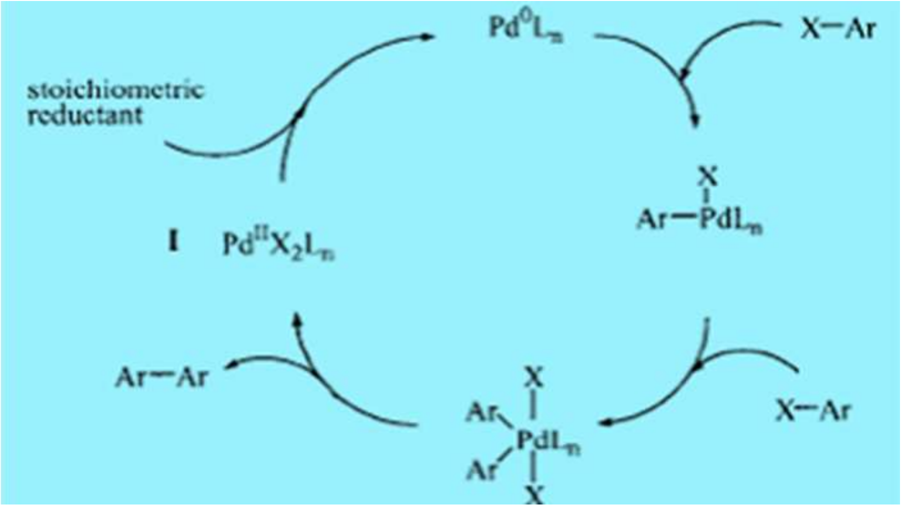


Fig.(1-30): **Catalyst cycle for the Suzuki coupling reaction**

Bidentate chelating ligands are often used to fix the active coordination sites of Pd(II) complexes in a *cis*-arrangemen[140]. P,O ligands which are used in the industrial, P,P and N,N ligands are applied in catalytic olefin homo- and copolymerization reactions [141]. P,N palladium complexes are among the most active and most stable catalysts for olefin/CO copolymerizations[142]. Palladium Complexes with Bidentate P,N Ligands are shown in figures (1-31) :

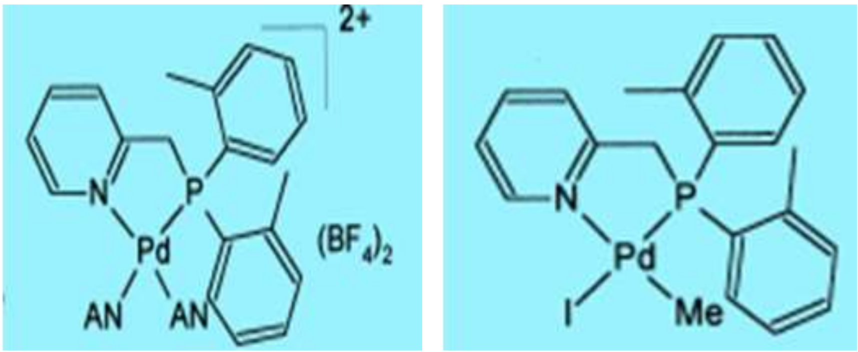


Fig.(1-31): Palladium Complexes with Bidentate P,N Ligands

1.11. Platinum Complexes

Common oxidation states of platinum are II and IV but more state used is II. In more recent times, a stable metal coordination complex based on the element platinum, cis-[$PtCl_2(NH_3)_2$] (cisplatin), has become the most well known of all metal based drugs and hundreds of articles have been published on the synthesis and activity of complexes derived from the parent cisplatin molecule[143]. Despite the clinical anti-cancer utility of cisplatin, carboplatin, oxaliplatin, and several other complexes in clinical trials, there is a continued interest in the design of new complexes that shows anti-tumor activities equivalent or better than these agents[144]. The continued interest in platinum-based antitumor compounds is stimulated by the fact that certain tumors are resistant to the clinically used drugs cisplatin and carboplatin.

Many derivatives of cisplatin also inhibit growth, and these compounds have at least one N-H group, which is responsible for important hydrogen-bond donor properties, either in the approach of the biological target or the final structure. Most of the well-known platinum anticancer complexes have the general formula *cis*-[$PtX_2(NHR_2)_2$], in which R = organic fragment and X = leaving group, such as chloride or (chelating *bis*)carboxylate. Many other active Pt(II) compounds are known now, even with *trans* geometries[145]. The second-generation platinum drug carboplatin, [$Pt(C_6H_6O_4)(NH_3)_2$], has fewer toxic side effects than cisplatin and is more easily used in combination therapy. Its low reactivity allows a higher dose to be administered. Carboplatin is used more for ovarian cancer treatment, whereas oxaliplatin is known to be most effective in colon cancer treatment [146]. These compound are shown in figure (1-32) :

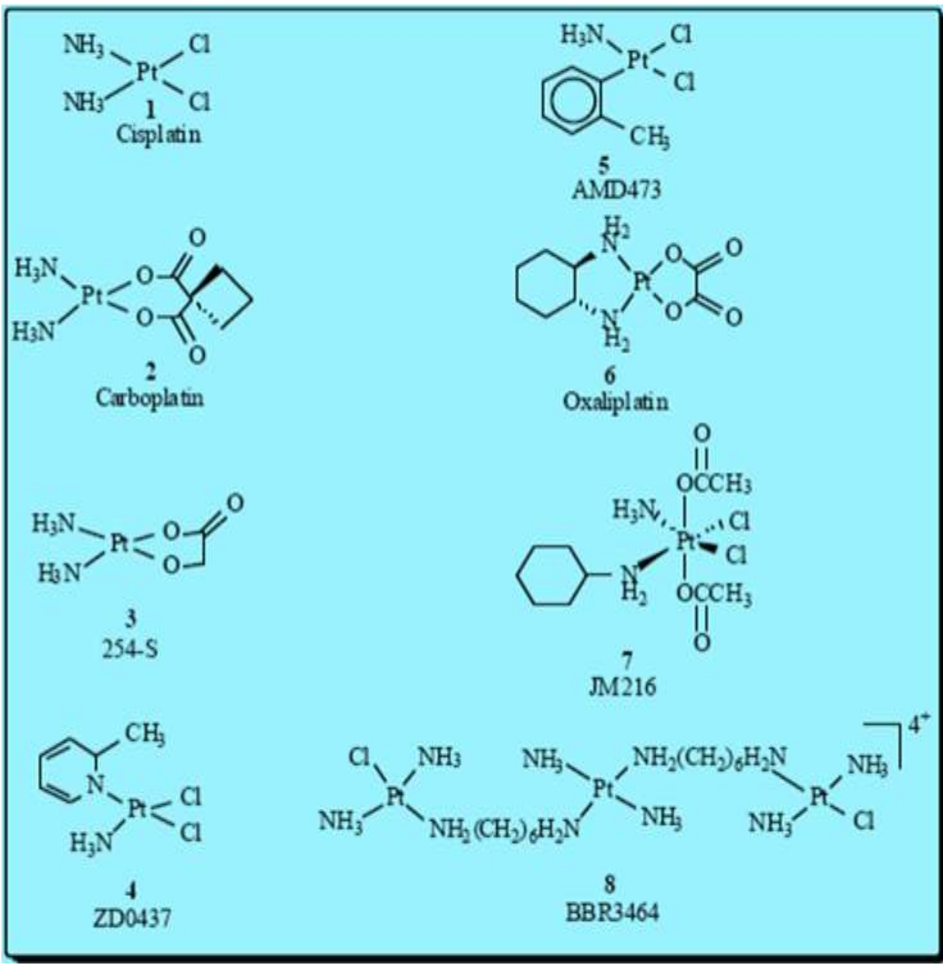


Fig.(1-32): platinum anticancer complexes

The mechanism of action of cisplatin at the molecular level, involving interaction of the labile Pt(II) ion with DNA[147]. However, it has several limitations including toxicity (nephrotoxicity, neurotoxicity, ototoxicity and emetogenesis) and intrinsic or acquired resistance[148], for instance, Pt(II) compounds have a strong thermodynamic preference for binding to sulfur donor ligands, hence, before antitumor platinum drugs reach DNA in the tumor cells, they may interact with various compounds, including sulfur-containing, these interactions are generally thought to play a primary mechanism underlying tumor resistance to platinum compounds, their inactivation and their side effects[149]. Equilibrium process for cisplatin in cancer cells[150] are shown in figure (1-33):

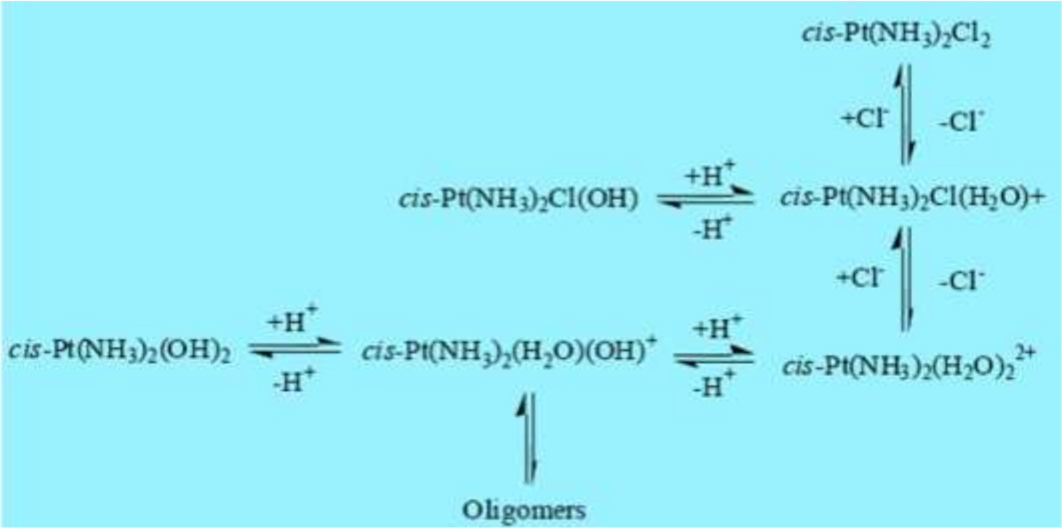


Fig.(1-33): Equilibrium process for cis-platin in cancer cell

There has also been interest in Pt(IV) complexes[151] for their potential as orally active agents. It is hoped that they will overcome Pt drug resistance in tumors and be applicable to a broader range of cancers. Novel platinum (IV) complexes having potent antitumor activity and high water solubility with low toxicity and pharmaceutical compositions were provided. Water insolubility and low bioavailability prevent cisplatin from being an orally active drug . Therefore, a new class of Pt(IV) compounds has been developed to get increased solubility in water. These drugs could represent a clinical advantage in terms of ease administration, particularly in patients who could not be treated systematically and allow the possibility of treatment on an outpatient basis, thus substantially reducing hospitalization costs. These compounds are typically neutral, water soluble, and robust enough to survive the gastric environment. Platinum(IV) complexes are known to be much more tolerant to ligand substitution reactions than their Pt(II) counterparts[152]. Some water soluble octahedral antitumor platinum(IV) complexes are shown in figure(1-34):

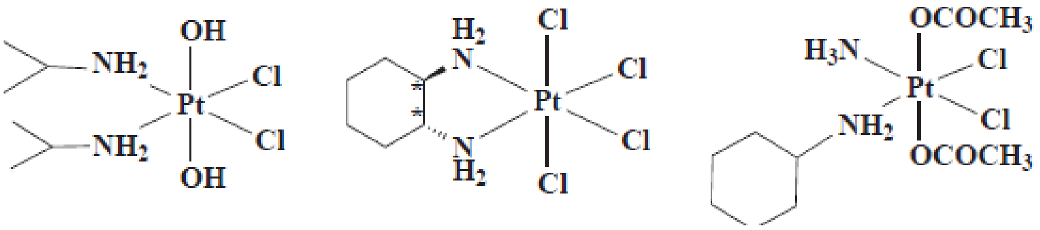


Fig.(1-34): platinum (IV) complexes

The similarity between the coordination chemistry of platinum(II) and palladium(II) compounds supports the theory that palladium complexes can act successfully as antitumor drugs and show fewer side effects relative to other heavy metal anticancer compounds[153]. Pd(II) analogues of Pt(II) complexes are well suited for kinetic and mechanistic studies by application of rapid-mixing techniques. Recently interactions of Pt(II) anticancer drugs and their Pd(II) analogues with sulfur containing amino acid chains have attracted much attention in studies on the biological activity of cisplatin[154] and carboplatin. These compounds usually prefer soft sulfur donors over nitrogen donors. Structure-activity relationships for a class of platinum coordination compounds confirmed that only those compounds having *cis* geometry block cell growth. The most active complex, cisplatin, was found to exhibit antitumor activity, whereas its *trans* isomer showed no such activity[155].

Octahedral platinum (IV) complexes with schiff base derived from dithiooxamide and benzaldehyde derivatives have been prepared Figure (1-35)[156,157]. These studies indicated that the complexes have biological activities as antitumor agents and anti bacterial.

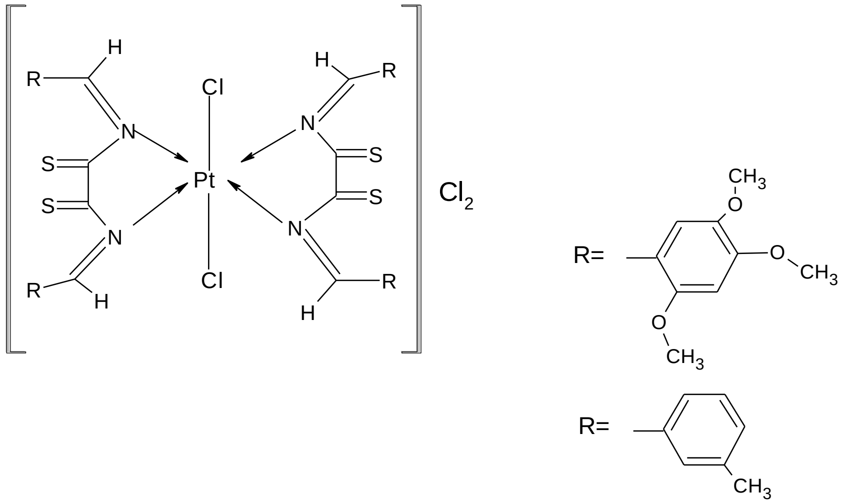


Fig.(1-35): platinum (IV) complexes with dithiooxamide derivatives

1.12. Aim of the Project

This work aims at synthesizing and characterizing some transition metal complexes with a schiff bases derived from dithiooxamide and two different aldehydes , as possible antifungal and antitumour agents . These include:

1- Preparation of [*N*,*N'*-bis(2-hydroxybenzylidene)dithiooxamide (LH1)]and[*N*,*N'*-bis(3,4,5-trimethoxybenzylidene) dithiooxamide (LH2)].

2- Preparation of Co(II),Ni(II),Cu(II),Pd(II) and Pt(IV) complexes of LH1.

3- Preparation of Co(II),Ni(II),Cu(II),Pd(II) and Pt(IV) complexes of LH2.

5- Screening of the prepared ligands and some of their complexes as antifungal agent, using dermatophytes *Aspergillus niger*.

CHAPTER

2

EXPERIMENTAL

The first part of this chapter constitutes chemicals and Instruments. The second part includes the synthesis of LH1 and its complexes. The third part includes the synthesis of LH2 and its complexes. The last part includes table (2-1) that shows color, melting points, yield% and purification solvents for ligands and their complexes.

2.1 Chemicals and Instrumentations

Dithiooxamide 99% (BDH), 2-hydroxybenzaldehyde 99% (Fluka), 3,4,5-trimethoxybenzaldehyde 98% (BDH), $CoCl_2.6H_2O$ (BDH), $NiCl_2$. $6H_2O$ (BDH), $CuCl_2.2H_2O$(BDH), $PdCl_2$. H_2O (BDH), K_2PtCl_6. $6H_2O$ (BDH), ethanol absolute 99% (Fluka) and Methanol 98% (Fluka). While the techniques that were used in this work are:

1-FT-IR 8000_S (Shimadzu), by KBr disc method, in University of Kufa.

2- UV-Vis.(Shimadzu), in University of Kufa.

3-Elemental analysis (E uroEA Elemental Analyser), in the University of Kufa.

4- Melting point of compounds produced was measured by using Gallen kamp melting point, in the University of Kerbala.

5-The molar the conductivity for complexes were measured using inluba WTW balance, in the University of kerbala.

6-The magnetic susceptibility of prepared complexes were measured by using magnetic sufcetitility balance, in the University of AL-Nahrain.

7-^{1}H NMR, was measured by BRUKER(300MHZ) in the University of Kashan-Iran.

8-Atomic Absorption Spectrometry (AAS) , in the University of Babylon.

2.2. Synthesis

2.2.1. Synthesis of *N,N′*-bis(2-hydroxybenzylidene) dithiooxamide (LH1).

The ligand was synthesized by dissolving (10mmol) of dithiooxamide in 20 mL of a hot absolute ethanol and then (20 mmol) of 2-hydroxybenzyaldehyde was added after that 2-3 drops of triethylamine was added to the mixture. The reaction was stirred and refluxed for 6 hours. The precipitate was filtered and washed with cold ethanol several times and then dried at 45 ºC for 5 hours. The ligand was partial soluble in dichloromethane, chloroform, toluene, non-soluble in n-Hexane and soluble in DMF and DMSO. Physical properties of the ligand are shown in Table(2-1).

2.2.2. Synthesis of Cobalt(II) Complex CoLH1 From (LH1 and $CoCl_2.6H_2O$)

10 mmol of ligand (LH1) was dissolved in 30 mL of methanol and 10 mmol of cobalt salt ($CoCl_2.6H_2O$) was dissolved in 10 mL of methanol. Ligand solution and cobalt salt solution were mixed and refluxed for 2 hours. Idealism conditions of complex is (pH = 7, λ_{max} = 491 nm and the concentration 0.009 M).The final product was filtered and washed with cold methanol several times and lastly dried at 45 ºC for 5 hours. The complex was partial soluble in dichloromethane , chloroform, toluene, non-soluble in n-Hexane, and soluble in DMF and DMSO. Physical properties of the complex are shown in Table(2-1) and the name of complex shows in table (2-2).

2.2.3. Synthesis of Nickel(II) and Copper(II) Complexes NiLH1 and CuLH1 (From LH1 and $NiCl_2.6H_2O$,$CuCl_2.2H_2O$ respectively).

Both of Nickel and copper complexes were synthesized using the 10 mmol of ligand (LH1) was dissolved in 30 mL of methanol and 10 mmol of salts dissolved in 10 mL of methanol. Ligand solution and salt solution were mixed and refluxed for 1.5 hours. The idealism conditions for two complexes were at pH = 10 and λ_{max}= 390 nm, 478 nm respectively and the concentration 0.008 M. The complexes were partial soluble in dichloromethane, chloroform, non-soluble in n-Hexane, toluene, and soluble in DMSO and DMF. Physical properties of the synthesis complexes are shown in Table (2-1) and the name of complexes shows in table (2-2).

2.2.4. Synthesis of Palladium(II) Complex PdLH1 From (LH1 and $PdCl_2$. H_2O.

10 mmol of ligand (LH1) was dissolved in 30 mL of methanol and 10 mmol of Palladium salt ($PdCl_2$. H_2O) was dissolved in 10 mL of methanol. Ligand solution and Palladium salt solution were mixed and refluxed for 1 hours. Idealism condition of complex is (pH = 10, λ_{max} = 590 nm and the concentration 0.01 M).The final product was filtered and washed with cold methanol several times and lastly dried at 45 ºC for 5 hours. The complex was partial soluble in dichloromethane , non-soluble in n-Hexane, toluene, chloroform and soluble in DMF Physical properties of the complex is shown in Table(2-1) and the name of complex shows in table (2-2).

2.2.5. Synthesis of Platinum(IV) Complex PtLH1 From (LH1 and $K_2PtCl_6.6H_2O$) .

10 mmol of ligand (LH1) was dissolved in 30 mL of methanol and 10 mmol of Platinum salt (K_2PtCl_6 .$6H_2O$) was dissolved in 10 mL of methanol. Ligand solution and Platinum salt solution were mixed and refluxed for 3 hours. Idealism condition of complex is (pH = 10, λ_{max} = 591 nm and the concentration 0.01 M). The final product was filtered and washed with cold methanol several times and lastly dried at 45 ºC for 5 hours. The complex was partial soluble in dichloromethane, non-soluble in n-Hexane, toluene, chloroform and soluble in DMF. Physical properties of the complex are shown in Table(2-1) and the name of complex shows in table (2-2).

2.2.6. Synthesis of *N,N*′-bis(3,4,5-trimethoxybenzylidene) dithiooxamide (LH2).

The ligand was synthesized by dissolving (10mmol) of dithiooxamide in 20 mL of a hot absolute ethanol and then (20 mmol) of 3,4,5-trimethoxybenzaldehyde was dissolved in 20 mL of absolute ethanol was added after that 2-3 drop of Piperidine ($C_5H_{11}N$) was added to the mixture. The reaction was stirred and relaxed for 12 hours. The precipitate was filtered and washed with cold ethanol several times and then dried at 45 ºC for 5 hours. The ligand was partial soluble in dichloromethane, chloroform, toluene, non-soluble in n-Hexane, and soluble in DMF. Physical properties of the ligand are shown in Table(2-1).

2.2.7 Synthesis of Cobalt(II) Complex CoLH2 From LH2 and $CoCl_2.6H_2O$

20 mmol of ligand (LH2) was dissolved in 50 mL of methanol and 10 mmol of cobalt salt ($CoCl_2.6H_2O$) was dissolved in 10 mL of methanol. Ligand solution and cobalt salt solution were mixed and refluxed for 2 hours. Ideal conditions of complex are (pH = 7, λ_{max} = 384 nm and the concentration 0.009 M).The final product was filtered and washed with cold methanol several times and lastly dried at 45 °C for 5 hours. The complex was partial soluble in dichloromethane, chloroform, non-soluble in n-Hexane, toluene, and soluble in DMF and DMSO. Physical properties of the complex are shown in Table(2-1) and the name of complex shows in table (2-2).

2.2.8 Synthesis of Nickel(II) and Copper(II) Complexes NiLH2 and CuLH2 From LH2 and $NiCl_2.6H_2O$, $CuCl_2.2H_2O$ respectively.

Nickel complex was synthesized using the 20 mmol of ligand (LH2) was dissolved in 50 mL of methanol and 10 mmol of salt dissolved in 10 mL of methanol. Ligand solution and salt solution were mixed and refluxed for 1.5 hours. The same method that was used to synthesize Copper complex but the ideal conditions were at pH = 10 and λ_{max}= 385 nm, 390 nm respectively and the concentration 0.008 M. The complexes were partial soluble in dichloromethane, chloroform, non-soluble in n-Hexane, toluene, and soluble in DMF. Physical properties of the synthesis complexes are shown in Table(2-1) and the name of complexs shows in table (2-2).

2.2.9. Synthesis of Palladium(II) Complex PdLH2 From LH2 and $PdCl_2.H_2O$.

20 mmol of ligand (LH2) was dissolved in 50 mL of methanol and 10 mmol of Palladium salt ($PdCl_2.H_2O$) was dissolved in 10 mL of methanol. Ligand solution and Palladium salt solution were mixed and refluxed for 2 hours. The Ideal condition of complex is (pH = 10, λ_{max} = 601 nm and the concentration 0.01 M). The final product was filtered and washed with cold methanol several times and lastly dried at 45 ºC for 5 hours. The complex was partial soluble in dichloromethane, non-soluble in n-Hexane, tolune, chloroform and soluble in DMF Physical properties of the complex are shown in Table(2-1) and the name of complex shows in table (2-2).

2.2.10 Synthesis of Platinum(IV) Complex PtLH2 From LH2 and $K_2PtCl_6.6H_2O$.

20 mmol of ligand (LH2) was dissolved in 50 mL of methanol and 10 mmol of Platinum salt ($K_2PtCl_6.6H_2O$) was dissolved in 10 mL of methanol. Ligand solution and Platinum salt solution were mixed and refluxed for 3 hours. The Ideal condition of complex is (pH = 10, λ_{max} = 550 nm and the concentration 0.01 M). The final product was filtered and washed with cold methanol several times and lastly dried at 45 ºC for 5 hours. The complex was partial soluble in dichloromethane, non-soluble in n-Hexane, toluene, chloroform and soluble in DMF. Physical properties of the complex are shown in Table(2-1) and the name of complex shows in table (2-2).

Table (2-1) Color, Melting Point, Yield% and Purification Solvent for Ligands and Its Complexes.

Compound	**Color**	**Melting Point ºC**	**Yield %**	**Suitable Solvent**
LH1	Orange	256- 259	82 %	DMF
Co(LH1)	Brown	280	86%	DMSO
Ni(LH1)	Deep orange	265- 270	64%	DMSO
Cu(LH1)	Black-Brown	289	75%	DMSO
Pd(LH1)	Deep brown	290	65%	DMF
Pt(LH1)	Black-Brown	292	60%	DMF
LH2	Deep orange	182 dec.	90%	DMF
$Co(LH2)_2$	Deep green	190 dec.	85%	DMSO
$Ni(LH2)_2$	Orange	172 dec.	60%	DMSO
$Cu(LH2)_2$	Black	191 dec.	65%	DMSO
$Pd(LH2)_2$	Deep brown	188 dec.	60%	DMF
$Pt(LH2)_2$	Black green	189 dec.	70%	DMF

Table (2-2) Nomenclature of prepared complexes according to IUPAC system.

Complexes	formula	Name of complexes
CoLH1	$[Co(LH1)(Cl)(H_2O)]Cl$	aquachloro*N*,*N*′-bis(2-hydroxybenzylidene) dithiooxamidecobalt(II) chloride
CuLH1	$[Cu(LH1)(H_2O)_2]$	diaqua*N*,*N*′-bis(2-hydroxybenzylidene)dithiooxamidecopper(II)
NiLH1	$[Ni(LH1)]$	*N*,*N*′-bis(2-hydroxybenzylidene)dithiooxamidenickel(II)
PdLH1	$[Pd(LH1)]$	*N*,*N*′-bis(2-hydroxybenzylidene)dithiooxamidepalladium(II)
PtLH1	$[Pt(LH1)(Cl_2)]$	dichloro*N*,*N*′-bis(2-hydroxybenzylidene) dithiooxamideplatinum(IV)
CoLH2	$[Co(LH2)_2(H_2O)_2]Cl_2$	diaquabis(*N*,*N*′-bis(3,4,5-trimethoxybenzylidene)dithiooxamide) cobalt(II) chloride
NiLH2	$[Ni(LH2)_2(H_2O)]Cl_2$	aquabis(*N*,*N*′-bis(3,4,5-trimethoxybenzylidenedithiooxamide) nickel(II) chloride
CuLH2	$[Cu(LH2)_2(H_2O)_2]Cl_2$	diaquabis(*N*,*N*′-bis(3,4,5-trimethoxybenzylidene)dithiooxamide) copper(II) chloride
PdLH2	$[Pd(LH2)_2]Cl_2$	bis(*N*,*N*′-bis(3,4,5-trimethoxybenzylidene) dithiooxamide)palladium(II) chloride
PtLH2	$[Pt(LH2)_2Cl_2]Cl_2$	dichlorobis(*N*,*N*′-bis(3,4,5-trimethoxybenzylidene)dithiooxamide)platinum(IV) chloride

CHAPTER

3

RESULTS œ DISCUSSION

This chapter includes the properties of the ligands and their complexes that were prepared. Several techniques used in this chapter, these techniques are: Elemental analysis (EA) used to measure the ratio of elements in the ligands. Infra red FT-IR, UV-Visible and ^{1}H NMR techniques were used to identify the various natures of chemical bonds present in the structure of ligands and their complexes. The magnetic susceptibility was measured to determine the structure of complexes. We measured the molar conductivity of complexes that were synthesized. This looked at in this chapter. Atomic absorption used for measuring quantities of chemical elements present in environmental samples by measuring the absorbed radiation by the chemical element of interest. Finally the antifungal activity of ligands and some of their complexes have been tested for the in vitro growth inhibitory activity against the *Aspergillus niger* (this fungi effect to the dermatophytes) by using the disc diffusion method.

3.1. Elemental Analysis

Elemental analysis technique was used to identify and determine the amount of elements that are present in a sample. This method is used as a qualitative and quantitative method, as it can be employed to identify the types of elements in the sample and it can be used to determine the ratio of elements in the sample material. For example the ratio of carbon, hydrogen, nitrogen and sulfur can be measured using this method[158]. In this project the elemental analysis technique is used to study ratio of elements for ligands that were prepared. It is clear from the table (3-1) the experimental values were the same as the theoretical values. This is indicting the formation the ligand. Table (3-1) shows the theoretical and practical values of elements of ligands LH1 and LH2.

Table (3-1). Theoretical and Practical Values of Elements of the Ligands LH1 and LH2

Ligand LH1	**% C**	**% H**	**% N**	**% S**
Theory value	58.5	3.6	8.5	19.5
Experiment value	57.6	3.3	10.5	19.9
Ligand LH2				
Theory value	55.4	5.0	5.5	13.5
Experiment value	57.0	4.9	6.5	21.6

3.2. Infrared Spectroscopy

It is necessary to identify the various natures of chemical bonds present in the structures of ligands and Its complexes that were prepared. The best way to identify types of bonds and structures of ligand and complexes are using infrared spectroscopy [159]. The basic principle of this technique is that the bonds will absorb infrared rays, where this can be led to change in the vibration energy of molecules. If the dipole of non-symmetrical bond has a frequency that is the same frequency of the electromagnetic radiation(emr), the energy will transfer to the bond and then the change in amplitude of the molecule vibration will occur[160] . Since every type of bonds has a different natural frequency of vibration, and since two of the same type of bond in two different compounds are in two slightly different environment, no two molecules of different structure have exactly the same infrared absorption pattern, or **infrared spectrum.** Although some of the frequencies absorbed in the two cases might be the same, in no case of two different molecules will their infrared spectra (the patterns of absorption) be identical. Thus, the infrared spectrum can be used for molecules much as a fingerprint can be used for humans. By comparing the infrared spectra of two substances thought to be identical, you can establish whether they are, in fact, identical. If their infrared spectra coincide peak for peak (absorption for absorption), in most cases the two substances will be identical. A second and more important use of the infrared spectrum is to determine structural information about a molecule. The absorptions of each type of bond (N-H, C-H, O-H, C-X, C=O, C-O, C-C,C=C, C=N and so on) are regularly found only in certain small portions of the vibrational infrared region. A small range of absorption can be defined for each type of bond. Outside this range, absorptions are normally due to some other type of bond[161].

3.2.1.FT-IR Spectroscopy of Ligand (LH1) and Its Complexes

The general bonds and their wavenumbers for ligand (LH1) and their complexes that were synthesized [162] . Table (3-2) the important bands of the LH1 and its complexes.

Wave number (cm^{-1})	Bonds
1650-1580cm^{-1}	C=N stretching
1360-1200	C=S stretching
1260-1000 cm^{-1}	C-O stretching
1000-700 cm^{-1}	H_2O coordination
700-325 cm^{-1}	M-N stretching

The C=N bond has sp^2-Hybridized carbon and absorbs in about the same range as a C=C bond. Although the H-C=N band varies in intensity from compound to compound, it usually is more intense than that obtained from the C=C bond. An imine (R-CH=N-R) gives a C=N absorption in the range 1650-1580cm^{-1} [163]. The former exhibits υ(C=S) near 1200-1360cm^{-1} as a single band, whereas the latter shows a doublet in the same range[164]. The strong C-O single-bond stretching vibrations is observed in the range from 1260 to 1000 cm^{-1}. Since the C-O absorption is coupled with the adjacent C-C stretching vibrations, the position of the band may be used to determine whether a phenolic compound is present

[165].The C-O-H bending vibration is coupled to H-C-H bending vibrations to yield some weak and broad peaks in the 1440 to 1220 cm^{-1}region. υ (C-O-H) shifts to higher frequency by complex formation. When these shifts are dependent on the metal ions, the magnitudes of the shifts follow the well-known ***Irving -Williams*** order :Mn(II) <Fe(II) <Co(II) <Ni(II) <Cu(II) >Zn(II) [166]. The M-N stretching mode in the low frequency region is of particular interest since it provides direct information about the structure of the MN skeleton and the strength of the M-N bond[167]. In general, If the spectrum is examined under high resolution, the fine structure of these bands is observed[168].

3.2.1.1. FT-IR Spectrum of Ligand (LH1)

Figure (3-1) shows IR peaks of LH1. It is clear from the figure that there is a peak at 1610 cm^{-1} this represents the azomethine stretching band υ (H-C=N). The peak at 1213 cm^{-1} is due the thio carbonyl band υ (C=S). There is a peak at 1180 cm^{-1} which corresponds to υ (C-O) stretching, while the peak at 1276 cm^{-1}corresponds to υ (C-O-H)bending. Table (3-3) contains the most characteristic bands of LH1[162].

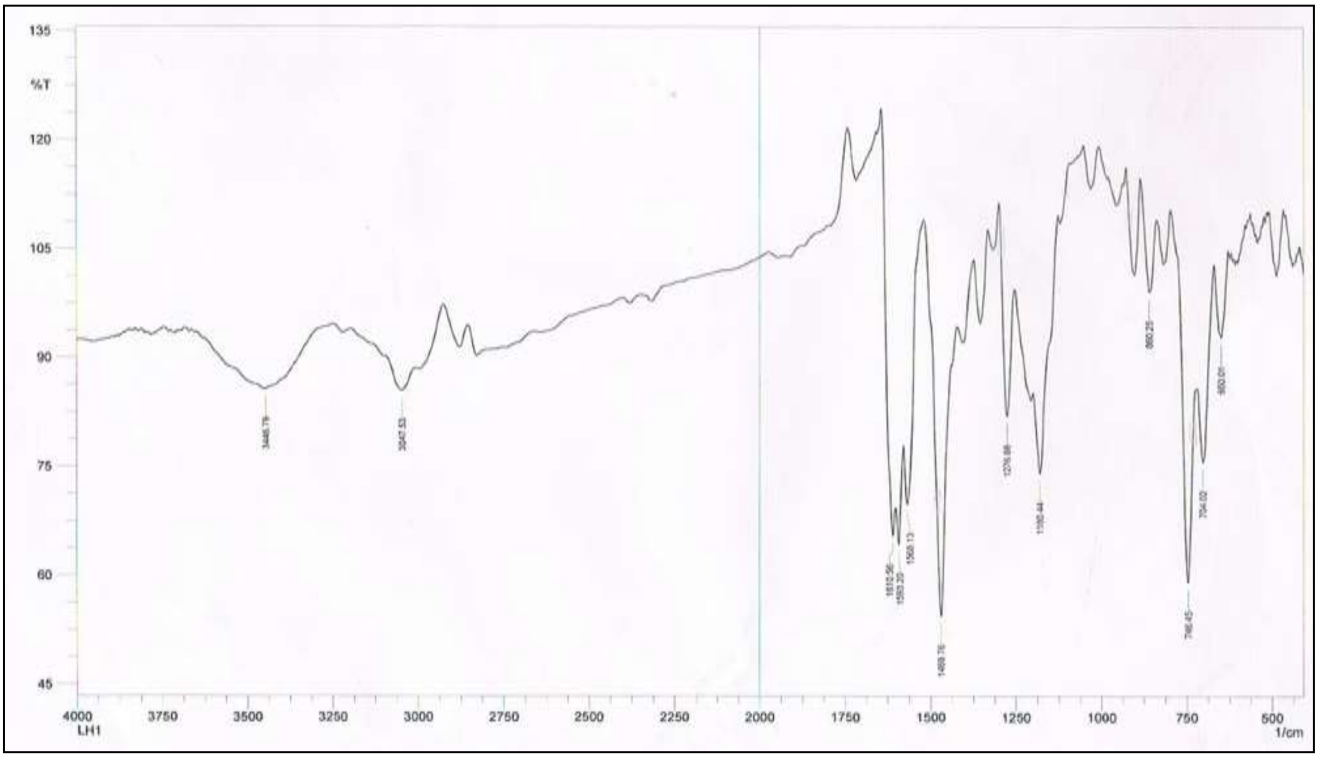


Fig. (3-1): FT-IR spectrum of ligand(LH1)

3.2.1.2. FT-IR Spectrum of Cobalt(II) Complex (CoLH1).

Cobalt (II) complex spectrum is shown in figure (3-2). There is a peak at 1597 cm^{-1} can be assigned to azomethine stretching band υ (H-C=N) which is shifting from 1610 to 1597cm^{-1}. This shifts occurred in lower frequency because decreasing of bond order between carbon and nitrogen due to occurred (π- back bonding)[169]. The peak at 1215 cm^{-1} relates to the thio carbonyl band υ (C=S). There is a strong peak at 1182 cm^{-1} which may represent to υ (C-O)stretching, whilst the peak at at 746cm^{-1} relates to υ (H_2O) coordination. In addition, there is a peak at 554 cm^{-1}, 704 cm^{-1} corresponds to υ (Co-N) and υ (Co-O)[170,171].Table (3-3) contains the most characteristic bands of CoLH1.

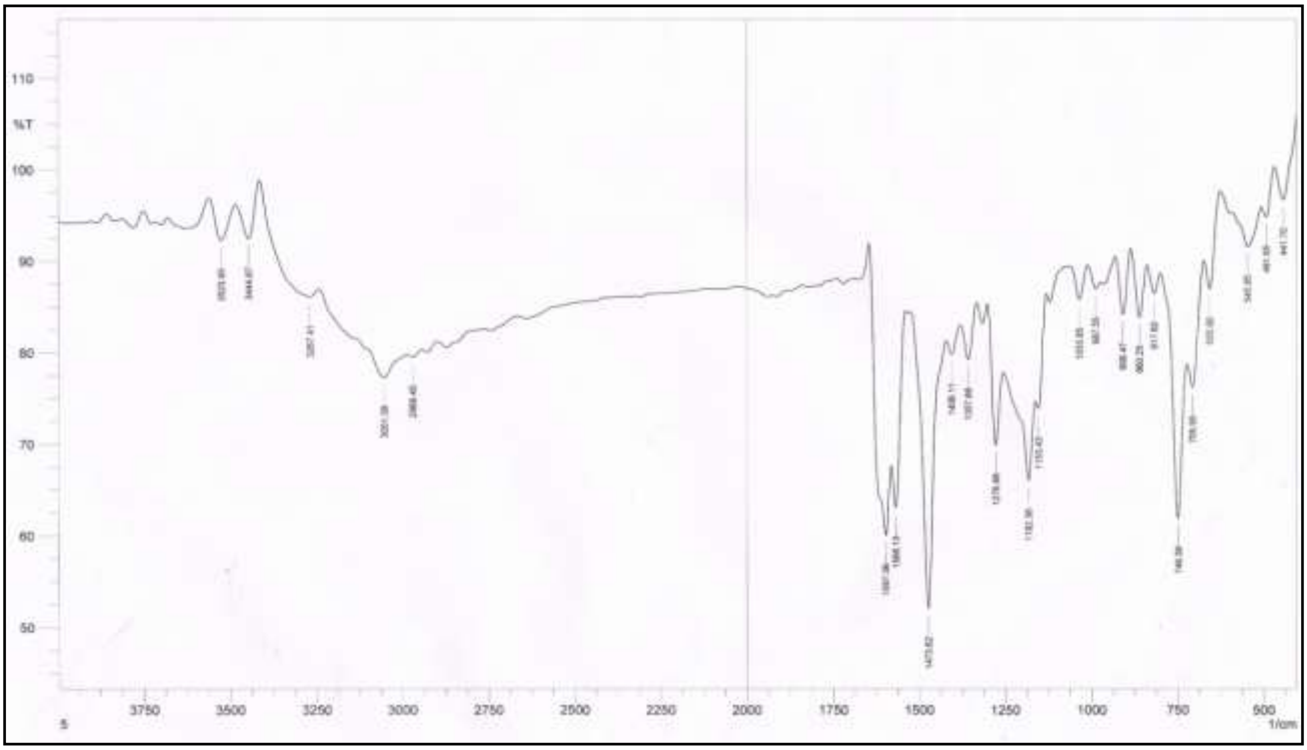


Fig. (3-2): FT-IR spectrum of CoLH1

3.2.1.3. FT-IR Spectrum of Nickel(II) Complex (NiLH1).

Figure (3-3) illustrates peaks of nickel (II) complex. The peak at 1622 cm^{-1} corresponds to azomethine stretching band υ (H-C=N) which is shifting from 1610 to 1622cm^{-1}. This shifts occurred in higher frequency because increasing of bond order between carbon and nitrogen[169] . There is peak at 1205 cm^{-1} which belongs to thio carbonyl υ (C=S). The peak at 1180 cm^{-1} can be related to υ (C-O) stretching. There is peak at 489 cm^{-1}, 750 cm^{-1} is due υ (Ni- N) and υ (Ni-O)[170,171].

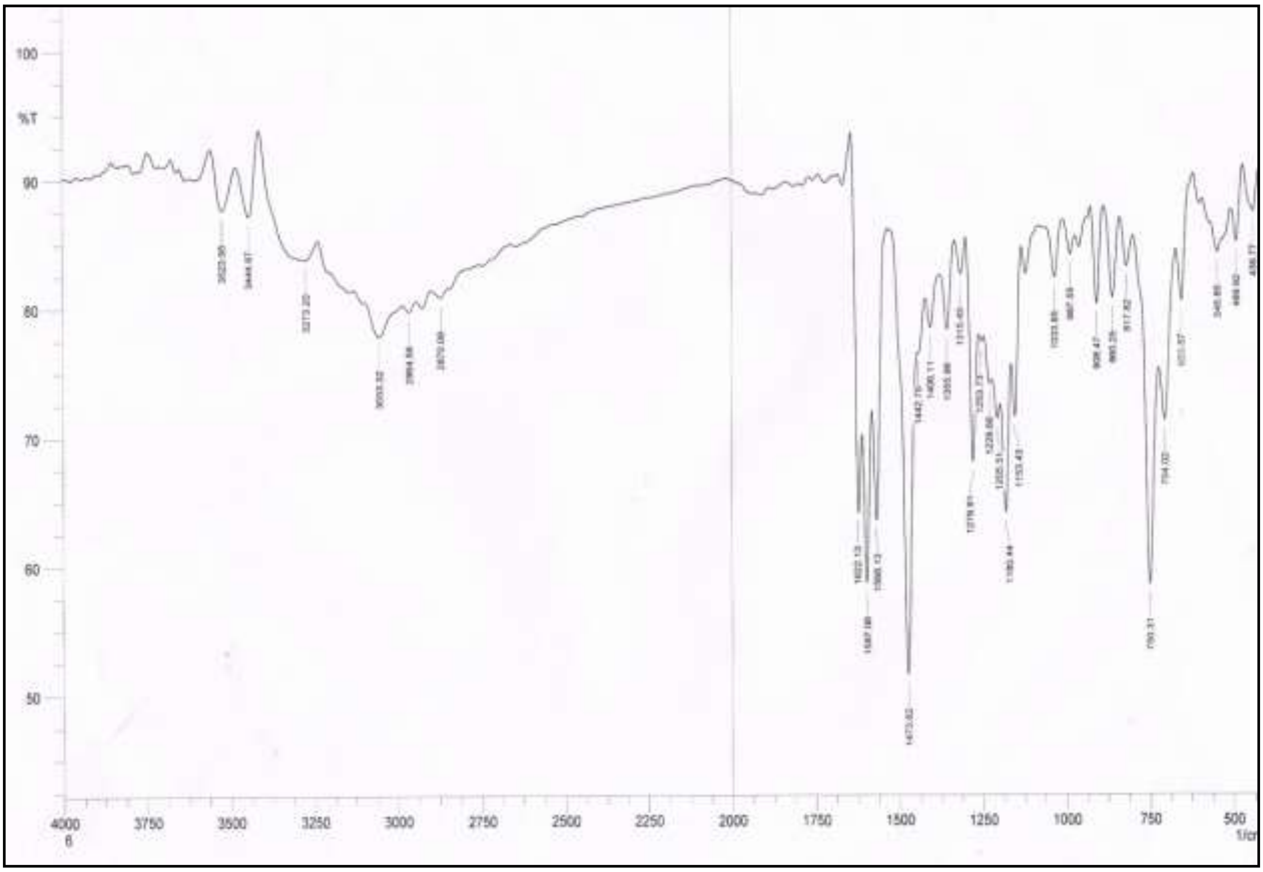


Fig. (3-3): FT-IR spectrum of NiLH1

3.2.1.4. FT-IR Spectrum of Copper(II) Complex (CuLH1).

IR Spectrum of copper complex CuLH1 is shown in figure (3-4). It is clear from this figure that is peak at 1602 cm^{-1} assigning to azomethine stretching band υ (H-C=N) which is shifting from 1610 to 1602cm^{-1}. This shift occurred in lower frequency because of the decrease of bond order between carbon and nitrogen due to occurred (π-back bonding)[169]. There is peak at 1203 cm^{-1} which relates to thio carbonyl υ (C=S)[170]. And another one at 3446 cm^{-1} due to υ(O-H) of the hydrogen bonding. The peak at 1159 cm^{-1} corresponds to υ (C-O) stretching. The small peak at 586 cm^{-1}, 756 cm^{-1} can be related to υ (Cu-N) and υ (Cu-O) [171]. The peak at 740 cm^{-1} belong to H_2O coordination.

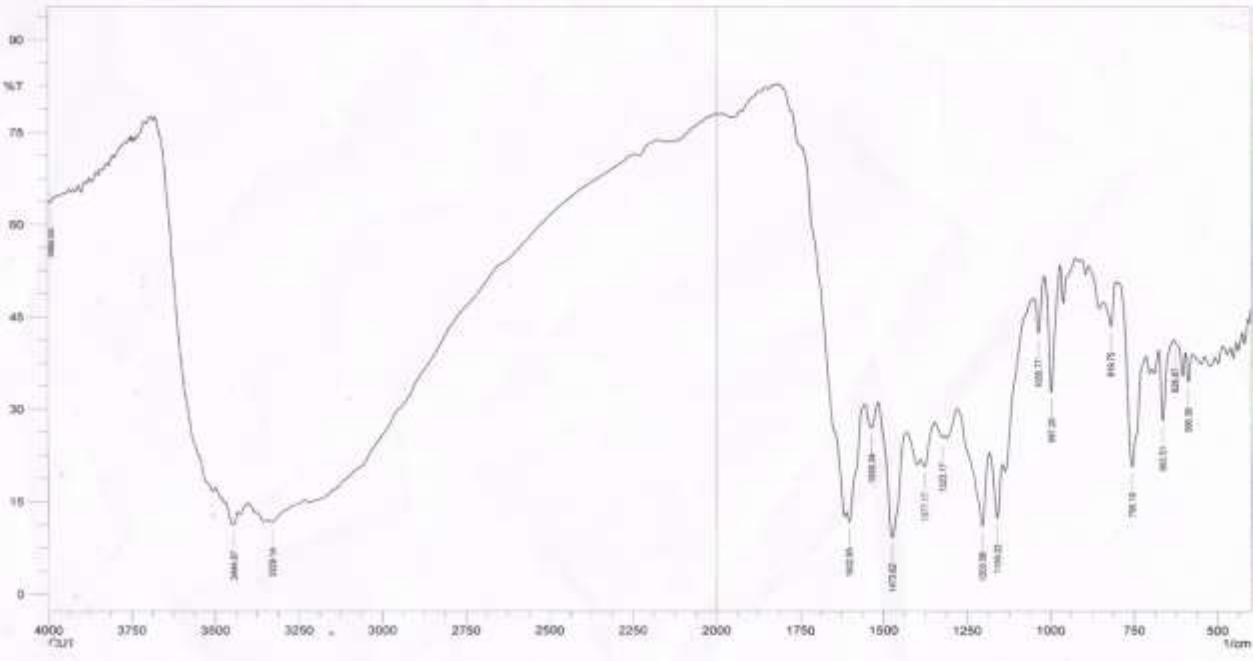


Fig. (3-4): FT-IR spectrum of CuLH1

3.2.1.5. FT-IR Spectrum of Palladium(II) Complex (PdLH1).

The FT-IR spectrum of PdLH1 is shown in Figure (3-5) The peak at 1593 cm^{-1} corresponds to azomethine stretching band υ (H-C=N) which is shifting from 1610 to 1593cm^{-1}. This shift occurred in lower frequency because of the decrease of bond order between carbon and nitrogen due to occurred (π- back bonding)[169] . there is peak at 1315 cm^{-1} that belongs to thio carbonyl υ (C=S). The peak at 1182 cm^{-1} can be related to υ (C-O) stretching. There is peak at 540 cm^{-1}, 751 is due υ (Pd- N) and υ (Pd-O)[170,171].

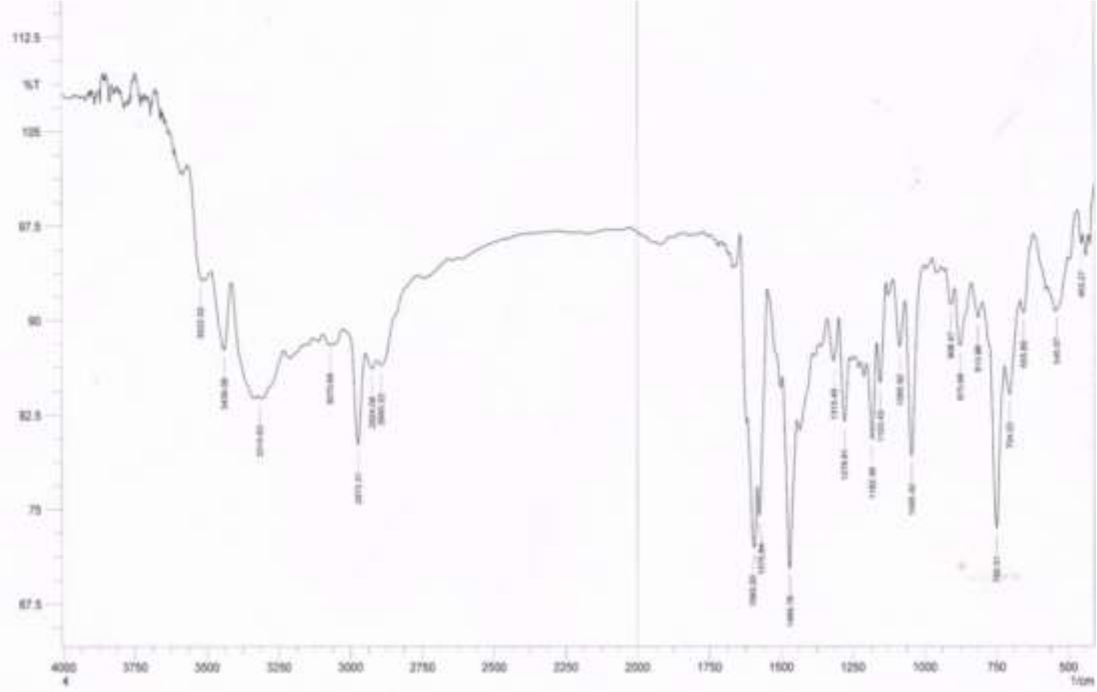


Fig. (3-5): FT-IR spectrum of PdLH1

3.2.1.6. FT-IR Spectrum of Platinum(IV) Complex (PtLH1).

Figure (3-6) illustrates peaks of Platinum (IV) complex. The peak at 1595cm^{-1} corresponds to azomethine stretching band υ (H-C=N) which is shifting from 1610 to 1595cm^{-1}. This shift occurred in lower frequency because of the decrease of bond order between carbon and nitrogen due to occurred (π- back bonding)[169] . There is peak at 1354cm^{-1} that belongs to thio carbonyl υ (C=S). The peak at 1178 cm^{-1} can be related to υ (C-O) stretching. There is peak at 491 cm^{-1}, 746 cm^{-1} is due υ (Pt- N) and υ (Pt-O) [170,171].

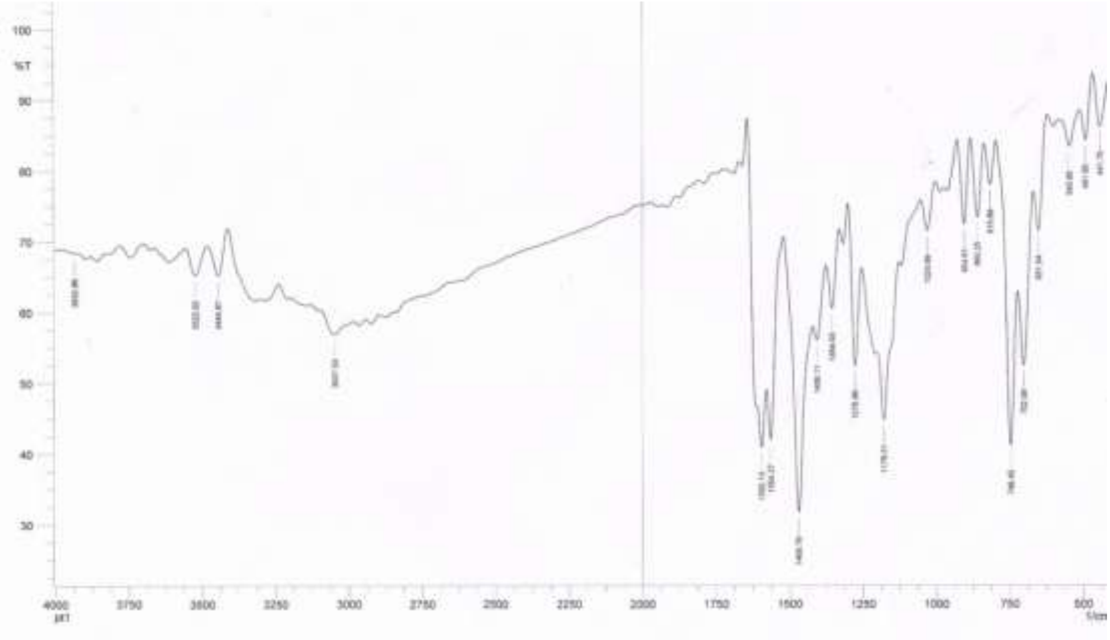


Fig. (3-6): FT-IR spectrum of PtLH1

Table(3-3): Number of The Most Bands of FT-IR To Prepared Ligand (LH1) and Its Complexes In (cm^{-1}).

Compound	**Azomethine H-C=N**	**Thio carbonyl bands (C=S)**	**υ C-O**	**H_2O (Coor.)**	**υ (M-O)**	**υ M-N**
LH1	1610$_{(s)}$	1213$_{(w)}$	1180$_{(s)}$	-		-
CoLH1	1597$_{(s)}$	1215$_{(w)}$	1182$_{(s)}$	746	704$_{(s)}$	554$_{(w)}$
NiLH1	1622$_{(s)}$	1205$_{(w)}$	1180$_{(s)}$	-	750$_{(s)}$	489$_{(w)}$
CuLH1	1602$_{(s)}$	1203$_{(w)}$	1159$_{(s)}$	740	745$_{(s)}$	586$_{(w)}$
PdLH1	1593$_{(s)}$	1315$_{(w)}$	1182$_{(s)}$	-	751$_{(s)}$	540$_{(w)}$
PtLH1	1595$_{(s)}$	1354$_{(w)}$	1178$_{(s)}$	-	746$_{(s)}$	491$_{(w)}$

w= weak, s= strong, m= medium

3.2.2.FT-IR Spectroscopy of Ligand(LH2) and Its Complexes.

The general bonds and their wavenumbers for ligand (LH2) and their complexes that were synthesized[162] . Table (3-4) the important bands of the LH2 and its complexes.

Wave number (cm^{-1})	**Bonds**
1650-1580 cm^{-1}	C=N stretching
1360-1200 cm^{-1}	C=S stretching
850-1000 cm^{-1}	C-O-C symmetric
1300-1220 cm^{-1}	C-O-C asymmetric
700-325 cm^{-1}	M-N stretching
3150-3050 cm^{-1}	CH_3 stretching
900-690 cm^{-1}	CH_3 out-of-plane bending

An imine (R-CH=N-R) gives a C=N absorption in the range 1650-1580cm^{-1}. This frequency occurred in lower frequency at coordinate with metal ions because of the decrease of bond order between carbon and nitrogen due to occurred (π- back bonding) and in higher frequency because of the increase of bond order between carbon and nitrogen. The former exhibits ʋ(C=S) near 1200cm^{-1} as a single band, whereas the latter shows a doublet in the same range. The ʋ (C-O-C) give rise to two strong bands: an asymmetric C-O-C stretch near 1250 cm^{-1}and a symmetric stretch near 1040cm^{-1}. The shift in the asymmetric stretching frequencies to values are higher than were found in this compounds can be explained through resonance [172]. The M-N stretching mode in the low frequency region is of particular interest since it provides direct information about the structure of the MN skeleton and the strength of the M-N bond. In general, the CH_3 stretching has strong intensity at 3150-3050cm^{-1} while the CH_3(out-of-plane) bending also has strong intensity at 900-690cm^{-1} [173].

3.2.2.1. FT-IR Spectrum of Ligand (LH2)

Figure (3-7) shows IR peaks of LH2. It is clear from the figure that there is a peak at 1583 cm^{-1} this represents the azomethine stretching band υ(H-C=N). The peak at 1186 cm^{-1} is due the thio carbonyl band υ (C=S). There is a peak at 1236 cm^{-1} which corresponds to υ (C-O-C)asymmetric stretching, while the peak at 1002 cm^{-1}corresponds to υ(C-O-C) symmetric. The peak at 3150cm^{-1} is due the υ(CH_3)stretching, while the peak at 819cm^{-1} corresponds to CH_3(out-of-plane) bending[162].

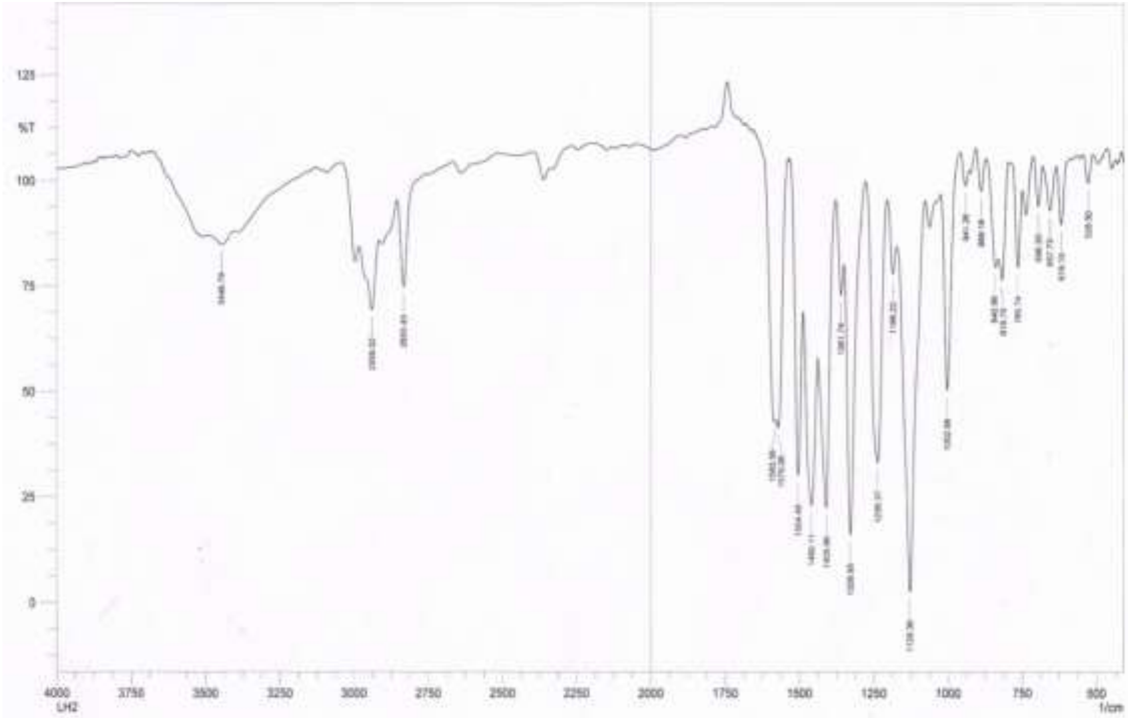


Fig. (3-7): FT-IR spectrum of Ligand(LH2)

3.2.2.2. FT-IR Spectrum of Cobalt(II) Complex (CoLH2).

The most significant difference in the IR spectra of the ligand and its cobalt complex, figure (3-8) was the shift of H-C=N stretching frequencies of LH2 to higher frequencies and the change in shape of the peak due to metal - ligand coordination[169]. Furthermore, new bands have been observed around 528 cm^{-1}, 653cm^{-1} and 3442cm^{-1} which are due to υ (Co-N), υ (H_2O) coordination water and hydrogen bonding[170] . Table (3-4) contains the most characteristic bands of CoLH2.

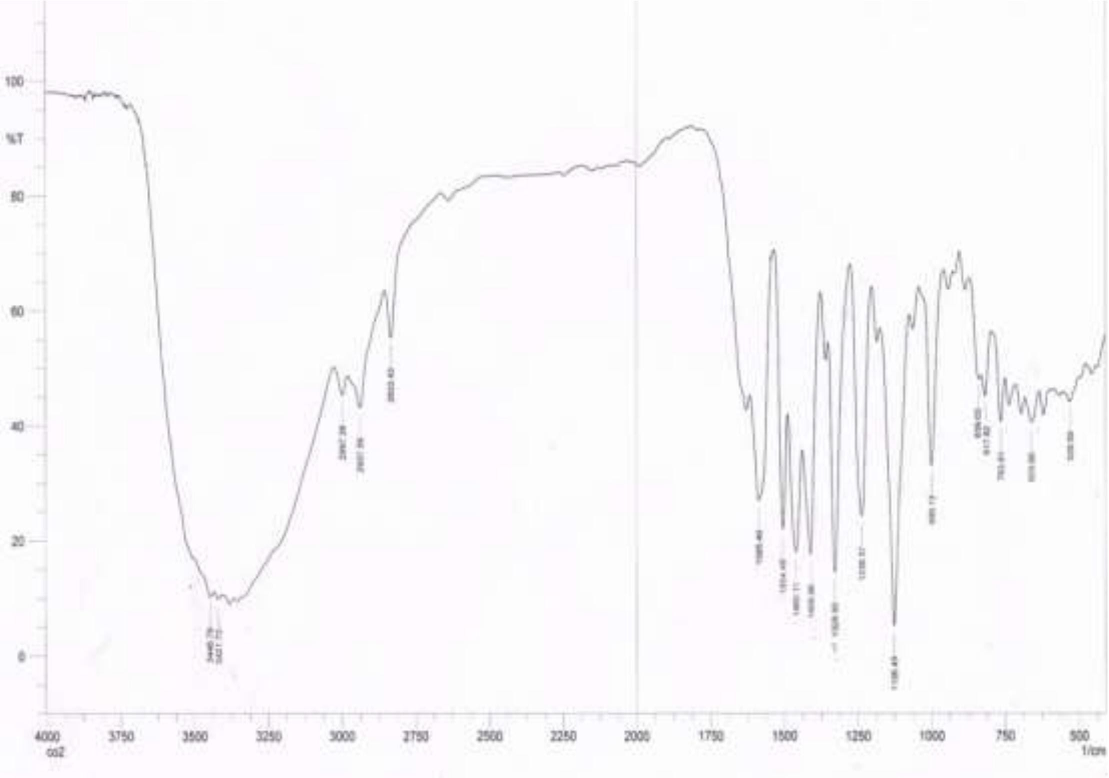


Fig. (3-8): FT-IR spectrum of CoLH2

3.2.2.3. FT-IR Spectrum of Nickel(II) Complex (NiLH2).

The FT-IR spectrum of NiLH2 is shown in Figure (3-9). The peak at 1587 cm^{-1} corresponds to azomethine stretching band υ (H-C=N). There is peak at 1184 cm^{-1} that belongs to thio carbonyl υ (C=S). The peak at 1232 cm^{-1} can be related υ (C-O-C)asymmetric stretching, while the peak at 1002 cm^{-1} represents υ (C-O-C) symmetric[169]. Furthermore, new bands have been observed around 547 cm^{-1}, 735cm^{-1} and 3382cm^{-1} which are due to υ (Ni-N), υ (H_2O) coordination water and hydrogen bonding [170]. The peak at 3150cm^{-1} is due the υ (CH_3) stretching, while the peak at 835cm^{-1} corresponds to CH_3(out-of-plane) bending[171].

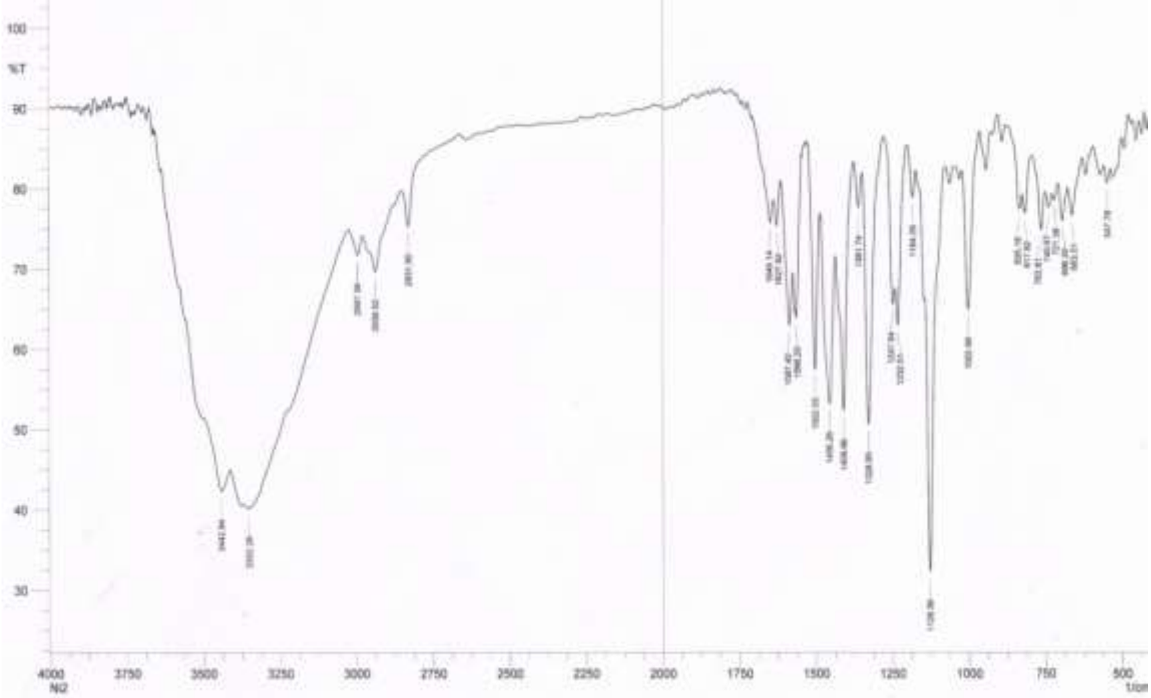


Fig. (3-9): FT-IR spectrum of NiLH2

3.2.2.4. FT-IR Spectrum of Copper(II) Complex (CuLH2).

The most significant difference in the IR spectra of the ligand and its copper complex, figure (3-10), was the shift of H-C=N stretching frequencies of LH2 to higher frequencies and the change in shape of the peak due to metal - ligand coordination[169]. Furthermore, new bands have been observed around 530 $cm^{-1}$and 651cm^{-1} which are due to ʋ (Cu-N), ʋ (H_2O) coordination [170,171]. Table (3-5) contains the most characteristic bands of CuLH2.

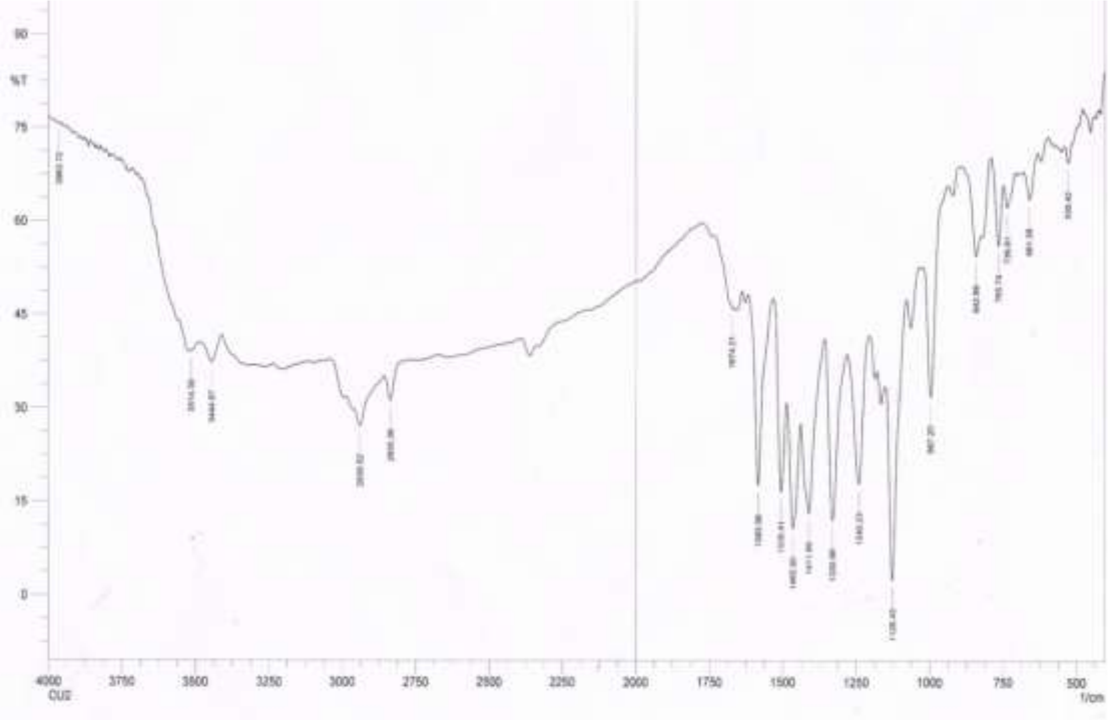


Fig. (3-10): FT-IR spectrum of CuLH2

3.2.2.5. FT-IR Spectrum of Palladium(II) Complex (PdLH2).

In PdLH2 spectrum, figure (3-11) azomethine peak frequency was changed by splitting and shifting to 1673 cm^{-1} , indicating the coordination through azomethine nitrogen[169]. The bands at 659 cm^{-1} can be attributed to υ(Pd-N)[170, 171].

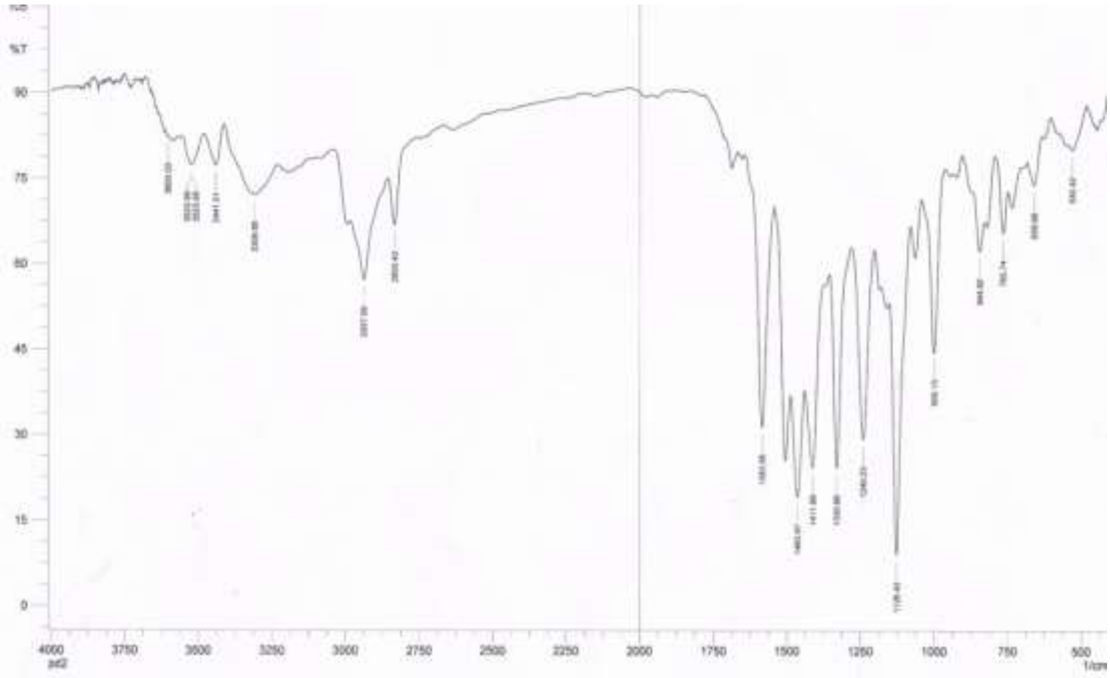


Fig. (3-11): FT-IR spectrum of PdLH2

3.2.2.6. FT-IR Spectrum of Platinum(IV) Complex (PtLH2).

Figure (3-12) illustrates peaks of Platinum (IV) complex. The peak at 1585 cm^{-1} corresponds to azomethine stretching band υ (H-C=N) which is shifting from 1583 to 1585cm^{-1}. This shifts occurred in higher frequency because of the increase of bond order between carbon and nitrogen [169]. There is peak at 1168cm^{-1} that belongs to thio carbonyl υ (C=S). The peak at 1242 cm^{-1} can be related to υ (C-O-C)asymmetric stretching, while the peak at 995 cm^{-1} represents υ (C-O-C) symmetric. There is peak at 665cm^{-1} is due υ (Pt- N)[170]. The peak at 3050cm^{-1} is due to υ (CH_3)stretching, while the peak at 837cm^{-1} corresponds to CH_3(out-of-plane) bending[171].

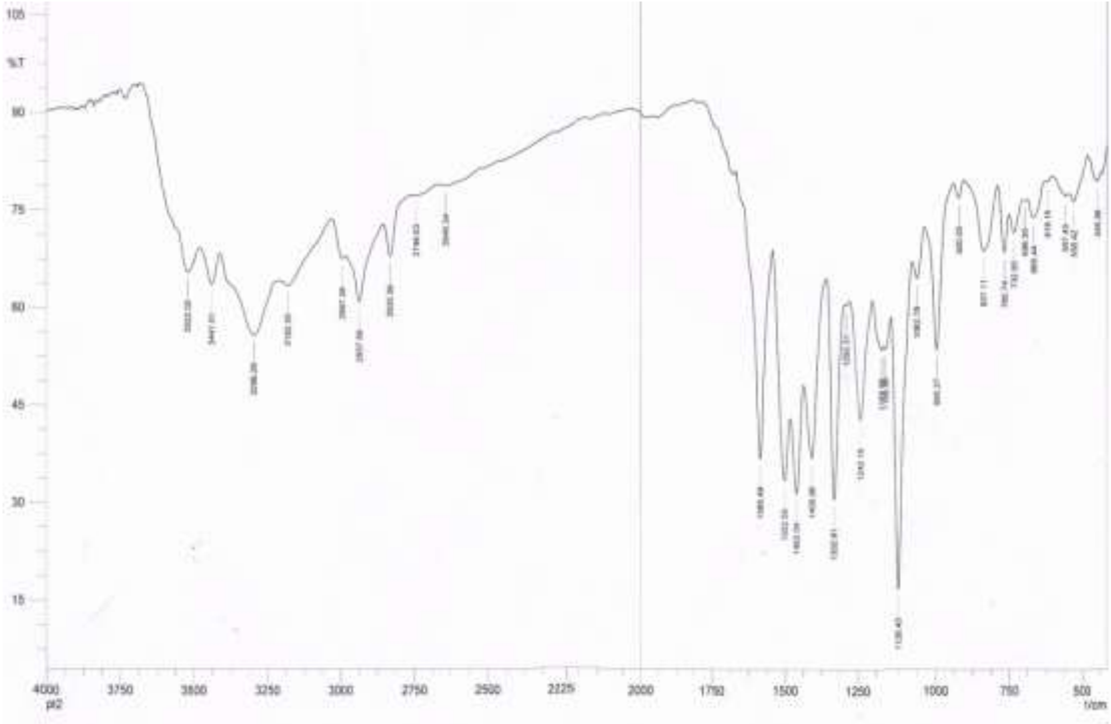


Fig. (3-12): FT-IR spectrum of PtLH2

Table (3-5): Number of The Most Bands of FT-IR To Prepared Ligand (LH2) and Its Complexes In (cm^{-1})

Compound	**υ H-C=N**	**υ C=S**	**Methoxy bands**		**υ (M-N)**	**Metheyl bands**		**H_2O (Coor)**
			υC-O-C) Asymmetric	**υC-O-C) Symmetric**		**CH_3 Stret.**	**CH_3 O.O.P.**	
LH2	$1583_{(s)}$	$1186_{(s)}$	$1236_{(w)}$	$1002_{(m)}$	-	3150	819	-
CoLH2	$1585_{(s)}$	$1184_{(s)}$	$1236_{(w)}$	$999_{(m)}$	$528_{(w)}$	3150	763	653
NiLH2	$1587_{(s)}$	$1184_{(s)}$	$1232_{(w)}$	$1002_{(m)}$	$547_{(w)}$	3150	830	735
CuLH2	$1674_{(s)}$	$1186_{(s)}$	$1240_{(w)}$	$997_{(m)}$	$530_{(w)}$	3050	842	651
PdLH2	$1673_{(s)}$	$1185_{(s)}$	$1240_{(w)}$	$999_{(m)}$	$659_{(w)}$	3050	844	-
PtLH2	$1585_{(s)}$	$1168_{(s)}$	$1242_{(w)}$	$995_{(m)}$	$665_{(w)}$	3050	837	-

W= weak, S= strong, m= medium, Stret.= Stretching, o.o.p.= Out of plane

3.3. Ultraviolet Spectroscopy (UV-Visible)

Most organic molecules and functional groups are transparent in the portions of the electromagnetic spectrum that we call the ultraviolet (UV) and visible (VIS) regions-that is, the regions where wavelengths range from 190 nm to 800 nm[174]. Consequently, absorption spectroscopy is of limited utility in this range of wavelengths. However, in some cases we can derive useful information from these regions of the spectrum. That information, when combined with the detail provided by infrared and nuclear magnetic resonance (NMR) spectra, can lead to valuable structural proposals[175]. For an atom that absorbs in the ultraviolet, the absorption spectrum sometimes consists of very sharp lines, as would be expected for a quantized process occurring between two discrete energy levels. For molecules, however, the UV absorption usually occur over a wide range of wavelengths because molecules (as opposed to atoms) normally have many excited modes of vibration and rotation at room temperature. In fact, the vibration of molecules cannot be completely "frozen out" eyen at absolute zero. Consequently, a collection of molecules generally has its members in many states of vibrational and rotational excitation. The energy levels for these states are quite closely spaced, corresponding to energy differences considerably smaller than those of electronic levels. The rotational and vibrational levels are thus "superimposed" on the electronic levels.

Because there are so many possible transitions, each differing from the others by only a slight amount, each electronic transition consists of a vast number of lines spaced so closely that the spectrophotometer cannot resolve them. Rather, the instrument traces an "envelope" over the entire pattern. What is observed from these types of combined transitions is that the UV spectrum of a molecules usually consists of a broad band of absorption centered near the wavelength of the major transition[176].

3.3.1. Electronic Spectrum of Ligand (LH1)

The spectrum of ligand Figure (3-13) show the first absorption band in 283 nm (35335 cm^{-1}) which can be attributed to (π - π^*) transition for the aromatic nucleus. The second band appearing in 374 nm (26737 cm^{-1}) is attributed to (π - π^*) transition in all molecules. The third band which appeared in (393,420) nm (25445,23809) cm^{-1} was attributed to (n- π^*) transition in imino group (C=N)[177].

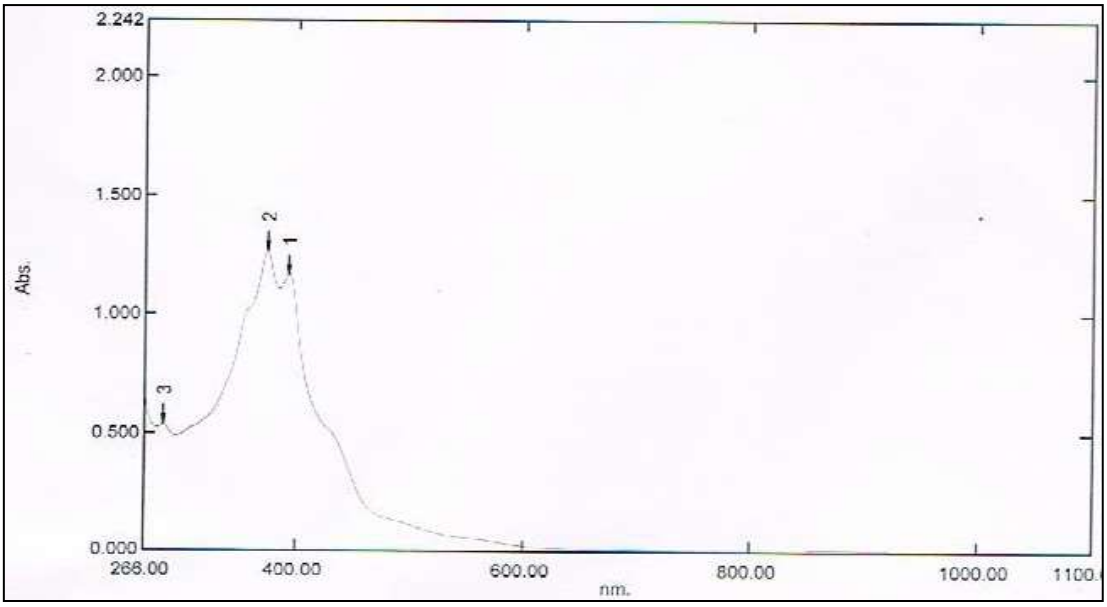


Fig. (3-13): UV-Vis- spectrum of ligand(LH1)

3.3.2. Electronic Spectrum of Cobalt (II) Complex (CoLH1).

In six coordinate cobalt (II) complex that have octahedral low spin the assignment of the one main absorption in the near 20000 cm^{-1}. Electronic spectrum for cobalt (II) complex Figure (3-14): was measured and it found one absorption band which is d-d transition in 456nm (21929 cm^{-1}) where this band can be assigned to electronic transition $^2Eg \rightarrow {}^2T_1g$ in Co(II) complexes which have octahedral[178].

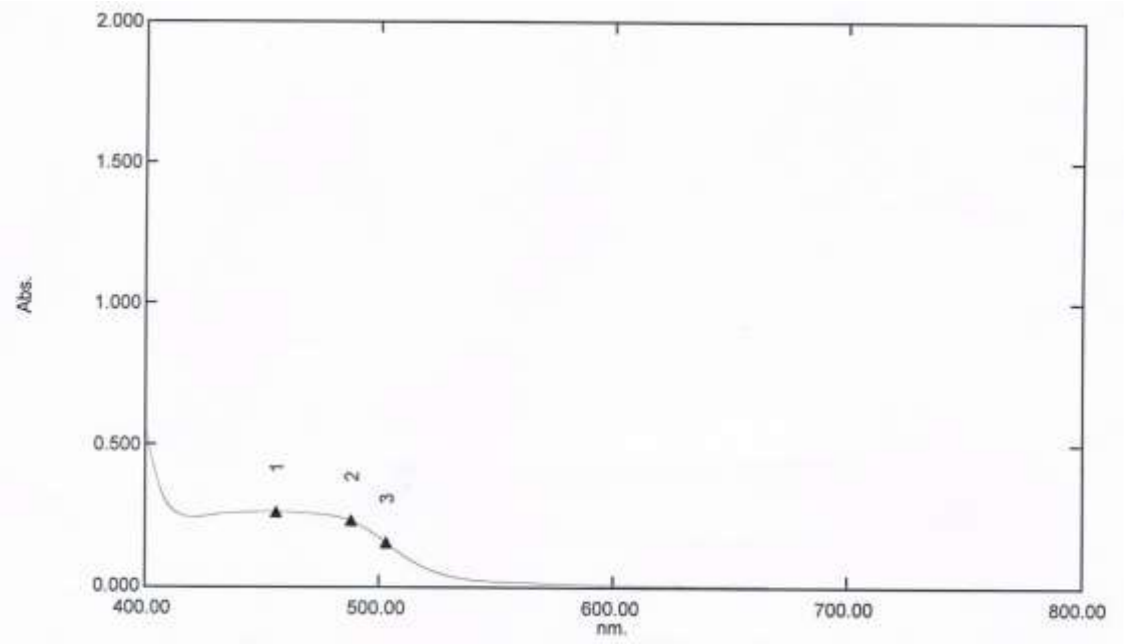


Fig. (3-14): UV-Vis- spectrum of CoLH1

3.3.3. Electronic Spectrum of Nickel(II) Complex (NiLH1).

Square planar derivatives of nickel (II) are commonly orange or red, but purple and green examples are known[179]. The majority of these complexes exhibit a strong absorption band (Ɛ, 50-500 l cm^{-1}mole^{-1}) in the visible region between 15,000 and 25,000 cm^{-1}, and in many cases referred to as υ_2 and υ_3. Square complexes of nickel with sulphur ligands [180] generally exhibit an additional well defined band to lower energies than υ_2: this is referred to as υ_1. The nickel (II) can form complexes with a square planer shape, the electronic spectra for these complexes show two bands of absorption belonging to $^{1}A_{1}g \rightarrow {}^{1}A_{2}g$, $^{1}A_{1}g \rightarrow {}^{1}B_{1}g$ respectively. Spectrum of the Ni(II) complex. Figure (3-15) shows two bands of absorption, one of them strong (15000 – 23000 cm^{-1}) (665-430 nm) belong to $^{1}A_{1}g \rightarrow {}^{1}A_{2}g$. while the second band (23000- 27000 cm^{-1}) (430-370nm) this belongs to $^{1}A_{1}g \rightarrow {}^{1}B_{1}g$, where this can be conformed this complex may to take a square planer shape.

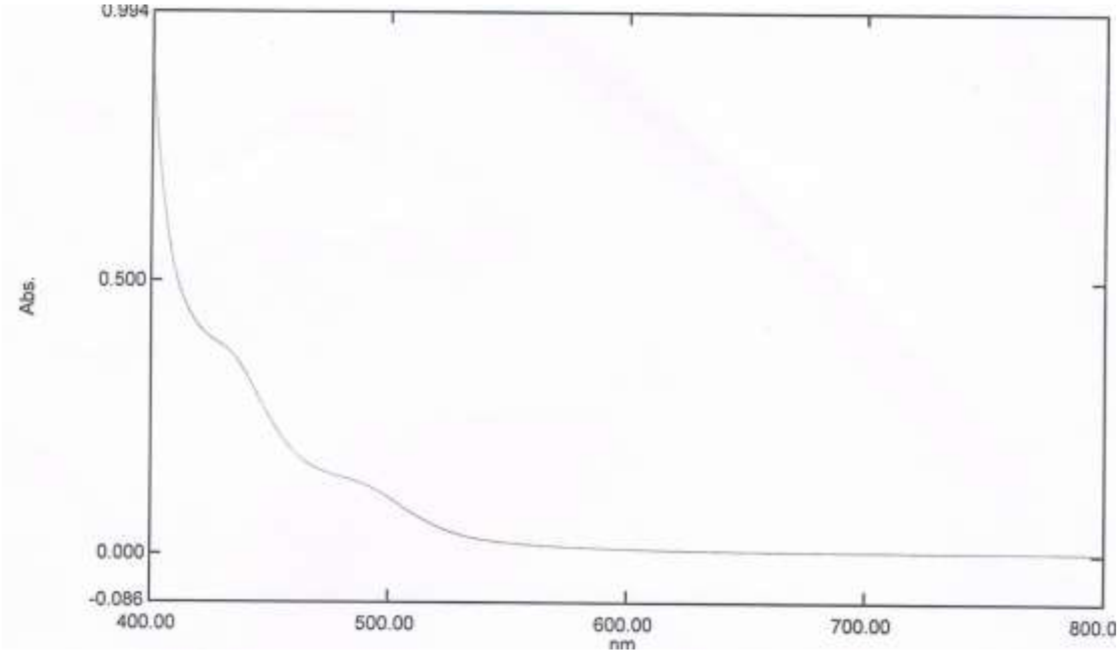


Fig. (3-15): UV-Vis- spectrum of NiLH1

3.2.4. Electronic Spectrum of Copper(II) Complex (CuLH1).

As the distortion towards a square continues it is predicted that both bands will move higher in energy .It is interesting that the structure of the compound is dependent upon the cation: the ion is distorted octahedral and has bands in the visible region[181] between 10,000-20,000 cm^{-1}. The spectrum of (CuLH1). Figure (3-16) has a broad band between (500-625)nm (20000- 16000) cm^{-1} due to a combination of two transitions, $^2B_1g \rightarrow ^2Eg$ and $^2B_1g \rightarrow ^2A_1g$ respectively. These transitions refer to distorted octahedral around Cu (II) ion [182].

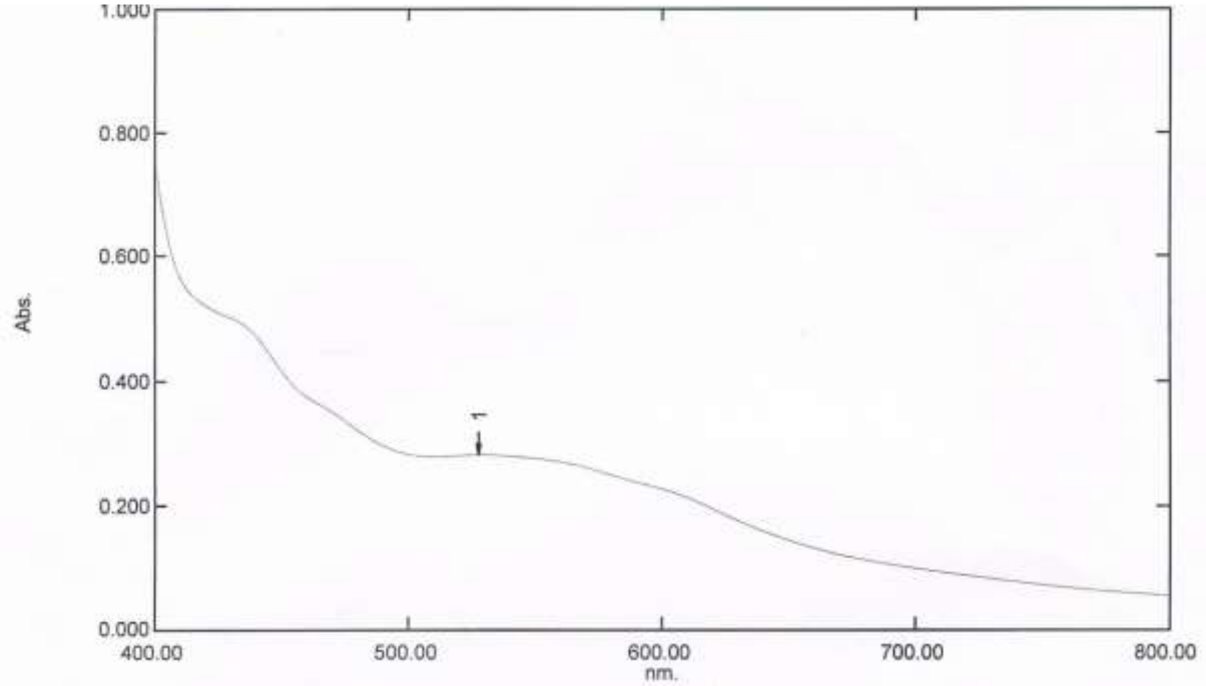


Fig. (3-16): UV-Vis- spectrum of CuLH1

3.3.5. Electronic Spectrum of Palladium(II) Complex (PdLH1).

The Palladium (II) complex coordinate as square planar shape when It was four coordination[183] because of a large volume ion palladium (II). This due to placed in second transition series this can be lead to increase of ligands field around centre atom[184]. Square complexes of Palladium (II) ion exhibit a broad band(Ɛ, $10\text{-}10^{2}\ l\ \mathrm{cm}^{-1}\ \mathrm{mole}^{-1}$) in the visible region resolvable into at least two components. Weaker bands are observed on the low energy side of this absorption, whilst several intense bands (Ɛ, $10^{4}\ l\ \mathrm{cm}^{-1}\ \mathrm{mole}^{-1}$) are observed on the high energy side in the near ultraviolet and ultraviolet region[185]. These last bands are undoubtably charge transfer in nature. In this complex figure (3-17) shows absorption band in 513nm (19493cm^{-1}) belonging to$^{1}A_{1}g\rightarrow{}^{3}B_{1}g$ transition and in 485nm (20597cm^{-1}) belonging to $^{1}A_{1}g\rightarrow{}^{1}B_{1}g$ transition that's equal to 10Dq value and another in 443nm (22573cm^{-1}) belonging to$^{1}A_{1}g\rightarrow{}^{1}Eg$ transition .therefore this complex can be suggested a square planar[186].

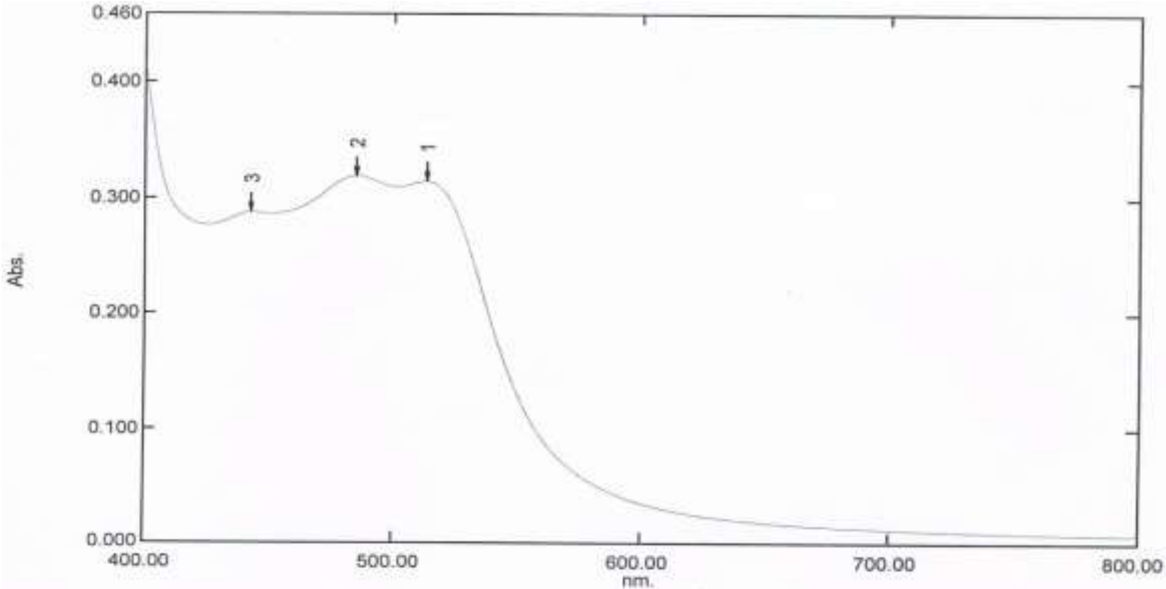


Fig. (3-17): UV-Vis- spectrum of PdLH1

3.3.6. Electronic Spectrum of Platinum (IV) Complex (PtLH1).

Figure (3-18) shows the spectrum of Pt (IV) complex that shows two bands in (530,497)nm, (18850,20100) cm^{-1} respectively belonging to transitions in octahedral field [186] .

(υ_2) $^1A_1g\ (t_2g)^6 \rightarrow\ ^3T_2g\ (t_2g)^5\ (eg)^1$

(υ_3) $^1A_1g\ (t_2g)^6 \rightarrow\ ^1T_1g\ (t_2g)^5\ (eg)^1$

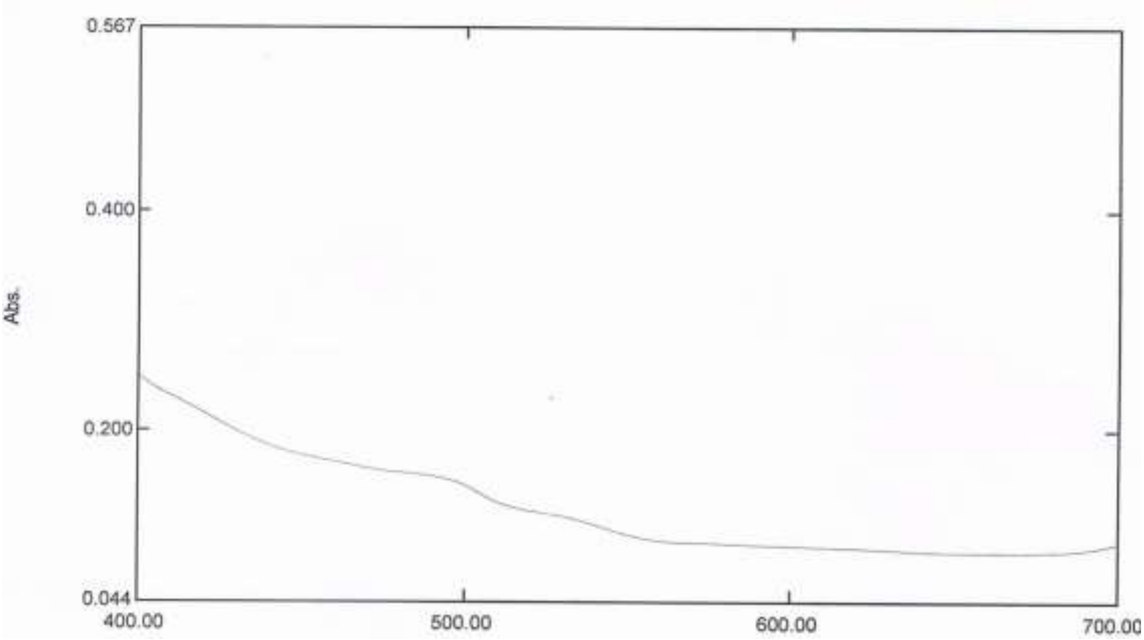


Fig. (3-18): UV-Vis- spectrum of PtLH1

3.3.7. Electronic Spectrum of Ligand (LH2).

The spectrum of ligand Figure (3-19) shows the first absorption band in 280 nm (357143 cm^{-1}) which can be attributed to (π - π^*) transition for the aromatic nucleus. The second band appearing in 377 nm (26737 cm^{-1}) is attributed to (π - π^*) transition in all molecules. The third band which appeared in 420 nm (238095 cm^{-1}) was attributed to (n- π^*) transition in imino group (C=N)[177].

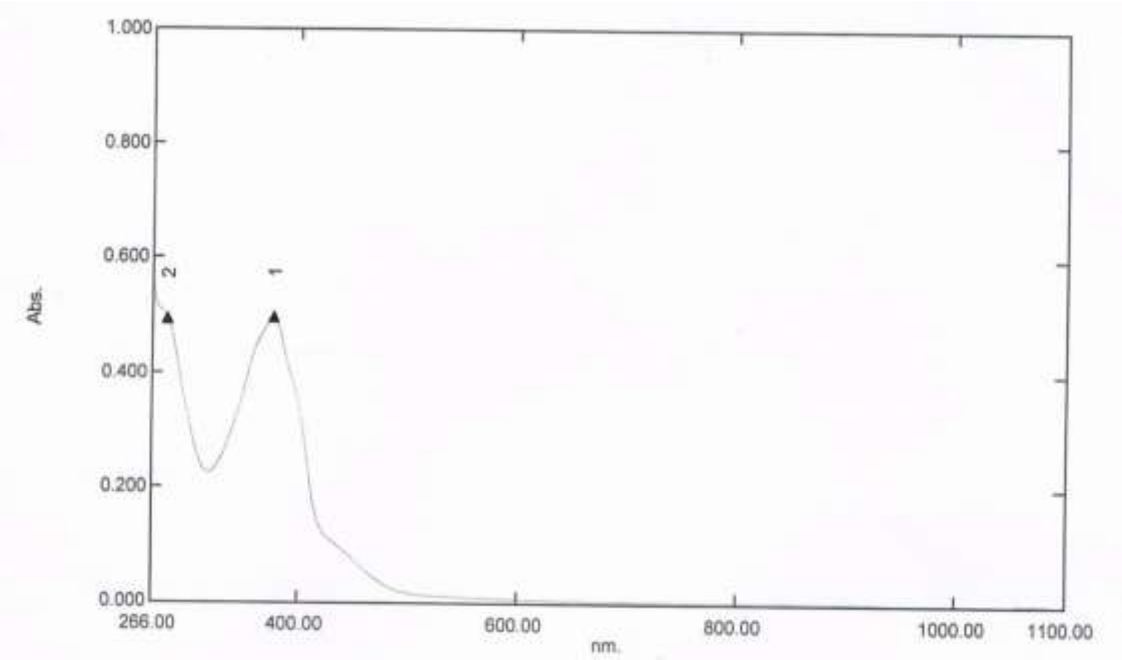


Fig. (3-19): UV-Vis- spectrum of Ligand(LH2)

3.3.8. Electronic Spectrum of Cobalt(II) Complex (CoLH2).

Figure (3-20) shows absorption band in visible region at 663nm (15083cm^{-1})belonging to (υ_2) $^4T_1g \rightarrow ^4A_2g$ (F) and absorption bands in (520,670) nm , (19230,14925)cm^{-1} respectively and from average give (υ_3)= 17630 cm^{-1} belonging to (υ_3) $^4T_1g \rightarrow ^4T_1g$ (P) in octahedral field. [178]. Using (Tanabe - Sugano) diagram for d^7, figure (3-21), and from υ_3/υ_2 ratio we could calculate υ_1 (6703cm^{-1}) assigned as $^4T_1g \rightarrow ^4T_2g$ (F) transition. This value refers to 10 D q [187]. The calculated value of β (0.77) indicates that the complex has covalent properties. The value ν_1 (6554 cm^{-1}) was calculated using the equation $15B' = \upsilon_3 + \upsilon_2 - 3\upsilon_1$. The resulting value is close to that obtained from using the Tanabe-Sugano diagram.

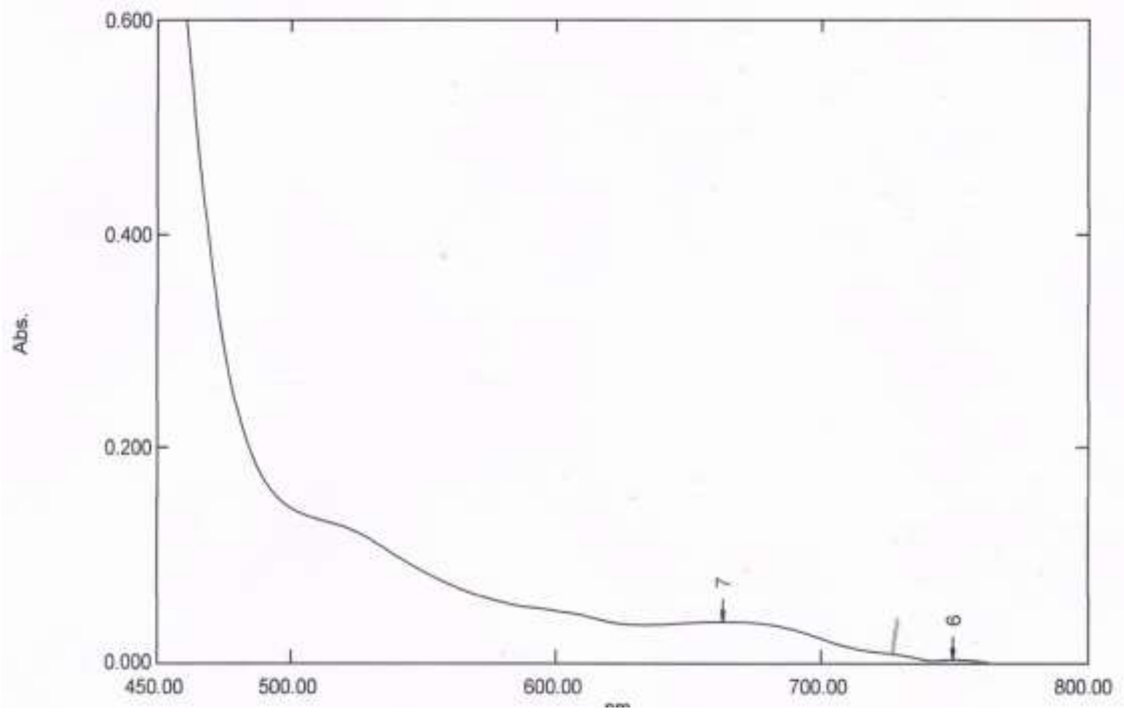


Fig. (3-20): UV-Vis- spectrum of CoLH2

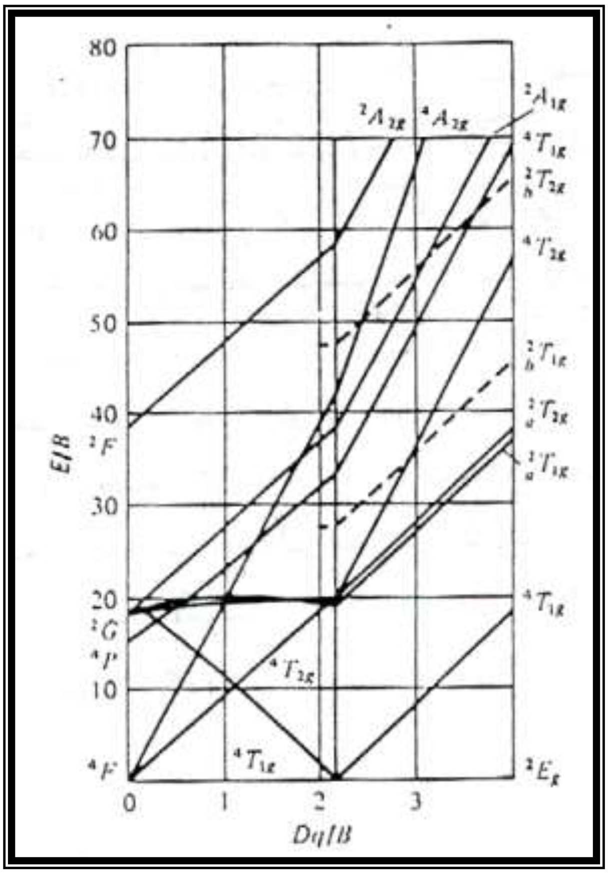


Fig. (3-21): Energy level diagram (Tanabe - Sugano) for d^7 ions in an octahedral field.

3.3.9. Electronic Spectrum of Nickel(II) Complex (NiLH2).

Figure (3-22) shows two absorption bands in visible region at (508,445)nm, (19665,22446)cm^{-1} respectively belonging to transitions (υ_2) $^3A_2g\rightarrow{}^3T_1g(F)$, $(\upsilon_3)$$^3A_2g\rightarrow{}^3T_1g(P)$ respectively in octahedral field[188]. From the value $\upsilon_3\backslash\ \upsilon_2$ and energy level diagram (Tanabe-Sugano) for d^8 ions in an octahedral field can calculate the value of υ_1 (8522cm^{-1}) from figure (3-23) that belongs to transition $^3A_2g\rightarrow{}^3T_2g(F)$ that's equal for 10Dq . This value is characteristic of octahedral field about nickel (II) complexes[189]. Furthermore, this band is not found in squar - planar or tetrahedral structures . The calculated value of β (0.86) indicates that the complex has covalent properties. The value ν_1 (8740 cm^{-1}) was calculated using the equation $\mathbf{15B' = \upsilon_3 + \upsilon_2 - 3\upsilon_1}$. The resulting value is close to that obtained from using the Tanabe-Sugano diagram.

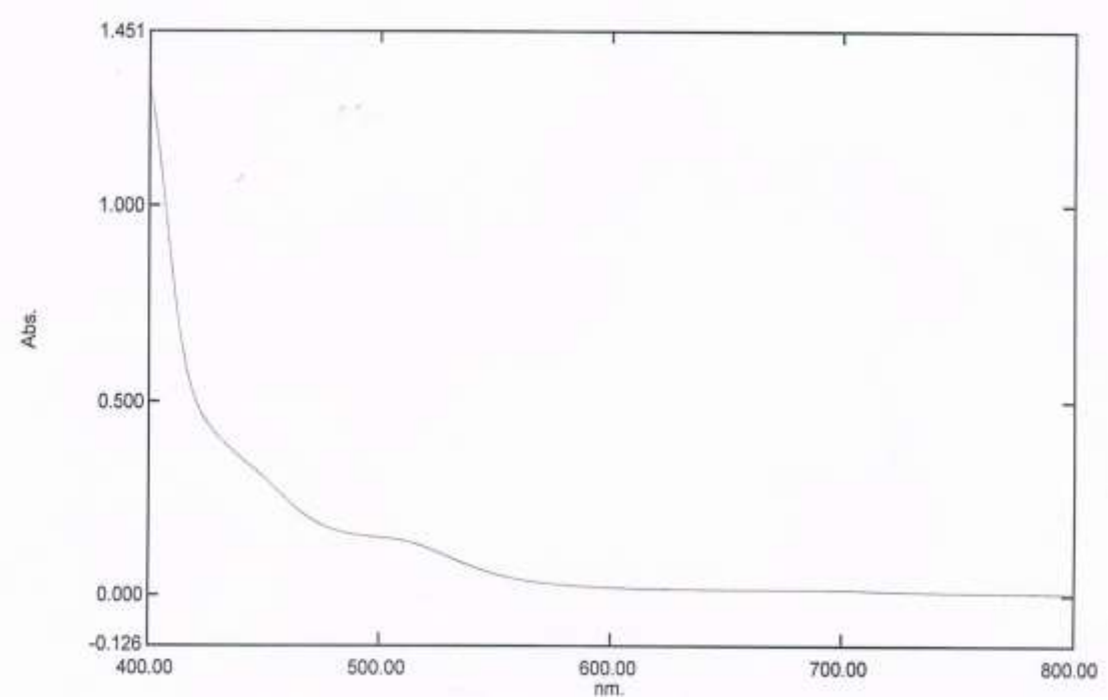


Fig. (3-22): UV-Vis- spectrum of NiLH2

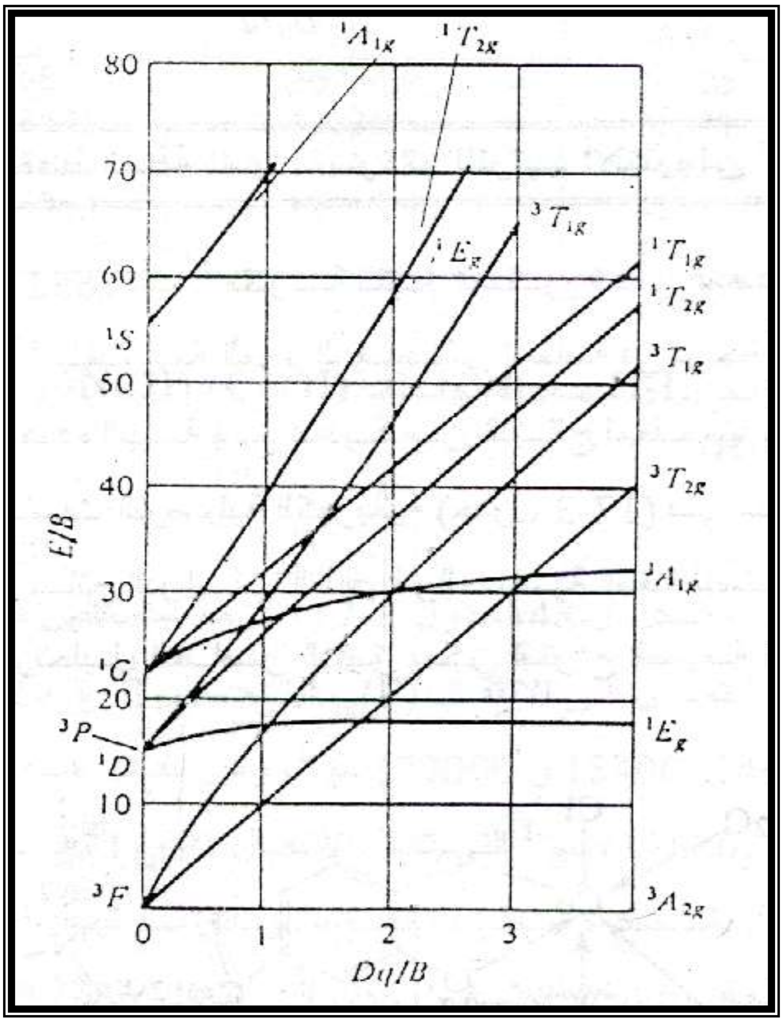


Fig. (3-23): Energy level diagram (Tanabe - Sugano) for d^8 ions in an octahedral field

3.3.10. Electronic Spectrum of Copper(II) Complex (CuLH2).

The ground state in an octahedral field is ^2Eg, it is subject to considerable Jahn-Teller distortion and in practice, the majority of copper(II) complexes which are usually green or blue are tetragonally distorted with four short metal-ligand bonds in one plane(xy) and two longer metal-ligand bonds lying along the z axis above and below this plane. In the limit, which is not generally reached, the molecule would be four coordinate and square planar. Such complexes give rise to one absorption band in the visible region near 17,000 cm^{-1} which can often be resolved into at least three components[190]. The band often exhibits a broad tail into the near infrared region[191]. Figure (3-24) shows band near 527nm (18957 cm^{-1}) and band at 445nm (22471 cm^{-1}) This bands belong to transitions $^2B_1g \rightarrow {}^2A_1g$, $^2B_1g \rightarrow {}^2B_2g$ respectively that's appears the coordinate octahedral distorted around copper(II) ion.

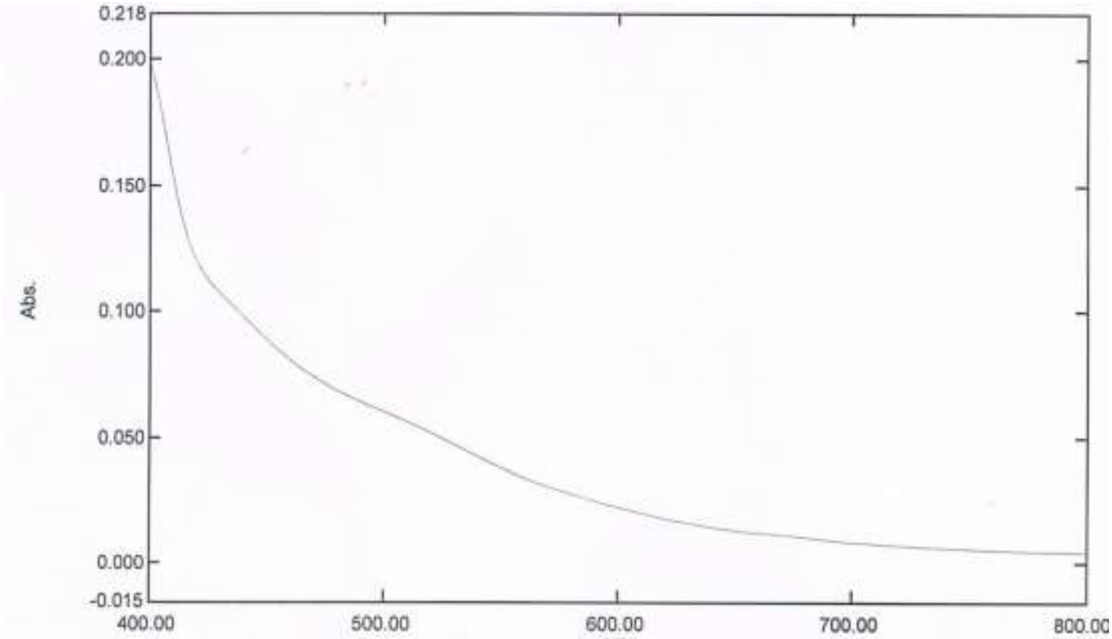


Fig. (3-24): UV-Vis- spectrum of CuLH2

3.3.11. Electronic Spectrum of Palladium (II) Complex (PdLH2).

In this complex figure (3-25) shows absorption band in (534nm) 18726 cm^{-1} belonging to $^1A_1g\rightarrow{}^1B_1g$ transition and another in (568nm) 17605cm^{-1} belonging to $^1A_1g\rightarrow{}^1Eg$ transition. therefore this complex was square planar[186].

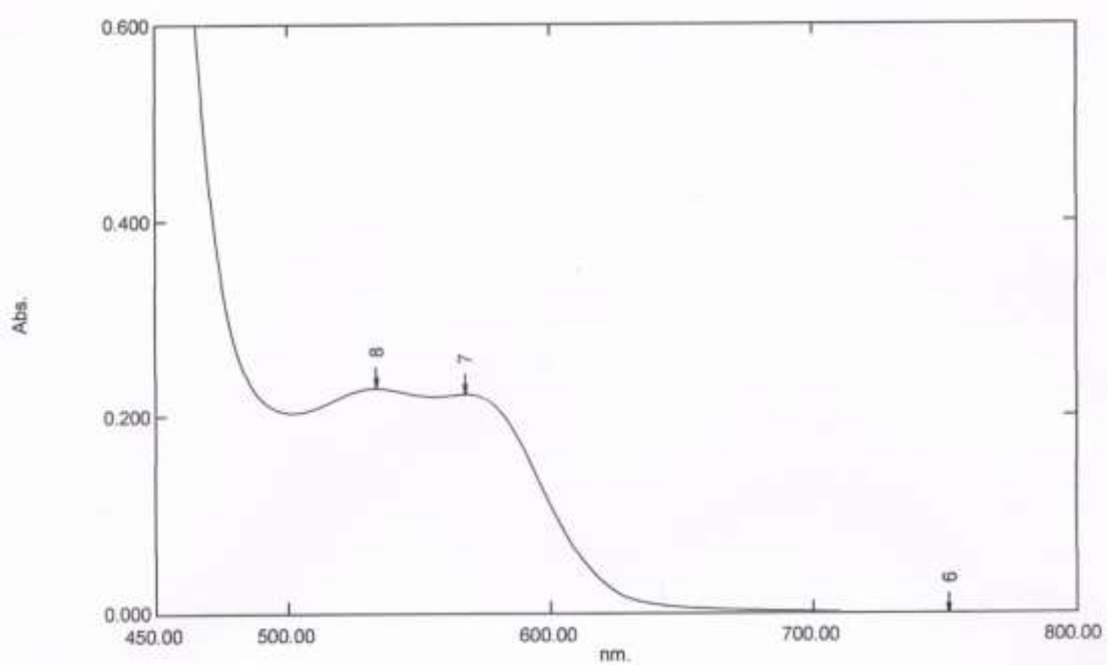


Fig. (3-25): UV-Vis- spectrum of PdLH2

3.3.12. Electronic Spectrum of Platinum (IV) Complex (PtLH2).

Figure (3-26) shows the spectrum of Pt (IV) complex that shows three bands in (443,486,513) nm, (22573,20576,19493) cm^{-1} respectively belonging to transitions in octahedral field[186].

(ʋ$_1$) $^1A_1g\ (t_2g)^6 \rightarrow {}^3T_1g\ (t_2g)^5\ (eg)^1$

(ʋ$_2$) $^1A_1g\ (t_2g)^6 \rightarrow {}^3T_2g\ (t_2g)^5\ (eg)^1$

(ʋ$_3$) $^1A_1g\ (t_2g)^6 \rightarrow {}^1T_1g\ (t_2g)^5\ (eg)^1$

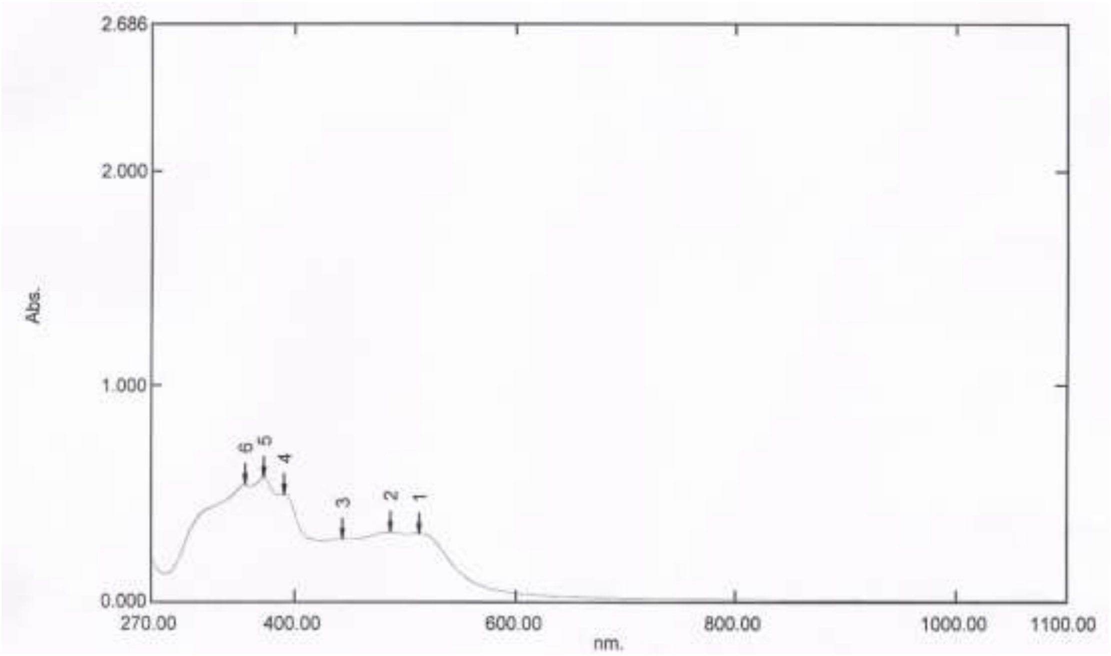


Fig. (3-26): UV-Vis- spectrum of PtLH2

Table (3-6) :Data of electronic spectra of prepared Complexes

Compound	*Bands absorption (cm^{-1})*	*Transitions*	*Shape*	β	10Dq
CoLH1	υ_1=21929	$^2Eg \rightarrow {}^2T_1g$	OCT	-	-
NiLH1	υ_1=15000-23000 υ_2=23000-27000	$^1A_1g \rightarrow {}^1A_2g$ $^1A_1g \rightarrow {}^1B_1g$	Sq.p	-	-
CuLH1	υ_1=18939 υ_2=20263	$^2B_1g \rightarrow {}^2Eg$ $^2B_1g \rightarrow {}^2A_1g$	OCT	-	-
PdLH1	υ_1=19493 υ_2=20597 υ_3=22573	$^1A_1g \rightarrow {}^3B_1g$ $^1A_1g \rightarrow {}^1B_1g$ $^1A_1g \rightarrow {}^1Eg$	Sq.p	-	-
PtLH1	υ_2=20100 υ_3=24067	$^1A_1g \rightarrow {}^3T_2g$ $^1A_1g \rightarrow {}^1T_1g$	OCT	-	-
CoLH2	υ_1=6554 υ_2=15082 υ_3= 17630	$^4T_1g \rightarrow {}^4T_2g$ (F) $^4T_1g \rightarrow {}^4A_2g$ (F) $^4T_1g \rightarrow {}^4T_1g$ (P)	OCT	0.77	6703
NiLH2	υ_1= 8740 υ_2= 19665 υ_3= 22446	$^3A_2g \rightarrow {}^3T_2g$(F) $^3A_2g \rightarrow {}^3T_1g$(F) $^3A_2g \rightarrow {}^3T_1g$(P)	OCT	0.86	8522
CuLH2	υ_1= 26809 υ_2= 10854	$^2B_1g \rightarrow {}^2A_1g$ $^2B_1g \rightarrow {}^2B_2g$	OCT		
PdLH2	υ_1= 17605 υ_2= 18726	$^1A_1g \rightarrow {}^1B_1g$ $^1A_1g \rightarrow {}^1Eg$	Sq.p		
PtLH2	υ_1= 19493 υ_2= 20576 υ_3= 22573	$^1A_1g \rightarrow {}^3T_1g$ $^1A_1g \rightarrow {}^3T_2g$ $^1A_1g \rightarrow {}^1T_1g$	OCT		

Sq.p =Squre planar , OCT = octahedral

3.4. ^{1}H NMR Spectroscopy

Nuclear magnetic resonance (nmr) is probably the chemists most valuable tool for determining the structures of compounds in liquid, dissolved state and solid states. In contrast to techniques such as X-ray diffraction and microwave spectroscopy (which are often capable of furnishing much more quantitative structural information for solids and gases, respectively), nmr spectroscopy is easily learned and yields spectra that are easily interpreted [192]. The nmr phenomenon occurs when nuclei aligned with an applied field are induced to absorb energy and change their spin orientation with respect to the applied field. The energy absorption is quantized process, and the energy absorbed must equal the energy difference between the two states involved.

$$E_{absorbed}=(E_{-1/2\ state} - E_{+1/2\ state}) = hv$$

In practice, this energy difference is a function of the strength of the applied magnetic field B_0 .

3.4.1. ^{1}H NMR Spectroscopy of Ligand (LH1).

^{1}H NMR spectrum figure (3-27a, 3-27b), (300MHz ,DMSO) of ligand (LH1) appeared the following signals at δ (ppm):

2.494 (S, DMSO), 3.353 (S, H_2O in DMSO), 6.607-6.626 (d,2H,2×Ha), 6.797-6.946 (m,2H,2×Hb), 7.248-7.290 (t,2H,2×Hc), 7.538 (d,2H,2×Hd), 8.046 (d,1H,He,imine), 8.701 (s,1H,He,imine), 11.089 (s,1H,Hf, phenolic O-H), 11.869 (S,1H,Hf,phenolic O-H)[192,193].

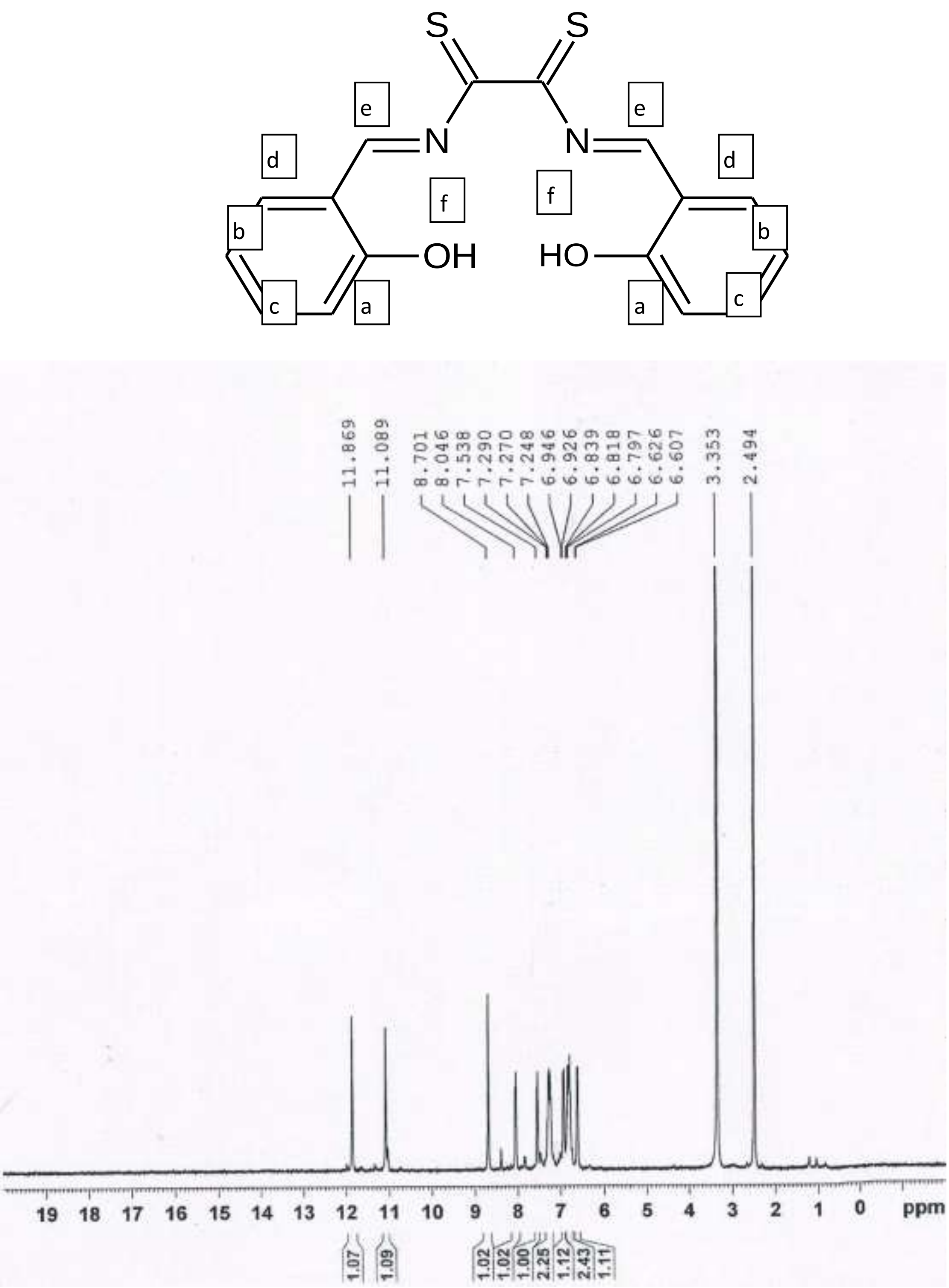


Fig.(3-27)a: ^{1}H NMR-Spectrum of ligand(LH1)

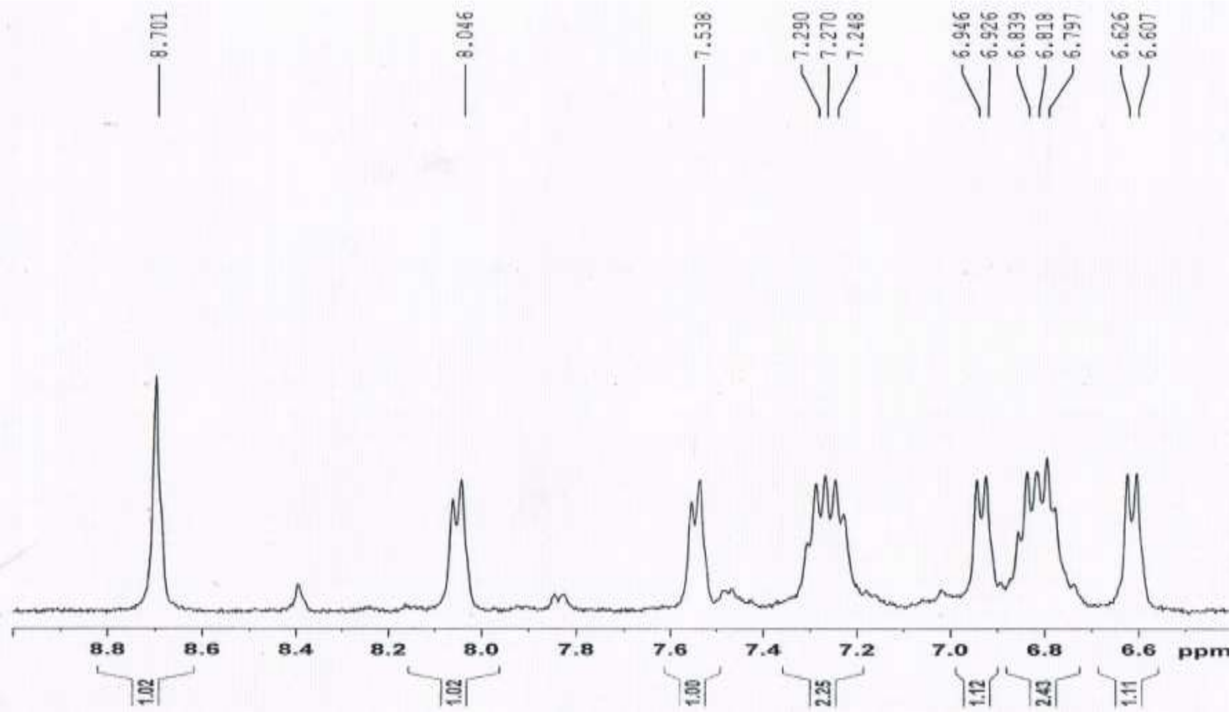


Fig.(3-27)b :^{1}H NMR -Expansion of Ligand(LH1)

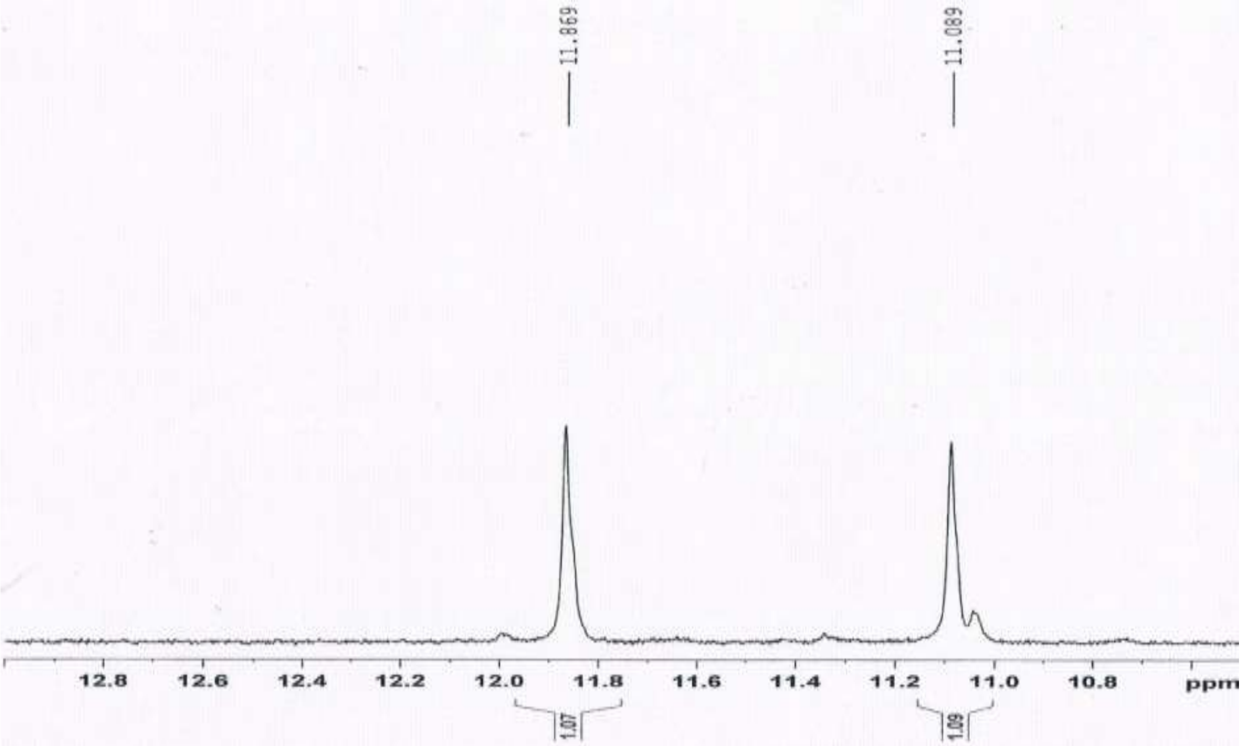


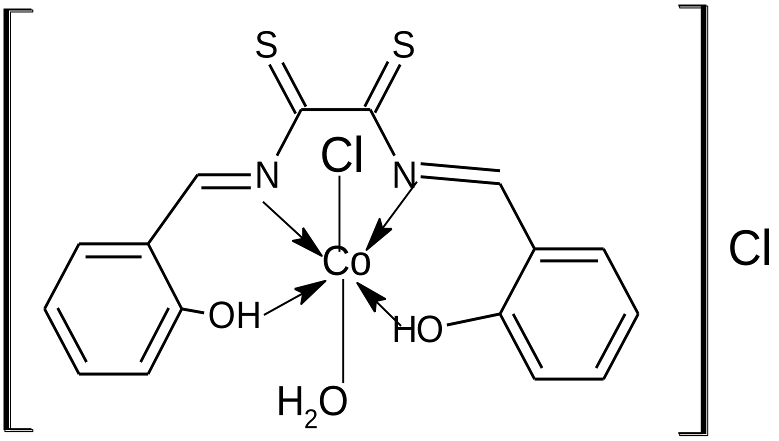
Fig.(3-27)c: ^{1}H NMR -Expansion of Ligand(LH1)

3.4.2. ^{1}H NMR Spectroscopy of Cobalt (II) Complex (CoLH1).

^{1}H NMR spectrum figures (3-28a, 3-28b), (300MHz , DMSO) of complex (CoLH1) appeared the following signals at δ(ppm):

2.480 (S,DMSO), 3.331 (S,H_2O in DMSO), 6.592-6.613(d,2H,2×Ha), 6.762-6.839 (m,2H,2×Hb), 7.212-7.290 (m,2H,2×Hc), 7.521-7.539 (d,2H,2×Hd), 8.023-8.042 (d,1H,He), 8.682 (S,1H,He), 11.071(S,1H,Hf, phenolic O-H), 11.849(S,1H,Hf, phenolic O-H)[194,195].

The signals of imine and hydroxyl groups are shifted towards the high field and this provide good evidence that the complex was formed.



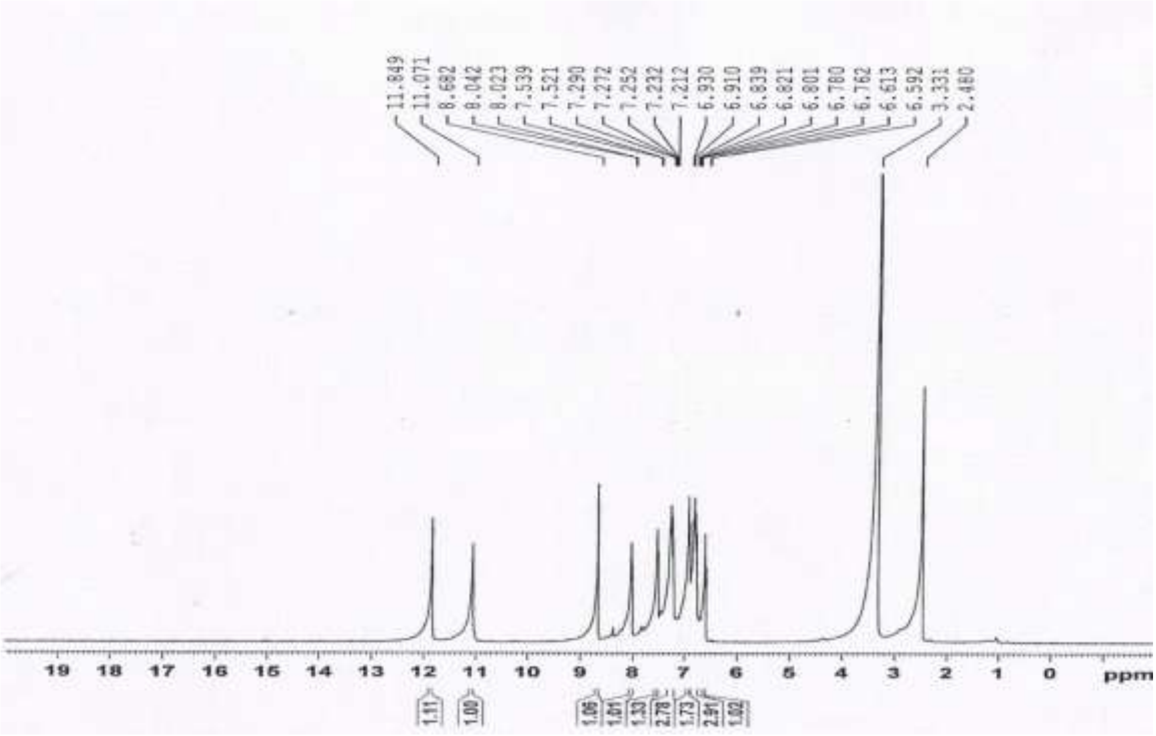


Fig. (3-28)a: ^{1}H NMR Spectrum of CoLH1

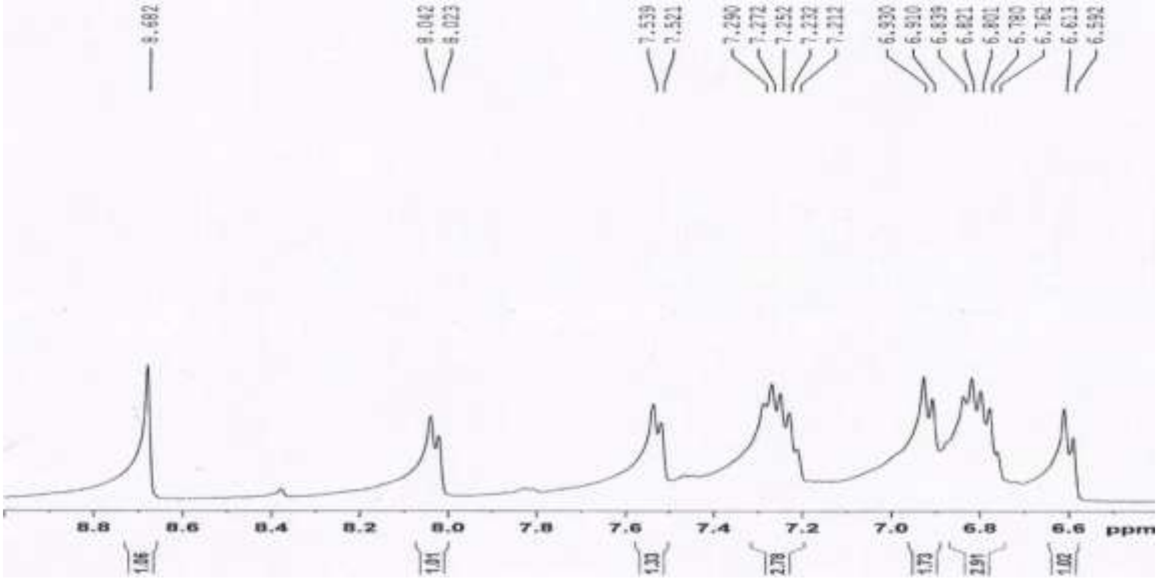
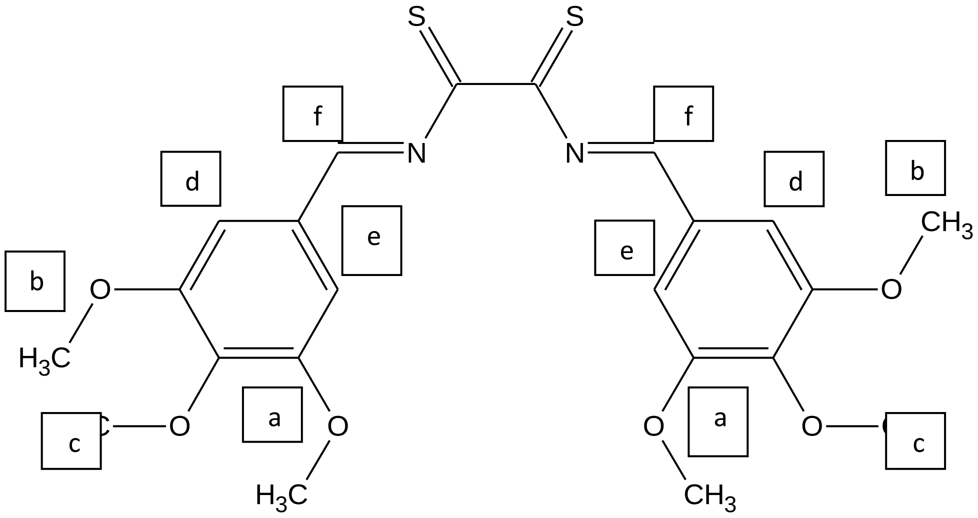


Fig.(3-28)b: ^{1}H NMR -Expansion of Co LH1

3.4.3. ^{1}H NMR Spectroscopy of Ligand (LH2).

^{1}H-NMR spectrum figures (3-29a,3-29b) (300MH$_Z$,DMSO) of ligand (LH2) showed the following signals at δ (ppm):

2.485 (S,DMSO), 3.330 (S, H_2O in DMSO), 3.607-3.641 (3H,3×Ha), 3.685-3.771 (3H,3×Hb), 3.752-3.776 (3H,3×Hc), 6.81 (d,2H,2×Hd), 7.01 (d,2H,2×He), 8.08 (S,1H,Hf,imine), 8.33 (S,1H,Hf,imine)[192,193].



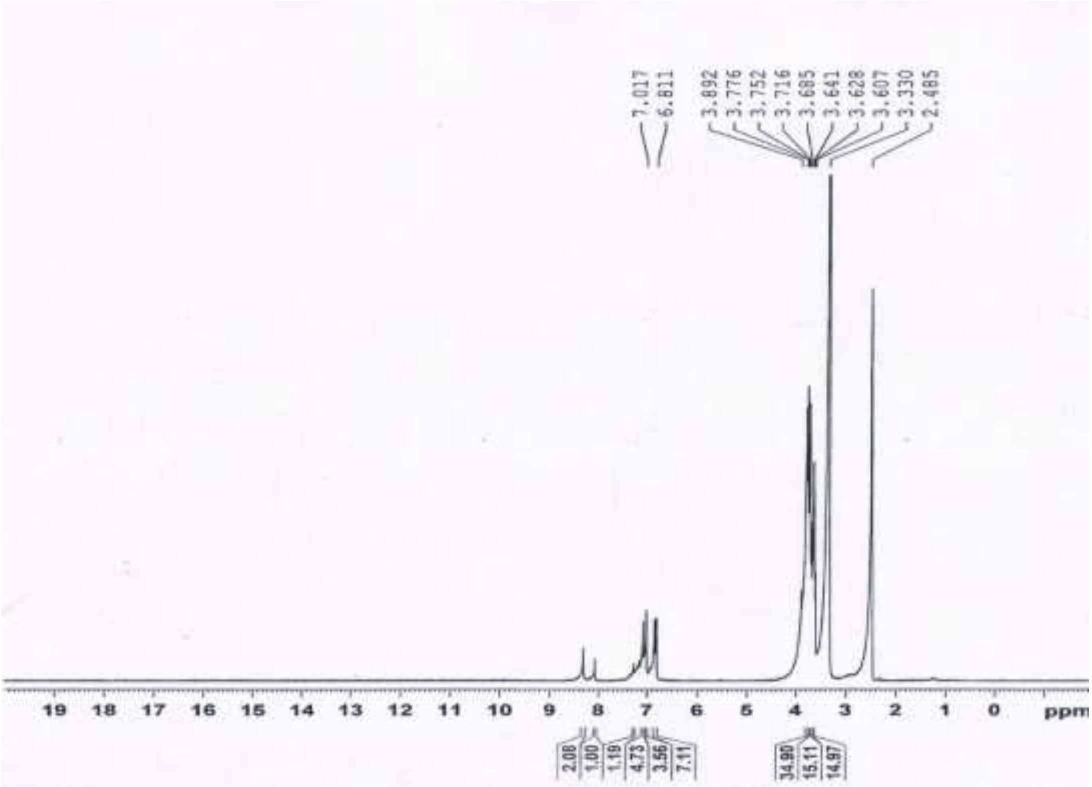


Fig. (3-29)a: ^{1}H NMR *-Spectrum of ligand(LH2)*

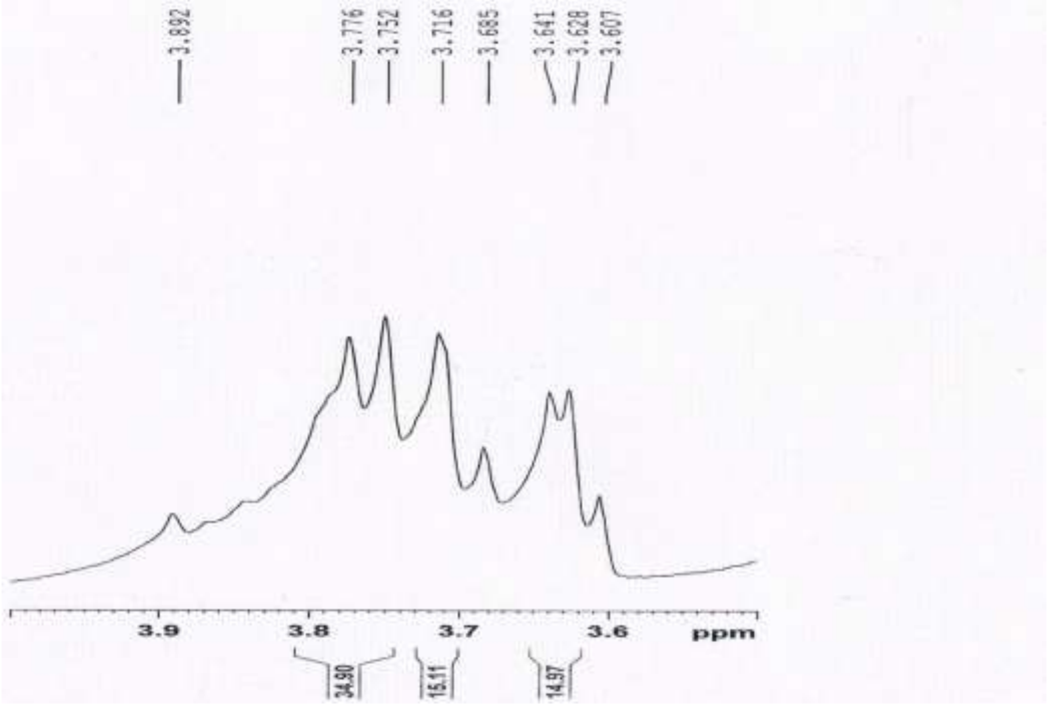


Fig. (3-29) b: ^{1}H NMR *-Expansion of Ligand(LH2)*

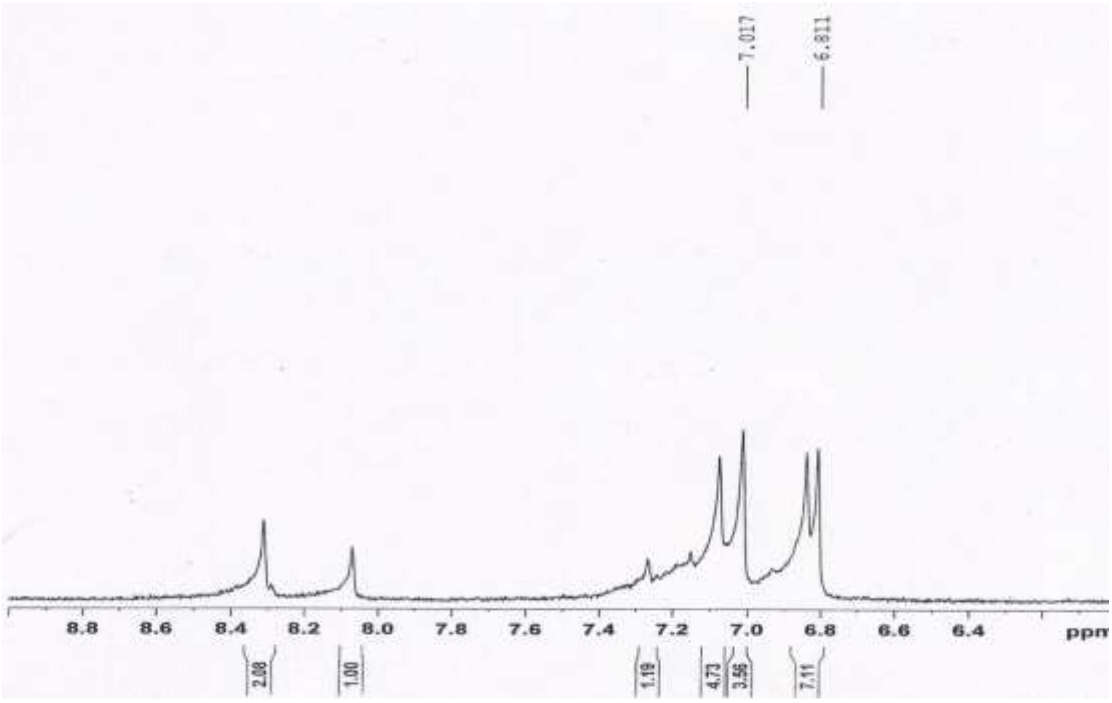


Fig. (3-29) c: ^{1}H NMR *-Expansion of Ligand (LH2)*

3.4.4. ^{1}HNMR Spectroscopy of Cobalt(II) Complex (CoLH2).

^{1}H NMR **s**pectrum figures (3-30a,3-30b,3-30c) (300MHZ ,DMSO) of complex (CoLH2) appeared the following signals at δ (ppm):

2.479-2.508 (DMSO), 3.544-3.579 (H_2O in DMSO), 3.608-3.697 (m,9H,3×CH_3, methoxy groups), 6.730-7.216(m,4H,aromatic), 7.216 (S,1H,azomethine proton), 8.193 (S,1H,azomethine proton), 8.193 (S,1H,azomethine proton)[194,195].

The signals of azomethine protons was shifted to the high field and this gives good evidence for formation of complex (CoLH2).

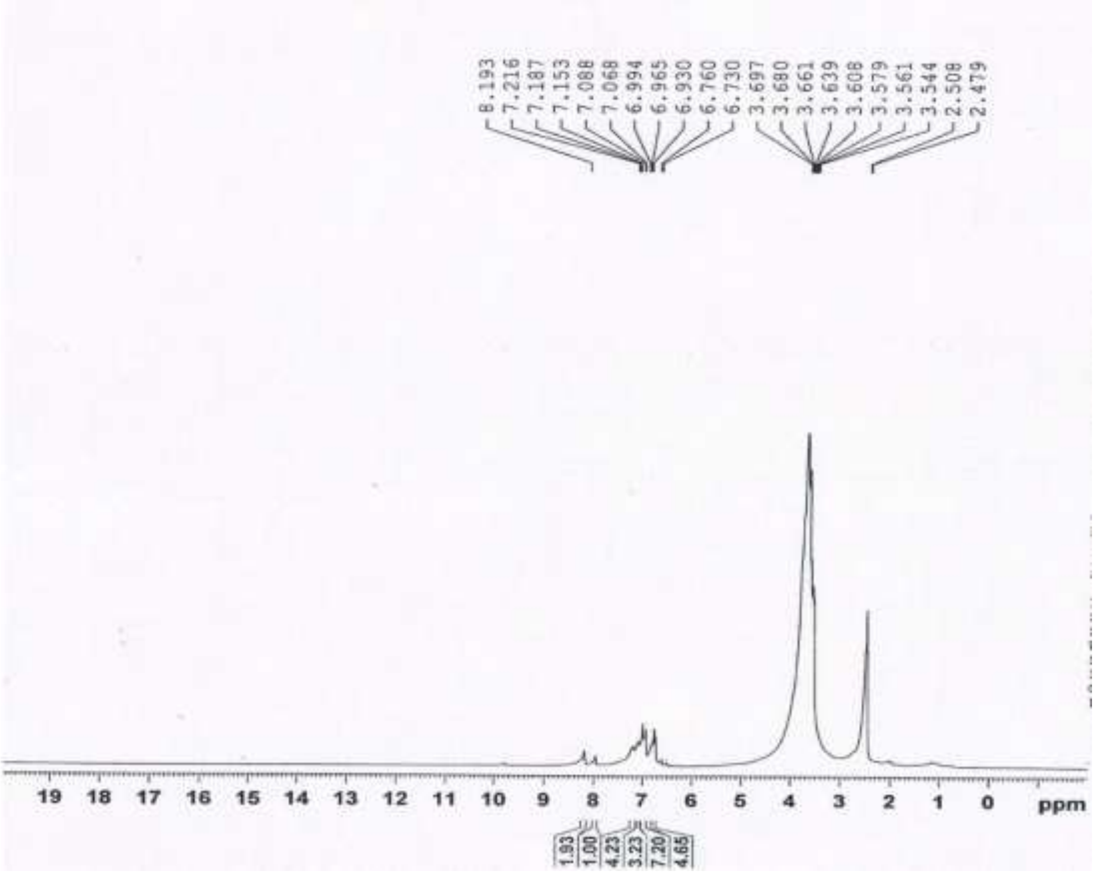


Fig. (3-30)a: ^{1}H NMR Spectrum of CoLH2

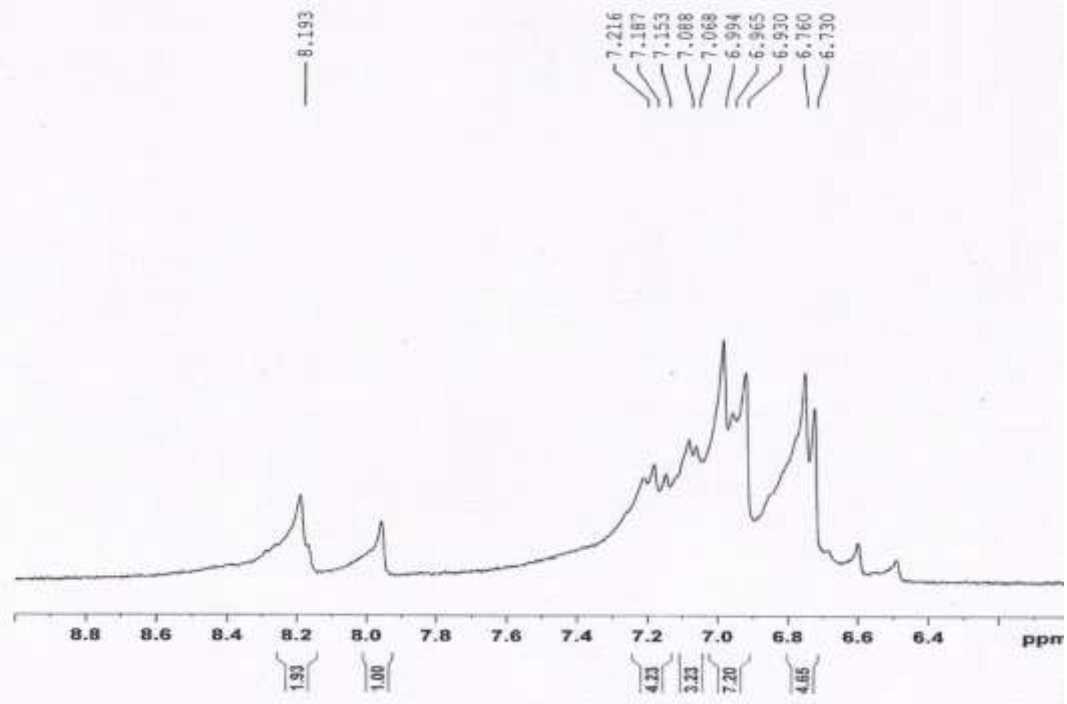


*Fig .(3-30)*b:^{1}H NMR *Expansion of CoLH2*

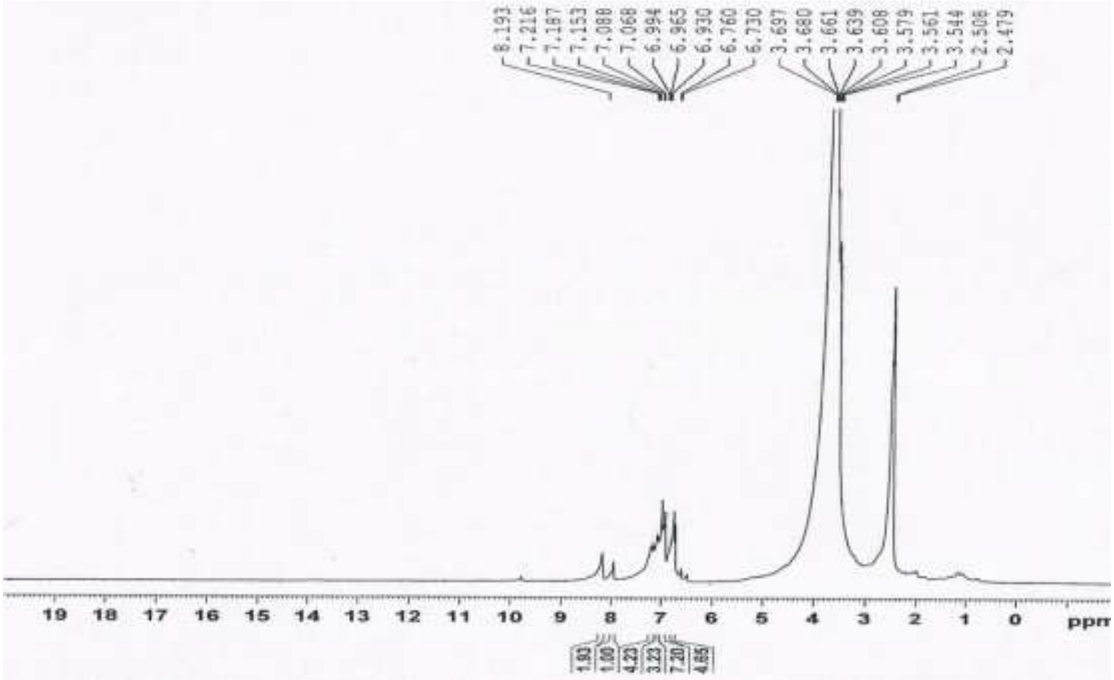


*Fig. (3-30)*C:^{1}H NMR *-Expansion of CoLH2*

Table(3-7):^{1}H NMR (DMSO-d_6) ppm of the Compounds

Compound	**^{1}H NMR (DMSO-d_6) ppm**
Ligand(LH1)	2.494(S,DMSO), 3.353(S,H_2OinDMSO), 6.607-6.626 (d,2H,2×Ha), 6.797-6.946 (m,2H,2×Hb), 7.248-7.290 (t,2H, 2×Hc), 7.538 (d,2H,2×Hd), 8.046 (d,1H,He,imine), 8.701 (s,1H,He,imine), 11.089 (s,1H,Hf, phenolic O-H), 11.869 (S,1H,Hf,phenolic O-H)
CoLH1	2.480 (S,DMSO), 3.331 (S,H_2O in DMSO), 6.592-6.613(d,2H,2×Ha), 6.762-6.839 (m,2H,2×Hb), 7.212-7.290 (m,2H,2×Hc), 7.521-7.539 (d,2H,2×Hd), 8.023-8.042 (d,1H,He), 8.682 (S,1H,He), 11.071(S,1H,Hf, phenolic O-H), 11.849(S,1H,Hf, phenolic O-H)
Ligand(LH2)	2.485 (S,DMSO), 3.330 (S, H_2O in DMSO), 3.607-3.641 (3H,3×Ha), 3.685-3.771 (3H,3×Hb), 3.752-3.776 (3H,3×Hc), 6.81 (d,2H,2×Hd), 7.01 (d,2H,2×He), 8.08 (S,1H,Hf,imine), 8.33 (S,1H,Hf,imine).
CoLH2	2.479-2.508 (DMSO), 3.544-3.579 (H_2O in DMSO), 3.608-3.697 (m,9H,3×CH_3, methoxy groups), 6.730-7.216(m,4H,aromatic), 7.216 (S,1H,azomethine proton), 8.193 (S,1H,azomethine proton), 8.193 (S,1H,azomethine proton).

3.5. Magnetic Susceptibility

Measurements of magnetic properties have been used to characterize a wide range of systems from oxygen, metallic alloys, solid state materials, and coordination complexes containing metals[196]. Most organic and main group element compounds have all the electrons paired and these are diamagnetic molecules with very small magnetic moments. Magnetic measurements, particularly for the first row transition elements, give information about the number of unpaired electrons. The number of unpaired electrons provides information about the oxidation state and electron configuration. The determination of the magnetic properties of the second and third row transition elements is more complex. The magnetic moment is calculated from the magnetic susceptibility, since the magnetic moment is not measured directly. There are several ways to express the degree to which a material acquires a magnetic moment in a field. The magnetic susceptibility per unit volume is defined by: [197].

$$K = \frac{I}{H}$$

where I is the intensity of the magnetization induced in the sample by the external magnetic field, H. The extent of the magnetic induction (I) depends on the sample. The induction may be visualized as an alignment of dipoles and/or by the formation of charge polarization in the sample. Generally, it is more convenient to use mass units, therefore the mass or gram susceptibility is defined as: [198]

$$X_g = \frac{K}{d}$$

where d is the density of the solid. The molar susceptibility is the mass susceptibility multiplied by the formula weight.

$$\chi_m = \chi_g \times \text{F.W. in g. mol}^{-1}$$

The terms ***k***, χ_g **,** χ_m and are all measures of the magnetic moment of a substance in a magnetic field.

The relationship between the applied magnetic field and the moments resulting in the diamagnetic and paramagnetic susceptibilities, combined with the contribution for other effects including Van Vleck paramagnetism, can be described in terms of the effective magnetic moment μ_{eff}, where k = Boltzmann's constant, T = absolute temperature, B = Bohr Magneton, N is Avogardo's number, and X_A is the susceptibility per gram of the paramagnetic ion [199].

$$\mu_{eff} = \sqrt{\frac{3k\chi'_A T}{N\beta^2}} = 2.84\sqrt{\chi'_A T} \quad B.M.$$

The units are in B.M. (Bohr Magnetons), which is a unit of magnetic moment and equal to $eh/4\pi mc = 9.27\times10^{-21}$ erg/gauss. The X_A is the atomic susceptibility corrected for the diamagnetic components of the ligands and associated ions.

The general mass magnetic susceptibility, Xg, by the use of an Evans balance is:

$$\chi_g = \frac{L}{m}\left\{C(R - Ro) + X'_v A\right\}$$

L = sample height in centimeters

m = sample mass in grams

C = balance calibration constant (printed on back of balance)

R = reading from the digital display when the sample and tube is in place in the instrument

Ro = reading from the digital display when the empty sample tube is in the instrument

$\chi v'$ = volume susceptibility of air (0.029×10^{-6} erg. cm^{-3})

A = cross-sectional area of the sample

There are two other measures of susceptibility, the mass magnetic susceptibility (χ_{mass} or χ_g, sometimes χ_m), measured in $m^3 \cdot kg^{-1}$ in SI or in $cm^3 \cdot g^{-1}$ in CGS and the molar magnetic susceptibility (χ_{mol}) measured in $m^3 \cdot mol^{-1}$ (SI) or $cm^3 \cdot mol^{-1}$ (CGS) that are defined below, where ρ is the density in $kg \cdot m^{-3}$ (SI) or $g \cdot cm^{-3}$ (CGS) and M is molar mass in $kg \cdot mol^{-1}$ (SI) or $g \cdot mol^{-1}$ (CGS).

The measured μ_{eff} can be compared to the calculated value μ_S, from the spin-only formula, where the orbital angular momentum is assumed to be quenched by the ligand field.

$$\mu_S = \sqrt{4S(S+1)}$$

$$S = n/2$$

$$\mu_{s.o} = \sqrt{n(n+2)}$$

where *S* is the total spin of the paramagnetic center with *n* unpaired electrons [200].

3.5.1. Magnetic Susceptibility Measurements of Complexes

The magnetic moment of CoLH1 Complex was 2.824 B.M. This indicates that the complex has octahedral low spin shape[201] and the magnetic moment for CoLH2 Complex was 2.6885 B.M. While the magnetic moment value for NiLH1 Complex was very low this showed diamagnetic properties because there is no individual electron. The magnetic moment of NiLH2 Complex was 3.394 B.M this indicate that it has octahedral shape where this complex can have paramagnetic properties and this is because it has two individual electrons in d^8 [202]. The magnetic moment value for CuLH1 and CuLH2 Complex were 1.67 and 1.56B.M, these value came within the range of to square planar and distorted octahedral because there is individual electron that has configuration t_2g^6 eg^3 [203]. The magnetic moment value for PdLH1 and PdLH2 were 0 B.M and this showed diamagnetic properties and had square planar shape[204]. While the magnetic moment value for PtLH1 was 0 B.M this showed diamagnetic properties and had octahedral shape and the magnetic moment for PtLH2 Complex was 0 B.M and this means that it has octahedral as well [205] .

Table(3-8): Magnetic properties of prepared complexes at 298K

No. of complex	Formula	$X_g \times 10^{-6}$	$X_m \times 10^{-6}$	$D \times 10^{-6}$	$X_A \times 10^{-6}$	μ_{eff}
1	CoLH1	6.8181	3108.596	238.32	3346.634	2.824
2	NiLH1	0.414	203.02	338.2	205.32	0.75
3	CuLH1	0.678	312.554	337.2	549.847	1.10
4	PdLH1	-	-	-	-	diamagnetic
5	PtLH1	-	-	-	-	diamagnetic
6	CoLH2	2.5	2704.825	328.2	3033.025	2.6885
7	NiLH2	4.464	4507.142	328.2	4835.342	3.394
8	CuLH2	0.8152	827.02	327.2	1154.22	1.65856
9	PdLH2	-	-	-	-	diamagnetic
10	PtLH2	-	-	-	-	diamagnetic

3.6. Molar Conductivity

Molar conductivity is defined as the conductivity of an electrolyte solution divided by the molar concentration of the electrolyte, and so measures the efficiency with which a given electrolyte conducts electricity in solution. Its units are siemens per meter per molarity, or siemens meter-squared per mole. The usual symbol is a Capital lambda, Λ, or Λ_m. ***Friedrich Kohlrausch*** established that to a high accuracy in dilute solutions, molar conductivity is composed of individual contributions of ions. This is known as the law of independent migration of ions [206]. From its definition, the molar conductivity is given by:

$$\Lambda_m = \frac{\kappa}{c}$$

Where:

κ is the measured conductivity

c is the electrolyte concentration.

For strong electrolytes, such as salts, strong acids and strong bases, molar conductivity is only weakly dependent on concentration and, to a good approximation, fits into the Debye - Huckel - Onsager equation :

$$\Lambda_m = \Lambda_m^\circ - K\sqrt{c}$$

where:

$\Lambda_m^\circ$is the molar conductivity at infinite dilution (or *limiting molar conductivity*)

K is the Kohlrausch coefficient, which depends on the nature of the specific salt in solution.

In contrast, Friedrich Kohlrausch showed that the molar conductivity is strongly concentration dependent for weak (incompletely dissociated) electrolytes; the more dilute a solution, the greater its molar conductivity, due to increased ionic dissociation.

The value of equivalent conductance increases with dilution. This is due to the fact that the degree of ionization increases with dilution thereby increasing the total number of ions in solution. A solution which contains a large number of ions compared to another solution of the same concentration at the same temperature has more conductance and is said to be stronger electrolyte . Table(3-9) shows molar conductivity for different types of electrolytes in different solvents[207].

Table(3-9) : The Value of Molar Conductivity (10^{-3}M) for Different Types of Electrolytes In Different Solvents

Solvent	**Non electrolyte**	**Types of electrolyte**			
		1:1	**1:2**	**1:3**	**1:4**
Water	0	120	240	360	480
DMSO	0-20	40-70	70-90	90-120	120-240
DMF	0-30	65-90	130-170	200-240	300
Ethanol	0-20	35-45	70-90	120	160
Methyl cyanide	0-30	120-160	220-300	340-420	500

3.6.1. Molar Conductivity Measurements of The Complexes.

By using the relation :

$$\Lambda_m = K / C$$

The molar conductance (**Λ_m**) of prepared complexes table(3-10) can be calculated, where **C** is the molar concentration of the metal complex.

Table(3-10): Molar conductivities of prepared complexes at (DMSO* as a solvent ,T=25 ± 2 °C and *Concentration=10^{-3}M)

sample of complex	*Conductivity (µs/cm)*
CoLH1	**43**
NiLH1	**18**
CuLH1	**12**
PdLH1	**14**
PtLH1	**24**
CoLH2	**73**
NiLH2	**84**
CuLH2	**86**
PdLH2	**74**
PtLH2	**88**

From this table shows the CoLH1 was ionic but the NiLH1,CuLH1, PdLH1and PtLH1 were not ionic.

And the table Shows the CoLH2,NiLH2,CuLH2 PdLH2 , PtLH2 as ionic.

3. 7. Atomic Absorption

Atomic Absorption Spectrometry (AAS) is a technique for measuring quantities of chemical elements present in environmental samples by measuring the absorbed radiation by the chemical element of interest [208]. This is done by reading the spectra produced when the sample is excited by radiation. The atoms absorb ultraviolet or visible light and make transitions to higher energy levels. Atomic absorption methods measure the amount of energy in the form of photons of light that are absorbed by the sample[209]. A detector measures the wavelengths of light transmitted by the sample, and compares them to the wavelengths which originally passed through the sample. A signal processor then integrates the changes in wavelength absorbed, which appear in the readout as peaks of energy absorption at discrete wavelengths[210]. The energy required for an electron to leave an atom is known as ionization energy and is specific to each chemical element. When an electron moves from one energy level to another within the atom, a photon is emitted with energy **E**. Atoms of an element emit a characteristic spectral line[211]. Every atom has its own distinct pattern of wavelengths at which it will absorb energy, due to the unique configuration of electrons in its outer shell. This enables the qualitative analysis of a sample [212]. The concentration is calculated based on the Beer-Lambert law. Absorbance is directly proportional to the concentration of the analyte absorbed for the existing set of conditions. The concentration is usually determined from a calibration curve, obtained using standards of known concentration. However, applying the Beer-Lambert law directly in AAS is difficult due to: variations in atomization efficiency from the sample matrix, non- uniformity of concentration and path length of analyte atoms (in graphite furnace AA). The chemical methods used are based on matter interactions, i.e. chemical reactions. For a long period of time these methods were essentially empirical, involving, in most cases, great experimental skills. In analytical chemistry, AAS is a technique used mostly for determining the concentration of a particular metal element within a sample. AAS can be used to analyze the concentration of over 62 different metals in a solution [213].

Theoretical percentage for metals in complexes were calculated, where found that the experiment percentage roughly similar to theory values. This shows in table (3-11).

Table(3-11) Theoretical and experimental value of metal ratio for prepared complexes

	% of metal	
Compound	**Theory value**	**Experiment value**
CoLH1	12.3	12.1
NiLH1	15.25	15.1
CuLH1	16.3	15.8
CoLH2	9.18	9.3
NiLH2	9.41	9.4
CuLH2	9.8	9.5

3.8. Antifungal activity

The antifungal activity of ligands and some of their complexes have been tested for the in vitro growth inhibitory activity against the *Aspergillus niger* (this fungi effect to the dermatophytes) by using the disc diffusion method. The fungus was cultured in Potato dextrose agar medium and used as inoculums for this study. Studied compounds were dissolved in DMSO to final concentration of 10 mg per ml and soaked in filter paper discs of 6mm diameter. These discs were placed on the already seeded plates and incubated at 25-28 °C for 10 days [214,215,216] .

Table (3-12) gives the results which show the inhibition of growth of the fungi. The compounds LH1 ,LH2, CoLH1, CuLH1, NiLH2 and CuLH2 showed greater activity against *Aspergillus niger*. while the compounds NiLH1, PdLH1, PtLH1, CoLH2, PdLH2 and PtLH2 do not show any activity against these fungi. There are some figures of discs shown in appendix.

Table (3-12): Antifungal activity for some complexes and their parent ligands

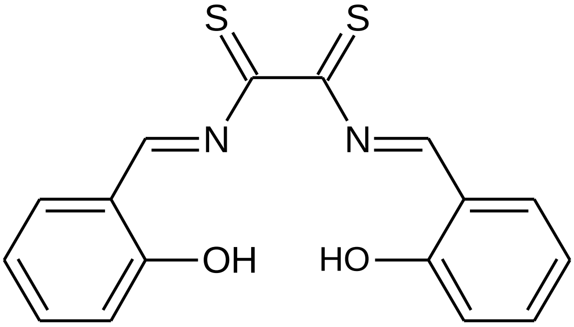
Compound	*Aspergillus niger*(10mg/ml)
LH1	+
CoLH1	+
NiLH1	-
CuLH1	+
PdLH1	_
PtLH1	_
LH2	+
CoLH2	-
NiLH2	+
CuLH2	+
PdLH2	-
PtLH2	-

(-) No-inhibition, (+) Inhibition

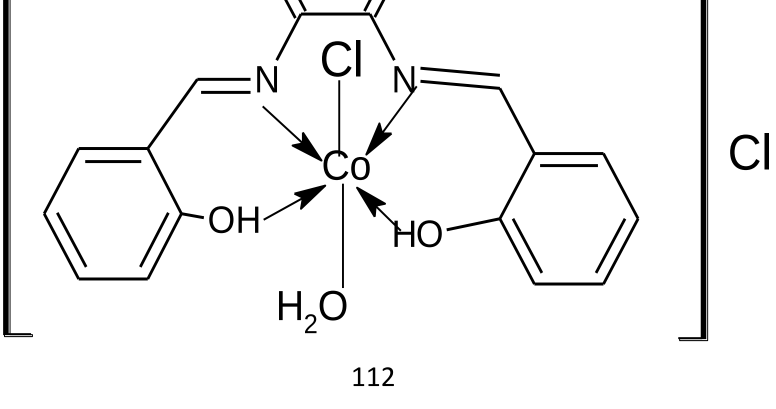
3.9. The proposed structure of the ligands and its Complexes

From the results of UV-Visible technique, Magnetic Susceptibility measurement , Molar conductivity and Atomic absorption technique of ligands and its complexes the proposed structure of this compounds were:

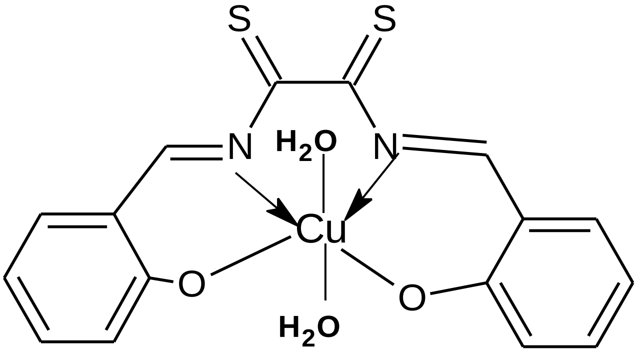
1- *N,N′*-bis(2-hydroxybenzlidene) dithiooxamide (LH1).



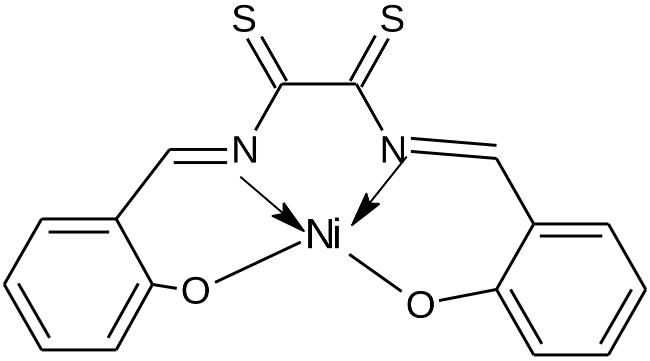
2- CoLH1



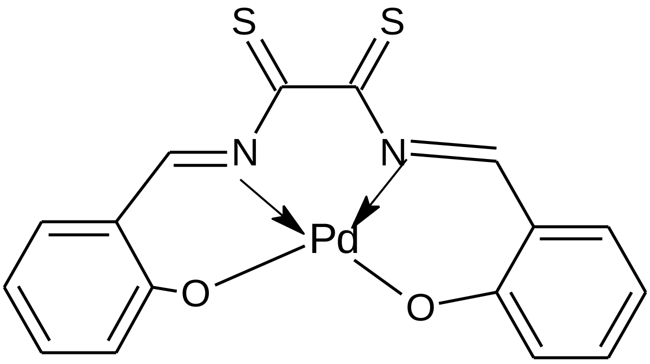
3- CuLH1



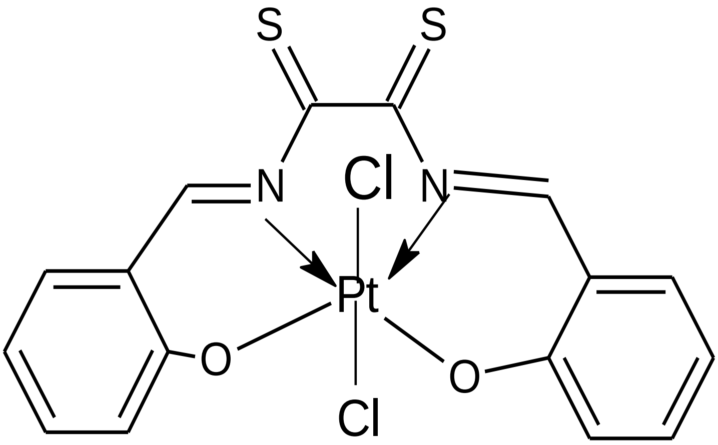
4-NiLH1



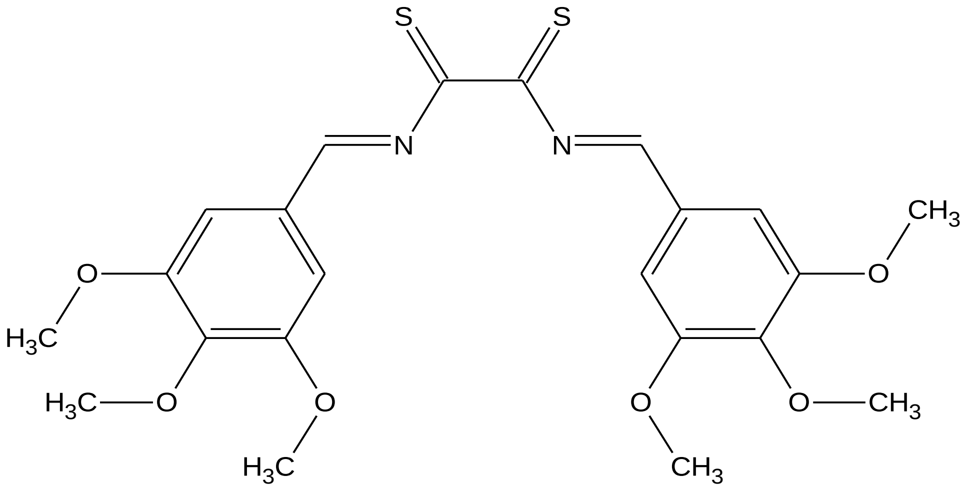
5-PdLH1



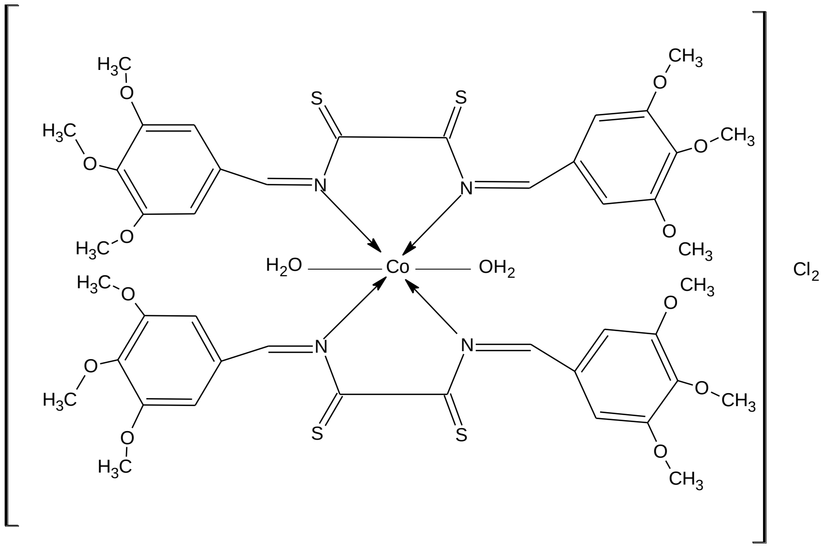
6-PtLH1



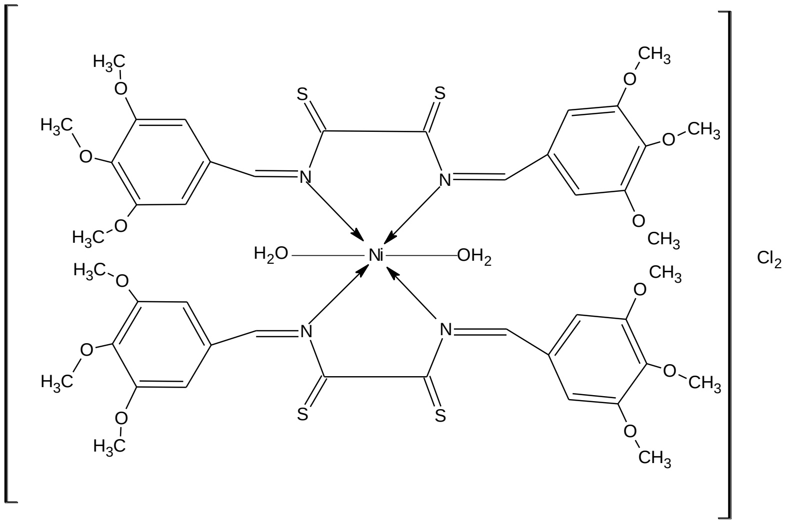
7- *N,N′*-bis(3,4,5-trimethoxybenzlidene) dithiooxamide (LH2).



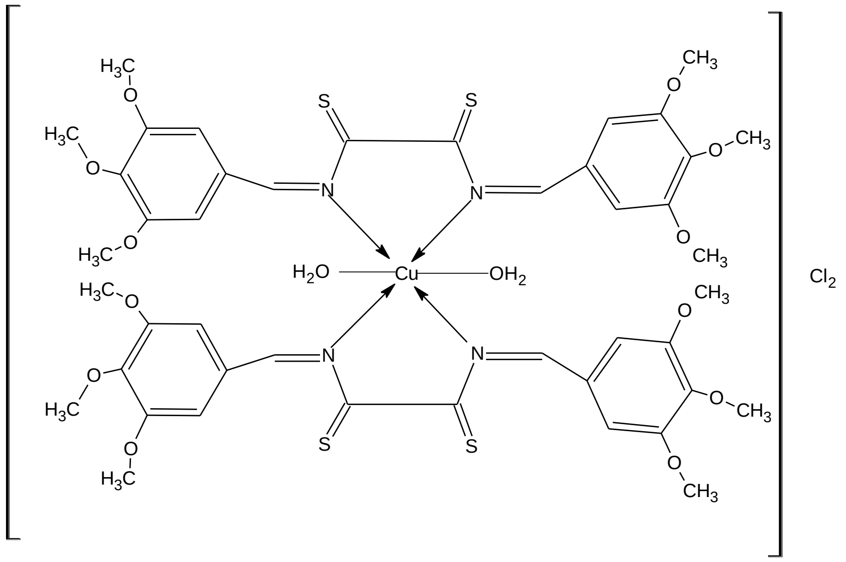
8-CoLH2



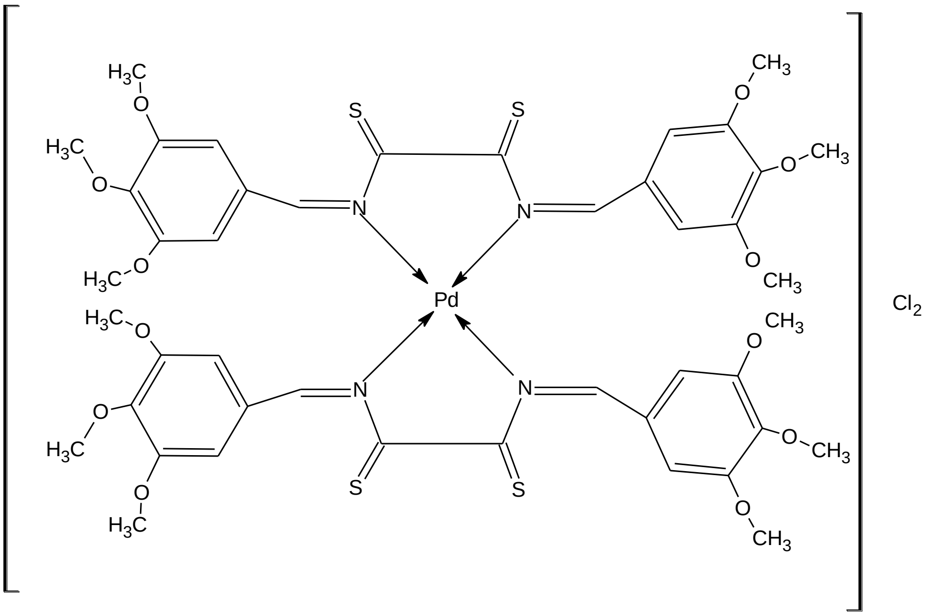
9-NiLH2



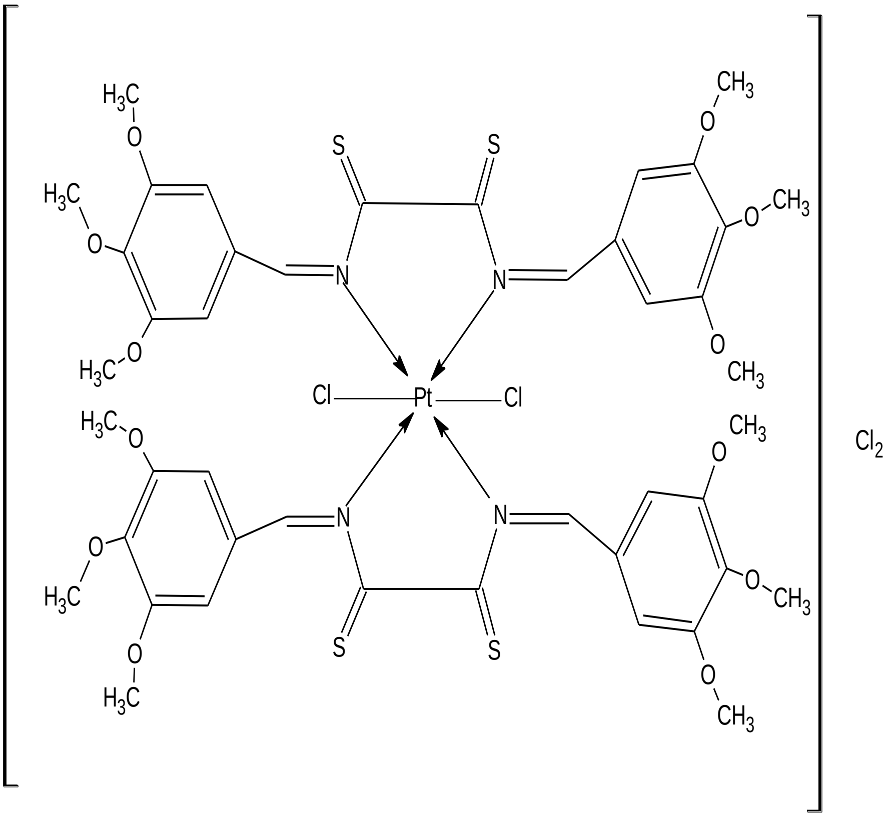
10-CuLH2



11-PdLH2



12-PtLH2



CHAPTER
4

CONCLUSION

This chapter includes the final results that were obtained. There were differences in the behavior of the two types of ligands that were synthesized. In this work a different ligand and its complexes have been prepared and different techniques were investigated.

4- Conclusion

Dithiooxamide, 2-hydroxybenzaldehyde and 3,4,5-trimethoxybenzaldehyde were used as raw materials for synthesizing two types of ligands. Ten types of complexes were prepared by refluxing the two ligands with five types of metals. Triethylamine and pipyridine were involved as dopants in synthesising the two ligands. The ligands are *N*,*N*′-bis(2-hydroxybenzylidene) dithiooxamide (LH1) and *N*,*N*′-bis(3,4,5-trimethoxybenzylidene) dithiooxamide (LH2) while the complexes that were prepared are CoLH1, NiLH1, CuLH1, PdLH1, PtLH1, CoLH2, NiLH2, CuLH2, PdLH2 and PtLH2.

The elemental analysis technique was used to identify the ligands that were synthesized. In addition ^{1}H NMR spectroscopy, UV-Visible spectroscopy and Infrared spectroscopy were used to identify the structure of the compounds that were produced.

Nature of structure LH1 gave square planar complexes with ions Ni(II),Cu(II) and Pd(II),while the ligand LH2 gave octahedral complexes with ions Ni(II) and Cu(II).

Magnetic Susceptibility Measurements of Complexes determine, were the magnetic moment of CoLH1 Complex was 2.824 B.M , this value agreement with octahedral low spin of cobalt complexes ,the magnetic moment value for NiLH1, PdLH1, PdLH2 and PtLH2Complexes were very low this appeared diamagnetic properties ,the magnetic moment of NiLH2 Complex was 3.394 B.M , Magnetic moment value for CuLH2 Complex was 1.7 B.M this agreement with distorted octahedral of Cu(II) complexes.

Molar conductivity was measured for prepared complexes and indicates that the CoLH1 was ionic but the NiLH1,CuLH1, PdLH1and PtLH1 were not ionic. As well as the CoLH2,NiLH2,CuLH2, PdLH2 , PtLH2 were ionic.

Atomic Absorption Spectrometry (AAS) technique was used to determine amount of the metal in the complexes. Theoretical percentage of metals in complexes were calculated and we found that the experiment percentage approximately the same to theory percentage.

It can be concluded from the result that was obtained, that Ligands and some of their complexes have antifungal activity against *Aspergillus niger*. These compound are LH_1 ,LH2, CoLH1, CuLH1, NiLH2 and CuLH2 greater activity against *Aspergillus niger*. while the NiLH1, PdLH1,PtLH1, CoLH2, PdLH2 and PtLH2 do not show any activity against these fungi.

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Appendix

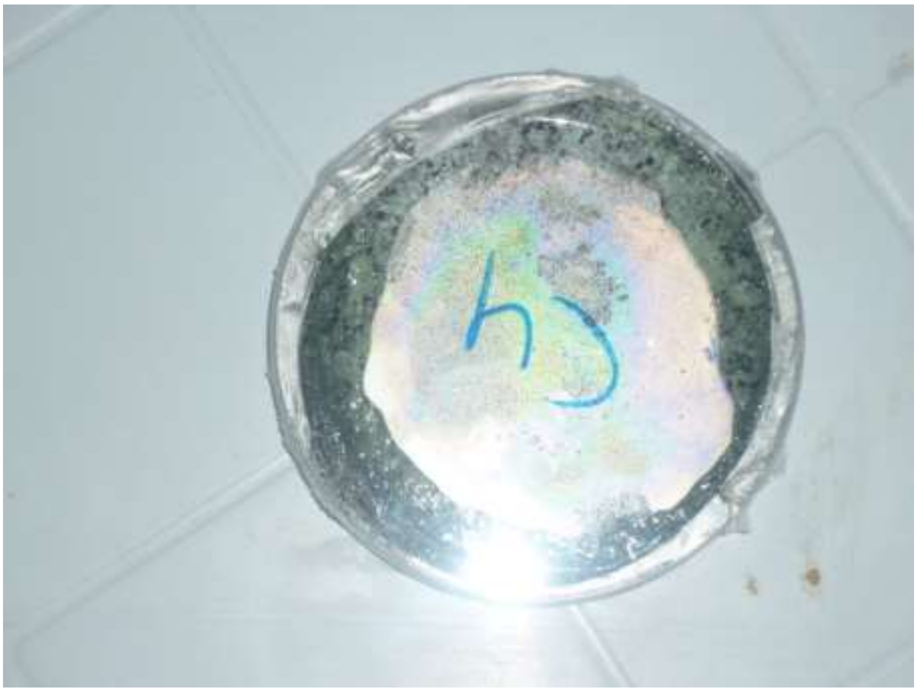
1- *N,N′*-bis(2-hydroxybenzlidene) dithiooxamide (LH1).

2- CoLH1

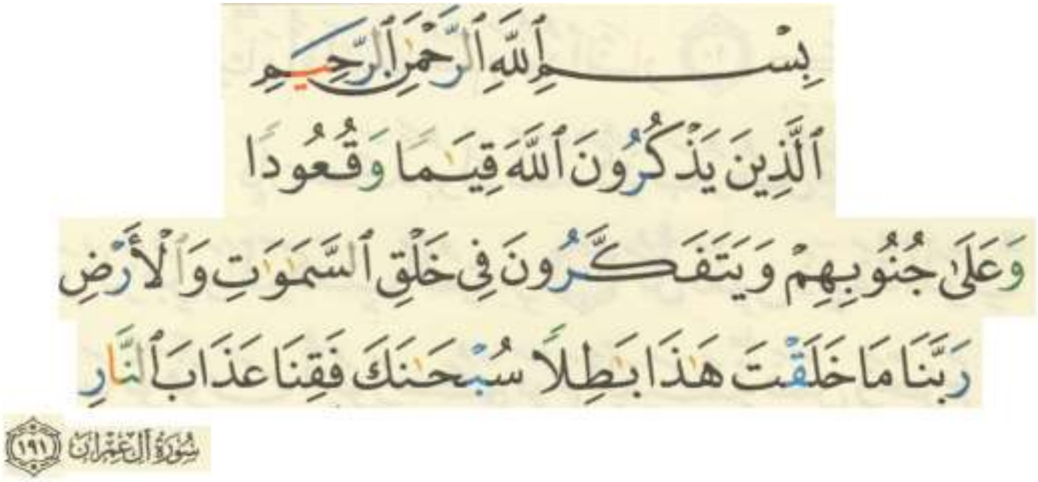
3-CuLH1

4- *N*,*N*′-bis(3,4,5-trimethoxybenzlidene) dithiooxamide (LH2).

5-NiLH2



6-CuLH2



بِسۡمِ ٱللَّهِ ٱلرَّحۡمَٰنِ ٱلرَّحِيمِ
ٱلَّذِينَ يَذۡكُرُونَ ٱللَّهَ قِيَٰمٗا وَقُعُودٗا
وَعَلَىٰ جُنُوبِهِمۡ وَيَتَفَكَّرُونَ فِي خَلۡقِ ٱلسَّمَٰوَٰتِ وَٱلۡأَرۡضِ
رَبَّنَا مَا خَلَقۡتَ هَٰذَا بَٰطِلٗا سُبۡحَٰنَكَ فَقِنَا عَذَابَ ٱلنَّارِ

سورة آل عمران ١٩١

صدق الله العلي العظيم

الخلاصه

الجزء الأول من من هذا العمل يتضمن تحضير اليكند . LH1

N,N'-bis (2-hydroxybenzlidene) dithiooxamide (LH1) والمشتق من تفاعل مادة الدايثايوكسمايد مع2-هيدروكسي بنزالديهايد. صعد التفاعل لمدة 6 ساعات وبدرجة 70 م . ومن خلال هذا الليكند تم تحضيرخمسة انواع من المعقدات الفلزية -بأستخدام الايونات Ni^{+2} , Co^{+2} Pt^{+4} , Pd^{+2} , Cu^{+2} , . شخصت المركبات المحضره ودرست خواص هذه المركبات بأستخدام عدة تقنيات مثل تقنية تحليل العناصر (CHNS) المستخدمه لتشخيص وتعين كمية العناصر الموجوده في الليكند ومطيافية الأشعه فوق البنفسجيه-المرئيه ومطيافية الأشعه تحت الحمراء ومطيافية الرنين النووي المغناطيسي التي أستخدمت لتشخيص تركيب هده المركبات . كذلك قيست الحساسيه المغناطيسيه للمركبات وقد وجد أن العزم المغناطيسي لمعقد ال CoLH1 بحدود 2.82 بورمغناطون أما بالنسبه لمعقدات ال NiLH1, CuLH1, PdLH1, PtLH1 كانت دايامغناطيسيه أي انها تملك عزم مغناطيسي واطئ جدا.

أما التوصيليه المولاريه للمعقدات قيست بأستخدام المذيب ثنائي مثيل سلفوكسايد (DMSO) حيث وجد أن المعقدات كانت أيونيه بنسبة 1:1 بالنسبه لمعقد ال CoLH1 بينما غير أيوني بالنسبه للمعقدات NiLH1, CuLH1, PdLH1, PtLH1 . أما الامتصاصيه الذريه للمعقدات حسبت ووجد أن القيمه العمليه كانت مقاربه جدا للقيمه النظريه . لذلك ومن خلال التفسير أعلاه أقترحت الأشكال التركيبيه للمعقدات حيث وجد أن الشكل المقترح لمعقد ال CoLH1 كان ثماني السطوح واطي البرم . أما بالنسبه لمعقدات NiLH1, CuLH1, PdLH1 كانت ذات اشكال مربع مستوي . أما معقد ال PtLH1 فقد وجد أن له تركيب ثماني السطوح .

أخيرا قيست الفعاليه البايولوجيه لليكند ومعقداته وقد وجد أن LH1,CoLH1, CuLH1 أظهرت أعظم فعاليه ضد الفطر ***Aspergillus niger*** وهو نوع من أنواع الفطريات الجلديه أما المعقدات NiLH1, PdLH1, PtLH1 لم يظهروا أي فعاليه بايولوجيه ضد هذا الفطر.

الجزء الثاني من من هذا العمل يتضمن تحضير اليكند (LH2)

N,N'-bis(3,4,5-trimethoxybenzlidene)dithiooxamide (LH2). والمشتق من تفاعل مادة الدايثايوكسمايد مع 5,4,3-ثلاثي ميثوكسي بنزالديهايد . صعد التفاعل لمدة 12 ساعات وبدرجة 70 م . . ومن خلال هذا الليكند تم تحضيرخمسة انواع من المعقدات الفلزية

بأستخدام الايونات Co^{+2} , Ni^{+2} , Cu^{+2} , Pd^{+2} , Pt^{+4} . شخصت المركبات المحضره ودرست خواص هذه المركبات بأستخدام عدة تقنيات مثل تقنية تحليل العناصر (CHNS) المستخدمه لتشخيص وتعين كمية العناصر الموجوده في الليكند ومطيافية الأشعه فوق البنفسجيه-المرئيه ومطيافية الأشعه تحت الحمراء ومطيافية الرنين النووي المغناطيسي التي أستخدمت لتشخيص تركيب هده المركبات . كذلك قيست الحساسيه المغناطيسيه للمركبات وقد وجد أن العزم المغناطيسي لمعقد ال CoLH2 بحدود 2.6885 بورمغناطون أما بالنسبه لمعقدات ال NiLH2, كان بحدود 3.394 بور مغناطون أما بالنسبه لمعقد ال CuLH2 كان بحدود 1.65856 بور مغناطون أما معقدي ال PdLH2 وPtLH2 كانت دايامغناطيسيه أي انها تملك عزم مغناطيسي واطئ جدا.

أما التوصيليه المولاريه للمعقدات قيست بأستخدام المذيب DMSO حيث وجد أن المعقدات كانت أيونيه بنسبة 1:2 بالنسبه لمعقدات CoLH2, NiLH2, CuLH2, PdLH2, PtLH2 أما الامتصاصيه الذريه للمعقدات حسبت ووجد أن القيمه العمليه كانت مقاربه جدا للقيمه النظريه . لذلك ومن خلال التفسير أعلاه أقترحت الأشكال التركيبيه للمعقدات حيث وجد أن الشكل المقترح لمعقد ال CoLH2, NiLH2, CuLH2, PtLH2 كانت ثماني السطوح. أما معقد ال PdLH2 فقد وجد أن له تركيب المربع المستوي.

أخيرا قيست الفعاليه البايولوجيه لليكند ومعقداته وقد وجد أن LH2, NiLH2, CuLH2 أظهرت أعظم فعاليه ضد الفطر ***Aspergillus niger*** وهو نوع من أنواع الفطريات الجلديه أما المعقدات CoLH2, PdLH2, PtLH2 لم يظهروا أي فعاليه بايولوجيه ضد هذا الفطر.

جمهورية العراق
وزارة التعليم العالي والبحث العلمي
جامعة كربلاء
كلية العلوم

تحضير وتشخيص بعض معقدات العناصر الأنتقاليه عن طريق قواعد شيف المشتقة من الدايثايوكسمايد وألديهايدات مختاره

رساله مقدمة الى

كلية العلوم -جامعة كربلاء

وهي جزء من متطلبات نيل درجة الماجستير في علوم الكيمياء

من قبل

رواء عبد الخالق عبد الغني الموسوي

بكالوريوس علوم كيمياء جامعة كربلاء-2005

بأشراف

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1434-2013