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Synthesis and Characterization of New Transition Metal Complexes with Schiff Bases Derived from Quinones with Different Amines

A Thesis

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By

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بسم الله الرحمن الرحيم

قَالُوا سُبْحَانَكَ لَا عِلْمَ لَنَا إِلَّا مَا عَلَّمْتَنَا ◌ۖ إِنَّكَ أَنتَ الْعَلِيمُ الْحَكِيمُ

صدق الله العظيم

الآية 32 من سورة البقرة المباركة

Supervisor Certification

I certify thesis entitle

Synthesis and characterization of new transition metal complexes with Schiff bases derived from quinones with different amines

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Dedication

To my supervisor, assistant professor Dr. Suad-Taha Saad

Those who supported me and helped me in achievement of this work…

I also express my thanks and gratitude to the deanship of the college of science for women and the head of the department of chemistry, Dr. Sadiq and all my professors who helped me and provided their valuable pieces of advice Dr. Noor , Prof. Dr. Mohammed Hamid and Dr. Hazim Al- Jeboree .

Acknowledgments

To one of my first teachers, my mother, how I wish you were there on this day...

To my patience and stamina

To everyone who supported me and increased my strength and determination

Riyam

Abstract:

This study included two steps to prepare Schiff base complexes from quinones with different primary amines. The first step was to prepare Schiff bases that included the interaction of ketones (quinones) 9,10-phenomethrin quinone، 2,5-dihydroxy-1,4-benzoquinone with amines. The first preparation is from the reaction of 9,10-phenomethrin quinone with 2-aminothiophenol, and the preparation ratio was (1:1) and the second preparation resulted from the reaction of 9,10-phenomethrin quinone with 5-amino2-methylphenol to produce a Schiff base, and the preparation ratio was (1:1) As for the third preparation, it resulted from the interaction of 2,5-dihydroxy-1,4-benzoquinone with 5-amino2-methylphenol, and the preparation ratio was (2:1). Schiff bases interact with aqueous salts of chlorides (cobalt iron, nickel and copper) in a second step to prepare complexes with different physical properties from each other. Many tests and techniques were conducted on ligands and complexes. Infrared spectroscopy, thermal analyzes, atomic mass, nuclear magnetic resonance, and techniques that were conducted on the complexes are ultraviolet-visible spectroscopy, infrared, thermal analyzes, atomic absorption, magnetic sensitivity, and molar conductivity. Complexes are two applied procedures on this thesis. The first application is to measure anticancer effects on the first and third ligands and cobalt complexes for the first and third ligands and compare them in terms of the healthy cell and the infected cell. Also, the application of anticorrosion agents for the first ligand and iron-copper complexes. Copper was more efficient with respect to iron and the first ligand

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List of abbreviation

DMSO-d6	Hexa deuterodimethyl sulfoxide
FTIR	Fourier-transform infrared spectroscopy
^{1}HNMR	Proton nuclear magnetic resonance
L_1	9,10phenanthrenequinone, 2-Aminothiophenol
L_2	9,10phenanthrenequinone, 5-Amino -2-methylphenol
L_3	2,5-dihydroxy-1,4-benzoquinon, 5-Amino -2-methylphenol
EDTA	Ethylene di Amin tetra acetic acid
Oh	Octahedral
Td	Tetrahedral
MLCT	Metal ligand transfer
C-T	Charge Transfer
TNAP	N-[2-thienylmethylidene]-1-propanamine
PHEN	1,10-phenanthroline
ASP	Aspirin
MCF10A	The non-malevolent breast epithelial cells
MCF7	The humanoid being breast cancer cell line
MTT	[3-(4, 5-dimethylthiazol-2-yl)-2, 5-diphenyltetrazolium Bromide]
UV-Vis	Ultraviolet-Visible Spectroscopy
AAS	Atomic Absorption Spectrometry

Chapter One

Introduction

1.1 Coordination Compound

Bonds are often classified based on whether they are ionic or covalent in nature[1, 2] .An importance type bond is called coordinate covalent bonds. This kind of bond forms when a single pair of electrons from one chemical species is transferred to an orbital on another chemical species.[3,4] Coordination covalent and donor-acceptor bonds are some names for this type of relationship. Therefore, coordination compounds are substances that include such bonding which contain a metal atom or ion and a molecule with one or more unshared electrons (ligand) combine to generate coordination compounds. The resulted coordination compound might be neutral or anionic species[5,6]. Both neutral substances and anions can function as ligands. Fig (1-1) displays a sample of this complex.

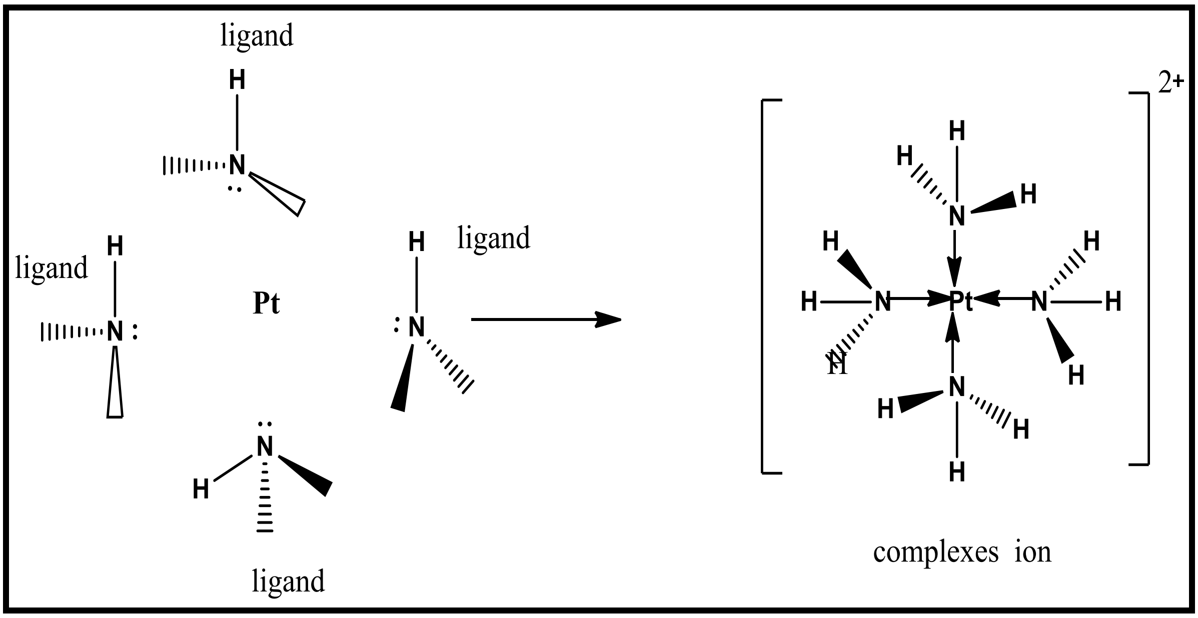


Fig (1-1) Coordination Compound

The well-known tetra ammine copper(II) ion $[Cu(NH_3)_4]$ is the first entirely inorganic coordination complex to be discovered. [7] In addition, not even the first name of the chemist who prepared it is known. Several of them imply or assert that he invented the parent chemical form $[Co(NH_3)_6]$.Hexamine cobalt (III) chloride, represented in Figure (1-2) in 1798, was only used to record the hue of a solution produced by adding more aqueous ammonia to a $CoCl_2$ or $Co(NO_3)_2$solution [8].

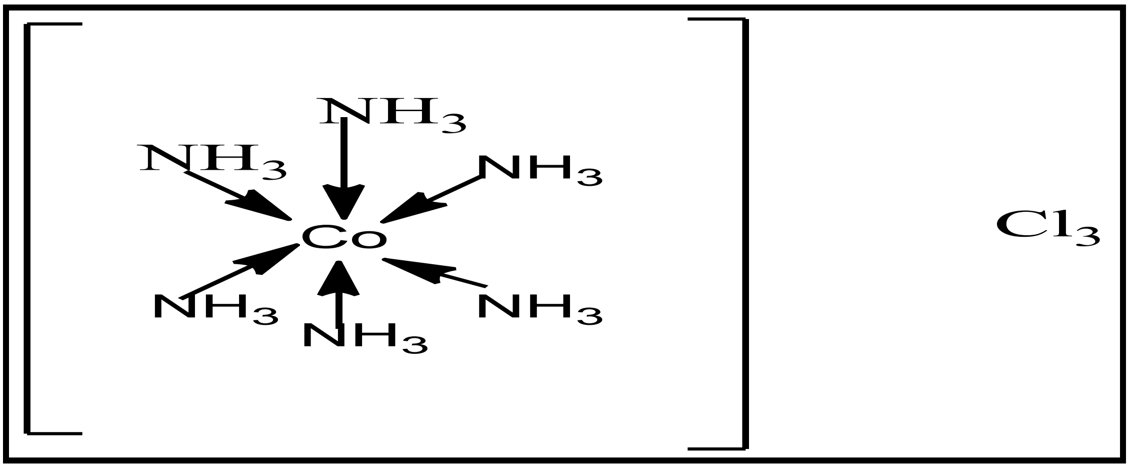


Fig (1-2)Hexamine cobalt (III) chloride.

Louis-Nicolas Vauquelin made the discovery of the pink compound tetra ammine Palladium (II), ([pd $(NH_3)_4$][pd Cl_4]) in 1813. Palladium is coordinated in both the cationic and the anion of Vauquelin's salt. Heinrich Gustav Magnus found the equivalent compound ($[Pt(NH_3)_4][PtCl_4]$) in 1828[9]. Nils' Green Salt is the first of all studies of hydrazine complexes to be discovered iridium led to the discovery of $H[Ir(N_2Hs)Cl_6]$salt . The color of Magnus' Green Salt and Vauquelin's Salt both differ noticeably from that of their constituent ions [10].

1.2 Types of Ligands.

The number of donor atoms in different ligands can be used to classify ligand therefore, these ligands can be classified in to:

1.2.1 Mono dentate ligand :

One electron pair is given to the metal or metal ion [11].Fig(1-3) includes examples of such ligands

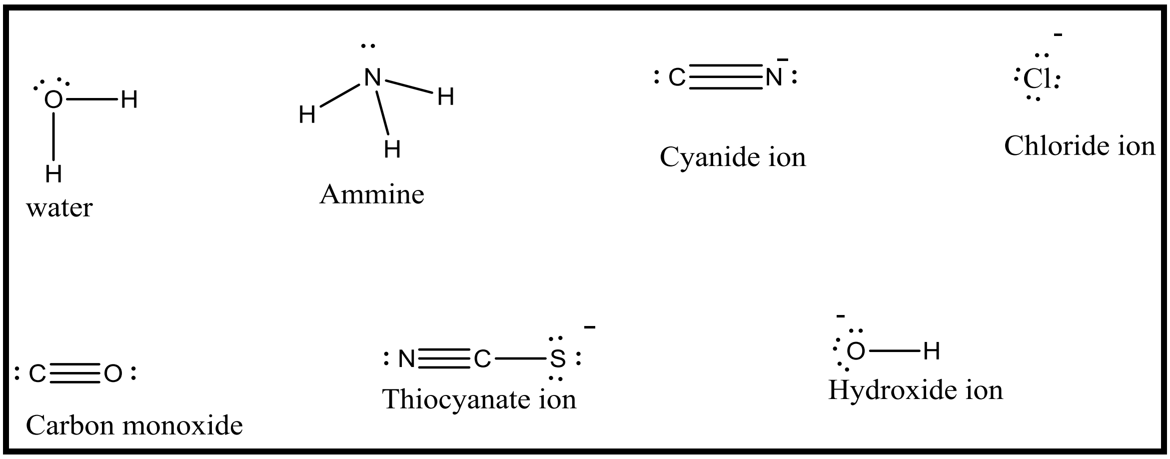
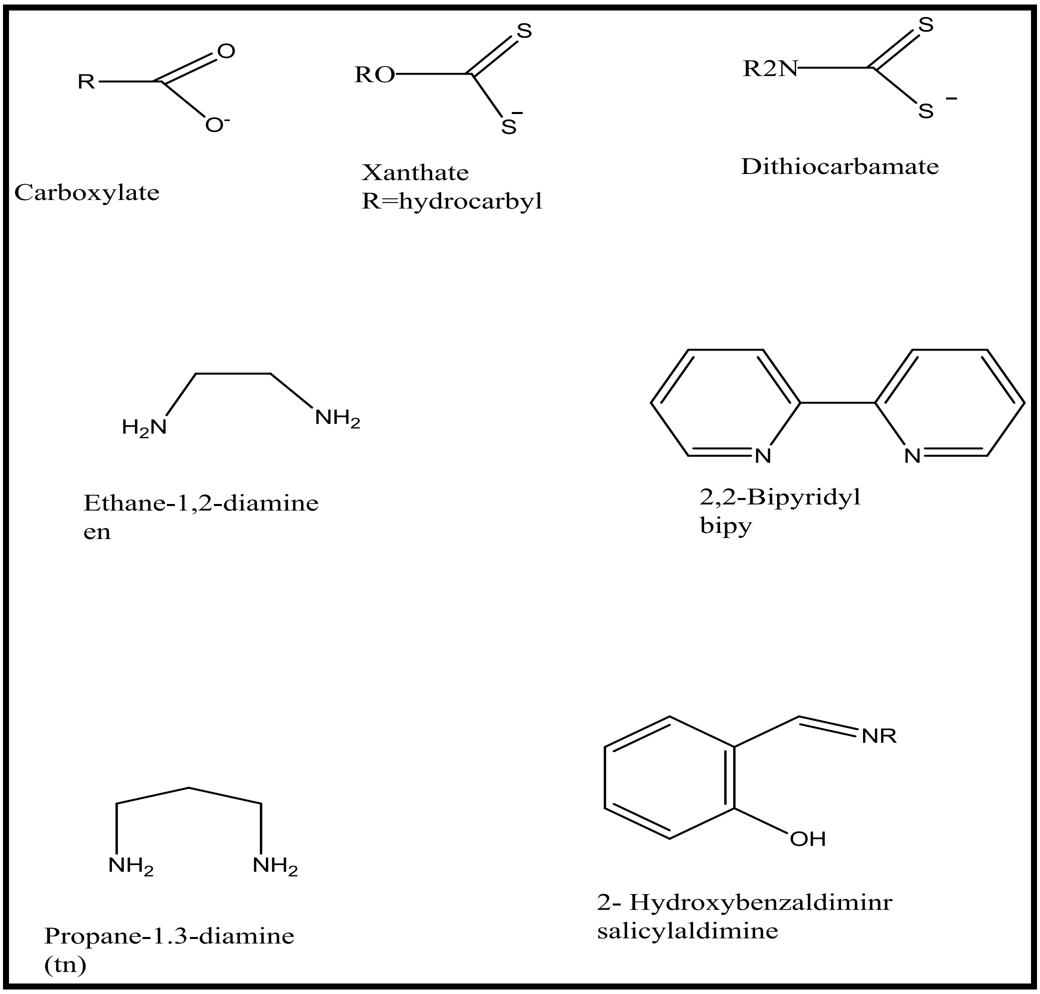


Fig (1-3) Example of common Mono Dentate Ligands

1.2.2Bientate Ligand :

The metal or metal ion accept two electron pairs from a dentate ligand[12]Figure (1-4)showed an examples of Bi dentate Ligands



Carboxylate

Xanthate
R=hydrocarbyl

Dithiocarbamate

Ethane-1,2-diamine
en

2,2-Bipyridyl
bipy

Propane-1.3-diamine
(tn)

2- Hydroxybenzaldiminr
salicylaldimine

Fig (1-4) Examples of Bi Dentate Ligands

1.2.3 Poly dentate Ligands

having more than two granter atoms Tridentate,tetradentate, pentadentate, hexdentate, etc can be classified under the term of poly dentate ligands [13]. Fig(1-5) and (1- 6) give examples of tridentate and tetradentate ligands.

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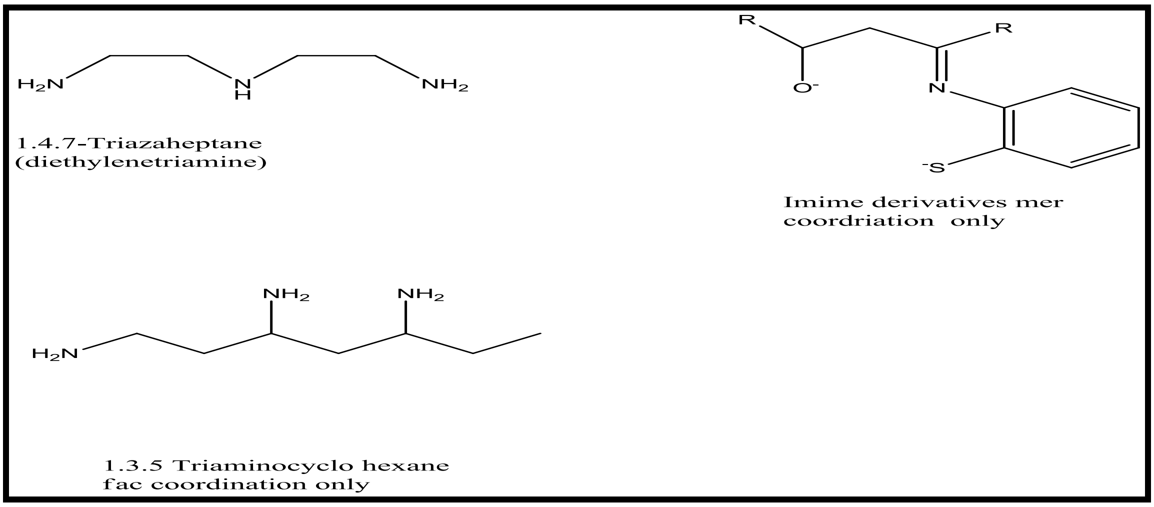


Fig (1-5) Tridentate ligands.

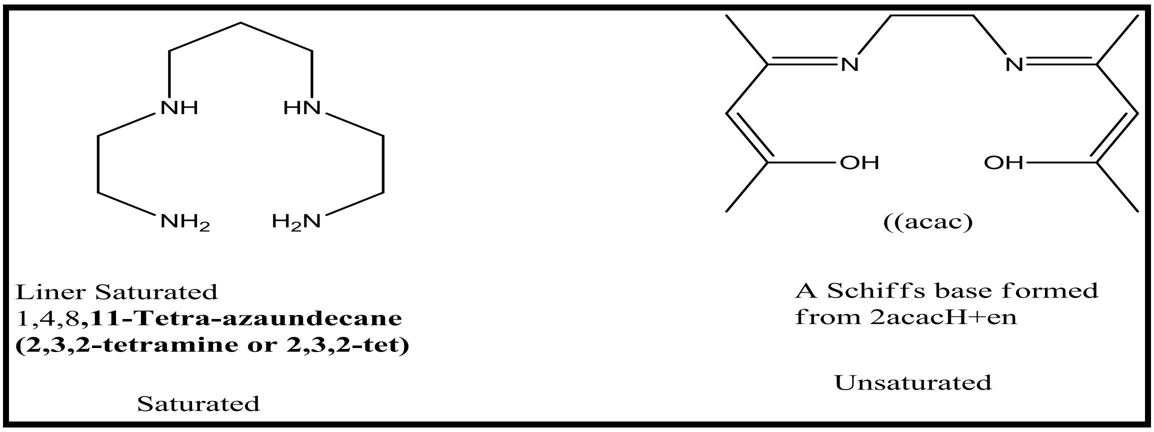


Fig (1-6) Types of tetra dentate ligands.

Penta dentate ligand, consists of five nitrogen with the ability to form coordinating bonds, replaced by an methyl group, replaced by a benzene ring.. [14] Penta dentate acetate ion Fig(1-7) Type of penta dentate ligand .

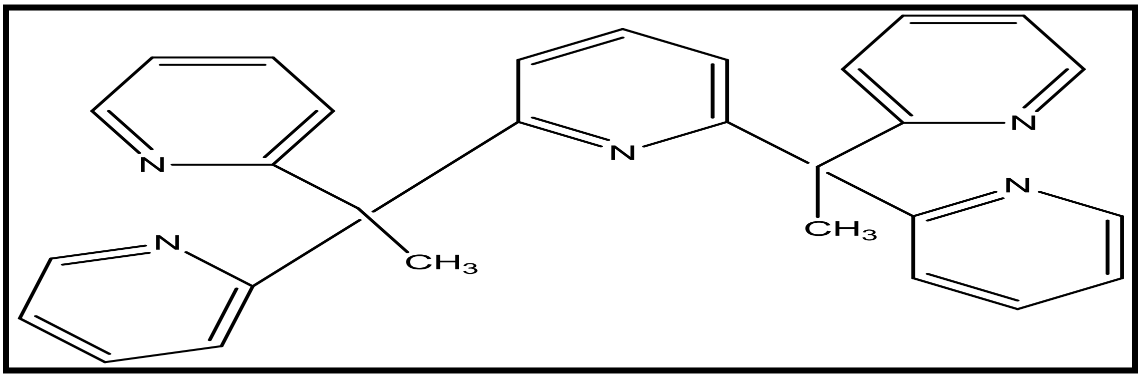


Fig (1-7) Type of penta dentate ligand.

Hexadentate ligand, such as ethylenediaminetraaceto ($EDTA^{-4}$). Thus, the two nitrogen atoms and four oxygen atoms of the acetate group can coordinate to the metal atom. Fig (1-8) shows a hexadentate ligand ethylene di amine tetra acetate ion ($EDTA^{4-}$)[15].

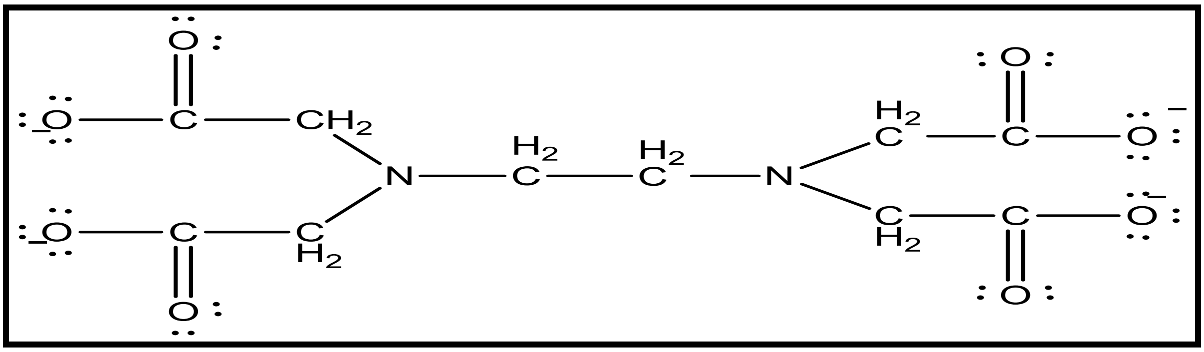


Fig (1-8) Type of hex dentate ligand Ethylene di amine tetra acetate ion ($EDTA^{4-}$)

In the complexes of these ligands the central metal atom is bound to these ligands at two or more coordination site which results in the formation of rings which is called a chelating ring. Fig (1-9) Types of chelating rings which can be either five or six membered ring.

Fig (1-9)Example of formation Five and six member rings in coordination process

1.3 Schiff Base

A Schiff base, named by Hugo Schiff, is a compound with a functional group that contains a carbon-nitrogen double bond with the nitrogen atom connected to an aryl or alkyl group, not hydrogen[16] Hugo Joseph Schiff, a German scientist, called these compounds after his discovery of them in 1864[17]. In these compounds the nitrogen of primary amine replaces the oxygen atom of the carbonyl group of an aldehyde or ketone.[18-20]

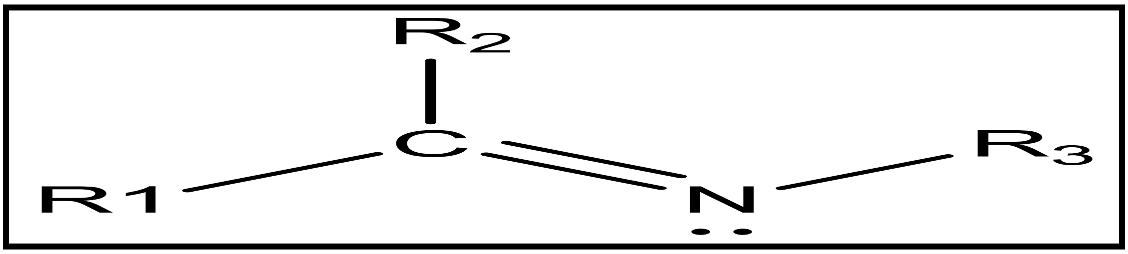


Fig (1-10)general structure of compound Schiff Base

Higher reaction temperatures and longer time reaction times are necessary because aliphatic ketones and amines create imines more slow than they do aldehydes. Reaction yields can approach 80%-95% levels with the use of acid catalysts and water taking out of from the reaction mixing Aromatic ketones are low reactive then aliphatic ones and must undergo difficult reaction in order to transform into imines[21]

The first step in the mechanism of the condensation reaction between the carbonyl compound and the amine is the initial addition of the amine to the carbonyl compound, creating a carbinol amine. The second step is the dehydration to create the imine product, which has the (-C=N-) bond. Fig (1-11) mechanism of Schiff Base acid synthesis[22].

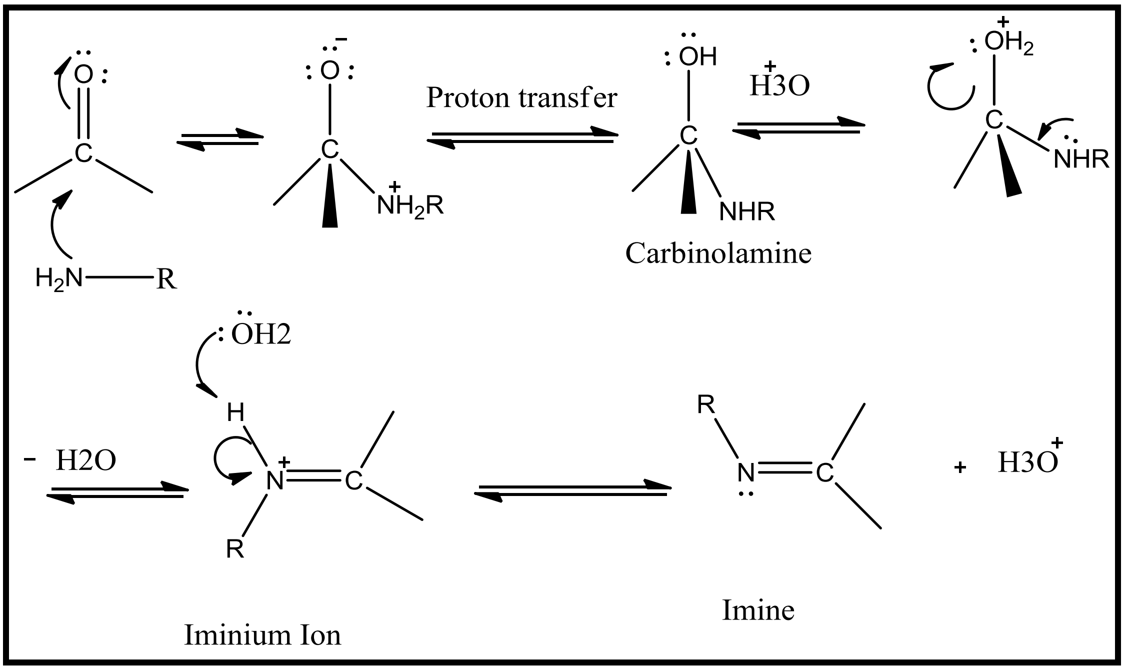
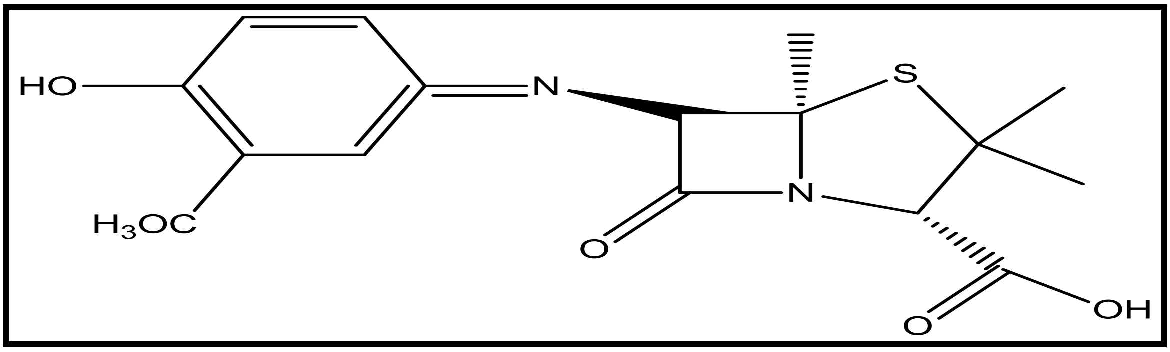


Fig (1-11)Mechanism of Schiff base formatiom

Many investigations revealed the significant chemical and biological investigations of a lone pair on electrons during inSP^2hybridized orbital of the nitrogen atom of the azomethine. he imines generated degrade or polymerize[23] Due to their strong group if the nitrogen or carbon atom is not bound by at least one aryl group thermal stability, high conductivity, and favorable luminescence characteristics, metal complexes of the Schiff base have expected a lot of attention. In general, the imine nitrogen atom is connected to with metals[24] The application for industrial reasons in textiles, such as stain bleaching and dye-transfer inhibition, transition metal complexes containing Schiff base ligands have drawn a lot of interest.[25, 26] Schiff bases are also of interest as metal agents catalyst carriers and inhibitors of corrosion in biological systems several uses including azo dyes and antioxidants[27,28]

Y. H. Sabah,(2017) have used the Primary amine compound to interact with the carbonyl compound to give the final compound azomethin Fig(1-12) the Synthesis of Schiff base use Synthesis, Characterization and Biological evaluation of penicillin derivatives complexes [29].



Fig(1-12) The structure of penicillin derivatives complexes

[M. A. Latif, et. al., (2019)] 4-(dimethylamino)benzaldehyde and S-benzyl dithiocarbamate were used to make the chemical azomethine. Fig(1-13)demonstrates how Schiff base is made.[30]

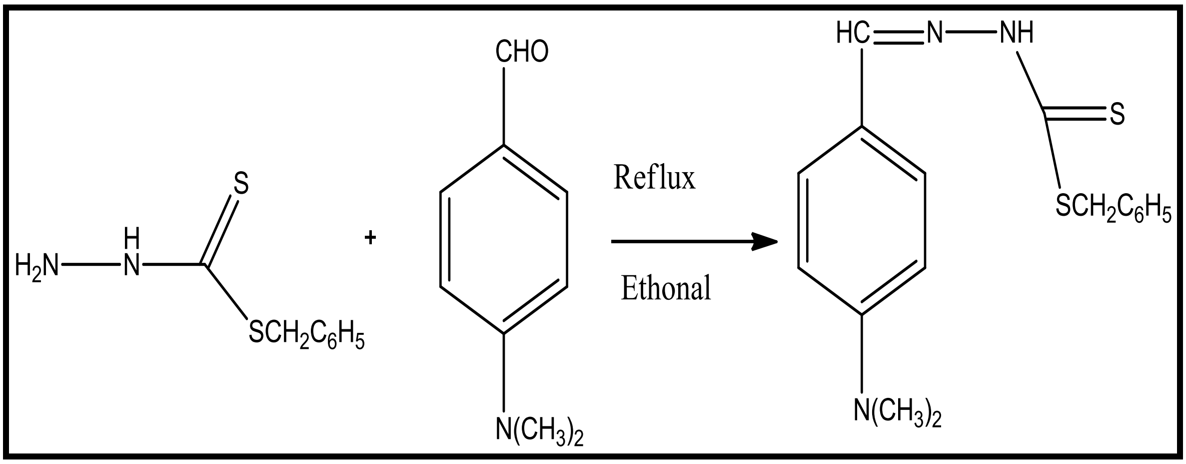
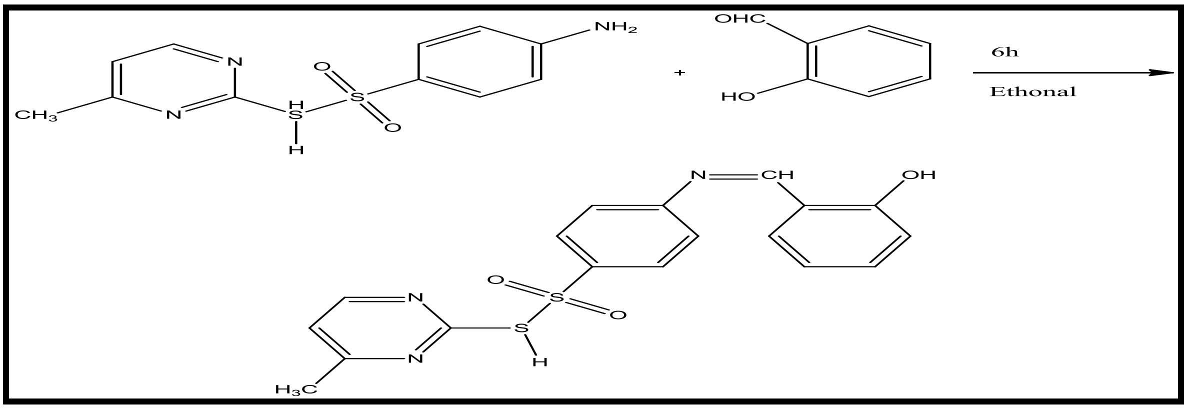


Fig (1-13)The Structure benzaldehyde and S-benzyl dithiocarbamate Synthesis for Schiff base

The researchers have produced the final molecule, azomethine salicylaldehyde-sulfamerazine, by using the primary amine component to interact with the carbonyl compound used the complex antimicrobial activity Figure (1-14) The Structure azomethine salicylaldehyde-sulfamerazine Synthesis of Schiff base [31]



Fig(1-14)The Structure azomethine salicylaldehyde-sulfamerazine Synthesis of Schiff base

The researchers have created the final molecule, azomethine, by using the primary amine compound to interact with the carbonyl component measurement enzymatic activities of novel hexadentate Schiff base Fig (1-15)Shows the Synthesis of Schiff base[32]

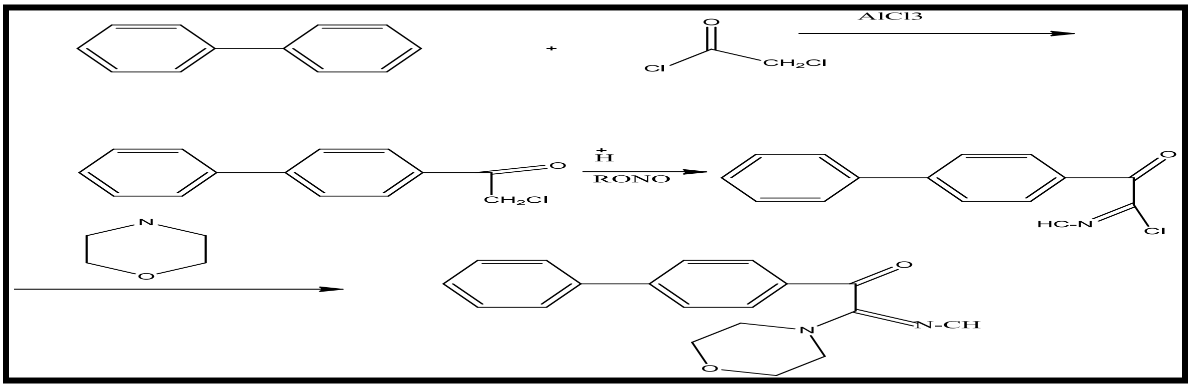
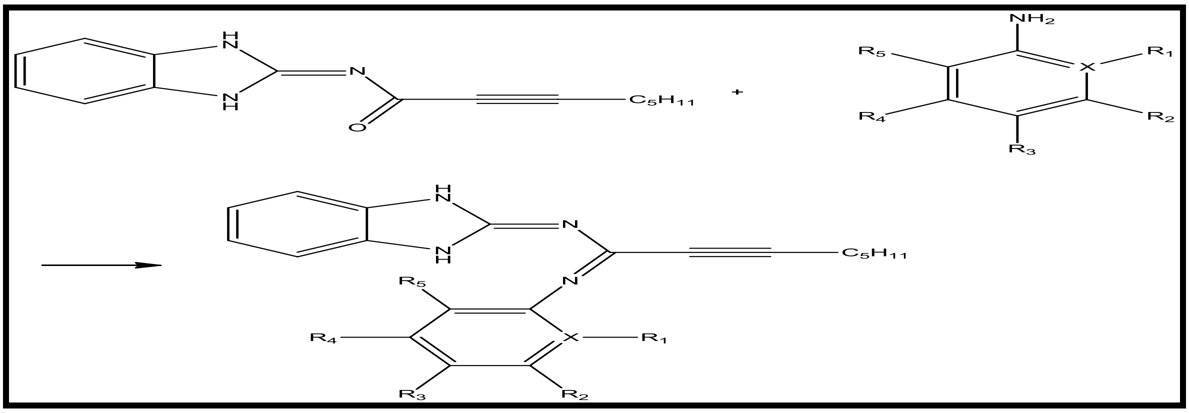


Fig (1-15) The Structure of novel hexadentate Synthesis of Schiff base

The researchers have been in accordance with the steps depicted in the picture below. The initial material was oct-2-ynoic acid (1,3-dihydro benzo imidazole-2-ylidene) amides[33]. Fig(1-16) The Structure oct-2-ynoic acid (1,3-dihydro benzo imidazole-2-ylidene) amides Synthesis of Schiff base



Fig(1-16) The Structure oct-2-ynoic acid (1,3-dihydro benzo imidazole-2-ylidene) amides Synthesis of Schiff base

1.4 Schiff Bases Synthesis Methods

Schiff base metal complexes are often created by reacting the Schiff base with readily available metal salts in an ethanol media. Clearly easy and effective, this method. For the creation of Schiff base metal complexes, there are basically five possible synthetic pathways that can be found[34]

1.4.1. Interactions Between Amines and Aldehydes or Ketone

The original reaction that Schiff found is the most popular technique for prepared imines.[35-37]. The reaction form an aldehyde or ketone, together with prime amine and the removal of one water molecule. A reflux reaction is used for the combination of a carbonyl combination and an amine in order to remove the water from this reaction, which can be sped up through acid catalysis., Lewis acids like $ZnCl_2$, $TiCl_4$ or even mineral acids like H_2SO_4 or HCI and organic acids[38] Fig (1-17) General condination reaction to prepare Schiff base compounds

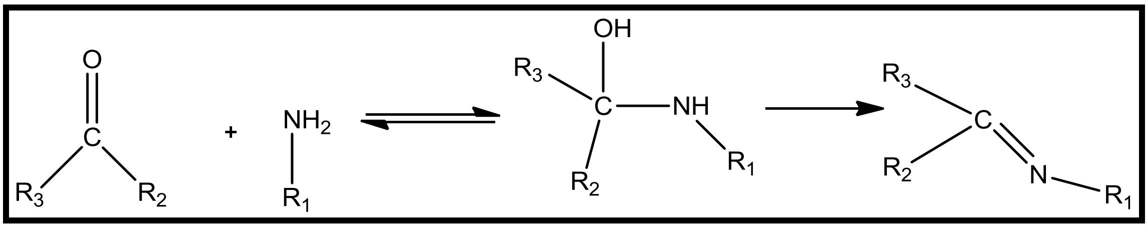


Fig (1-17)General condination reaction to prepare Schiff base compounds.

1 .4.2 The Use of Aerobic Oxidative Synthesis to Produce Schiff's Bases.

A simple method of producing(C=N) of amines and alcohols using tandem oxidative methods has recently been devised because aldehydes and ketones are often produced by oxidizing the corresponding alcohols Fig(1-18)oxidation synthesis of imine from alcohol and amine[39-41].

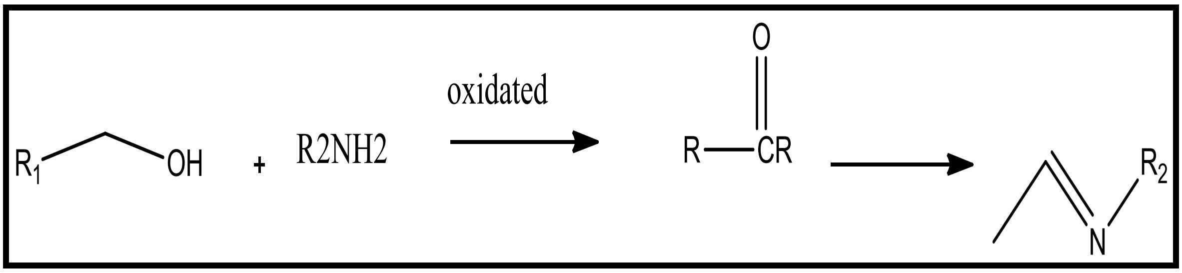


Fig (1-18)Oxidation synthesis of imine from alcohal and amine.

1.4.3. Cyanides are Given Organometallic Additives.

Aryl cyanides can be converted to substituted Keto imines by adding Grignard or organ lithium reagents. Depending upon the hydrolysis conditions use in to break down the metallic imine moderate, these Keto imines can then be elaborated to the timely ketones .[42] the Mg-imine intermediate is treated by anhydrousCH_3OH , producing very large yields of Keto imines Fig (1-19)Addition of organometallic reagents in to cyanides.[43].

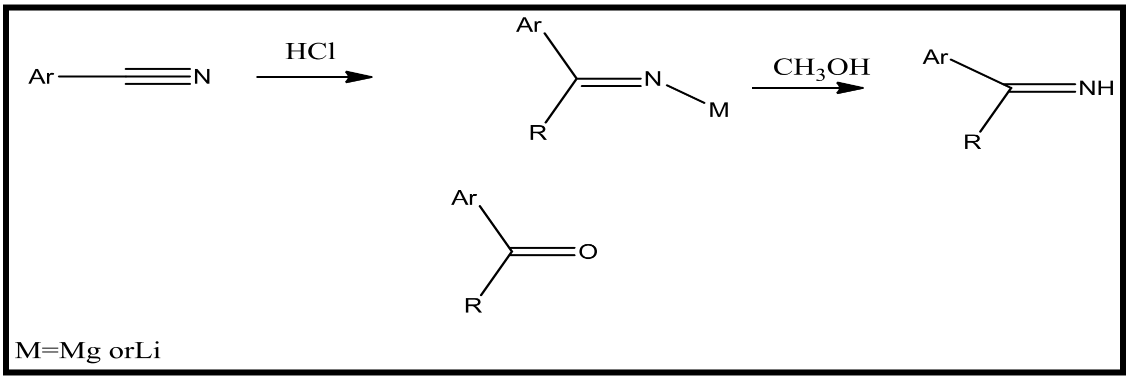


Fig (1-19)Addition of Organometallic Reagents to Cyanides.

1.4.4. Nitriles Interaction with Phenol and Phenol Ethers

Alkyl and aryl cyanides easily respond for phenols and their ethers to create Keto amines in a high yield when an acid catalyst is present. The response is passed outside by combining nitrile and phenolduring ether and saturating the solution through gassy HCl since $ZnCl_2$ must be used for minus than reactive phenols Fig(1-20) Combination of ketamine from phenol and nitriles.[44-46]

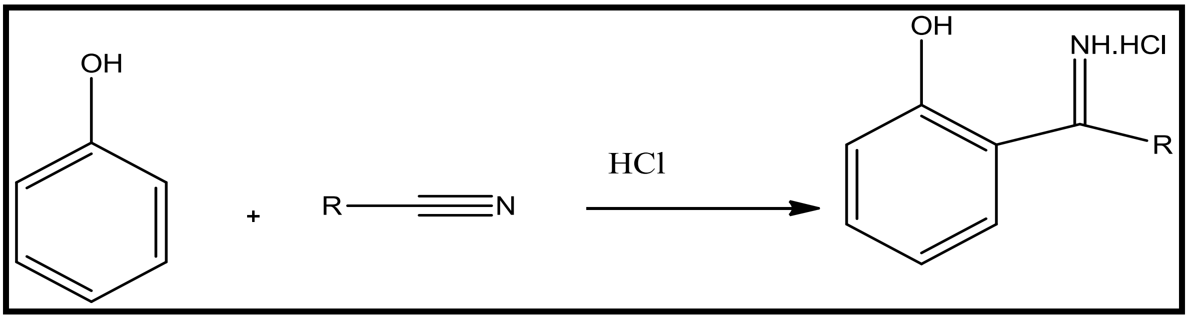


Fig (1.20) Synthesis of ketamine from phenol and Nitriles.

1.4.5. Amide Metal Reaction.

This method involved Reaction of Alkali metal with aromatic ketones to produce Ketamine compounds ,the range of this type of reaction expanded as shown in figure(1-21)that explained the oxidation of metal amine by using 2-bromo anisole [47].

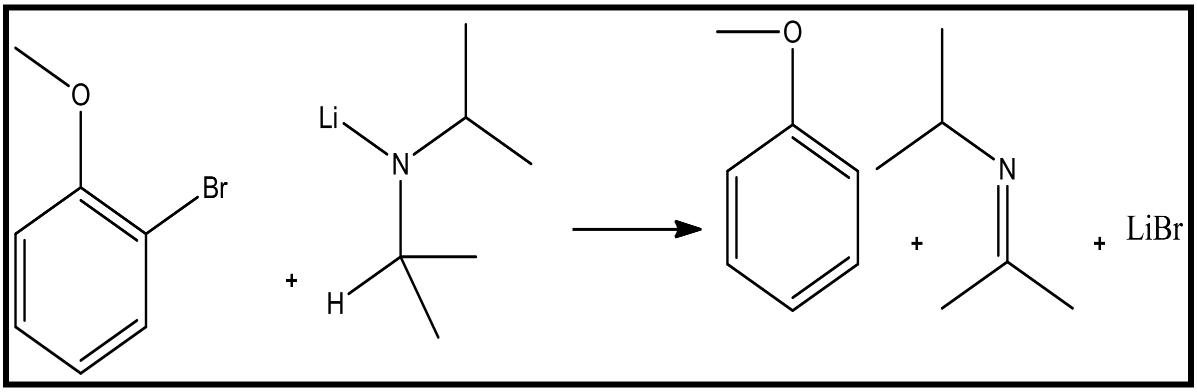


Fig (1-21) Oxidation of Metal Amine to Imine by 2-BromoAnisole

1.4.6 OtherMethods

Amino acid and sodium hypochlorite reactions can also produce imines. The creation of a chloramine intermediate as a by- product of this reaction which eliminates carbon dioxide and sodium chloride results in the imine Fig (1-22)Conversion of alpha amine acid in to imine.[48].

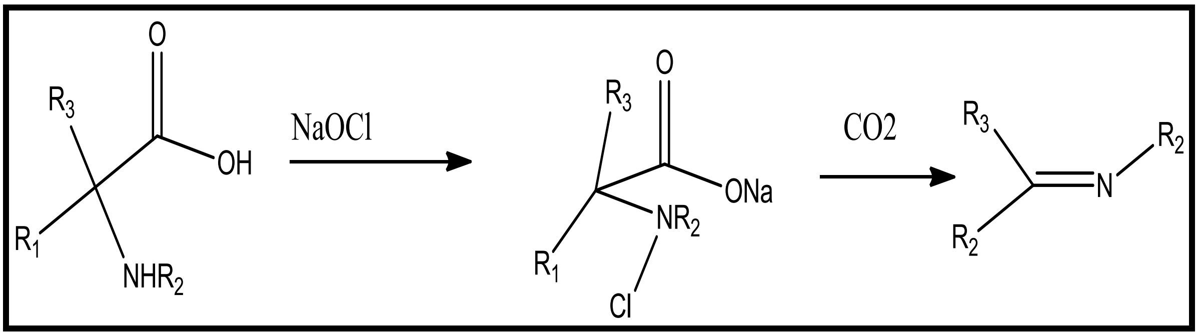


Fig (1-22) Conversion of alpha amine acid in to imine.

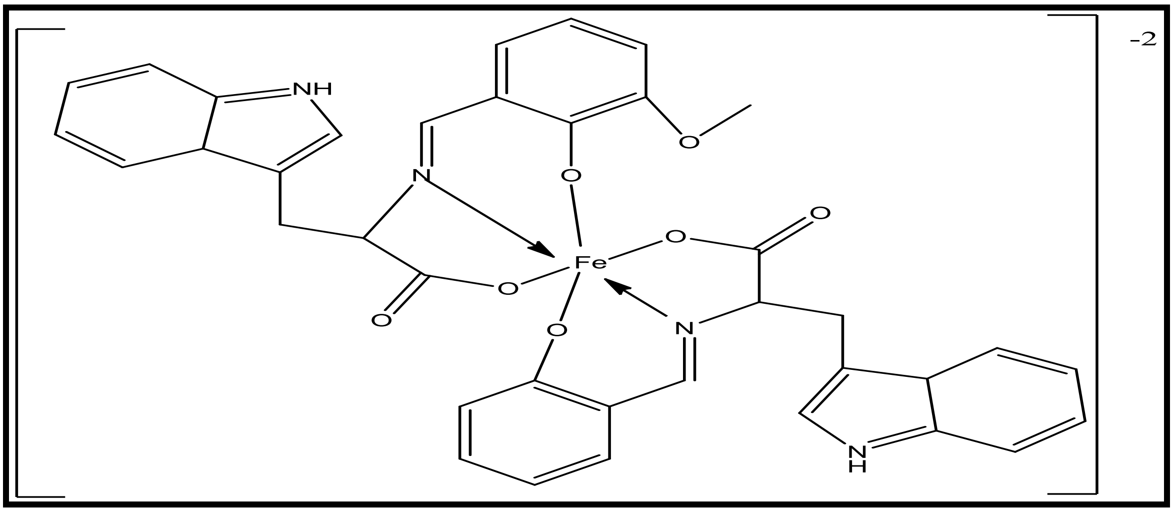
1.5 Metal Complex of Schiff Base

The Schiff base complexes of several metallic ions, primarily those in the first row of the periodic table, have attracted a lot of attention over the past twenty years. The significance of these complexes in a variety of implementation , such as medical, analytical, industrial, and catalytic activity in organic chemistry [49] Schiff base compounds function well as chelating agents by coordinating with the metal ion through the nitrogen atom of the azo 16ethane group. However, the inclusion of specific coordinating sites like hydroxyl and thiol groups in the skeleton of Schiff base ligands can improve the characters of the synthesized Schiff base ligand and support the building of stable six- or four different rings[50] As a result these, Schiff base ligands find their way in various applications as mentioned above.

1.5.1 Iron Complexes

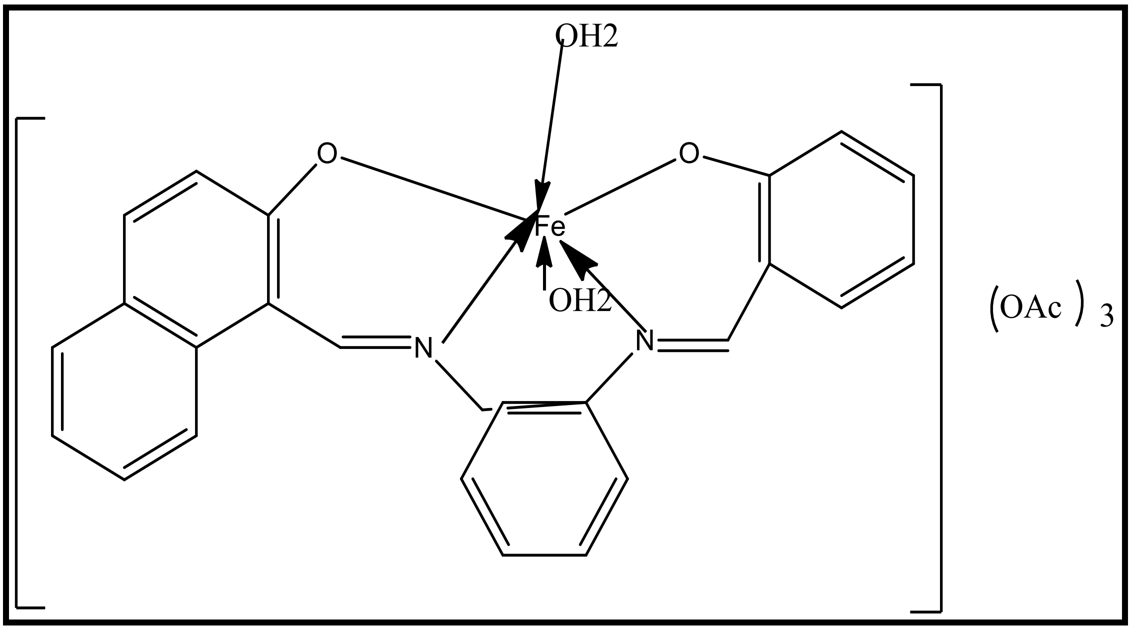
The most frequent oxidation states of Fe are +2 and +3 and in six-coordinate compounds with octahedral shape (Oh)[51] although the four-coordinate tetrahedral (Td)[52] .Hexa coordinate complexes, of iron with the electronic configuration d6 and d5 in high spin as well as lower spin in the two main oxidation states dominate the iron chemistry complexes are also found. Iron is included in the composition of the body of a living being because of its great importance and included in the composition of red blood cells, as they have the ability to carry oxygen and transport it inside the body[53, 54].

Iron forms complexes with different ligands and one of them is Schiff bases. For example, the Schiff base is ligand derived of the of 3-methoxysalicylaldehyde or 4-diethylaminosalicylaldehyde together α-amino acids were synthesized [55] Fig (1-23) Azo Methine Amino ligand for Fe(II)Complex.All Interaction of the got azomethine amino ligands with metallic salts created unique nano sized Fe(II)



Fig(1-23) Azo Methine Amino ligand for Fe(II)Complex.

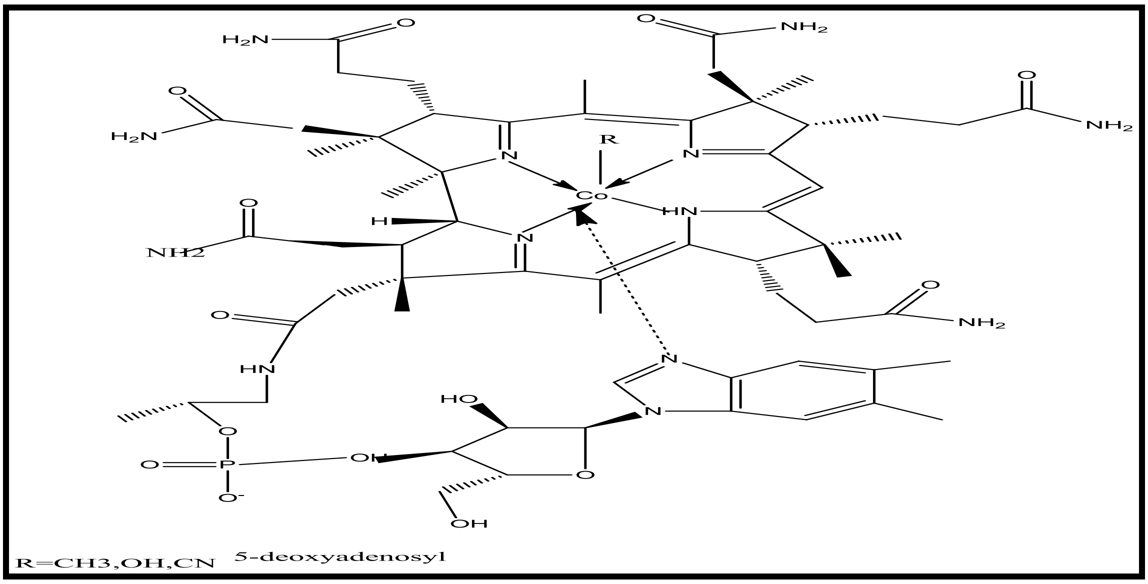
The process of creating Fe(III) complexes with Schiff base ligand that is produced by the from o-phenylenediamine, is limited to the stoichiometry of the type [ML $(H_2O)_2$] $(Oac)_3$Fig(1-24) Fe(III) complexes with Schiff base ligands. The metallic component were tested out for their ability to fight against germs and fungi[56].



Fig(1-24) Fe(III)Complexes with Schiff Base ligands

1.5.2 Cobalt Complexes

Cobalt compounds are part of the class of coordination complexes which are cobalt-containing ion bounds to different ligands to create the Schiff bases [57]. The oxidation states +2 and +3 of cobalt are the most prevalent. An important example of cobalt complex is its vitamin B12Fig(1-25) structure of vitamin B12 compound which is necessary for animals Similarly cobalt serves as a food for fungi ,algae and bacteria[58]



Fig(1-25)The structure of vitamin B12

The reaction of furane-2-carbaldehyde with 2-aminobenzoic acid produced the bioactive Co(II) composite with Schiff base Ligand , which has been produced and studied.[59] Through the coordination of the amine nitrogen atom, furan oxygen ring, and carboxyl group oxygen, octahedral geometry is formed[60].

Due to their use in bioinorganic implementation and thermal stability heterocyclic bases have been reported in a significant number of mixed ligand complexes. In addition to playing a crucial role in organic synthesis and catalysis, the complex has a wide range of applications in the biological, clinical, analytical, and industrial fields[61] It has been possible to create Co(II), ligands-metallic complexes from (PHEN) and (ASP) the outcomes Fig(1-26) Proposed Structure of the [Co (ASP)(PHEN)$(H2O)_2$]Cl_2

The ligands' status as bidentate chelating agents was validated by physical and spectroscopic data. Coordination took place between the two pyridine nitrogen groups in 1, 10-phenanthroline. Complexes of acetylsalicylic acid coordinate via the carboxyl and ester group ' carbonyl oxygen. A six-coordinate geometry is created by the chemicals. The following bacteria and fungi were tested for antimicrobial action using the mixed ligand metal complexes and free ligands: Escherichia coli, staphylococcus aureus, klebsiella pneumonia, pseudomonas aeruginosa, and candida spp. While not so great active than the free 1, 10-phenanthroline ligand, the mixed up ligand metal complexes had higher activity when compared to the not at work acetylsalicylic acid ligands[62].

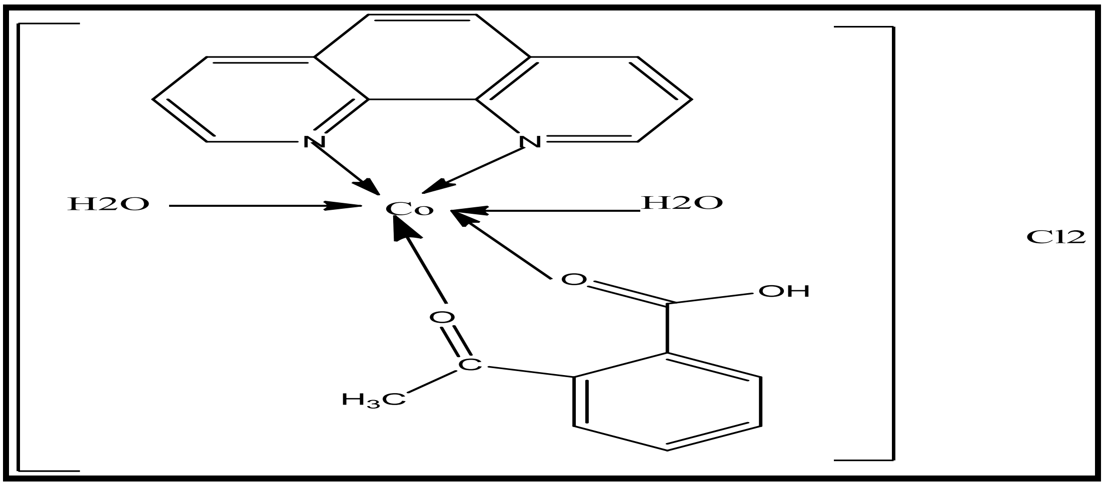


Fig (1-26) Proposed Structure of the [Co (ASP)(PHEN)$(H2O)_2$]Cl_2

1.5.3 Nickel Complexes

The coordination numbers 4, 5, and 6 exist for the nickel ion in nickel(II)-complexes. It is paramagnetic octahedral, trigonal bi pyramidal, quadratic pyramidal, and tetrahedral complexes are generally green or blue [63, 64] The diamagnetic quadratic planar nickel combined are often yellow, red, or brown in color[65] Various oxidation states of nickel can produce compounds, but the most important is +2[66].

An example of the Schiff base complexes is that produced by the condensation of 2-thiophenecarboxaldehyde and propyl amine to give the tetrahedral complex Ni(TNAP)$_2$Cl$_2$. Fig(1-27) shows the structure for Ni(TNAP)$_2$Cl$_2$ complexes [67].

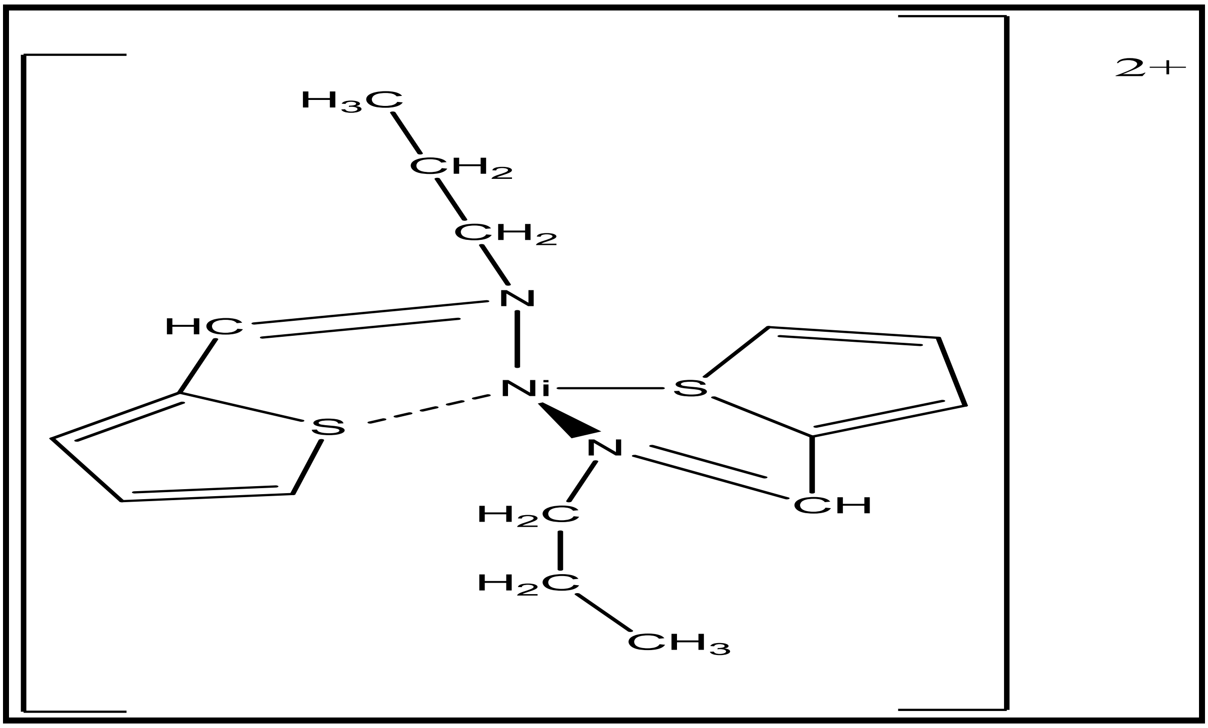


Fig (1-27) Structure of Ni(TNAP)$_2$Cl$_2$Complex

Schiff bases Complexes are produced from the presence biologically active tridentate amino acids (Alanine, Glycine, and Tyrosine) and Ni(II) have been synthesize characterized, and their potential to inhibit bacterial growth assessed. Effective against microorganisms including *Escherichia* coli, Staphylococcus aureus[68] Fig(1-28) The structure for amino acids Ni(II) complexes.

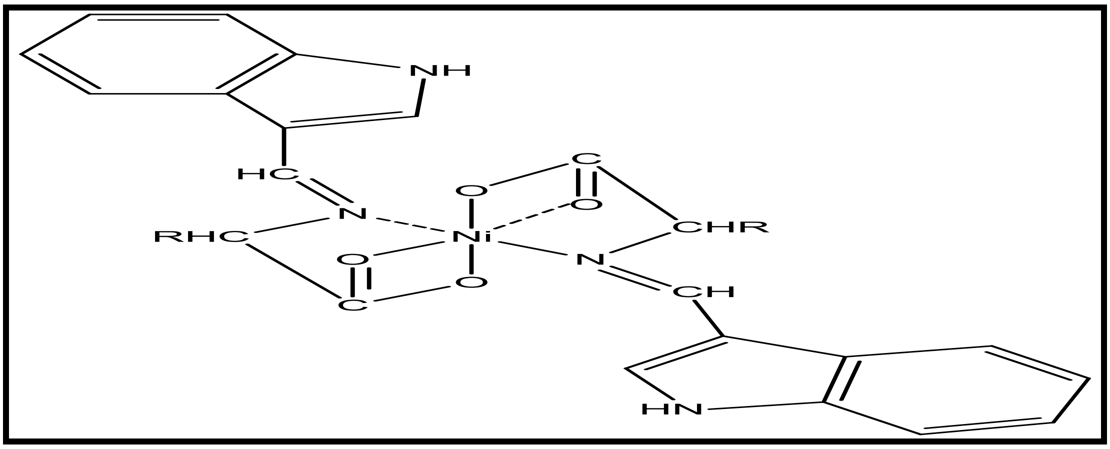


Fig (1-28) The Structure for Amino Acids Ni(II)Complex

1.5.4 Copper Complexes.

It was initially found in two ores, sulfides and oxides, and was first identified in 1776. It has a soft red appearance when it is metal[69]. Typically occurring oxidation states for Copper is +2[70]. Copper concentrations in Greenland ice were measured over a period of seven millennia, and results showed that values started to surpass natural levels around 2500 years ago.

Most Cu^{+2} compounds have four, five and six coordination numbers[71-73] Complexes of copper (II) exhibit d-d electronic transitions and charge transfer transitions, which give them a blue or green color (from metal to ligand and ligand to metal). A square planar form is preferred for tetra coordinated copper[74] N. K. Chaudhary and P. Mishra’s team produced an asymmetrical Schiff base ligand and Cu(II) using amoxicillin and formyl thiophene Fig (1-29) asymmetrical Schiff base ligand and Cu(II)[75].

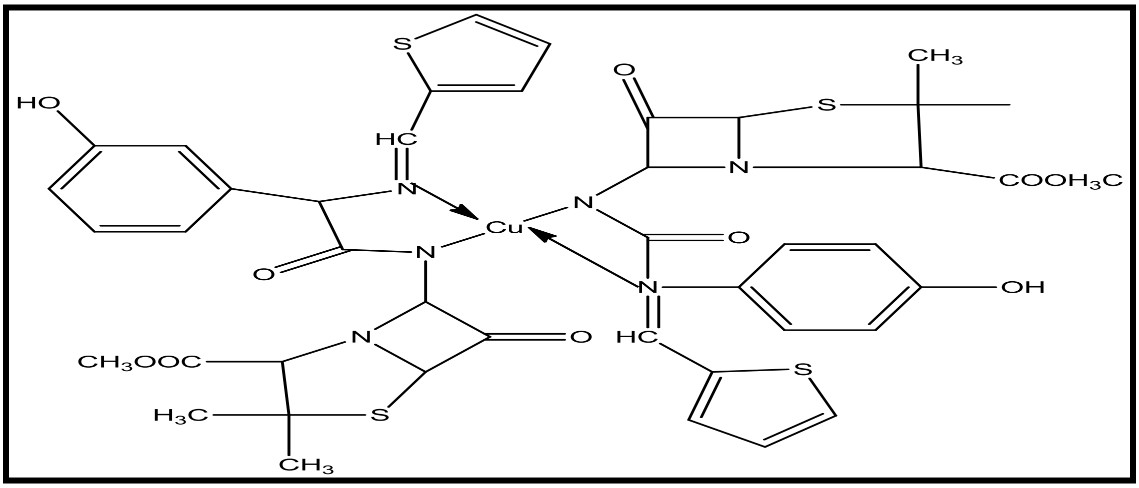


Fig (1-29) produced an Asymmetrical Schiff base ligand and Cu(II).

Salicylaldehyde and semi-aromatic diamines, which were made by reducing the respective dinitro compounds, were utilized to create novel Schiff base ligands, which were then used to create complexes with the Cu(II) metal ion Fig (1-30) Schiff base ligands and complexes with the Cu(II) metal ion[76].

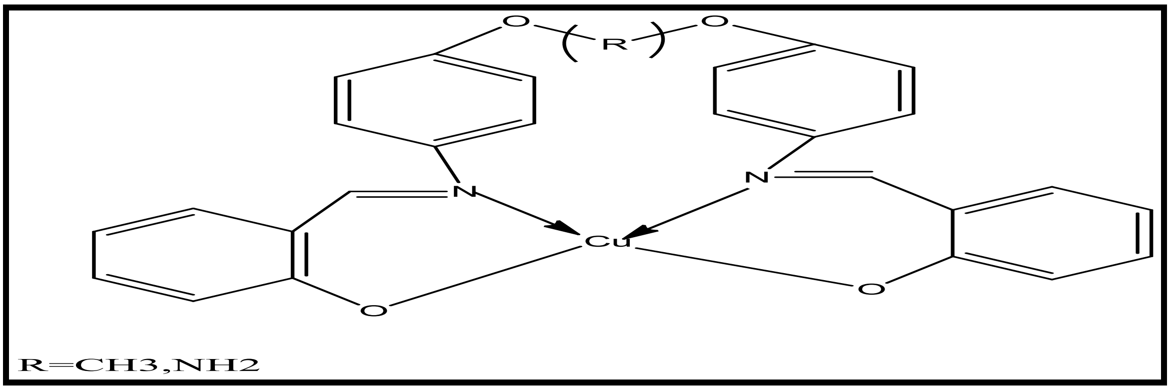
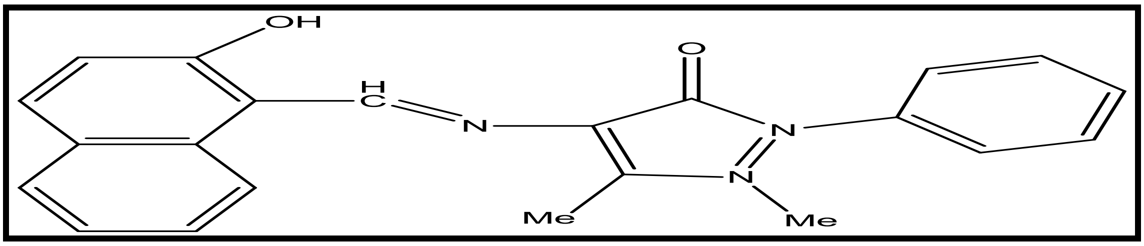


Fig (1-30) The structure Salicylaldehyde with semi-aromatic diamines with Cu(II)Metal ion

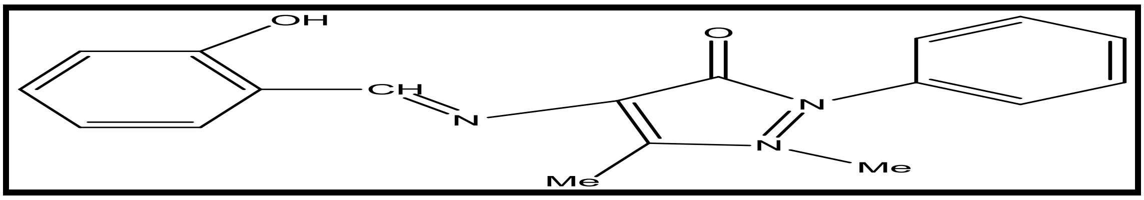
1.6 Applications of Schiff Bases

1.6.1 Corrosion Application of Schiff base

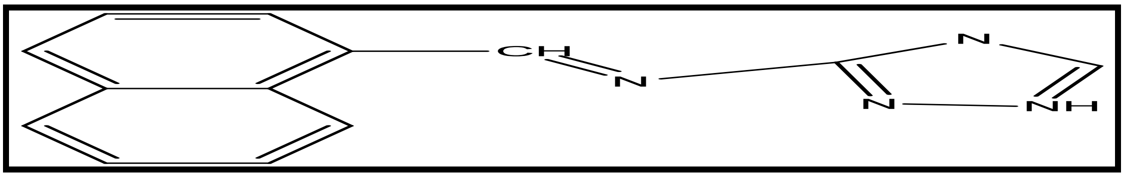
Corrosion is a chemical or electrochemical interaction that happens between materials, typically metals, and their environment, resulting in the corrosion of the materials and their properties are deteriorating. Corrosion is a problem that affects all uses of metals. Corrosion damage boosts the expense of maintaining and preserving the materials used. The creation of methods to control corrosion presents a challenge for researchers in this area. One of the appealing and most effective corrosion control methods for metals in contact with corrosive media is the use of an inhibitor. Inhibitors minimize corrosion by reducing metal consumption and dissolution[77]. Corrosion Inhibitors are frequently used to reduce the amount of undesirable base metal dissolution induced by these .The most of organic inhibitor compounds have heteroatoms like N, O, S, and many π bonds in their structures, aromatic rings, molecular planarity, electron distribution and steric variables is necessary for a corrosion inhibitor to operate well [78, 79] which facilitate adsorption on the steel surface to prevent corrosion in metallic components since they are frequently used to reduce metallic waste during production and the risk of material failure, both of which can cause the abrupt shutdown of industrial operations and result in additional costs, corrosion inhibitors are very useful anti-corrosion were performed on polydentate Schiff base composites (PSCs), act as corrosion resistance for iron in aerated 2.0 M HNO_3 characteristics of the inhibitor/surface[80] Fig(1-32) anti-corrosion were implemented on five polydentate Schiff base compounds (PSCs)



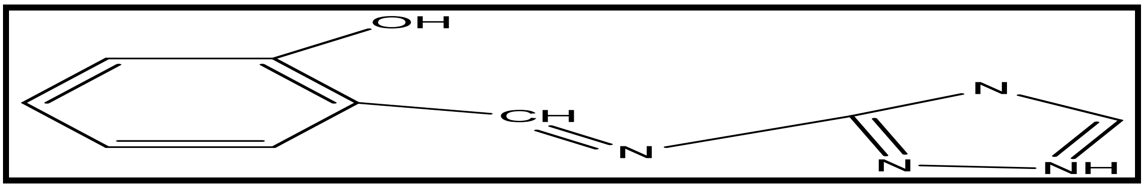
Fig(1-31) The structure of 4-(2-Hydroxynaphthylideneamino)antipyrine



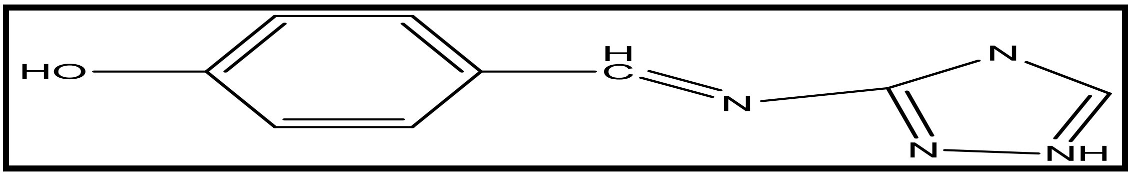
Fig(1-32) The structure of 4-(2-Hydroxybenzylideneamino)antipyrine



Fig(1-33) The structure of 3-(2-Hydroxynaphthyldieneamine)-1,2,4 triazole



Fig(1-34) The structure of 3-(2-Hydroxbenzylideneamine)-1,2,4-triazole



Fig(1-35) The structure of 3-(4-Hydroxybenzylideneamimo)-1,2,4-triazole

1.6.2 Anticancer Application of Schiff Base.

Cancer is a type of cell disease that, in some cases, causes those cells to develop uncontrollably. Chemotherapy and surgery are available treatments for cancer[81] The negative side effects of chemotherapy are its downside [82]. Therefore, chemical compounds have been used to treat cancer. For example, The reflux thickening of p-phenylenediamine with 2-hydroxy-1-naphthaldehyde and benzaldehyde, a novel Schiff base ligand known as 2-(€-((4-((€-benzylidene)amino)phenyl)imino)methyl)-naphthalene-1-ol was created. In order to create metal complexes, the ligand was combined with the metal salt $CoCl_36H_2O$. Co(II). When the ligand and its metal

complexes were examined in vitro anticancer effects on the PC-3, $SKOV_3$, and HeLa tumor cell streak, they showed more antitumor effects than commonly prescribed medications like cisplatin, estramustine, and etoposide Fig (1-36) anticancer Schiff base ligand and Co complex (€-((4-((€-benzylidene)amino)phenyl)imino)methyl)-naphthalene-1-ol[83]

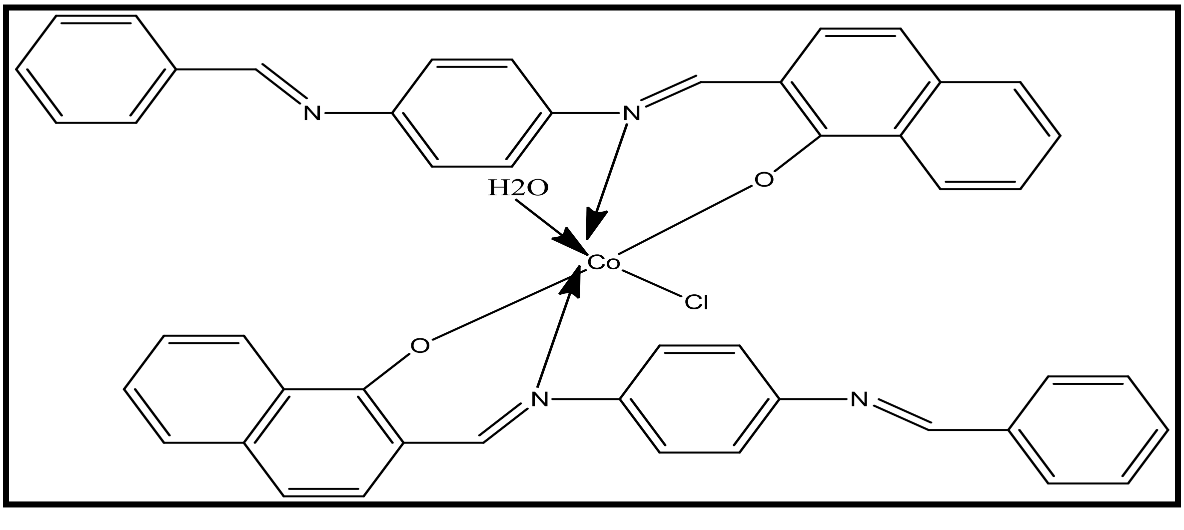
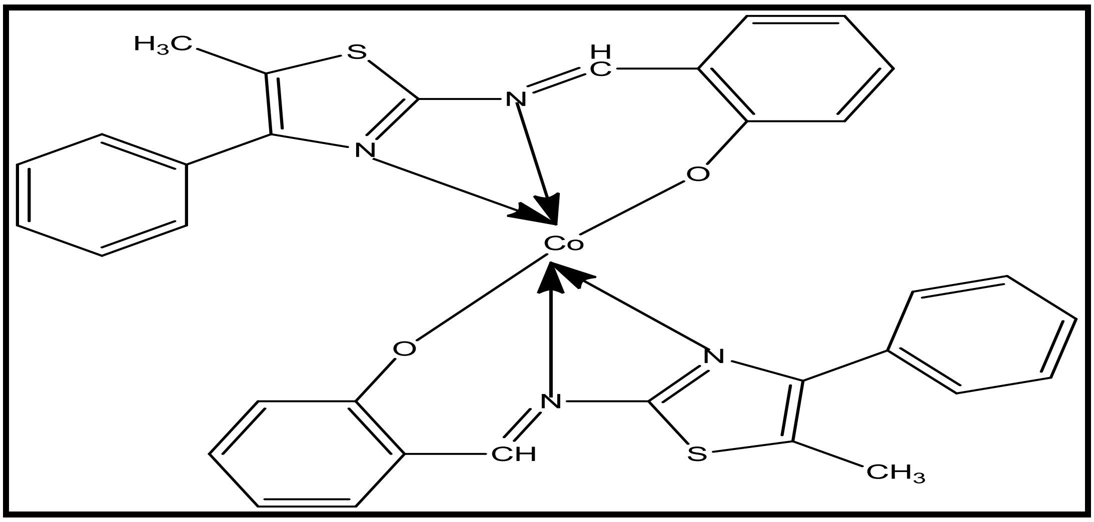


Fig (1-36) anticancer Schiff base ligand and Co complex (€-((4-((€-benzylidene)amino)phenyl)imino)methyl)-naphthalene-1-ol

In addition, the condensation of salicyaldehyde with 2-amino-4-phenyl-5-methyl thiazole, a Schiff base ligand was produced . The Co(II) complex was produced also. This complex was investigated against four dissimilar human tumor cell lines: breast cancer MCF-7, liver cancer HepG2, lung carcinoma A548, and colorectal cancer HCT116[84]. The anticancer action of the synthesized compounds were compared with that of doxorubicin, which was used as a reference medication, Fig(1-34) anticancer salicyaldehyde with 2-amino-4-phenyl-5-methyl thiazole, a Schiff base ligand and Co(II).



Fig(1-37) Anticancer Salicyaldehyde with 2-Amino-4-phenyl-5MethylThiazole, a Schiff Base ligand and Co(II)

The Aims of the project

5- Synthesis of Three Schiff base ligands (L_1- L_3)derived from Quinones with different amine.

2- preparation The complexes of(L_1-L_3)ligands with transition metal ion like Fe(II), Co(II), Ni(II)and Cu(II) .

3-Characterization of ligands and their synthezid metal complexes.

4- Studying the anticancer activity of some of the prepared compounds.

5- Studying the anticorrosion activity of some of the prepared compounds

Chapter Two

Experimental Part

The first part of this chapter constitutes of the used chemicals and the instruments. While the second part includes the synthesis of Schiff base ligands (L_1, L_2 and L_3) and their metal complexes.

2-1Chemicals

All of the chemicals that used with their molecular formula, suppliers and degree of purity were shown in table (2-1).

Table(2-1) Chemicals with their molecular formula, their suppliers and degree their of purity

No	Material	Molecular Formula	Company	purity
1	2,5-Dihyroxyl1,4 benzoquinone	$C_6H_4O_4$	Shanghai Macklin biochemical	98%
2	9,10 phenanthrene quinone	$C_{14}H_8O_2$	Shanghai Macklin biochemical	95%
3	2-Amino thiophenol	C_6H_7NS	Solarbio	98%
4	5-Amino -2-methylphenol		MACKLN	97%
5	Hydrochloric Acid	HCl	Thoms Baker	35%
6	Nickel(II) chloride hexa hydrate	$NiCl_2.6H_2O$	CDH	98%
7	Iron (II) chloride dihydrate	$FeCl_2.6\ H_2O$	CDH	98%
8	Cobalt (II) chloride hexa hydrate	$CoCl_2.6H_2O$	CDH	98%
9	Ethanol Absolute	C_2H_5OH	ECOCHEM	99.98%
10	Sodium Hydroxide	$NaOH$	CDH	97%
11	Cupper (II) chloride di hydrate	$CuCl_2.6\ H_2O$	Merck	97%

2.2 Instrument

2.2.1 Melting Point Apparatus.

SMP30 Stuart melting point apparatus was used. It is available at College of Science for women, University of Babylon.

2.2.2 FT-IR Spectra-Photometer.

FT-IR spectra for ligands and complexes used form (4000-400)were obtained by FT-IR – 8400S spectra-photometer. College of Science for women, University of Babylon. .

2.2.3 Conductivity Measurement.

The conductivity of the complexes was measured using WTW Cond 7300 digital conductivity meter. College of Science for women, University of Babylon..

2.2.4 UV- Visible Spectra Measurement.

UV-vis spectra of the prepared compounds were measured using PEAK/ INSTRUMENTS (C-7200) , College of Science for women, University of Babylon..

2.2.5 ^{1}H NMR Spectra.

These spectra were measured at University of Basra College for Education for pure Sciences using Bruker spectrometer instrument operating at (400Hz).

2-2-6 Mass Spectrometric.

Mass measurement in Iran Mashhad University of Medical Sciences.

2.2.7 Magnetic Moment Measurements.

Magnetic moments were determined at 25 °C with a magnetic susceptibility balance (Sherwood Scientific). This was carried out at the College of Science, AlMustansiriyah University

2.2.8 Thermal Analysis.

The thermal analysis was measured for all the compounds. differential thermal gravimeter (DTG-160-FC-60A) was used. It is available at College of Science for women, University of Babylon..

2.2.9 Atomic Absorption Spectrometry.

The metal contents in the complexes was carried out using Nova 350 Spectrophotometer. Ibn Sian Laboratories Ministry of Industry.

2.3 Synthesis of (L_1-L_3)Ligands

2.3.1 Synthesis of Schiff Base Ligand (L_1)

9,10-phenathrenquinon (1g, 4.8m mol) mixed with 2-aminothiopenol (0.6g,4.8mmol) in absolute ethanol (25 ml). to this mixture, three drops of HCl were added. The mixture was left under reflux for three hours. green precipitate of L_1 was collected, washed with water and ethanol and recrystallized from hot ethanol.

2.3.2 Synthesis of L_2

Absolute ethanol (25 ml) was used to dissolve 9,10-phenathrenquinon (1g, 4.8mmol). Three drops of hydrochloric acid and 0.5 g of 5-amino-2-methylphenol were added to the 9,10-phenathrenquinon solution. For four hours, the mixture was placed in reflux. It was possible to generate a brown L_2 precipitate that was washed with ethanol and water before recrystallizing.

2.3.3 Synthesis of L_3

2,5-dihydroxy-1,4-benzoquinon (1g, 7.1mmol) in ethanol (25ml) was mixed with 5-Amino -2-methylphenol (1.7g, 14.2mmol).The mixture left under reflux for six hours. The brown precipitate of L_3 was filtrated, washed with water and ethanol and recrystallized of ethanol.

2-4 Synthesis of Complexes

2.4.1 Synthesis From Complexes with L_1

All the metal complexes were synthesized by dissolving L_1 (0.5 g, 1.5 mmol)) in 20ml ethanol and mixing it with chloride salts Fe(II), Co(II), Ni(II) and Cu(II) hydrated chloride salts in (1:1) ligand: metal molar ratio. The reaction was refluxed for (12) hours. Then the metal complexes were formed which were filtered , washed with water and ethanol. Table (2-2) illustrates the used amounts of L_1 and the metal salts.

Table (2-2) Illustrates the Used Amounts of L_1 and the Metal Salts

Complex	Weight of metal salt	Weight of ligand L_1
[Fe (L_1)Cl_2 H_2O].3H_2O	0.3g, 1.5 mmol	0.5 g, 1.5mmol
[Co(L_1)Cl_2H_2O].3H_2O	0.3g, 1.5mmol	0.5g, 1.5mmol
[Ni(L_1)Cl_2H_2O].3H_2O	0.3g,1.5mmol	0.5g,1.5mmol
[Cu(L_1)Cl_2H_2O].3H_2O	0.2g,1.5mmol	0.5g,1.5mmol

2.4.2 Synthesis of Complexes withL_2

Four metal complexes were synthesis by refluxing L_2 (0.5 g., 1.5mmol) with Fe(II), Co(II) and Ni(II) hydrated chloride salts in (1:1) ligand: metal molar ratio using in ethanol 20ml as a solvent. The reaction mixtures were refluxed for (16) hours. The brown complexes were formed which were filtered , washed with water and ethanol. Table (2-3) illustrates the used amounts of L_2 and the metal chloride salts .

Table (2-3) Summarizes the Amount used of L_2 and the Metal Salts to Prepare the Metal Complexes with L_2

Complexes	Weight of metal salt	Weight of ligandL_2
[Fe (L_2)Cl.2H_2O] H_2O	0.3g, 1.5 mmol	0.5g, 1.5mmol
[Co(L_2)Cl.2H2O] H_2O	0.3g,1.5mmol	0.5g,1.5mmol
[Ni (L_2)Cl.2H_2O] H_2O	0.3g,1.5mmol	0.5g,1.5mmol

2.4.3 Synthesis of Complexes with L_3

All the multiplexes were synthesized by dissolving L_3 (0.5 g, 1.42mmol)) in 20ml ethanol and (2:1) ligand: metal molar ratio. The reaction was refluxed for (16) hours. Then the metal complexes were formed which were filtered , washed with water and ethanol. Table (2-4) illustrates the used amounts of L_3 and the metal salts.

Table (2-4) Illustrates the used Amounts of L_3 and the Metal Salts Prepare the Metal Complexes with L_3.

Complexes	**Weight of metal**	**Weight of ligandL_3**
$[Fe_2(L_3).(H_2O)_6]$	0.5g, 2.8 mmol	0.5g, 1.4mmol
$[Co_2(L_3).(H_2O)_6]$	0.6g , 2.8 mmol	0.5g ,1.4mmol
$[Ni_2(L_3).(H_2O)_6]$	0.6g, 2.8mmol	0.5g,1.4mmol
$[Cu_2(L_3).(H_2O)_6]$	0.4g, 2.8mmol	0.5g,1.4mmol

2-5 Cytotoxicity Assay

The non-malevolent breast epithelial cells MCF10A and the human being breast cancer cell line MCF7 were obtained since the Nationwide Cell Bank of Iran (Pasteur Institute). Lockups were cultured using Gibco's RPMI-1640 and DMEM:F12 moderate, 10% FBS, and (100 U/ml pencillin and 100 g/ml strep tomycin). at 37 °C in moistened air covering 5% CO_2, cells were way through trypsin/EDTA (Gibco) and (PBS) solution. The cells were full-grown as 3D colonies using the same monolayer cell state liquids and conditions. Study the energy of MTT cells. Lockup growing and viability were measured by the MTT [3-(4, 5-dimethylthiazol-2-yl)-2, 5-diphenyltetrazolium Bromide] test. In a nutshell, cells were isolated, triedpsinized, After creating a monolayer, cells were treated to 300-18 g/ml of the complexes over 24 hours on 37 °C in 5% CO_2. Later the treatment (24 h), the supernatant was with haggard, then 200 /fit of MTT solution phosphate-buffered saline (0.5 mg/ml in [PBS]) was add , leaving the monolayer culture in the original plate unaltered. The dish was then brood for a extra 4 h at 37 °C. Thru extracting the cell supernatant and adding 100 of dimethyl sulfoxide to each well, MTT solution was made. After being treated at cells were completely dissolved in crystals. at 37 °C on a shaker. Using an Elisa reader, absorbance at 570 nm was used to measure cell viability (Model wave xs2, Bio Tek, USA).

2-6 Corrosion Measurement

A computer, thermostat, magnetic stirrer, potentiostat (EmStat 4s, Palm Sens, Netherlands), and galvanostat are all components of the potentiostat setup. The Pyrex cell has a capacity of (250 ml) and is made up of interior and external bowls. The electrochemical corrosion cell is made up of three electrodes. The working electrode is carbon steel, the secondary electrode is a platinum electrode with a length of 10 cm, and the reference electrode is a saturated calomel (Hg/Hg_2Cl_2 sat.KCl). All through fifteen min, the employed electrode was flooded in the test sol to create a firm state exposed tour potential (Eocp). After that, measurements of electrochemistry were made in a potential range of (200) mV. The tests were carried out in a cooling-heating circulating water bath at 298 K.

The Corrosion Cell

Pyrex corrosion cell with a capacity of (250ml) Contains three electrodes and a corrosion cell in two vessels, one internal and one external. In a vessel inside the body, three electrodes and a thermostat were replaced..

The three electrodes can be explained as follows:

A. Allowing to the potential of a place electrode, a reference electrode was applied to calculate the working electrode potential. Reference electrode potential is a well-known and consistent value. Double tubes are combined in it. ; the inside tube contains Hg/Hg_2Cl_2 sat .KCl, The reference electrode stand at a distance 2 mm from the working electrode

B. The length of the Secondary Electrode, which is made of high purity platinum metal, is (10 cm).

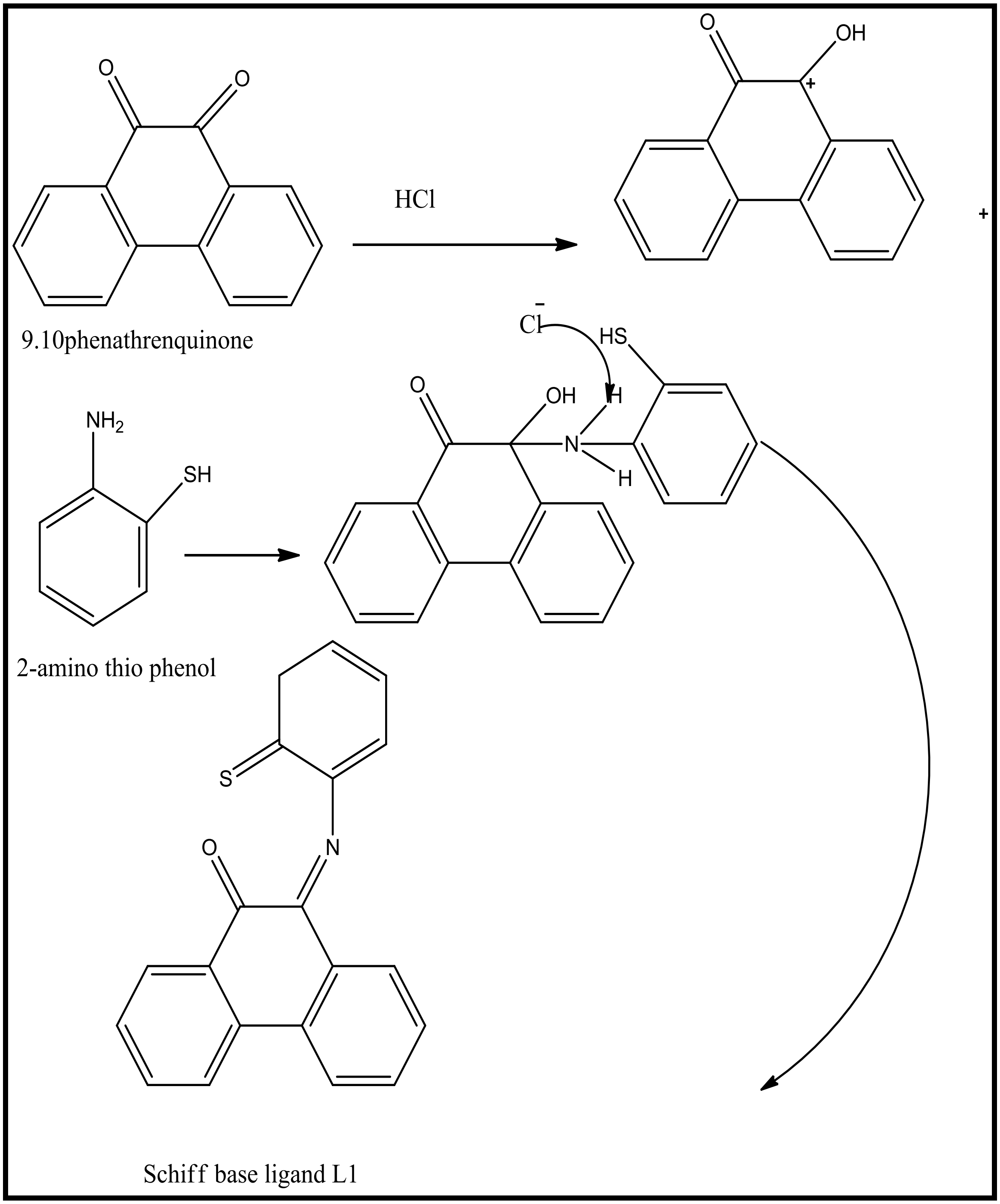
C. The Operational Electrode is the object of study, and its potential needs to be determined. This electrode was made from 20 cm of metallic wire and involved to the sample that was placed.

Chapter Three

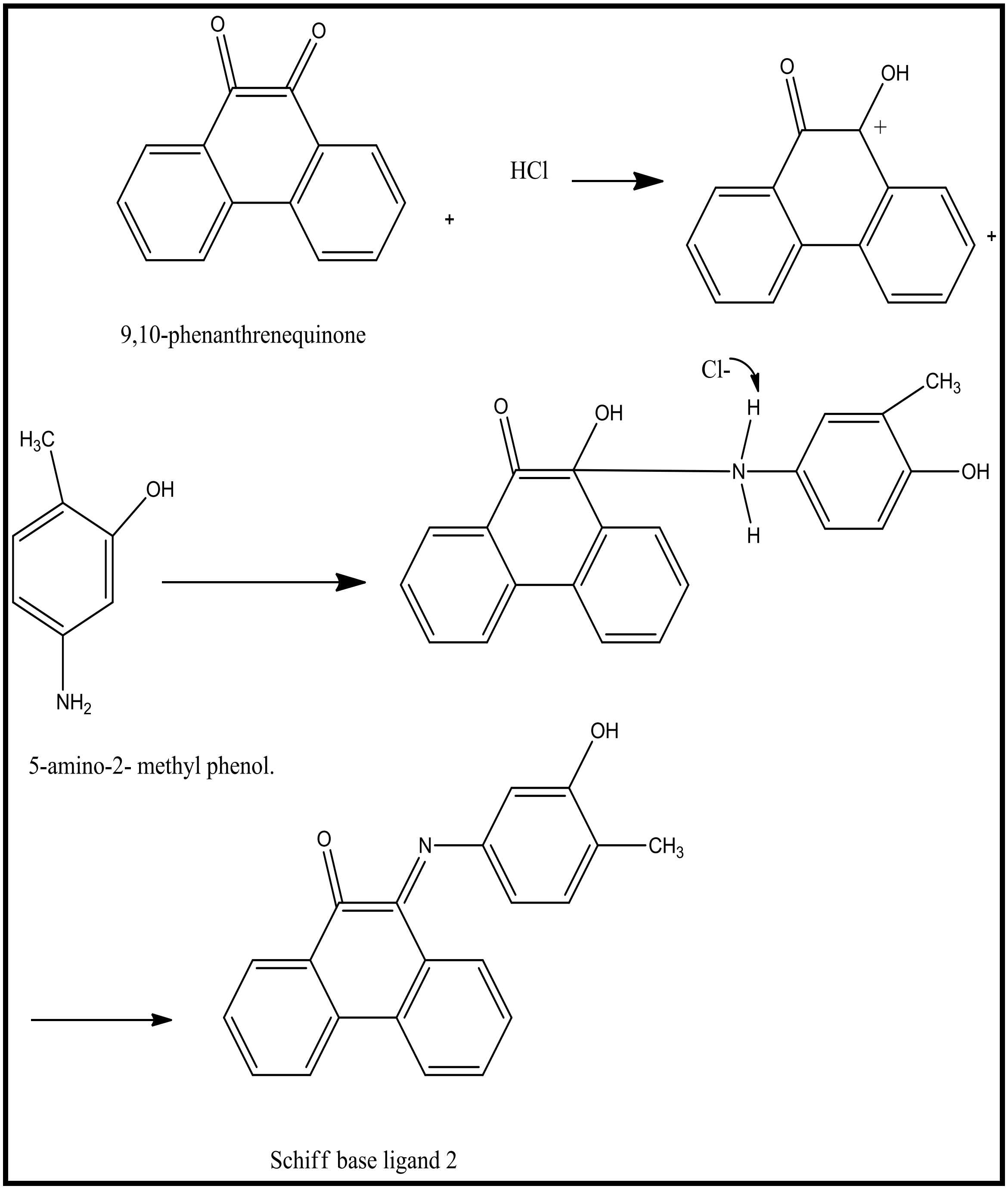
Results and Discussion

3.1Synthesis of Schiff Base Ligands L_1,L_2 and L_3

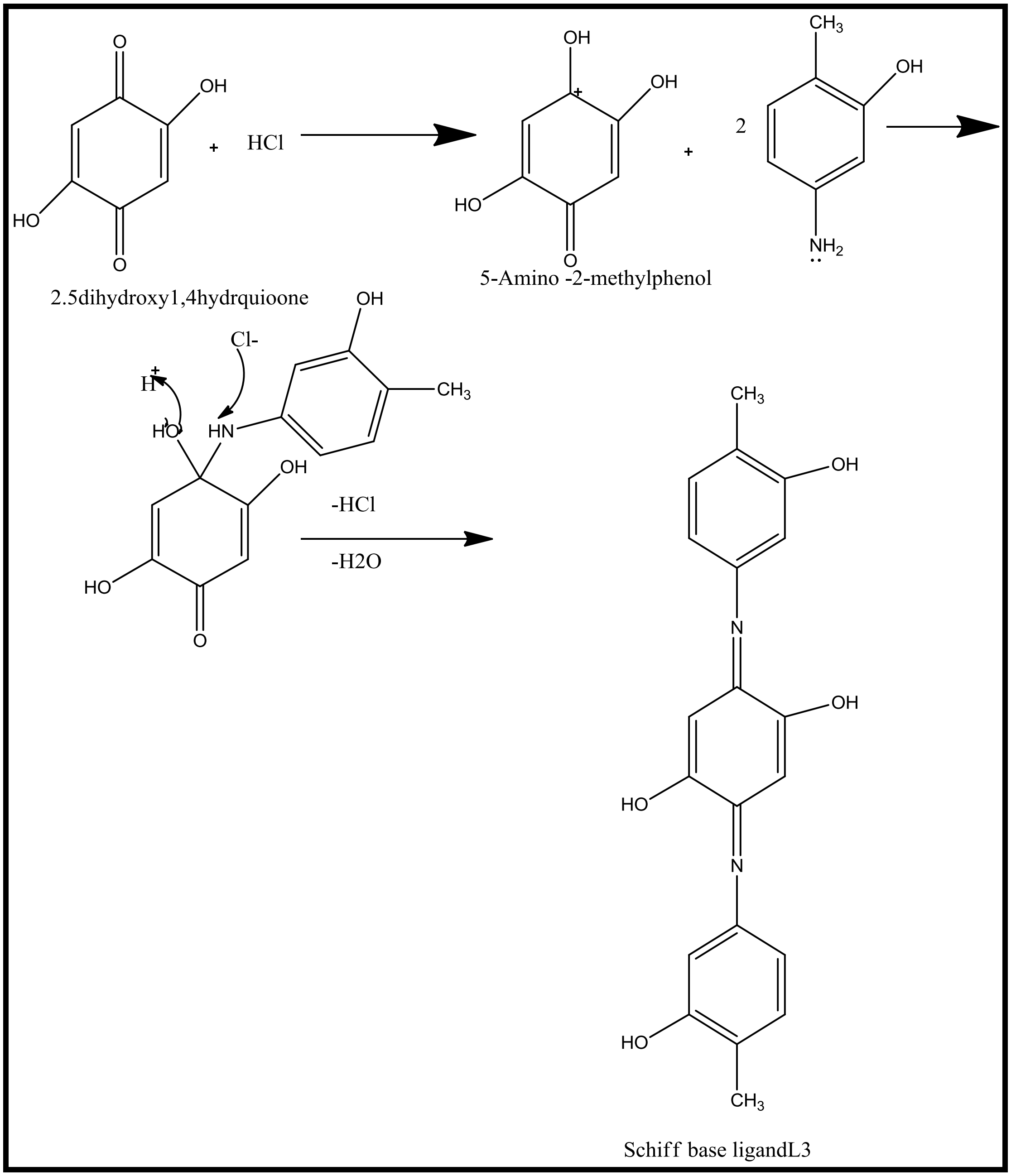
By reacting commercially available ketones, 9,10-phenanthrenequinone and 2,5-dihydroxy-1,4-benzoquinon, with 2-aminothiopenol and 5-amino-2-methyl phenol respectively. The Schiff base ligands L_1, L_2, and L_3 were prepared . The amines and the ketones combination reactions occur under the use of hydrochloric acid which act as a catalyst. This acid successfully catalyzed the reaction of both ketones with 2-aminothiophenol and 5-amino-2- methyl phenol. Where the latter acts as a nucleophile attacking the electrophiles 9,10-phenanthrenequinone and 2,5-dihydroxy-1,4-benzoquinon, leading to the formation of the Schiff bases and releasing of water molecule. The protonation of an oxygen atom in the carbonyl group, which produces the hydroxyl group and the carbonium ion, is the first step in the reaction's mechanism (electrophile). The attack of the nucleophile (represented by the primary amine group in the 2-aminothiophenol and 5-amino-2- methyl phenol molecules) favors this geometry of intermediate compound to attack it more than the 9,10-phenanthrenequinone molecule due to the low steric hindrance effect in the synthesis of the intermediate compound . When too much hydrochloric acid is added, a protonation reaction occurs that causes the water molecules to be released from the intermediate product. Deprotonating of amine protons to create an imine group (C=N) and give the target compound its final structure of a Schiff base is the procedure that completes the reaction. The following mechanism illustrates the ligands synthesis.



Scheme (3-1) Mechanism for the Synthesis of Schiff Base ligandsL_1



Scheme (3-2) Mechanism for the Synthesis of Schiff Base ligandsL_2

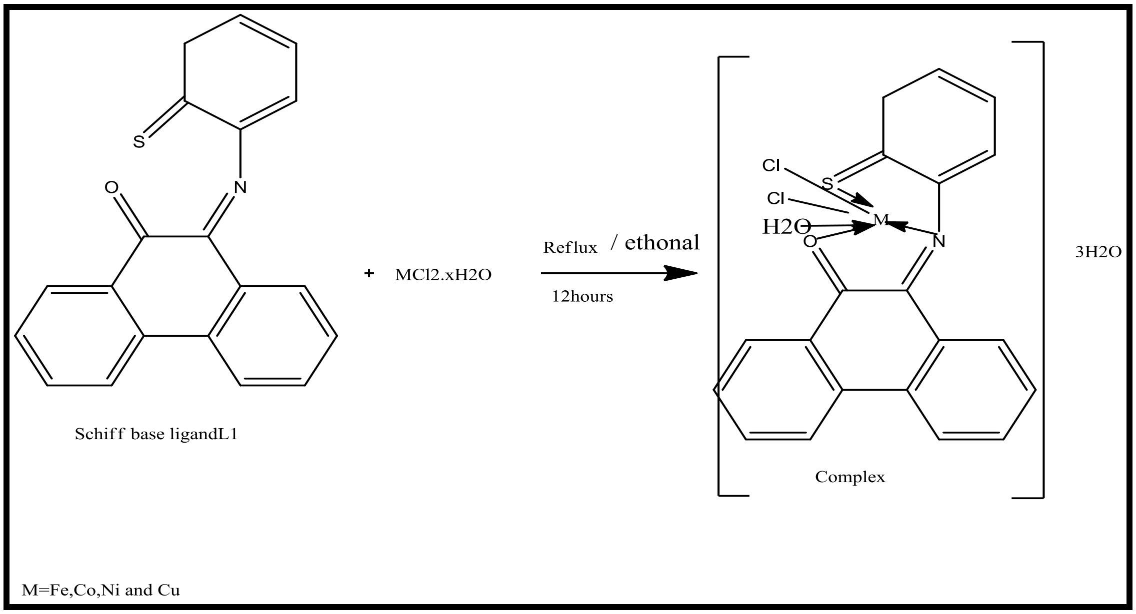


Scheme (3-3) Mechanism for the Synthesis of Schiff Base ligandsL_3

3.2 Synthesis of Metal Complexes

3.2.1 Metal Complexes with L_1

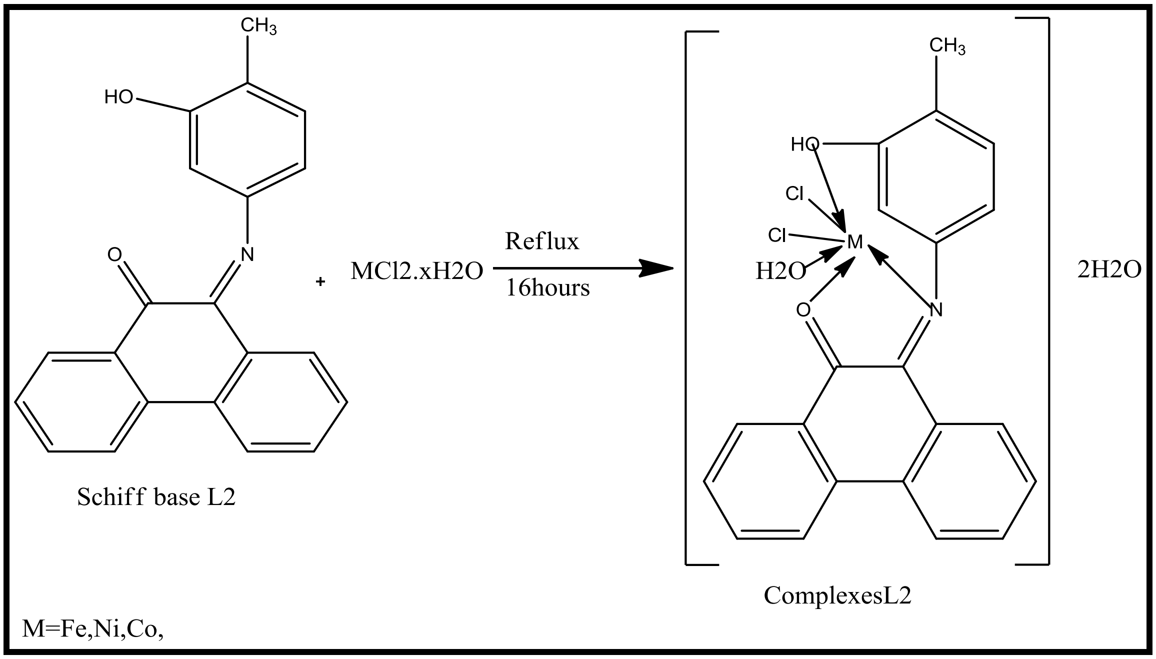
Scheme(3-4)showed Refluxing between (L_1)Ligand and metal chloride salts of Fe(II), Co(II) Ni(II)and Cu (II) at mole ratio (1:1)(M:L) to produce The solid Complexes of This Ligand .



Scheme(3-4) shows the Metal Complexes Synthesis withL_1

3.2.2 Metal Complexes with L_2

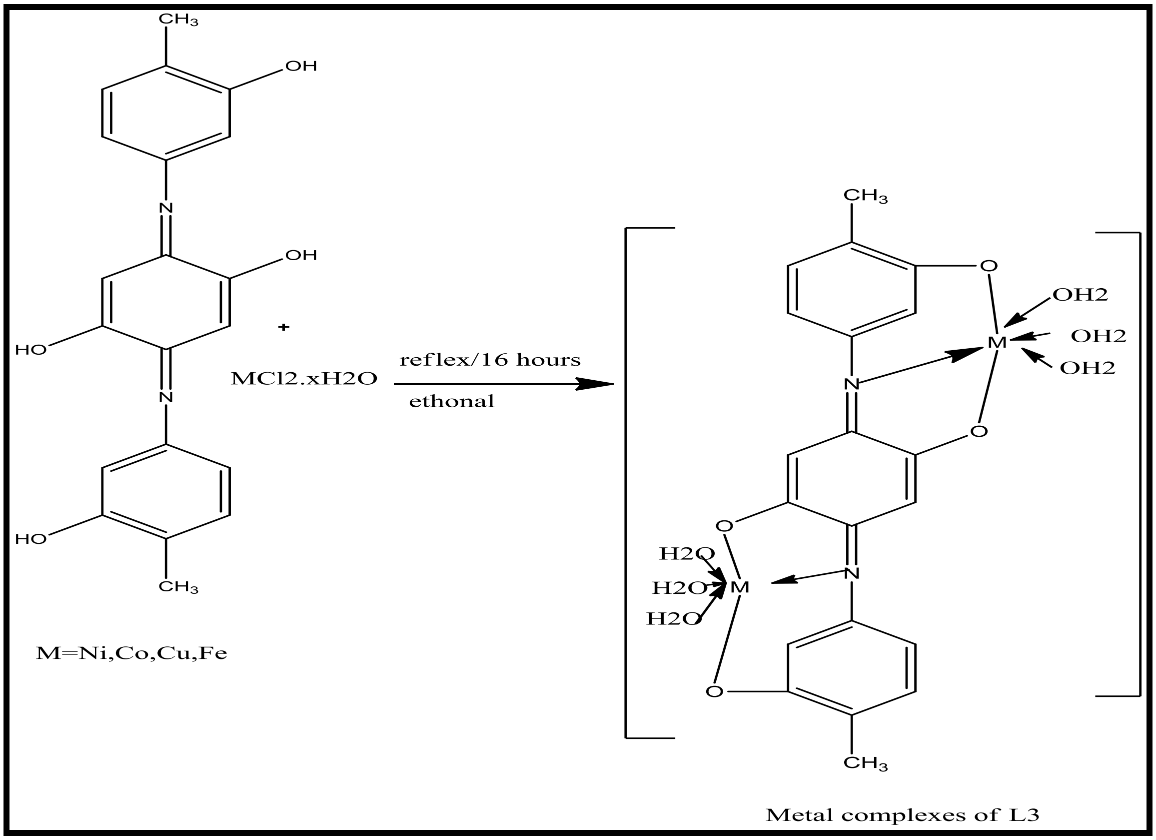
Metal complexes were produced by reacting L_2 with Fe(II), Co(II) Ni(II)and Cu (II) chloride salts in ethanol also in 1:1melat ligand molar ratio. scheme(3-5) shows the synthesis steps of L_2 metal complexes.



Scheme (3-5) metal Complexes Synthesis with L_2.

3.2.3 Metal Complexes with L_3

Metal complexes were produced by reacting L3 with Fe(II), Co(II) Ni(II)and Cu (II) chloride salts by using ethanol as solvent at mole Ratio (2:1)(metal:L_3) by reflexing each mixture for(16)hours ,as shown in Scheme (3-6)



Scheme(3-6)Show the metal Complexes Synthesis with L_3.

All of the synthesized compounds are soluble in most organic solvents and insolvable in water. Using analytical techniques such as ^{1}H-NMR,Mass, FTIR, UV-Vis, thermal analysis, and atomic absorption, the synthesis of the ligand and their complexes was confirmed.

Table (3-1) Some Physical Properties of the Prepared ligands and their Metal Complexes

Compound	**Color**	**m.p °C**	**Yield %**	**M.Wt g/mol**
LigandL_1	green	133-132	73%	315 .39 g/mol
$[Fe(L_1)Cl_2H_2O]3H_2O$	green	190-189	73%	430.71 g/mol
$[Co (L_{1)}Cl_2.H_2O]3H_2O$	green	150-152	42.7%	445 g/mol
$[Ni (L_1)Cl_2H_2O]3H_2O$	green	209-207	44%	446.57 g/mol
$[Cu(L_1)Cl_2H_2O]3\ H_2O$	blue	156-155	51%	451.43 g/mol
Ligand L_2	brown	183-181	97%	313.35 g/mol
$Fe (L_2)Cl .2H_2O]\ H_2O$	brown	210-208	77%	439.67 g/mol
$[Co(L_2)Cl.2H_2O]\ H_2O$	brown	228-226	39%	442.76 g/mol
$[Ni (L_2)Cl.2H_2O]\ H_2O$	brown	221-219	39%	442.37 g/mol
Ligand L_3	brown	207-205	78%	350 g/mol
$[Fe_2(L_3).(H2O)_6]$	brown	344-342	77%	567.13 g/mol
$[Co_2(L_3).(H2O)_6]$	brown	286-284	52%	572.29 g/mol
$[Ni_2(L_3). (H2O)_6]$	brown	235-233	75%	571.61 g/mol
$[Cu_2(L_3). (H2O)_6]$	brown	295-293	44%	585.53 g/mol

3-3 ^{1}H NMR

^{1}H NMR spectroscopy was used to determine the presence and the type of protons in the three Schiff base ligands using DMSO-d6 as a solvent which can be detected at δ 2.50 ppm signal detected. The spectrum of L_1 shown in figures (3-7)signals in at δ 6 -9 ppm which are related to the aromatic protons[85] And signal between δ 12-13 ppm w was identified to S-H bond in the ligand structure as shown in figure(3-9)(3-8)[86], Signals for the L2 and L3 have been seen in the ^{1}H NMR spectrum. Each -CH_3 and -OH group's proton signal show up at about 1 and 9.5 ppm respectively[87]. While several signals between 6 and 9 ppm are linked with the aromatic protons in both ligands as shown in figures (3-8) and (3-9).

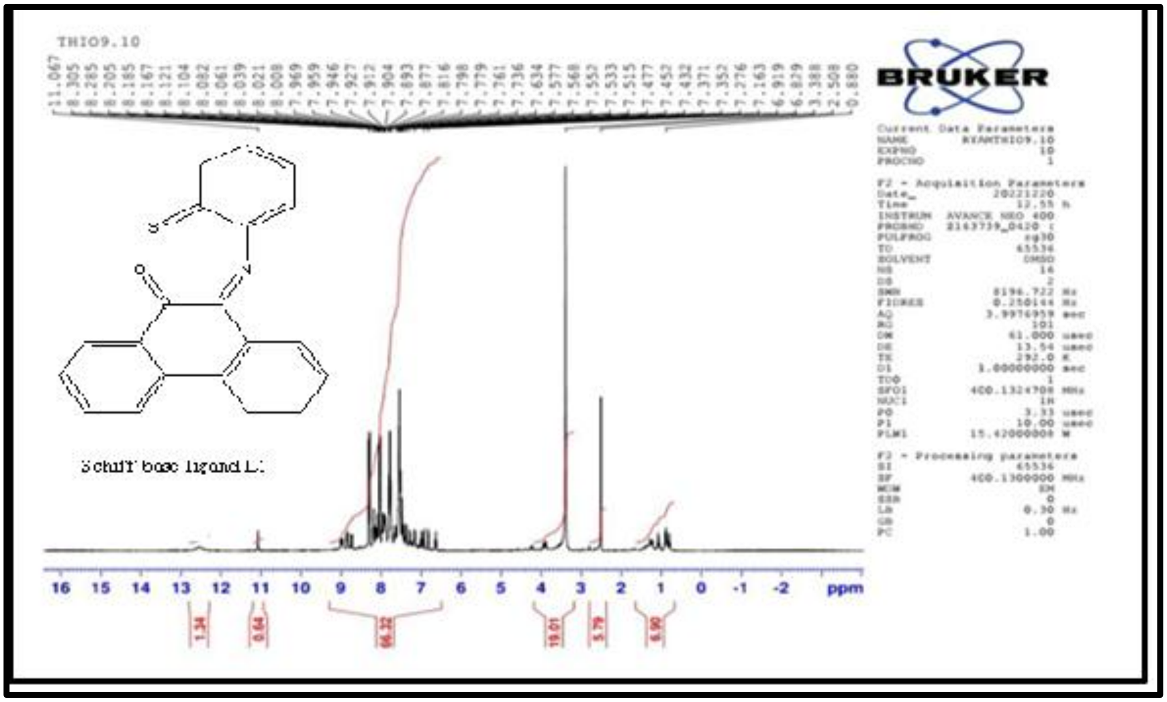


Fig (3-7) ^{1}HNMR of L_1

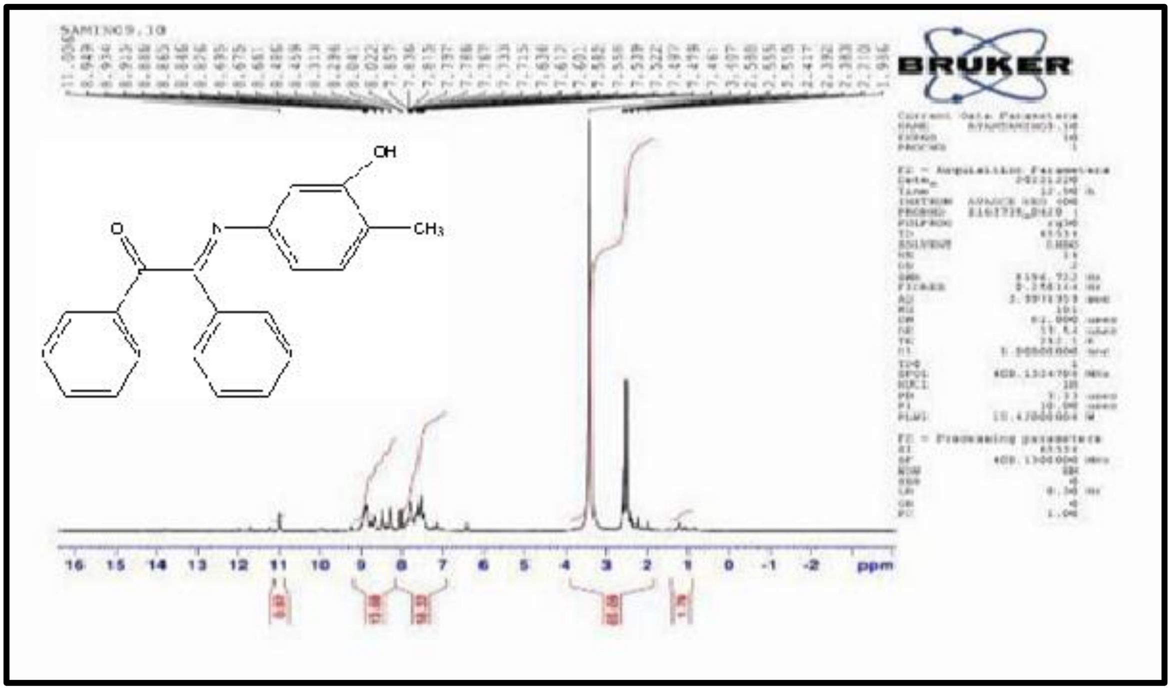


Fig (3-8)^1 HNMR of and L$_2$

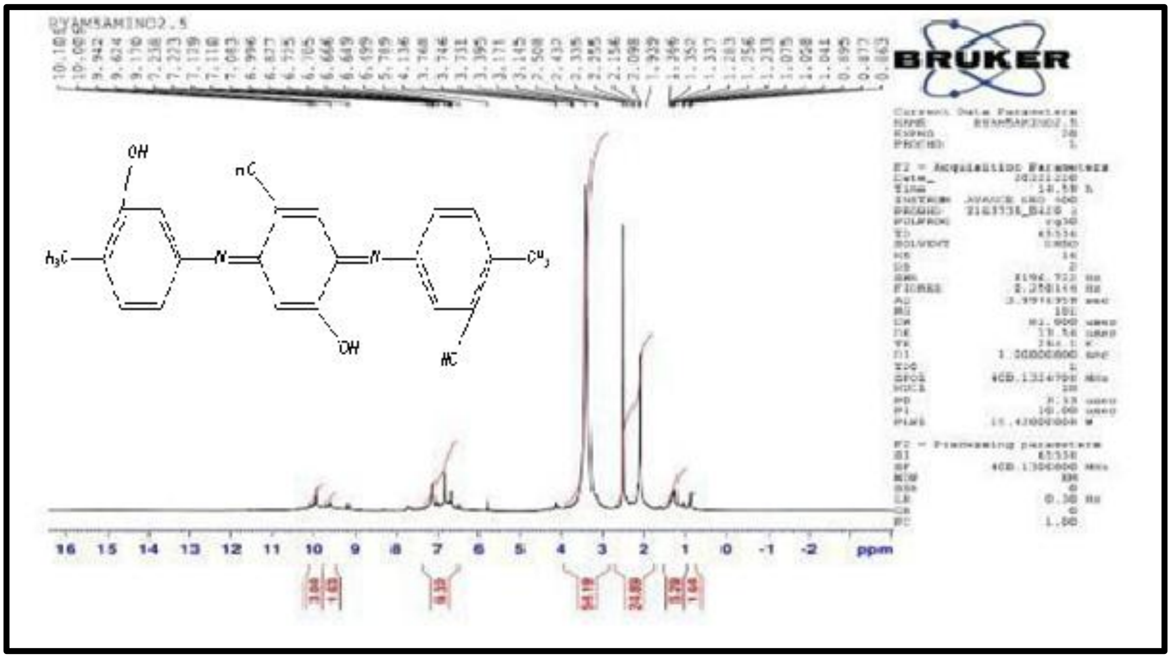


Fig (3-9)^1 HNMR of and L$_3$

3-4 Mass Spectra

Mass spectrometry has been successfully used to investigate molecular structure of compounds. The ligands were compared with their molecular formula weight. Mass values are in good agreement with the proposed molecular formula for the ligands. It also shows series of some peaks corresponding to various fragments. Figure(3-10) shows the mass spectra of ligand $L_1$315m\z Figure(3-11) shows the mass spectra of ligand $L_2$313m\zand Figure(3-12) shows the mass spectra of ligand L_3 350m\z.

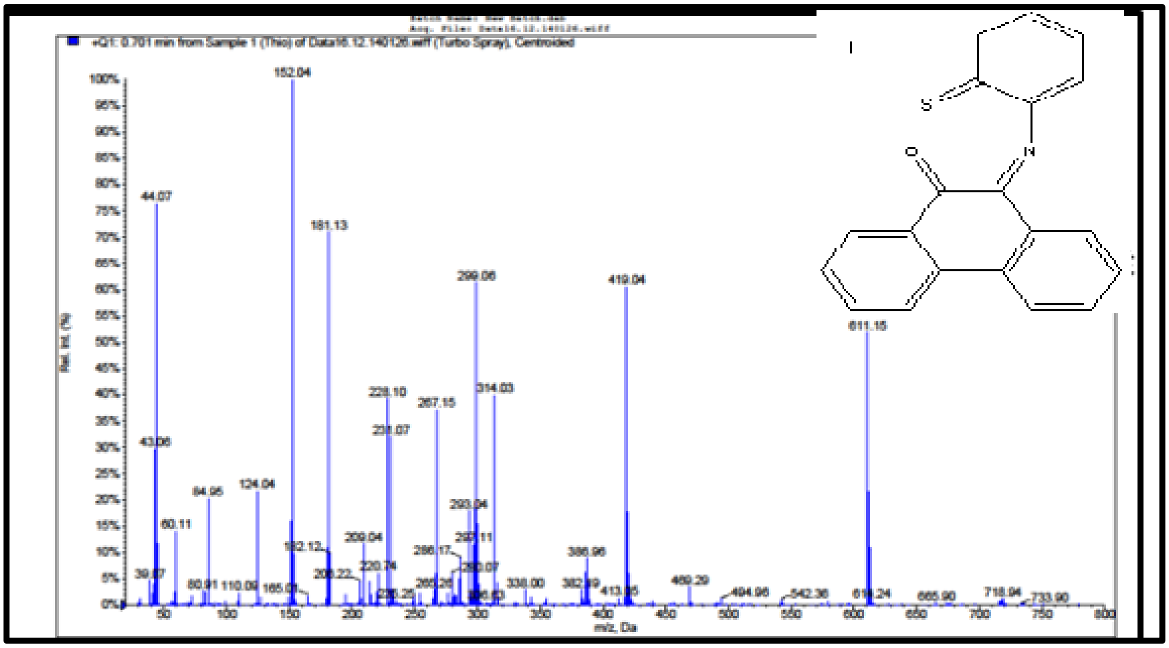


Fig (3-10) Mass Spectra of ligand L_1

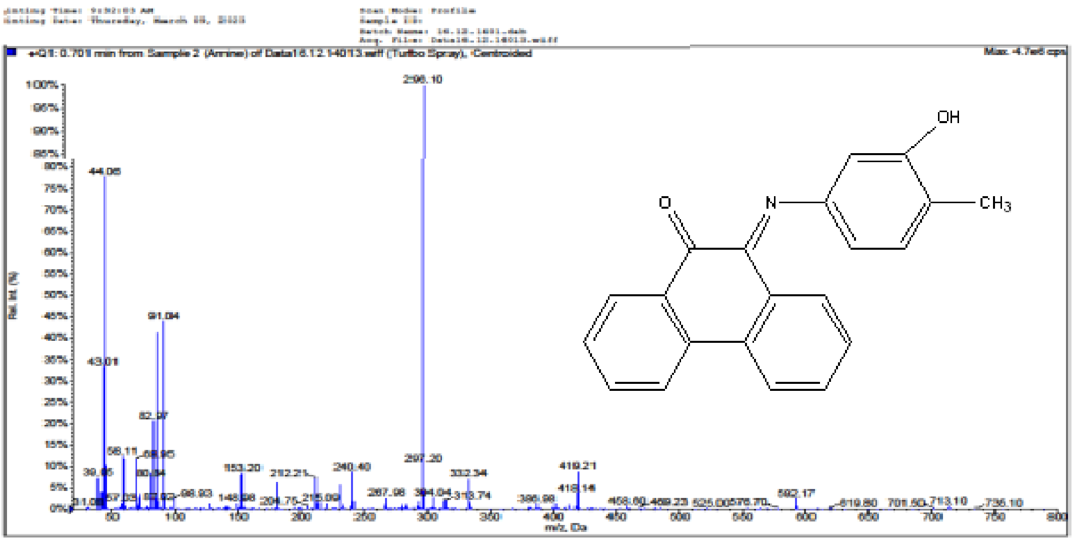


Fig (3-11) Mass Spectra of ligand L_2

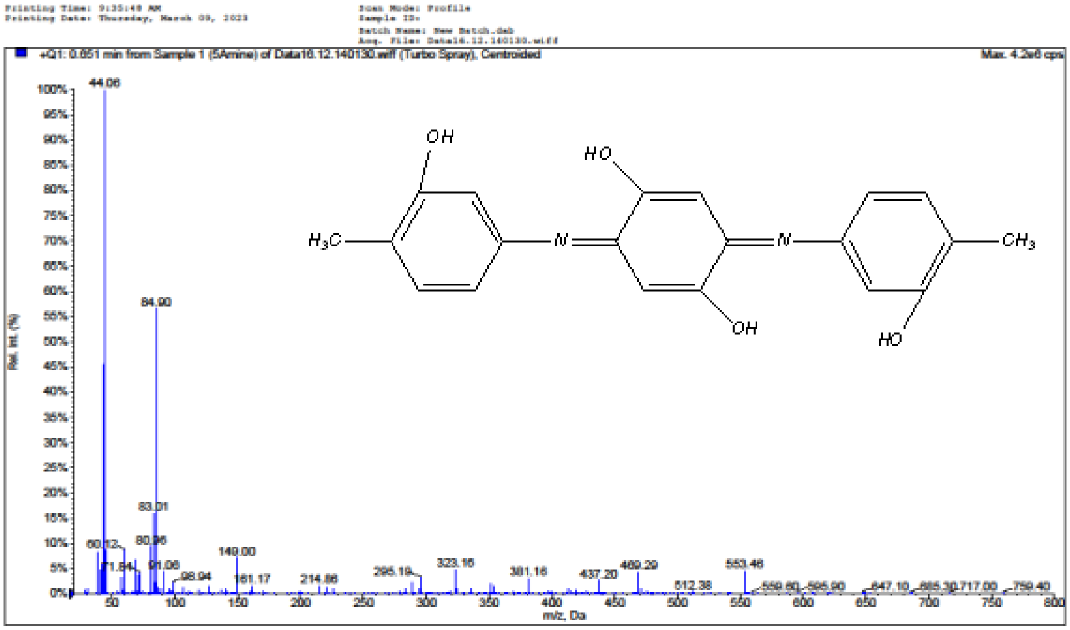


Fig (3-12) The Mass Spectra of ligand L_3

3-5 FT-IR Spectroscopy

It has been feasible to ascertain the chemical structure of the ligands and their metal complexes by utilizing Fourier transform infrared spectroscopy analysis, vibration modes, and the existence of functional groups like C=O, C=N, S-H, and O-H.

3-5-1 FT-IR Spectroscopy of L_1 and Metal Complexes

In addition to the absence of an absorption band for the- NH_2 group in the free 2-aminothiopenol at 3446cm^{-1} and 3356 cm^{-1} and the presence of the ʋ (C=O) group in the 9,10-phenathrenquinon absorption band at 1674 cm^{-1}, the FT-IR spectra of the Schiff base ligand (L_1) also reveal a new band at 1516 cm^{-1} that is attributed to imine group ʋ (C=N).When the ligand was formed, the characteristic ʋ(S-H) vibration frequency that is present in 2-Aminothiophenol as a single band at 2522 cm^{-1} also vanished, indicating that it was converted to the thione form ʋ (C=S), which is present at 1323 cm^{-1}.[88] When the metal complexes are created, these three bands ʋ (C=N) ,(C=S)and ʋ (C=O). Showed a change in their positions in complexes spectra which indicated the coordination process through these groups with metal ions [89].While the (C=S) was moved to 1338 cm^{-1} in the Fe^{2+} ,Cu^{2+},Ni^{2+} and Co^{2+} complex show that the metal coordinated with the ligand through the second coordination site (the thione group) Bonds (M-N) and (M-S) are referenced in new bands (400-600 cm^{-1}) that arise. The presence of hydrated water molecules outside the coordination sphere is shown by a broad band between 3200 and 3600 cm^{-1}. Figures(3-13,3-14,3-15,3-16,3-17) show the FT-IR spectra of the ligand L_1, Fe(II), Co(II) Ni(II)and Cu (II) complexes of the Schiff base ligand (L_1)[90] Table (3-2)gives a summary of the characteristic bands in the FT-IR spectrum of L_1 and how they were shifted upon complexes formation.

Table (3-2)FT-IR Frequencies data cm^{-1} of $L_1$and its complexes

Compound	H_2O	υ C=O	υ C=N	υ C=S	υ M-N	υ M-S	υ M-O
Ligand	------	1674	1516	1323	------	-----	-----
$[Fe(L_1)Cl_2H_2O]3\ H_2O$	3600-3200	1670	1508	1338	550	423	512
$[Co\ (L_1)Cl_2.H_2O]3H_2O$	3600-3200	1670	1508	1338	534	426	461
$[Ni\ (L_1)Cl_2H_2O]3H_2O$	3600-3200	1670	1508	1338	617	434	543
$[Cu(L_1)Cl_2H_2O]3H_2O$	3600-3200	1670	1508	1338	572	426	518

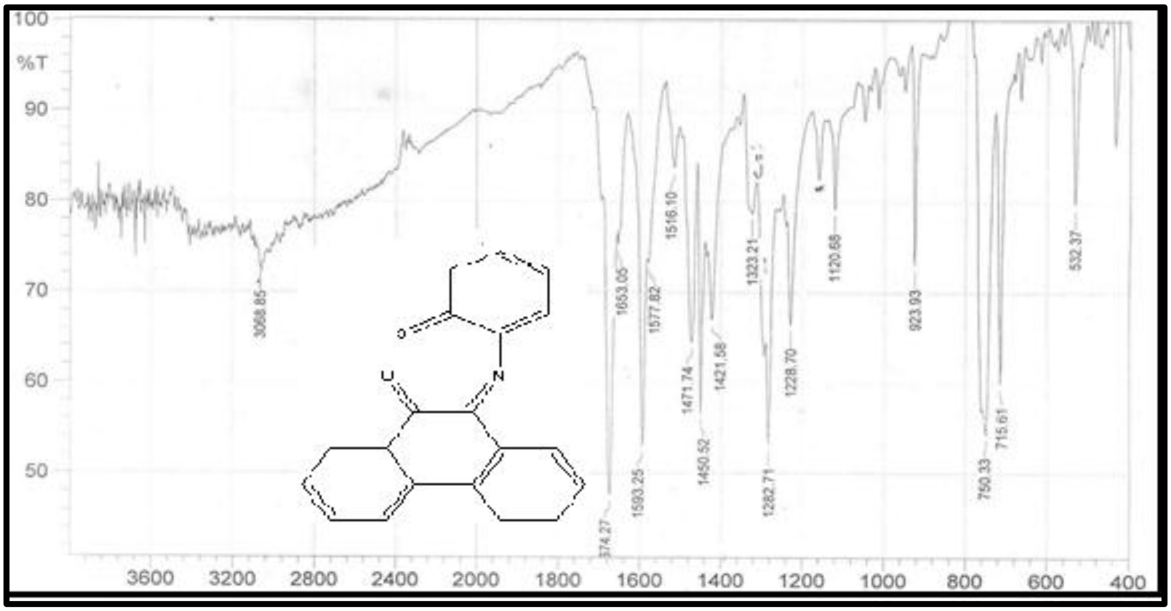


Fig (3-13) ligand L_1

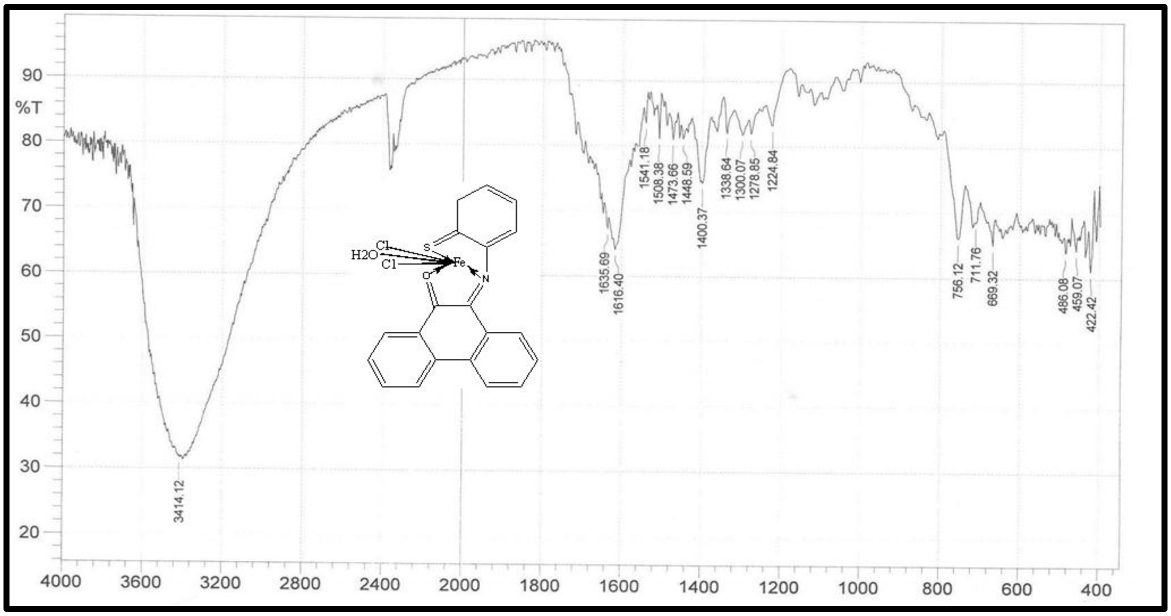


Fig (3-14)Fe(II) Complex and ligand L_1

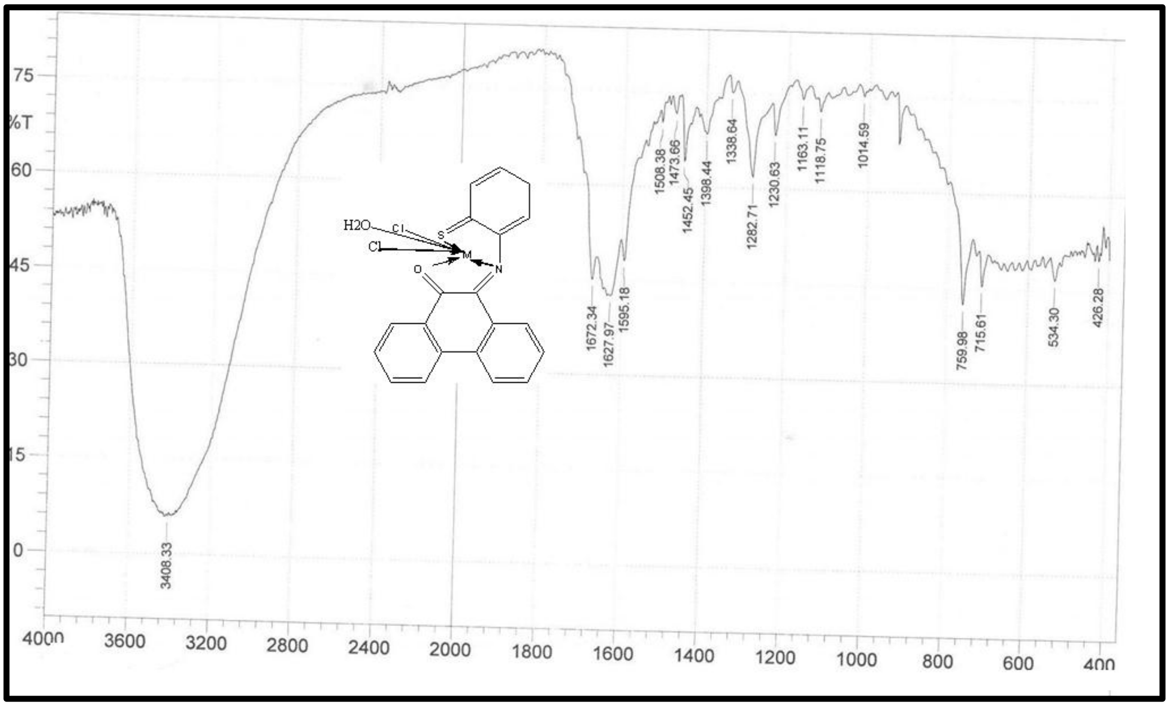


Fig (3-15)Co (II) Complex and ligand L_1

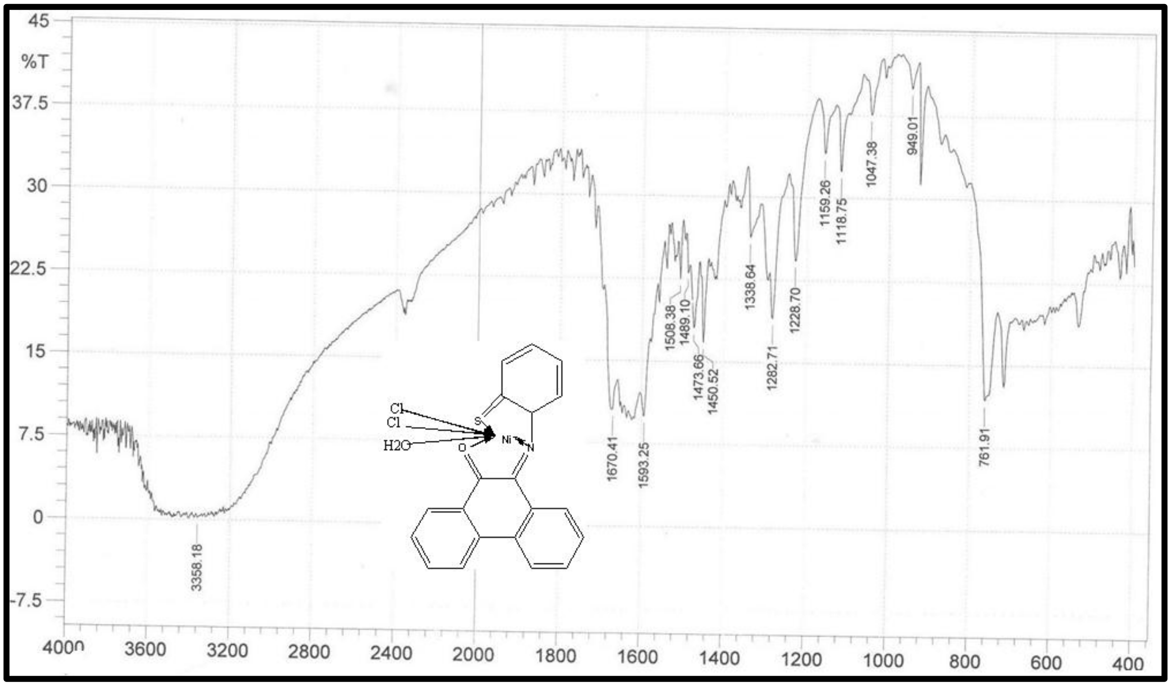


Fig (3-16)Ni (II) Complex and ligand L_1

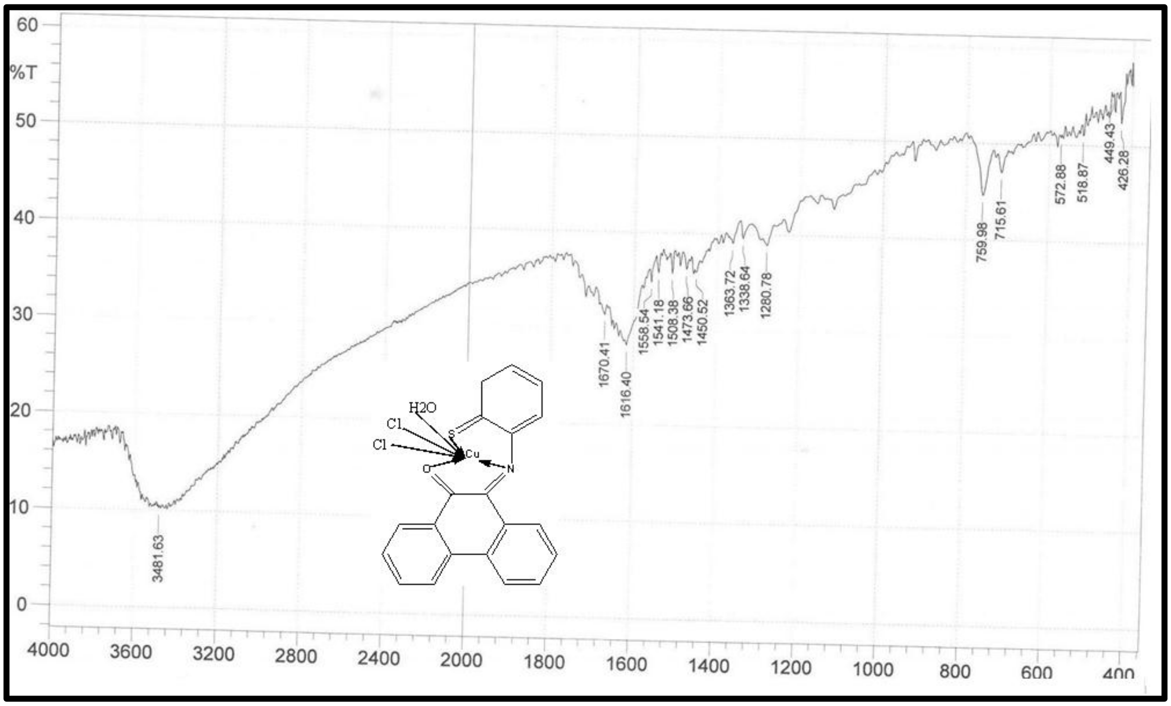


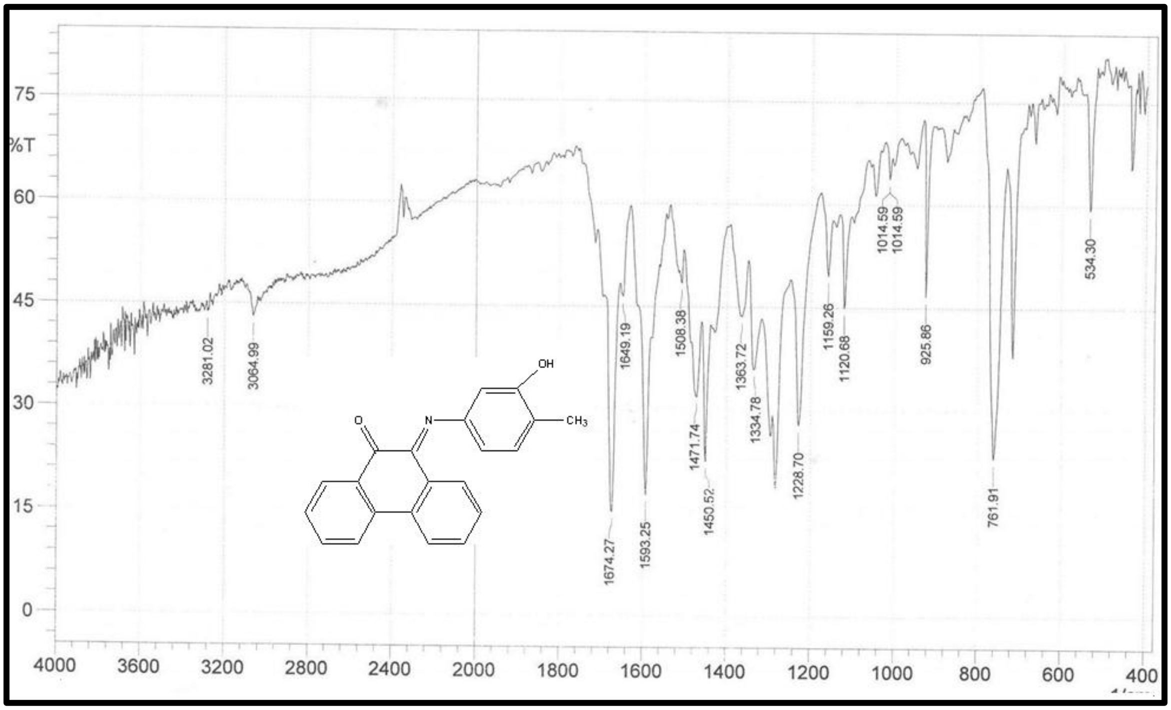
Fig (3-17)Cu (II) Complex and ligand L_1

3.5.2 FT-IR Spectra of L_2 and its Metal Complexes

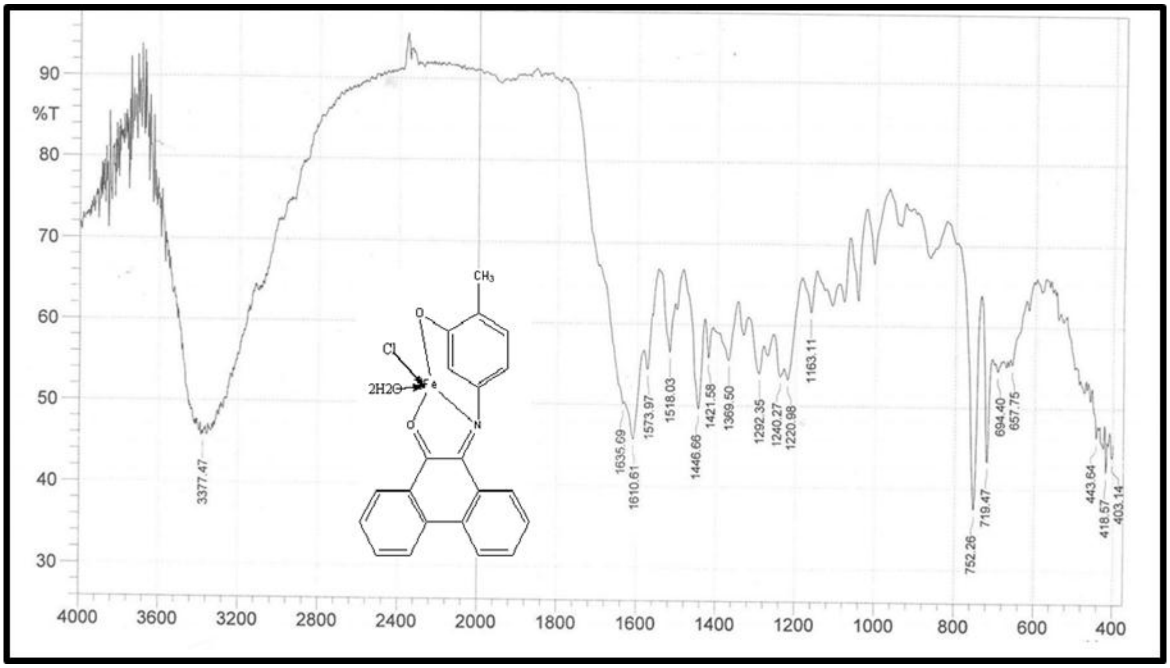
The FT-IR spectra of the Schiff base ligand (L_2) show a new band at 1508cm^{-1} that is attributed to an amino group (C=N) as well as the absence of an absorption band for the -NH2 group in the free 5-amino-2- methyl phenol at 3385 and 3319 cm^{-1} and the presence of the (C=O) group in the 9,10-phenathrenquinon absorption band at1674 cm^{-1}and absorption appears(OH)3323 cm^{-1}inL_2[91] When the metal complexes are created, these three bands (C=N) and (C=O) and (OH) Where the carbonyl group turned to 1635 cm^{-1} in the iron complex and 1647 cm^{-1}in the cobalt complex, the carbonyl group appeared at 1670 cm^{-1} in the nickel complex, while the OH group disappeared in all the prepared complexes are altered all metal complexes which showed a shift in the (C=N) frequency to 1508 cm^{-1}, which is suggestive of metal coordination with L_2 via the imine group's lone pair of nitrogen Bonds (M-N) and (M-O) are referenced in new bands (400-600 cm^{-1}) that arise.[92] The presence of hydrated water molecules outside the coordination sphere is shown by a broad band between 3200 and 3600 cm^{-1}[93] Figures(3-18,3-19,3-20,3-21) show the FT-IR spectra of the complexes of the Schiff base ligand (L_2) Table (3-3) gives a summary of the characteristic bands in the FTIR spectrum of L_2 and how they were shifted upon complexes formation.

Table (3-3)FT-IR data cm^{-1} of L_2 and Complexes.

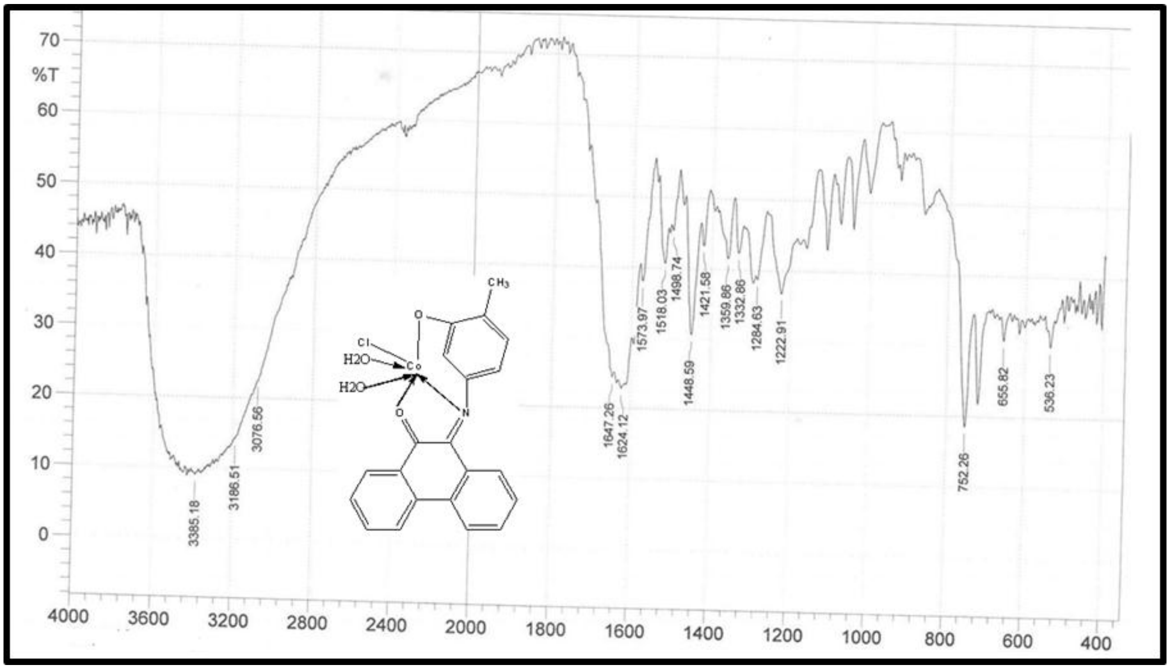
compound	H_2O	OH	C=O	C=N	M-O	M-N
Ligand L_2	--------	3323	1674	1508	-------	------
[Fe (L_2)Cl.2 H_2O] H_2O	3600-3200	--------	1635	1518	443	416
[Co(L_2)Cl.2 H_2O] H_2O	3600-3200	--------	1647	1518	568	576
[Ni (L_2)Cl.2H_2O] H_2O	3600-3200	--------	1670	1518	563	418



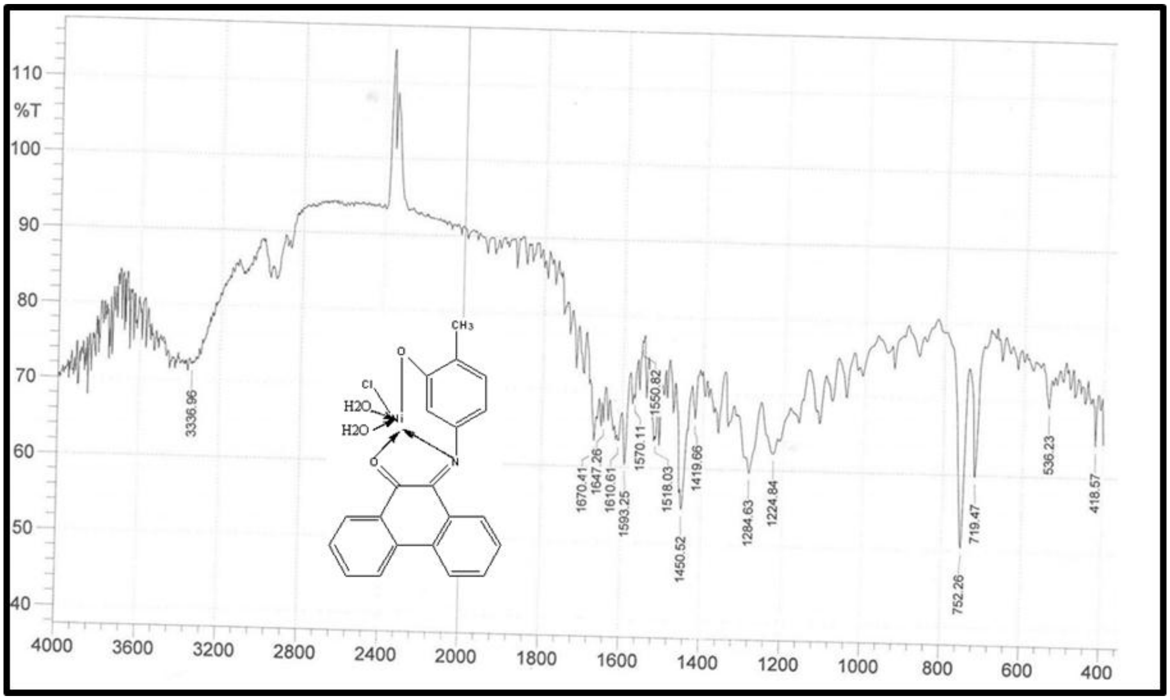
Fig(3-18)Ligand L_2



Fig(3-19)Fe(II) Complex and ligand L_2



Fig(3-20)Co (II) Complex and ligand L_2



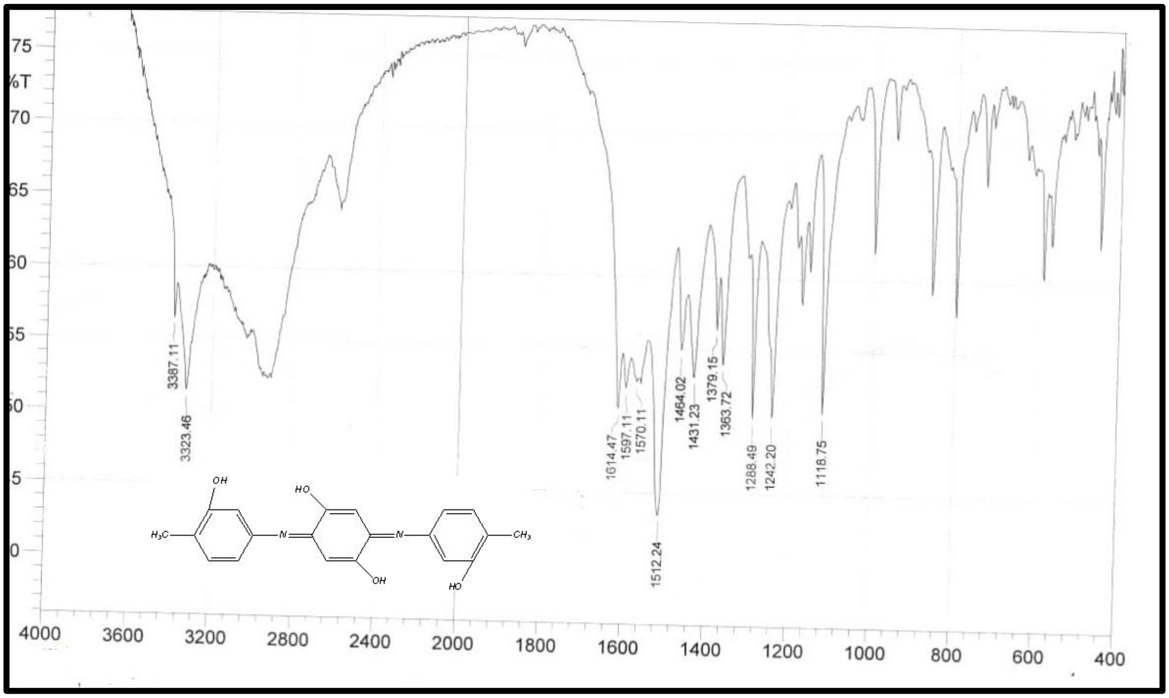
Fig(3-21)Ni (II) Complex and ligand L_2

3.5.3 FT-IR Spectra of L_3 and its Metal Complexes

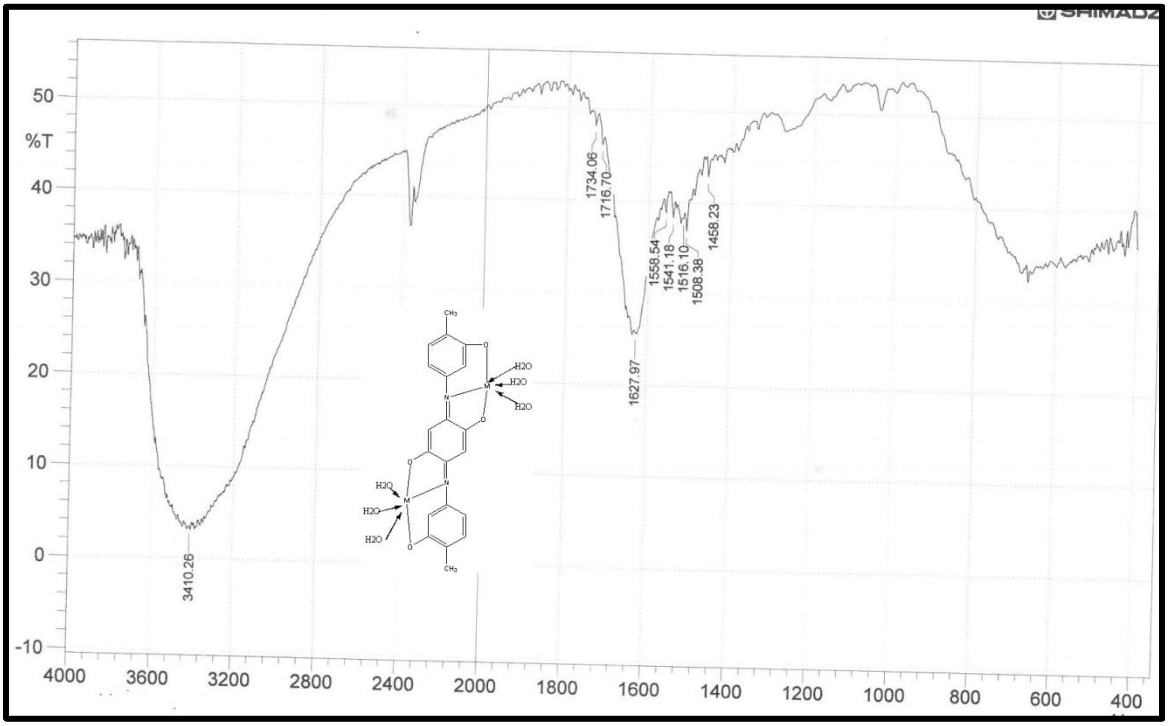
The FT-IR spectra of L_3 (Fig3-20) also shows the characteristic imine group band which is seen around1639 cm^{-1}. The formation of this band was supported with the absence of both absorption bands of the amino group in 5-amino-2- methyl phenol and the carbonyl group in 2,5-dihydroxy-1,4-benzoquinon which is found at 1674 cm^{-1}.The v(O-H) frequency is around 3323cm^{-1}as a single band in L3[94].upon complication these characteristic bands are changed and shifted (Fig3-22,3-23,3-24,3-25,3-26) For example the imine group frequency is shifted to a lower wavelength. From 1627cm^{-1}in,[Fe_2L_3 $(H_2O)_6$] the free ligand to 1600cm^{-1} in both [Co_2L_3 $(H_2O)_6$].,[$Cu_2(L_3)$ $(H_2O)_6$] and 1602cm^{-1} in,[Ni_2 L_3 $(H_2O)_6$] complexes which confirms the metal coordination with L_3. the hydroxyl group is deprotonated and coordinates with the metal ions through the oxygen atom to form (M-O) bonds which appears at 597 cm-1[Fe_2L_3 $(H_2O)_6$] ,472 cm^{-1} in [$Co_2L_3(H_2O)_6$] 550 cm^{-1} in and [Ni_2 L_3 $(H_2O)_6$] and 576 cm^{-1} in[Cu_2L_3 $(H_2O)_6$] [95,96]. An extra new bands in the metal complexes FT-IR spectra also appeared between 400-600cm^{-1} which are attributed to the v(M–N) and v(M–O) both bands .Table (3-4) gives a summary of the characteristic bands in the FTIR spectrum of L_3 and how they were shifted upon complexes formation.

Table (3-4)FT-IR Data cm^{-1} of L_3 and Complexes

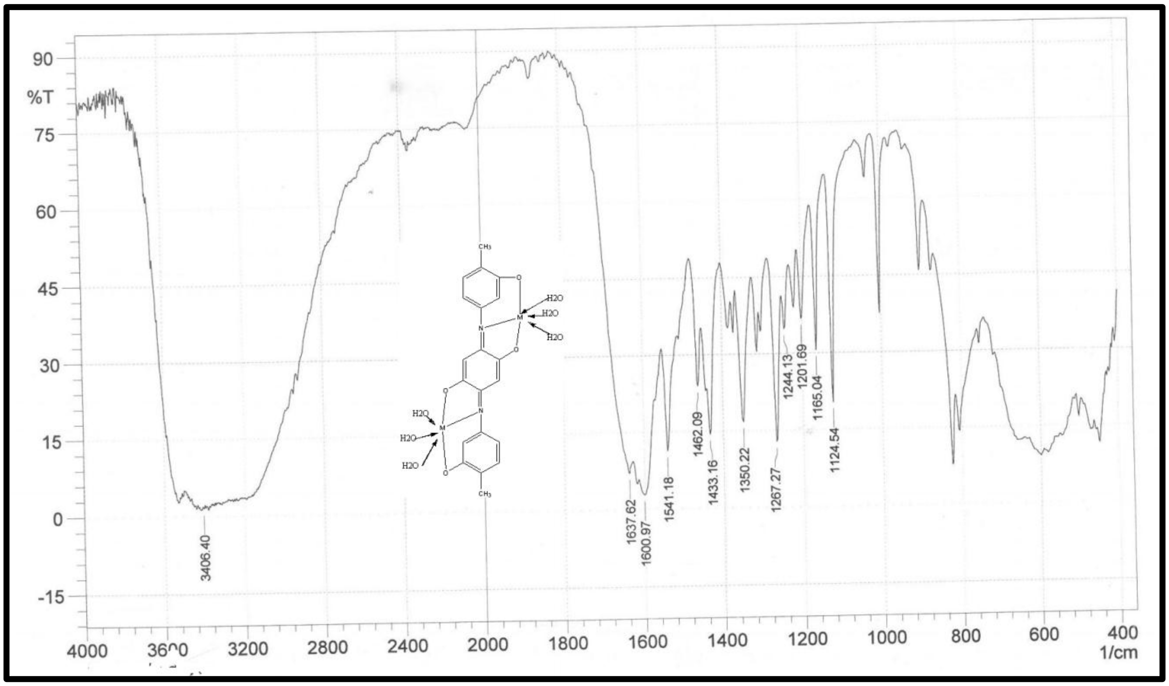
Compound	H2O	OH	C=N	M-O	M-N
Ligand L_3	--------	3323	1570	------	-------
$[Fe_2L3. (H_2O)_6]$	3600-3200	-------	1627	518	597
$[Co_2L3. (H_2O)_6]$	3600-3200	-------	1600	545	599
$[Ni_2L3. (H_2O)_6]$	3600-3200	-------	1602	522	559
$[Cu_2L3.(H_2O)_6]$	3600-3200	-------	1600	518	567



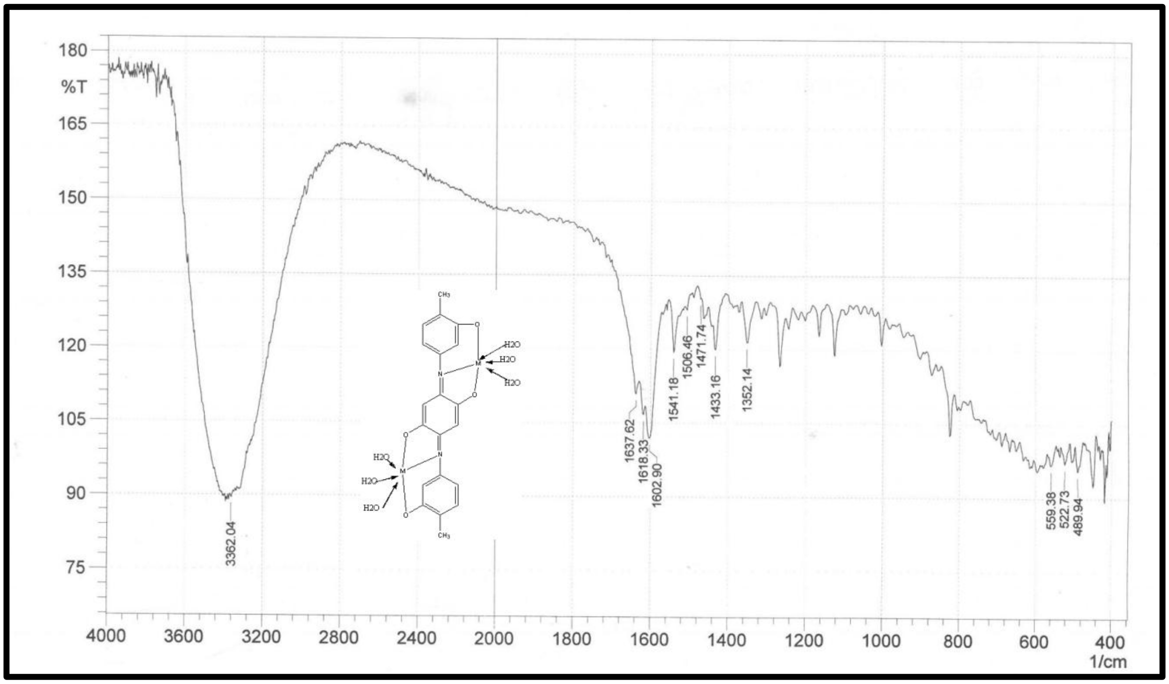
Fig(3-22)Ligand L_3



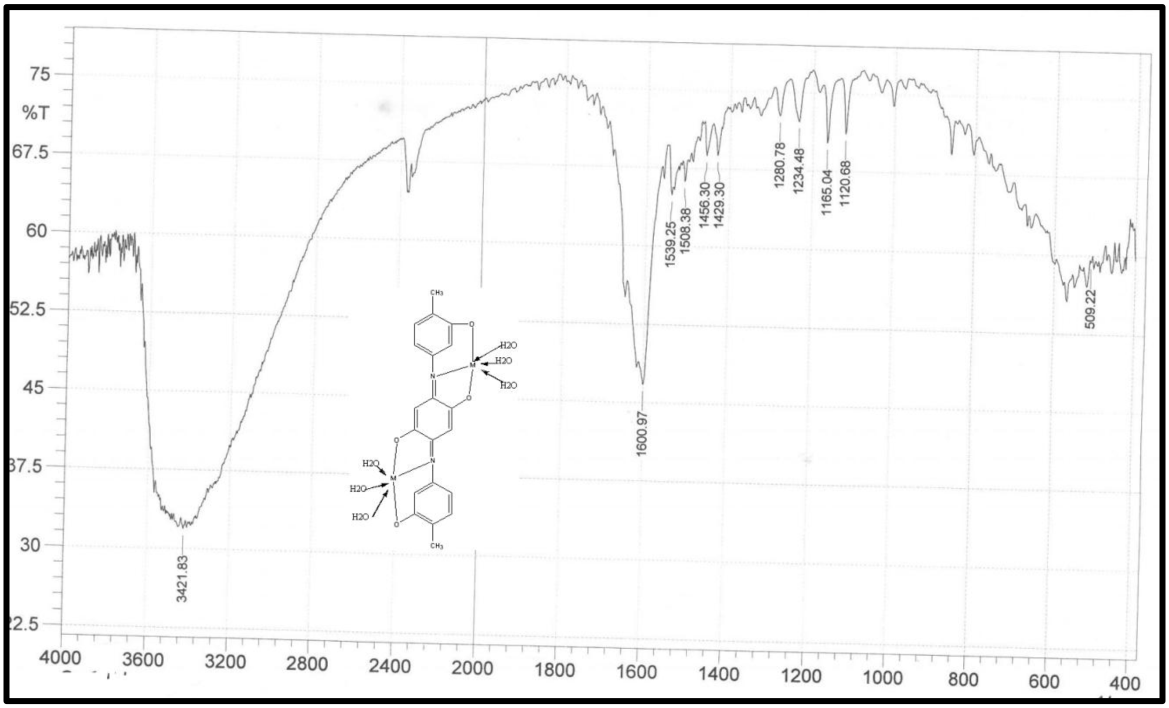
Fig(3-23) Fe (II) Complex and ligand L_3



Fig(3-24)Co (II) Complex and ligand L_3



Fig(3-25)Ni (II)complex and ligand L_3



Fig(3-26)Cu (II) Complex and ligand L_3

3-6 Atomic Absorption

The atomic absorption spectrometry (AAS) allows researchers to Therefore, this method was used to confirm the metallic ratio in the complexes[97]. Table (3-5) Theoretic and experimental value of metal part for prepared complexes.

Table (3-5)Theoretical and Experimental Value of Meta1 Ratio for Prepared Comp1exes.

Complexes	Theory value	Experiment value
$[Fe(L_1)Cl_2H_2O]3H_2O$	12.6	11.9
$[Co (L_1)Cl_2H_2O]3H_2O$	13.2	12.6
$[Ni (L_1)Cl_2H_2O]3H_2O$	13.1	12.5
$[Cu(L_1)Cl_2H_2O]3 H_2O$	14.08	13.5
$[Fe (L_2)Cl. 2H_2O] H_2O$	12.7	11.2
$[Co(L_2)Cl.2H_2O] H_2O$	13.3	12.5
$[Ni (L_2)Cl.2H_2O] H_2O$	13.2	12.4
$[Fe_2(L_3). (H_2O)_6]$	6.08	6.8
$[Co_2(L_3).(H_2O)_6]$	6.3	6.8
$[Ni_2(L_3).(H_2O)_6]$	6.3	7.2
$[Cu_2(L_3).(H_2O)_6]$	6.6	7.3

3.7 UV-Visible Electronic Spectra

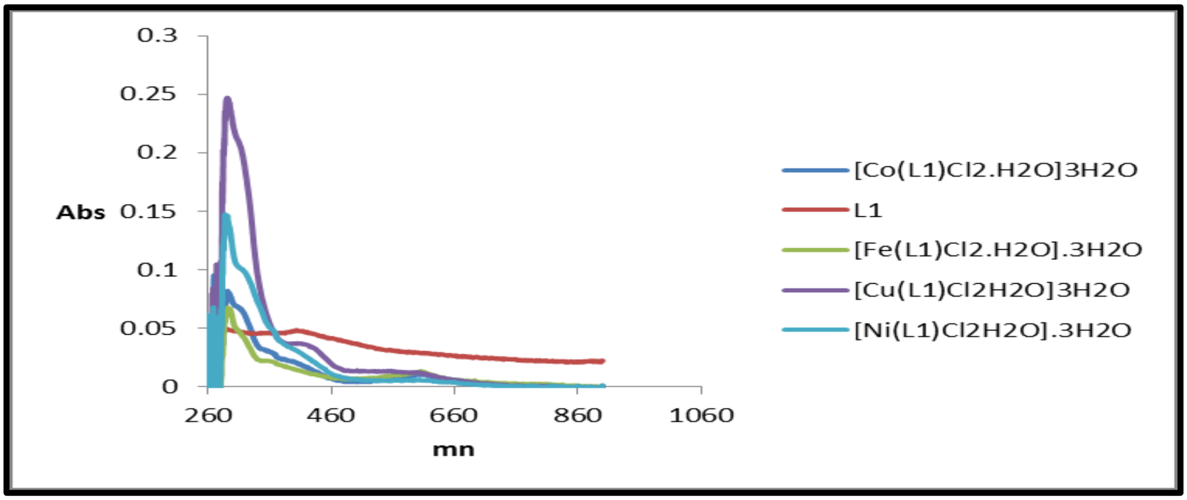
3-7-1UV-Visible Electronic Spectra of L_1 and Fe(II)Co (II) ,Ni(II) and Cu(II) Complexes

The ultraviolet-visible absorption spectrum includes absorption values for ligands and absorption peaks that belong to electronic transitions. The spectra of L_1 shows the first transition at235nm which is π-π* in the aromatic compound [98, 99]. While the second transition is due to electronic423 nm n-π*pairs present [100] .

The $[Fe(L_1)Cl_2H_2O]3H_2O$ spectrum shows d-d transition[101] $^5T_{2g}\rightarrow{}^5E_g$ transition appear in the iron complex at 624nm [102]. Cobalt (II) complex spectra shows also transitions appear at 370, 427 , 628 nm which are related to $^4T_{1g}\rightarrow{}^4T_{2g}$, $^4T_{1g}(F)\rightarrow{}^4T_{1g}$, $^4T_{1g}\rightarrow{}^4A_{2g}$. Nickel (II) transitions are $^3A_{2g}\rightarrow{}^3T_{2g}(F)$, $^3A_{2g}\rightarrow{}^3T_{2g}(p)$ $^3A_{2g}\rightarrow{}^3T_{2g}(F)$, $^3A_{2g}\rightarrow{}^3T_{2g}(p)$ at 327, 427, 635 nm respectively [103,104]. Copper transitions appear at $^2B_{1g}\rightarrow{}^2A_{1g}$, $^2B_{1g}\rightarrow{}^2B_{2g}$, $^2B_{1g}\rightarrow{}^2E_g$ appears at 439, 621 nm.

Table (3-6) Shows the absorption Peaks and their Assignments

compound	λ max(nm)	Type of Transition
Ligand (L_1)	235,423	π-π*, n-π*
[Fe(L_1)Cl_2H_2O]3H_2O	296, 379, 624	C-T $^5T_2g\rightarrow{}^5E_g$
[Co (L_1)Cl_2H_2O]3H_2O	295, 370, 427 , 628	C_T $^4T_1g\rightarrow{}^4T_{2g}$ $^4T_1g\rightarrow{}^4A_{2g}$ $^4T_1g_{(F)}\rightarrow{}^4T_{1g}$
[Ni (L_1)Cl_2H_2O]3H_2O	292, 327, 433, 635	C_T $^3A_{2g}\rightarrow{}^3T_{2g}$ $^3A_{2g}\rightarrow{}^3T_{2g(F)}$ $^3A_{2g}\rightarrow{}^3T_{2g(p)}$
[Cu(L_1)Cl_2H_2O] 3H_2O	298,446, 625	C_T $^{2B1g}\rightarrow{}^2A_{1g}$ $^2B_1g\rightarrow{}^2B_{2g}$ $^2B_1g\rightarrow{}^2E_g$



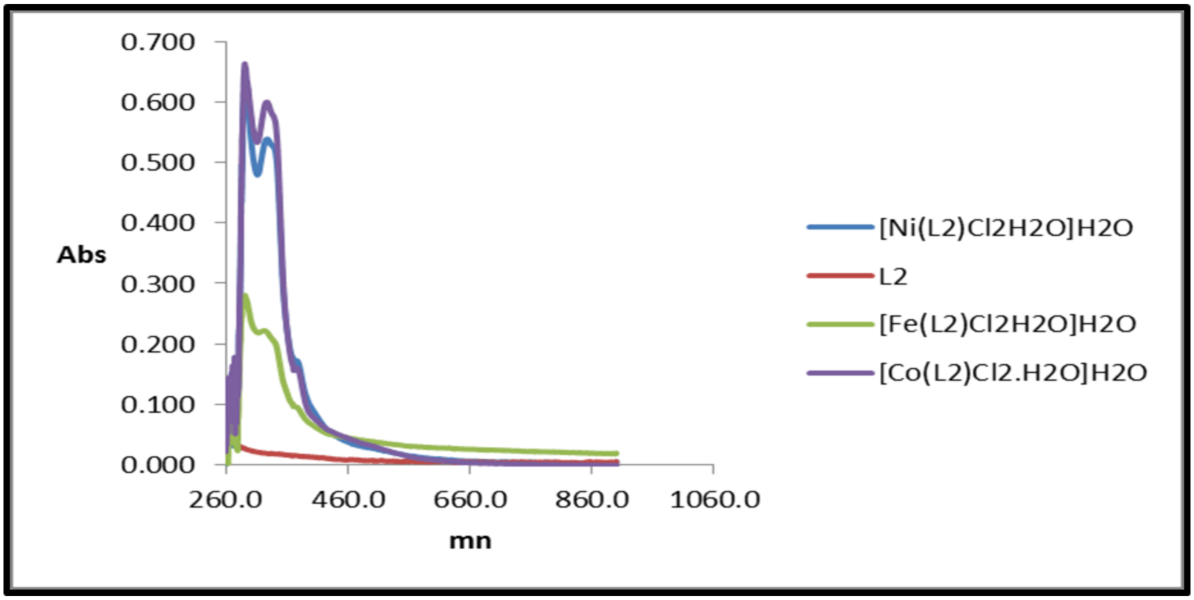
Fig(3-27)UV-Vis Spectra of ligand (L_1)and Complexes.

3.7.2 UV-Visible Electronic Spectra of L_2 and a Fe(II)Co (II) and Ni(II) Complexes

The ultraviolet-visible absorption spectrum includes absorption values for ligands and absorption peaks that belong to the electronic transitions. The first transition is due to aromatic compound215 nm π-π*[105]while the second transition is due to non-electronic pairs presen358t n-π* on the N and O and transition d-d between metal and ligand[106] $^5T_2g \rightarrow ^5E_g$ transitions appear in the iron complex[107], cobalt transitions and transitions appear at $^4T_{1g} \rightarrow ^4T_{2g}$, $^4T_{1g(F)} \rightarrow ^4T_{1g}$, $^4T_{1g} \rightarrow ^4A_{2g}$ and nickel transitions from $^3A_{2g} \rightarrow ^3T_{2g}$, $^3A_{2g} \rightarrow ^3T_{2g(F)}$, $^3A_{2g} \rightarrow ^3T_{2g\ (p)}$ [108] . Table (3-6) Shows the absorption Peaks and their Assignments

Table (3-7) Shows the absorption Peaks and their Assignments

compound	λ max(nm)	Type of Transition
Ligand L_2	215,358	π-π*, n-π*
[Fe L_2Cl.2 H_2O] H_2O	293, 330, 343,382	C_T $^5T_2g \rightarrow ^5E_g$
[Co(L_2)Cl.2 H_2O] H_2O	292, 342, 335,381	C_T $^4T_{1g} \rightarrow T_{2g}$ $^4T_{1g} \rightarrow A_{2g}$ $^4T_{1g(F)} \rightarrow T_{1g}$
[Ni (L_2)Cl. 2H_2O] H_2O	294,336,344, 380	C_T $^3A_{2g} \rightarrow T_{2g}$ $^3A_{2g} \rightarrow T_{2g(F)}$ $^3A_{2g} \rightarrow T_{2g(p)}$



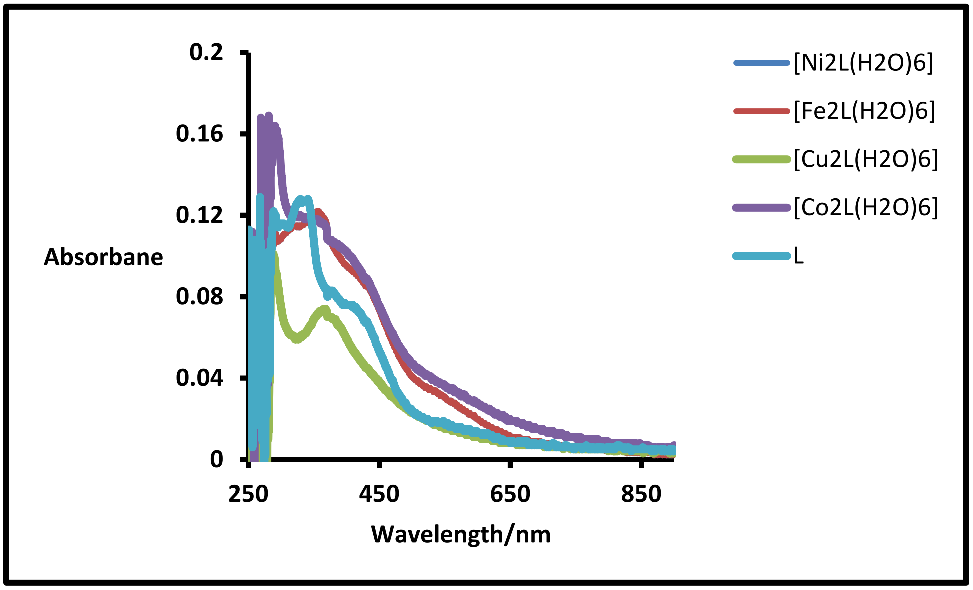
Fig(3-28)UV-Vis Spectra of ligand (L_2)and Complexes

3.7.3 UV-Visible Electronic Spectra of L_3 and a Fe(II)Co (II) ,Ni(II) and Cu(II) complexes

The ultraviolet-visible absorption spectrum includes absorption values for ligands and absorption peaks that belong to the electronic transitions. The first transition in the ligand spectra at 344 nm refers to π-π* transition [109].while the second transitions at 421, 594 nm is due to n-π* transition type for the non-electronic pairs present on the N and O [110] .in Fe (II), Co(II) and Ni(II) complexes these peaks are shifted which indicate the coordination between the metal and the ligand. While in copper complex a broad peak at 389 nm refers to two transitions $^2B_{1g}\rightarrow{}^2A_{1g}$ and $^2B_{1g}\rightarrow{}^2E_g$ [111]. Table (3-8) Shows the absorption Band and their Assignments.

Table (3-8) Shows the absorption Band and their Assignments.

Compound	λ max(nm)	Type of Transition
Ligand L_3	344,421, 594	π-π*, n-π*
$[Fe_2L_3 (H_2O)_6]$	365,438,573	C_T MLCT
$[Co_2 L_3 (H_2O)_6]$	369,411,578	C_T MLCT
$[Ni_2L_3 (H_2O)_6]$	367,436,562	C_T MLCT
$[Cu_2L_3 (H_2O)_6]$	290, 389	C_T $^2B_{1g}\rightarrow{}^2A_{1g}$ $^2B_{1g}\rightarrow{}^2E_g$



Fig(3-29)UV-Vis Spectra of ligand (L_3)and Complexes

3.8 Magnetic Susceptibility Measurement

This method is typically employed to look for single electrons in metal complexes. This method also help in showing the main ions' hybridization in their complexes, whether or do not have paramagnetic or diamagnetic properties, and lastly the structure of the metal complexes[112,113]**.** The calculated magnetic susceptibility of the prepared metal complexes was measured at (293 °K) using the following equations.

$\mu eff=2.828 \sqrt{}\ XAT$ B.M

$XA=XM-D$

$XM=Xg\times$ M.wt

$Xg= CL/109m \times (R-RO)$

They represent:

T = absolute temperature = 293°K

XA = atomic sensitivity.

XM = molar sensitivity.

Xg = Gram's (weight) sensitivity.

D = diamagnetic correction factor.

μeff = effective magnetic moment.

wt. M = gram molecular weight.

B.M= unit of magnetic moment (boermagnetone).

C=1.53

L=1 cm

R = sensitivity of the tube to the substance

RO = sensitivity of the empty tube

m = weight of the model = weight of pipe with material - weight of pipe empty Based on the obtained results of magnetic susceptibility measurement, it was found that all of complexes in L_1,L_2 and L_3 are paramagnetic and the suggested complexes structure is octahedral . The results magnetic susceptibility measurement, magnetic properties and the suggested structure for L1 ,L2 and L3metal complexes are listed in the table (3-9).

Table (3-9) Magnetic Measurements, Magnetic Properties and the Proposed Complexes Structure

Complexes	μeff (B.M)	Magnetic properties	Suggested structure
$[Fe(L1)Cl_2H_2O]3H_2O$	4.5	paramagnetic	octahedral
$[Co\ (L_1)Cl_2\ H_2O]3H_2O$	3.09	paramagnetic	octahedral
$[Ni\ (L_1)Cl_2\ H_2O]3H_2O$	3.37	paramagnetic	octahedral
$[Cu(L_1)Cl_2\ H_2O]\ 3H_2O$	2.27	paramagnetic	octahedral
$[Fe\ (L_2)Cl_2H_2O]2H_2O$	4.13	paramagnetic	octahedral
$[Co(L_2)Cl_2H_2O]2H_2O$	4.6	paramagnetic	octahedral
$[Ni\ (L_2)Cl\ _2\ H_2O]2H_2O$	1.8	paramagnetic	octahedral
$[Fe_2(L_3)\ (H_2O)_6]$	4.2	paramagnetic	octahedral
$[Co_2(L_3)\ (H_2O)_6]$	4.11	paramagnetic	octahedral
$[Ni_2(L_3)\ (H_2O)_6]$	2.97	paramagnetic	octahedral
$[Cu_2(L_3)\ (H_2O)_6]$	2.34	paramagnetic	octahedral

3.8.1 Fe(II) complexes of L_1, L_2 and L_3

It is apparent from the magnetic susceptibility values in table (3-8) that the Fe(II) complexes with a high spin electronic configuration with the presence of four single electrons in d-orbitals where the μ_{eff} are 4.5, 4.13 and 4.2 B.M for Fe(II) complexes with L_1, L_2 and L_3 respectively, and their structures are octahedral [114].

3.8.2 Co (II) Complexes of L_1, L_2 and L_3

Co(II) complexes are paramagnetic and also present as high spin complexes with a +2 oxidation state for Co. In agreement with the existence of three unpaired electrons in the d-orbital and the Co(II) complexes in octahedral geometry. The complexes magnetic susceptibility values are 3.09, 4.6 and 4.11 BM with L_1, L_2 and L_3 respectively [115].

3.8.3 Ni(II) Complexes of L_1, L_2 and L_3

Nickel (II)complexes have magnetic susceptibility values of 3.37, 1.8 and 2.97 BM with L_1, L_2 and L_3 respectively . These values suggest the presence of two unpaired electrons and paramagnetic character of Ni(II) complexes and their structures are octahedral [116-118].

3.8.4Cu (II) Complexes of L_1, and L_3

For the high spin Cu(II) complexes with μ_{eff} = 2.27and 2.34 BM also suggests the paramagnetic character of this ion and agrees with one electron in d- orbital and the octahedral structure of the Cu(II) complexes [119].

3.9 Molar Conductance Measurements.

As a solvent, ethanol was used to measure the conductivity of the produced complexes at a concentration of $1x10^{-3}$ M. All the complexes are non-electrolytes as shown by the conductance values in table (3-11) [120, 121]. The conductivity was measured at the laboratory temperature, and an $AgNO_3$ test was also performed for all complexes, and all complexes did not give a precipitate **. Table(3-10) : The Value of Molar Conductivity (10^{-3}M) for Different Types of Electrolytes In Different Solvents**

Solvent	Non 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	120-300	340-420	500

Table (3-11): The values of molar conductivity of complexes at (1×10^{-3}) M in ethanol

Compounds	Value of Molar Conductivity (10^{-3}M)
[Fe(L_1)Cl_2H_2O]3H_2O	4.6
[Co (L_1)Cl_2H_2O]3H_2O	5.7
[Ni (L_1)Cl_2H_2O]3H_2O	6.7
[Cu(L_1)Cl_2H_2O]3 H_2O	5.6
[Fe (L_2)Cl $_2$.H_2O]2H_2O	7.2
[Co(L_2)Cl_2.H_2O]2H_2O	3.2
[Ni (L_2)Cl_2.H_2O]2H_2O	4.6
[Fe_2(L_3)(H_2O)$_6$]	7.7
[Co_2(L_3) (H_2O)$_6$]	7.8
[Ni_2(L_3) (H_2O)$_6$]	8.9
[Cu_2(L_3)(H_2O)$_6$]	8.16

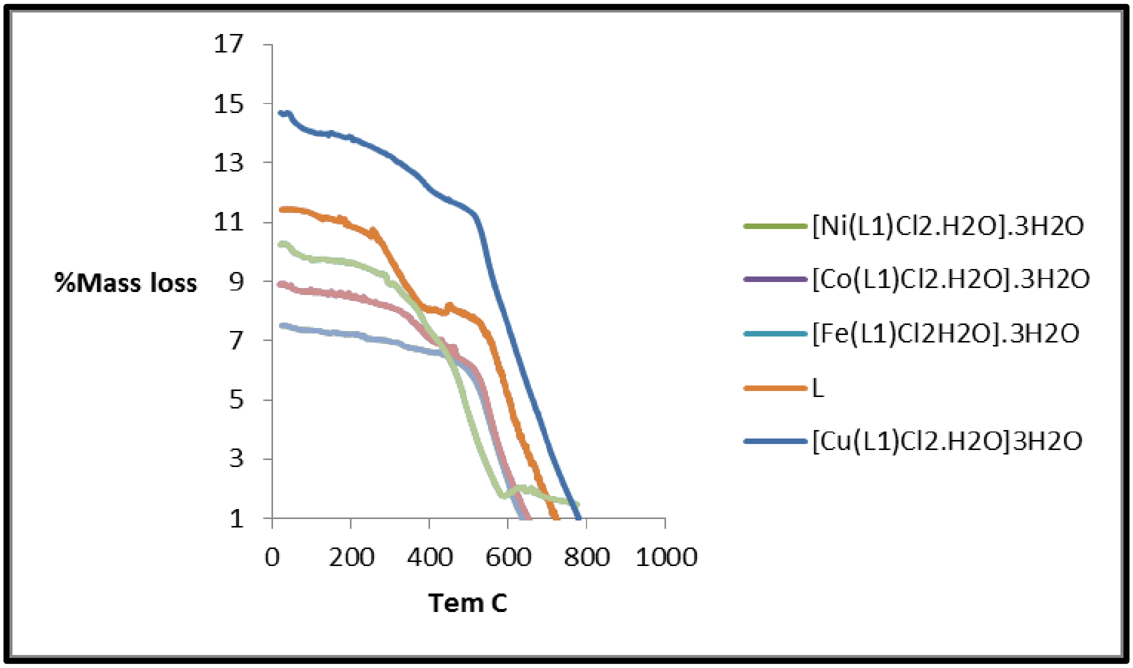
3.10 Thermal Analysis

3.10.1[Fe(L_1)Cl_2H_2O]3H_2O, [Co (L_1)Cl_2H_2O]3H_2O,[Ni (L_1)Cl_2H_2O]3H_2O and[Cu(L_1)Cl_2H_2O]3H_2O Complexes of ligandL_1

The thermal analysis took place between at 0-800°C under air. The loss of water at a temperature of 100-150°C has a thermal analysis of the complex[122]. Table (3-13) shows the breakdown temperature range and mass for all the chemicals under study. In Figure (3-30) The TG technique includes the decomposition of the ligand in two steps, the first through which Moisture substances are lost at a temperature40.82-184.ll°C and a percentage4.369%, while the second step was at a temperature184.11-582.06 and the percentage of loss43.656%. As for the measurement of the decomposition of the cobalt complex, it was found that it decomposed in three steps, the first step included the loss of four molecules of water and oxygen, while the second step included the loss of nitrogen and sulfur at a temperature383.31-487.57°C and the percentage of loss was10.81%and the third step was at a temperature487.57-572.17°C and a percentage of loss31.127%[123]. While Ni complexes the other two decomposition steps refer to the loss of some of the complexes moiety in the range36.07 - 580°C.The complexes of Cu(II)the other three decomposition steps refer to the loss of some of the complexes moiety in the range 33.42-586.23°C. As for iron, the number of decomposition steps was three steps, which included the loss of two molecules of water and two of chlorine at a temperature32.42 -514.03°C and a percentage of loss from4.949% to28.858 %

Table (3-12) shows the breakdown temperature range and mass for all the chemicals under study

Compound	**Steps of Degradation**	**Decomposition Temperature ° C**	**Mass Loss%**	**Type of Lost Species**
Ligand (L_1)	1	40.82-184.ll	4.369%	Moisture
	2	184.11-582.06	43.656%	$(C_6H_5)O,N$
$Fe(L_1)Cl_2.H_2O].3H_2O$	1	32.42 -122.05	4.949%	H_2O
	2	122.05-425.15	28.359 %	$3H_2O-2Cl$
	3	425.15 -514.03	28.858%	(C_6H_5) -S-O
$Co(L_1)Cl_2.H_2O].3H_2O$	1	40.68-383.31	17.650%	$4H_2O-O$
	2	383.31-487.57	10.81%	N-S- 6H
	3	487.57-572.17	31.127%	$2(C_6H_5)$-6H-2Cl
$[Ni(L_1)Cl_2H_2O].3H_2O$	1	36.07-468.91	16.25%	$4H_2O$
	2	468.91 -580	44.101 %	O-2Cl-(C_6H_5)
$[Cu(L_1)Cl_2.H_2O].3H_2O$	1	33.42-102.76	4.215 %	$2H_2O$
	2	102.76-492.53	17.780%	$2H_2O+2Cl$
	3	492.53-586.23	23.755%	C_6H_5S



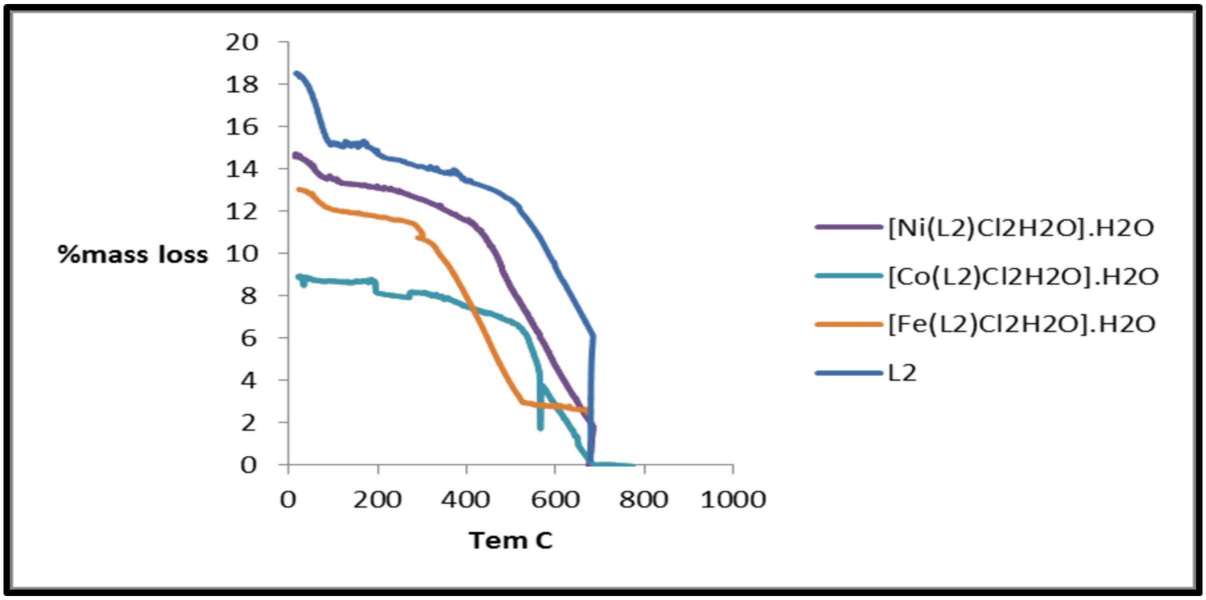
Fig(3-30)TG Curves for L_1 and Complexes .

3.10.2[Fe $(L_2)Cl_2H_2O]2H_2O$, $[Co(L_2)Cl_2.H_2O]2H_2O$and [Ni $(L_2)Cl_2.H_2O]2H_2O$ Complexes of ligandL_2

The thermal analysis was passed out under air with a temperature 0-800°C. The loss of water at a temperature of 100-150 has a thermal analysis of the complex [124]. It was found when measuring the decomposition of the Ligand L_2, it decomposes in three steps, the first step at a temperature of 22.99-95.55°C and the percentage of weight loss was17.474% and the second step was at a temperature was95.55-399.82 °C and at the third step was weight loss 24.763%and the temperature399.82-611.39 °C[125] was and when measuring the decomposition of iron complexes it was decomposed in three steps the first step was at a temperature 32.37-115.32°C and the second step was the percentage of weight loss17.840%) As for the third step, it was at a temperature305.23-431.84°C[126] ,the cobalt decomposition rate was in two steps, the first was at a temperature42.28 -282.21°C and weight loss7.533 %, while the second step was at a temperature282.21-541.78 °C and weight loss26.911 %[127]. As for the decomposition of nickel, it was also in two steps. The first step is the loss of water and oxygen at the temperature33.01-115.00°C, and the second step is the weight loss44.104% rate at a temperature115-541.1°C[128] table (3-13) gives a summary for the decomposition temperature range and the mass lose from all the willful compounds.

Table (3-13) Gives a Summary for the Decomposition Temperature Range and the Mass lose from all the Willful Compounds

Compound	Steps of Degradation	Decomposition Temperature	Mass Loss%	Type of Lost Species
Ligand (L_2)	1	22.99-95.55	17.474	OH,O,CH_3
	2	95.55-399.82	9.543	C=N
	3	399.82-611.39	24.763	C_6H_6
[Fe (L_2)Cl. $2H_2O$] H_2O	1	33.37-115.32	7.557	O,H_2O
	2	115.32-305.23	17.840	$2H_2O$,Cl
	3	305.23-431.84	30.626	CH_3,O,C=N,C_6H_6,
Co(L_2)Cl.$2H_2O$] H_2O	1	42.28 -282.21	7.533	O,H_2O
	2	282.21-541.75	26.911	CH_3,O,C=N,$2H_2O$,Cl
[Ni (L_2)Cl.$2H_2O$] H2O	1	33.01-115	7.376	O,H_2O
	2	115-541.1	44.104	$2H_2O$,CH_3,O,C=N,C_6H_6,Cl



Fig(3-31) TG curves for L_2 and complexes

3.10.3[$Fe_2(L_3)$ $(H_2O)_6$], [$Co_2(L_3)$ $(H_2O)_6$], [$Ni_2(L_3)$ $(H_2O)_6$] and [$Cu_2(L_3)$ $(H_2O)_6$]. Complexes of ligandL_3

The thermal analysis was approved out under the air temperature range 0-800°C.. table (3-14) gives a summary for the decomposition temperature range and the mass lose from all the studied compounds .The ligand decomposition two steps the temperature range 27.77-429.57 °C[129] . while Iron three step decomposition loss $2H_2O$ in 6.866%in temperature range34.94-258.46 the two steps of Iron loss $4H_2O$,4O,$2CH_3$ in temperature range 258.46-330.07°C in three steps of Iron loss of compound 2(C_5H_6),12H and C=N in temperature range 330.07 -420.2.The decomposition of Cobalt in three step in temperature range 44.13 -476.04 °C .while Nickel decomposition in two steps the range temperature 37.18-412.07 °C and

Copper the range temperature 43.49-332.47°C The decomposition in the three steps [130,131].

Table(3-14) Thermal Decomposition Data for $L_3$and Complexes

Compound	Steps of Degradation	Decomposition Temperature C	Mass Loss%	Type of Lost Species
Ligand (L_3)	1	27.77-331.88	13.88%	CH_3-2(OH)
	2	331.88-429.57	47.351%	C=N,OH, CH_3,C_5H_6
[$Fe_2(L_3)$ $(H_2O)_6$]	1	34.94-258.48	6.866%	$2H_2O$
	2	258.48-330.07	31.379%	$4H_2O$-4O-$2CH_3$
	3	330.07-420.26	35.035%	C=N,12H,2 C_6H_5
[$Co_2(L_3)$($H_2O)_6$]	1	44.13-342.60	25.506%	$3H_2O$,CH_3,4O
	2	342.60-476.04	46.689%	2(C_6H_5),12H,C=N
[$Ni_2(L_3)$($H_2O)_6$]	1	37.18-278.43	10.204%	$3H_2O$
	2	278.43-412.07	44%	$3H_2O$,4OH, $2CH_3$,C=N, 6H,C_6H_5S
[$Cu_2(L_3)$ $(H_2O)_6$]	1	43.49-237.62	13.357%	$3H_2O$,O
	2	237.62-261.27	19.55%	$3H_2O$,2O,2 CH_3
	3	261.27-332.47	27.542%	C_6H_5,C=N, O_2,6H

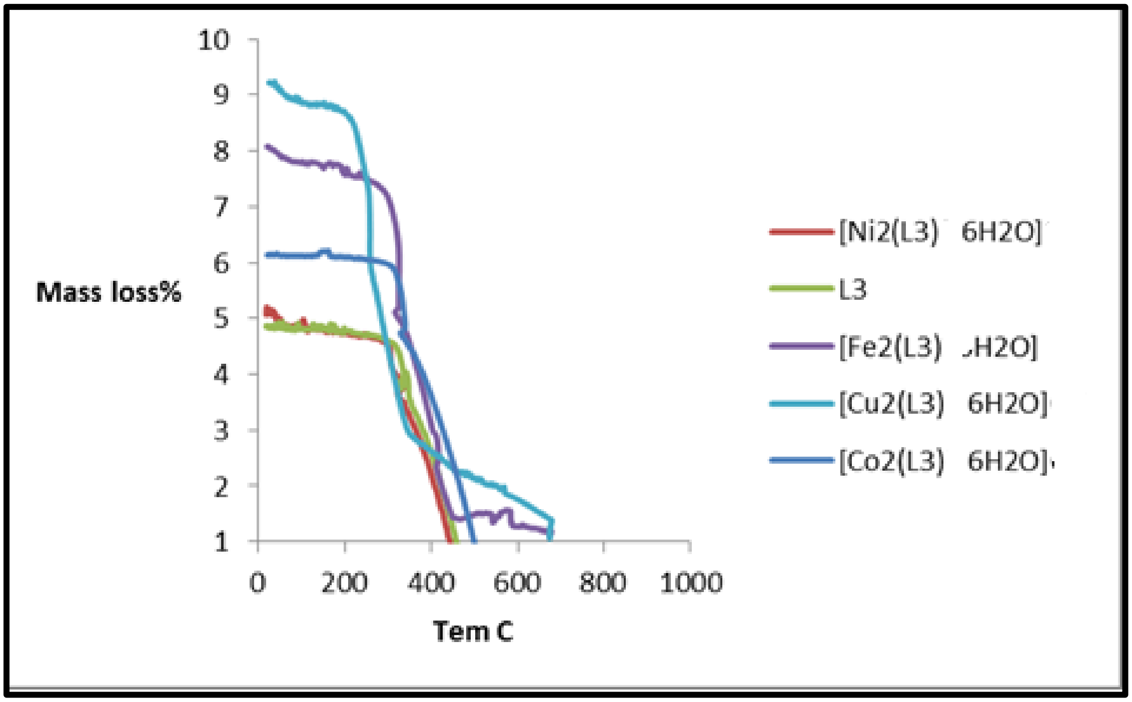


Fig (3-32)TG curves for L_3 and complexes

3.11 Cytotoxicity Assay

The concentration of the compounds that resulted in 50% of cell death (IC50) was determined from respective dose-response curves .The ligand and cobalt complex were measured to find out the effectiveness of measuring MTT for healthy and infected cells, as it was found that the complex$[Co (L_1)Cl_2H_2O]3H_2O$ was less effective than the ligandL_1.while The ligand L_3 less effective of cobalt complex$[Co_2(L_3).6 H_2O]$. were MTT for healthy and infected cells[132-134].

Table (3-15) Table Ic50 Shows the First and Third ligands and Cobalt Complexes for the First and Third ligands of a Healthy and Infected cell.

Compounds	IC50 healthy cell	IC50infected cell
Ligand L_1	66.90	26.45
Co $(L_1)Cl_2H_2O]3H_2O$	104.99	63.07
Ligand L_3	166.25	129.2
$[Co_2(L_3).6\ H_2O]$	153.95	101.24

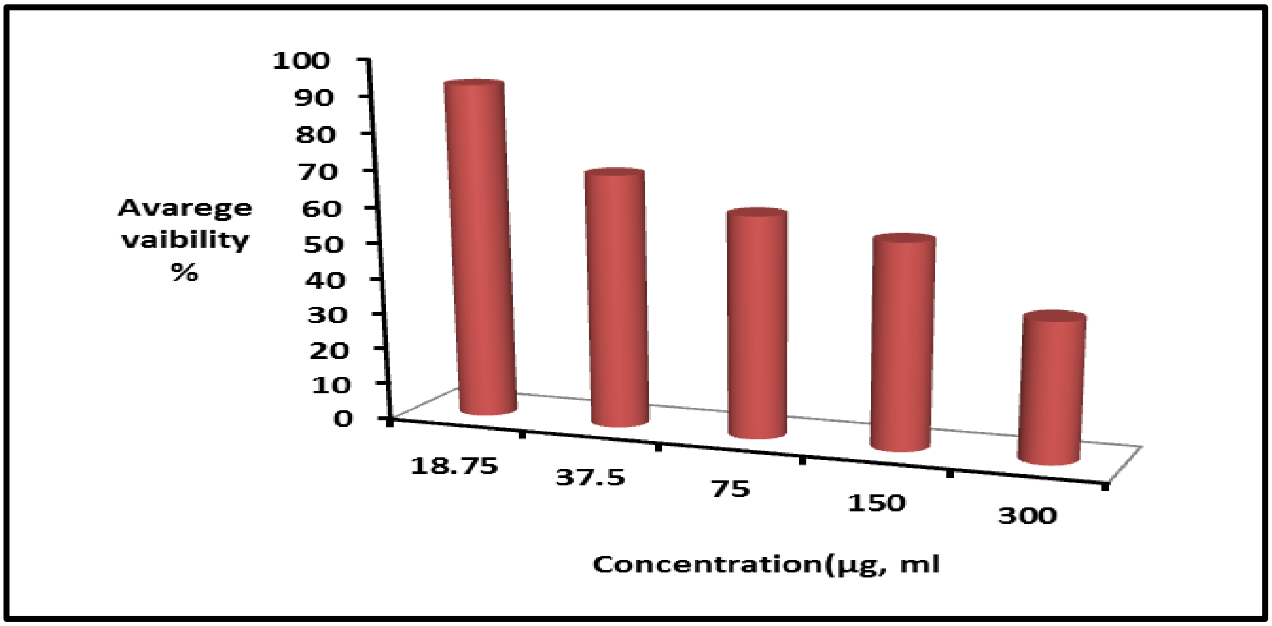


Fig (3-33)IC50 Curve for ligand L_1

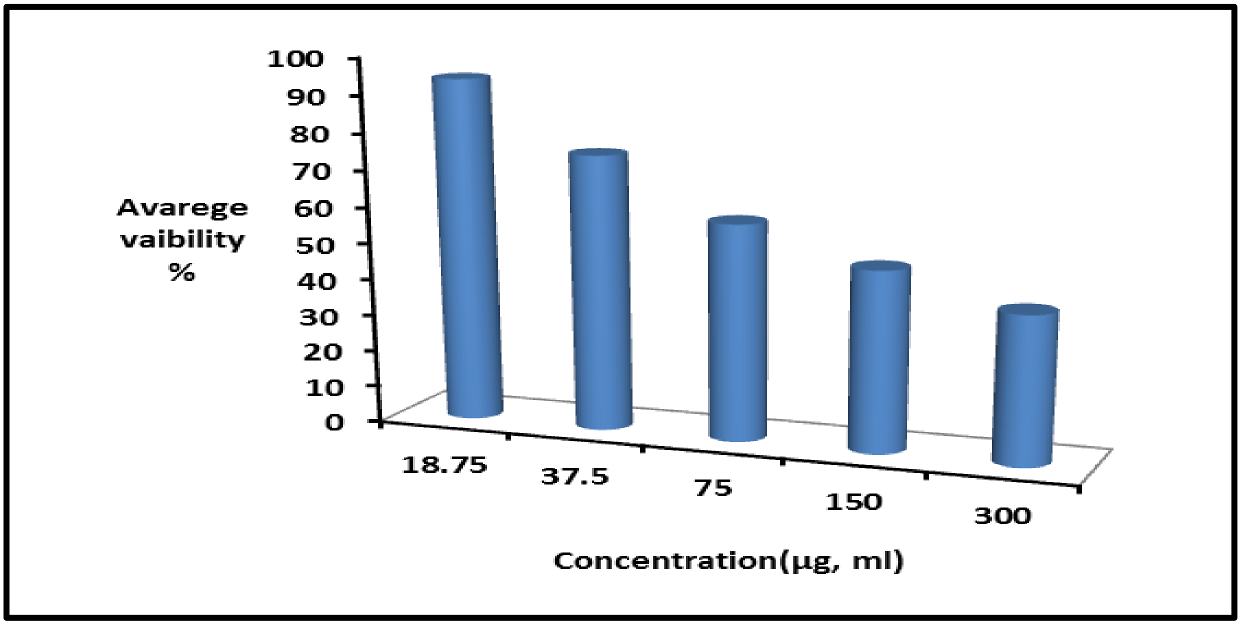


Fig (3-34)IC50 Curve for Co $(L_1)Cl_2H_2O]3H_2O$

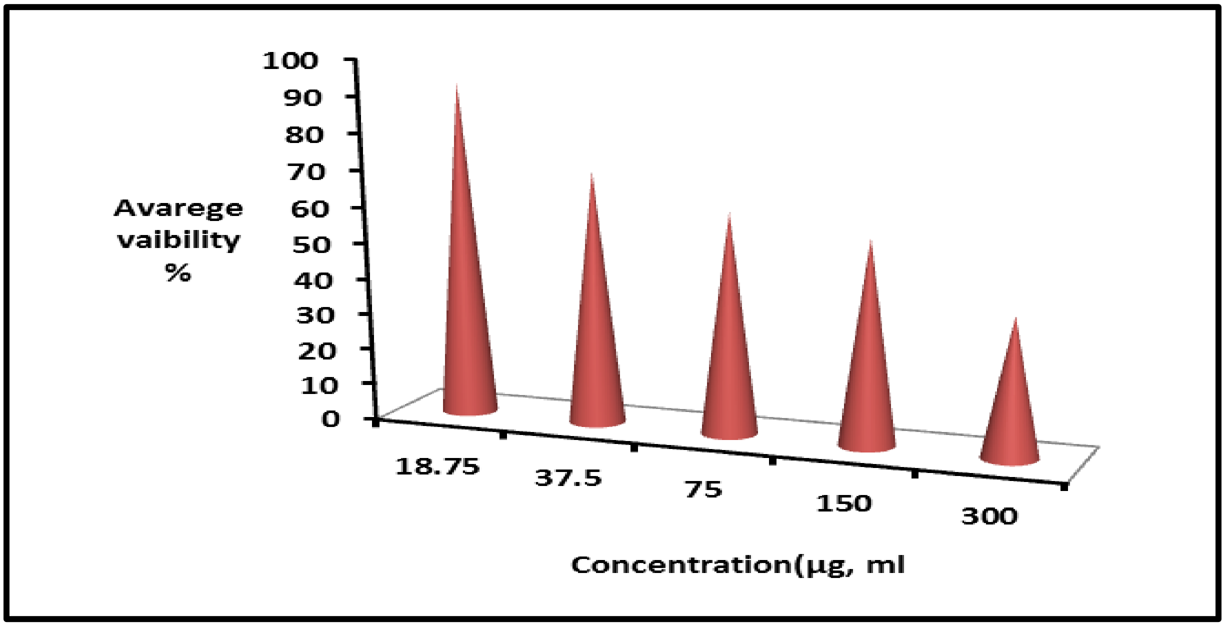


Fig (3-35)IC50 curve for Ligand L_3

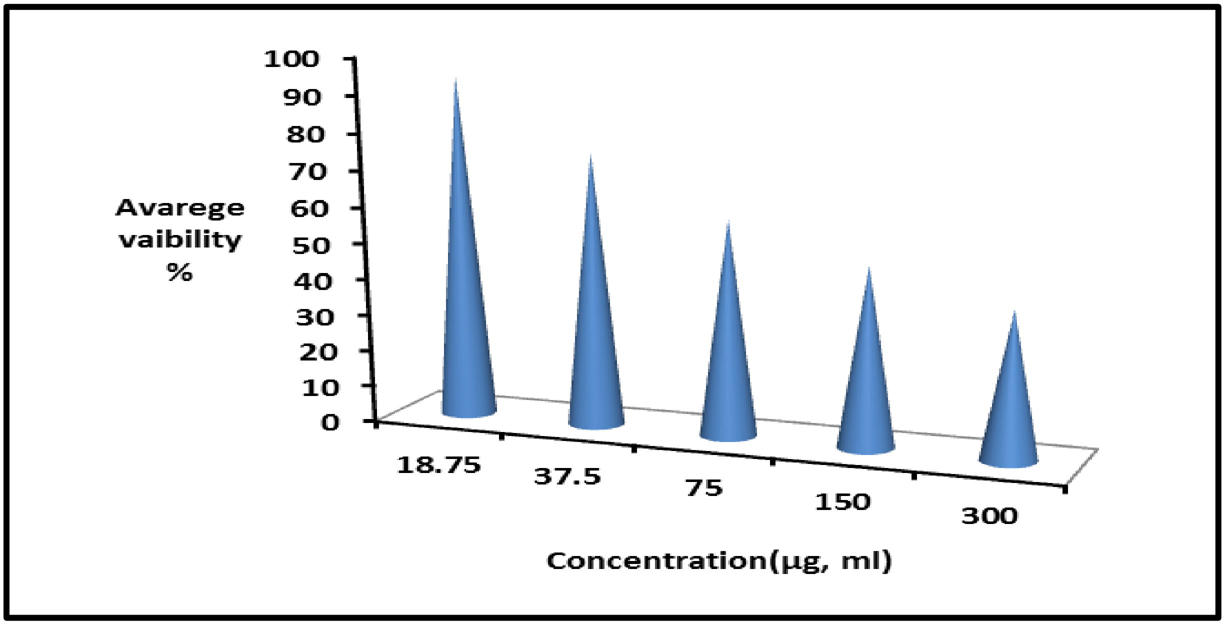


Fig (3-36)IC50 curve for $Co_2(L_3).6\ H_2O]$

3.12Corrosion Measurement

The corrosion inhibition of prepared compounds (L_1) $[(Fe(L_1)Cl_2.H_2O].3H_2O)$ and$[Cu(L_1)Cl_2H_2O]3\ H_2O$. have been examined on carbon Steele surface area in (0.1) M Hydrochloric Acid Solution at 298 K. Polarization technique was utilized to analyze the inhibition efficiency of the aforementioned compounds, IE%, was calculated in the equation below: %IE = (Icorr (blank) – (icorr) / Icorr (blank)) × 100

The results reveal that ring substitution in the proposed compounds have a substantial impact on the corrosion inhibition [135,136]Table (3-16) showed good inhibition efficiency for the synthesis compounds at 298 temperatures, giving the maximum inhibition efficiency IE%. The efficacy of ligand was 73%, iron 87%, and copper 89%[137].

Table (3-16)

Corrosion Parameters for Blank and Compound in HCl Solutions at 298 Temperature at Different Compound.

Comp.	E corr.	I corr.	Icorr./r	Resis.	Anodic	Cathodic	Corr. Rate,	IE%
Blank	-0.535	101.77	1.875E-4	169.3	0.103	0.057	0.920	----
L_1	-0.660	27.95	5.590E-5	1786	0.171	0.350	0.272	73
Fe L_1	-0.622	12.94	2.588E-5	2405	0.116	0.189	0.127	87
CuL_1	-6270.	11.70	2.339E-5	1888	0.091	0.115	0.115	89

E corrosion, V

I corrosion, µA

I corrosion per surface area, A/cm²

Polarization Resistance, Ω

Anodic β Tafel constant, V/decade

Cathodic β Tafel constant, V/decade

Corrosion rate, mm/year

IE% inhibition efficiency

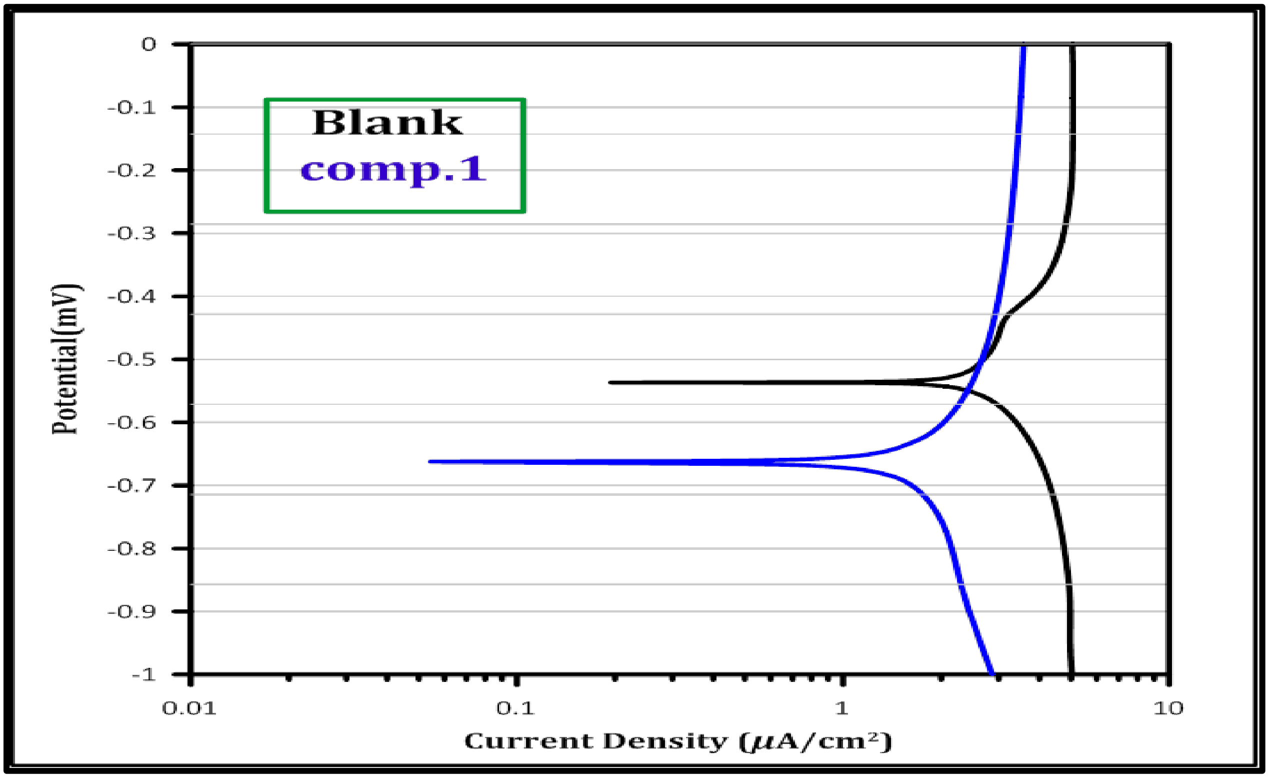


Fig (3-37) Polarization Curves form Corrosion of Blank HCl Solution Compound LigandL_1.

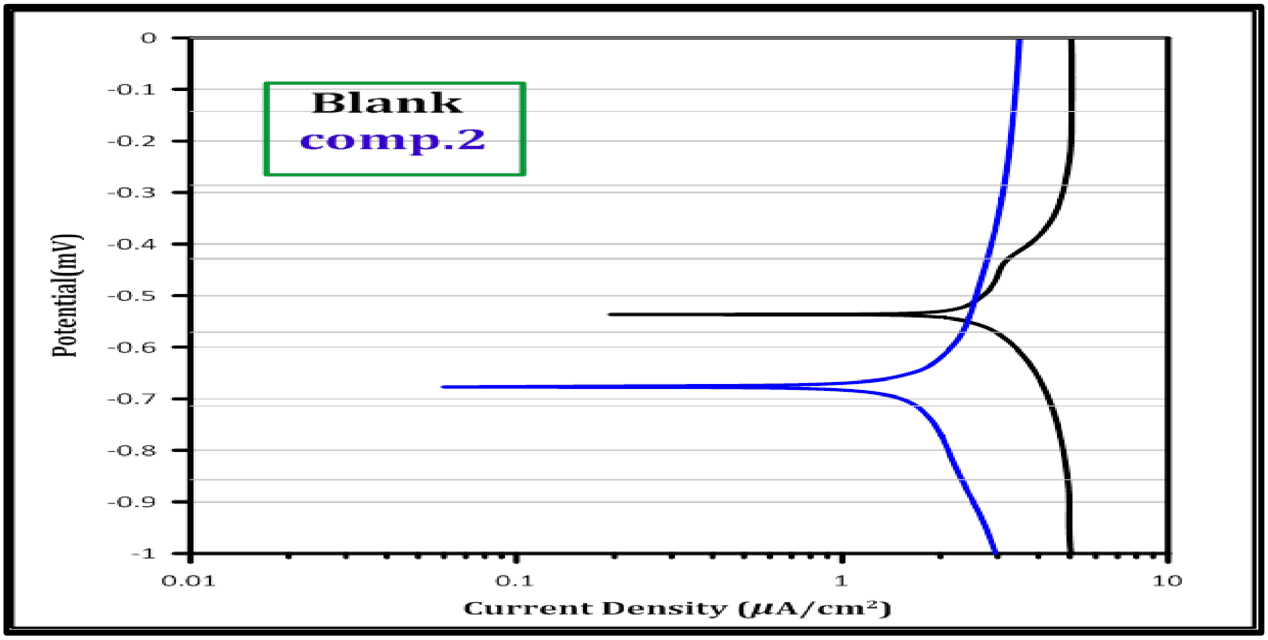


Fig (3-38)Polarization Curves for corrosion of blank HCl Settling Compound $[Fe(L_1)Cl_2.H_2O].3H_2O$

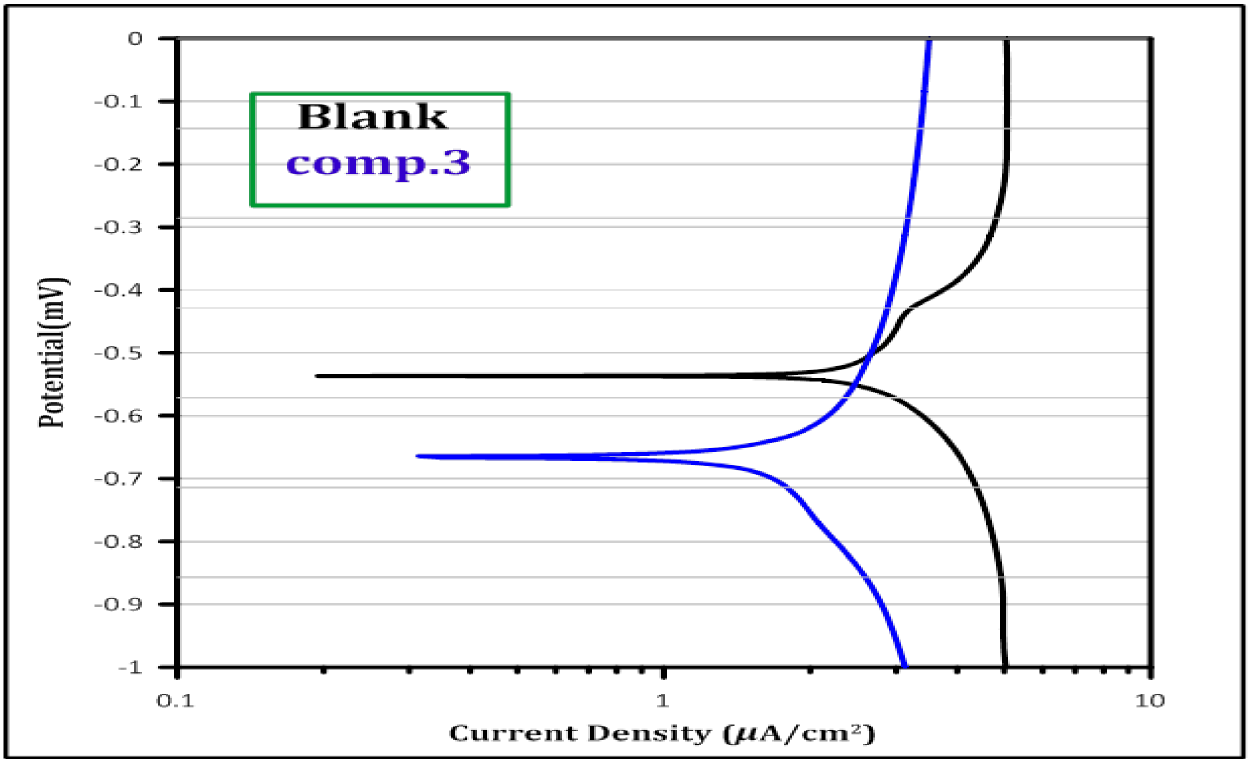


Fig (3-39)Polarization curves for rust of Blank HCl Solution Compound $[Cu(L_1)Cl_2.H_2O]3H_2O$

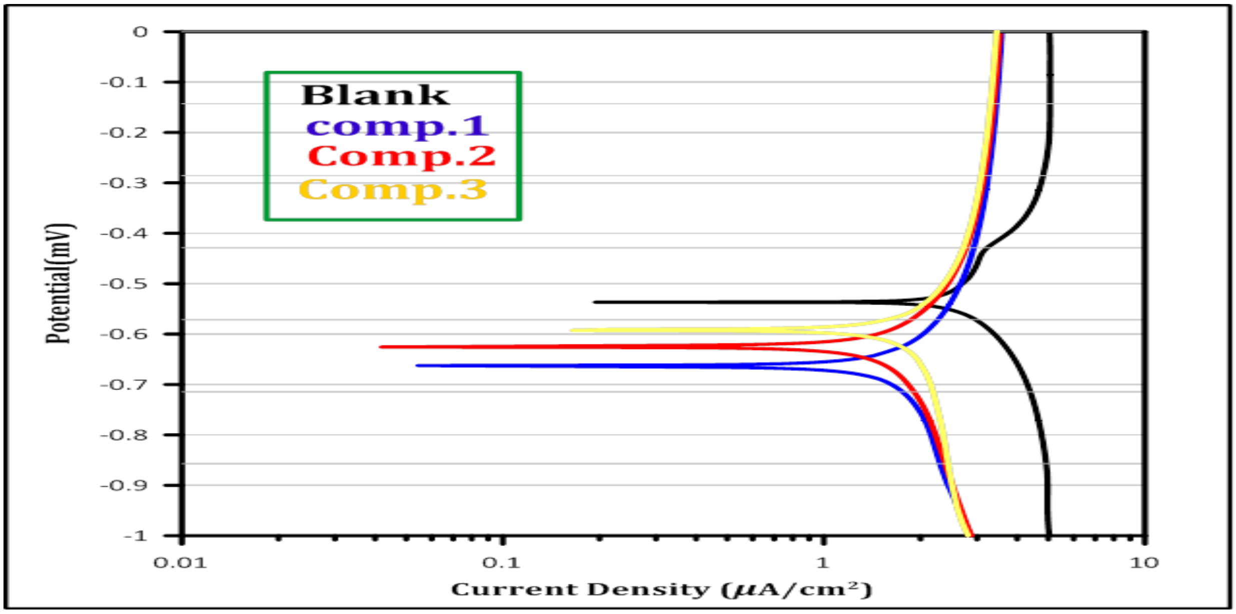


Fig (3-40)Polarization Curves for Corrosion of Blank HCl Solution

3.13. Conclusion

According to the above results, it can be concluded that:

1-The suggested structure for all complexes be octahedral geometries.

2-All the complexes are non-electrolytes.

3-The mole ratios [M:L] were[1:2] $L_3$and [1:1]L_2,L_1.

3.14 .Future work

1- The aforementioned ketones (9,10 phenanthrene quinone, 2,5-Dihyroxyl1,4 benzoquinone) can be mixed in different ratios with other amines to create a variety of ligands

2- L_2 can be used to prepare metal ion complexes with the molar ratio 1:2 ketone: amine.

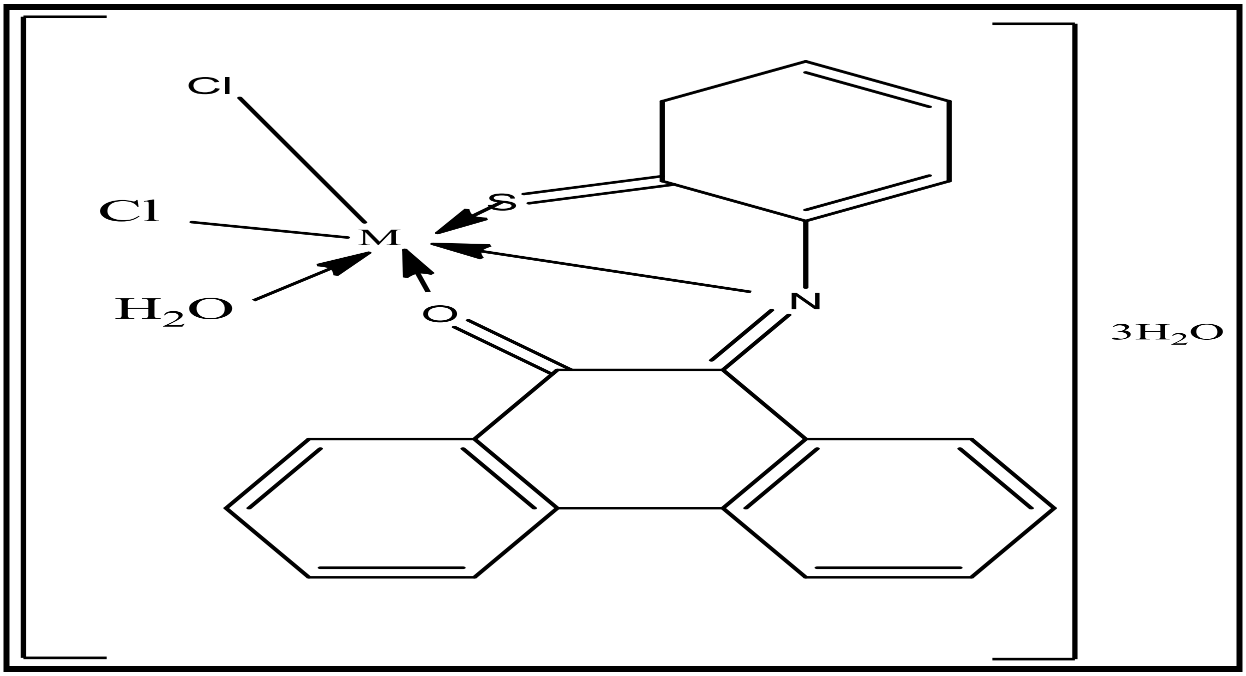
2 - Other new metal complexes using different metal ions can be prepared with L_1,L_2 and L_3 using both molar ratios.

3-Investigations can also be conducted on the production of various metal ion complexes with L_1, L_2, and L_3 Schiff base ligands.

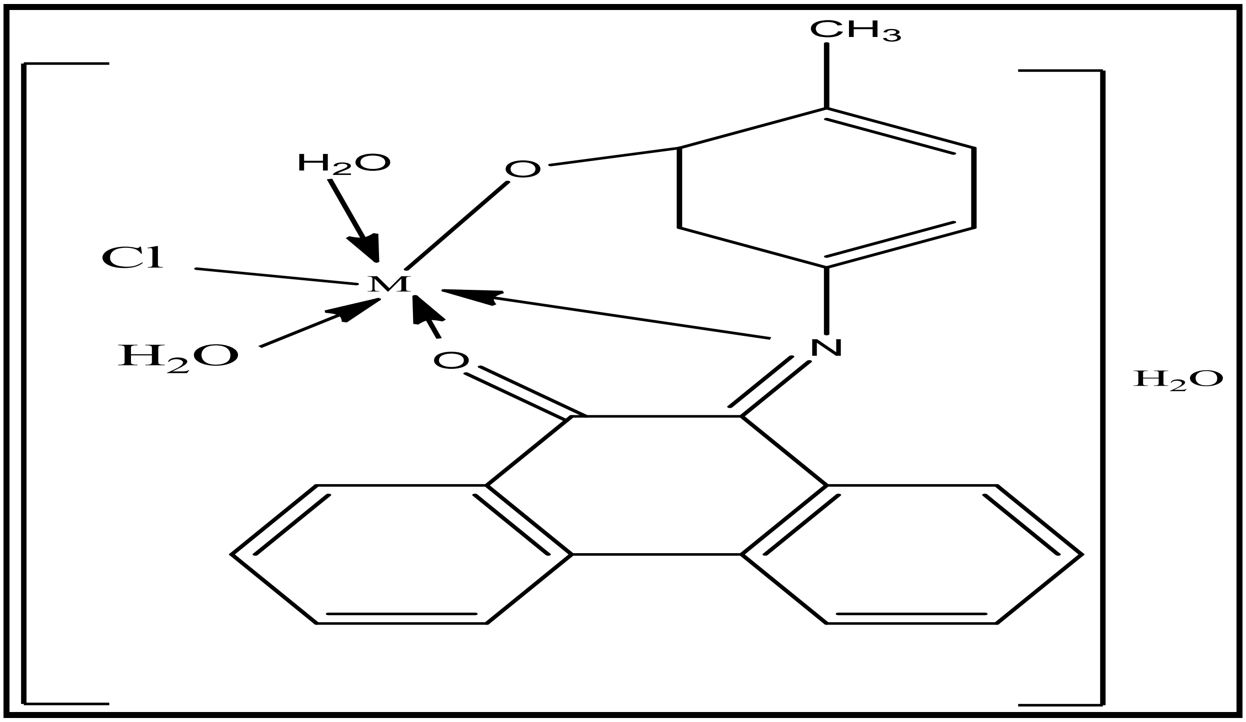
4-The application of the produced compounds in many industries and biological sectors.

3.15ThePropsed Building Of The Ligands And its Complexes

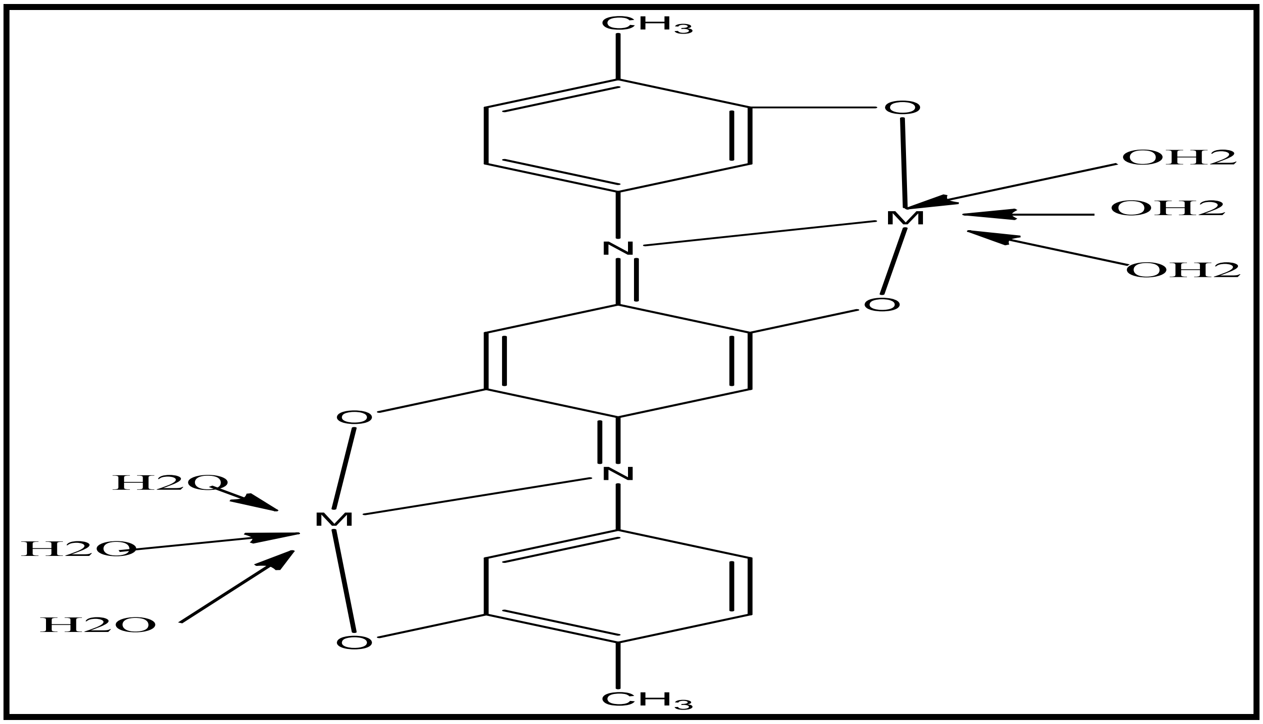
According to the obtained results from the different used techniques the proposed structure of the metal complexes with the ligands are :



M= Fe, Co, Ni and Cu L_1



M= Fe, Co and, Ni L_2



M= Fe, Co, Ni and Cu L_3

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الخلاصة

تضمنت هذه الدراسة خطوتين لتحضير معقدات قواعد شف من الكينونات مع الامينات الاوليه المختلفه فكانت الخطوة الاولى لتحضير قواعد شف تتضمن تفاعل الكيتونات(الكينونات)مع امينات. تحضير الاول من تفاعل 9، 10 فينو نثرين كينون مع 2 امينوثايو فينول وكانت نسبة التحضير(1 :1)والتحضير الثاني ناتج من تفاعل 10، 9 فينو نثرين كينون مع 5- امينو2 مثيل فينول لأنتاج قاعدة شف وكانت نسبة التحضير (1: 1) اما التحضير الثالث ناتج من تفاعل 2، 5-ثنائي هيدروكسي 1، 4-بنزوكوينون مع 5- امينو2 مثيل فينول وكانت نسبة التحضير (2:1) قواعد شف تتفاعل مع الاملاح الكلوريدات المائيه(الحديد الكوبلت، النيكل والنحاس)الثنائية في خطوه ثانيه لتحضير معقدات ذات خواص فيزيائية مختلفة عن بعضها البعض اجريت العديد من الفحوصات والتقنيات على الليكاندات والمعقدات وكانت التقنيات التي اجريت على الليكاندات هي الاشعة فوق البنفسجية-المرئية، الأشعة تحت الحمراء، التحاليل الحرارية، الكتله الذريه و الرنين النووي المغناطيسي والتقنيات التي اجريت على المعقدات هي مطيافية الأشعة فوق البنفسجية-المرئية، مطافيه الأشعة تحت الحمراء، التحاليل الحرارية، الامتصاص الذري، الحساسية المغناطسية و التوصيلية المولاريه وكان الشكل المقترح للمعقدات ثماني السطوح والصفات بارا مغناطسيه لكل المعقدات اجراء تطبقين على هذه الرسالة التطبيق الاول هي قياس مضادات السرطان على الليكاندات الاول والثالث ومعقدات الكوبلت لليكاند الاول والثالث والمقارنة بينهم من حيث الخلية السليمة والخلية المصابة وأيضا تطبيق مضادات التأكل لليكاند الاول ومعقدات الحديد والنحاس .وكان النحاس اكثر كفاءة بالنسبة للحديد والليكاند الاول .

جمهورية العراق

وزارة التعليم العالي والبحث العلمي

جامعة بابل – كلية العلوم للبنات

قسم الكيمياء

تحضير وتشخيص المعقدات المعدنية الانتقالية الجديدة مع قواعد شف المشتقة من الكينونات مع أمينات مختلفة

رسالة

مقدمه الى مجلس كلية علوم البنات - جامعة بابل

من متطلبات نيل درجة الماجستير في العلوم/ كيمياء

من قبل

ريام باقر ابراهيم

بكالوريوس علوم كيمياء. جامعة الكوفة (2012)

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