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Title

Synthesis and Characterization of New Metal Complexes with Schiff Bases Derived from Quinones and Substituted Quinones

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By

SALAM ABD ULSATTAR ASHIJ

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Supervised by

Asst. Prof.Dr.Suad Taha Saad

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بسم الله الرحمن الرحيم

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Title

Synthesis and Characterization of New Metal Complexes with Schiff Bases Derived from Quinones and Substituted Quinones

Signature

Dr.Suad Taha Saad
Scientific Order: Asst. Prof.
Address:
University of Babylon / College of
Science for Woman
Date: / /2022

Recommendation of Head of Chemistry Department

According to the available recommendation, I forward this thesis for Discussion.

Signature of Chemistry Department
Dr/ HazemYahya Mohammed
Scientific order : Asst. Prof.
Address : Head of Chemistry Department
University of Babylon / College of
Science for Woman

Dedication

To my father and my mother

To my supervisor, assistant professor Dr. Suad-Saad

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

To all my postgraduate colleagues

Acknowledgements

First and foremost, I would like to praise Allah the Almighty for His blessing and guidance

I would like to extend my special thanks and appreciation to Assistant Professor , Dr.Suad Taha Saad for his suggestions and guidance.

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Abstract:

The study involved synthesis of two types of Schiff base ligands. The first ligand (L1) is synthesized from the reaction between 2-aminothiophenol with 9,10-phenathrenquinon and the second ligand (L2) was synthesized from reaction between 2-aminothiophenol with 2,5-dihydroxy-1,4-benzoquinon. The first ligand coordinated with (Co(II) Ni(II) and Cu(II) in molar ratio (l:l) (M:L), while the second ligand coordinated with (Co(II) and Ni (II) in molar ratio (2:1) (M:L). Both ligands were characterized by (FTIR, UV-visble,^{1}HNMR and thermal analysis). The ligands complexes were characterized by (FTIR, UV-visible, molar conductivity, magnetic sensitivity and thermal analysis). It could be suggested the square planar geometry for (L1) complexes. While (L2) complexes suggested as tetrahedral. The biological activity of all the prepared ligands and complexes were tested against two types of bacteria, *Escherichia coli* and *Staphylococcus aureus*. The results show the biological activity of L1- metal complexes against the two types of bacteria in comparison with the two ligands and L2- metal complexes .

List of Subjects

CHAPTER TWO

EXPERIMENTAL PART

CHAPTERTHREE

RESULTS AND DISCUSSIONS

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	List of abbreviation	
NaOH	Hydroxide sodium	
DMSO	Dimethyl Sulfoxide	
FTIR	*Fourier-transform infrared spectroscopy*	
^{1}HNMR	*Proton nuclear magnetic resonance*	
HCl	Hydrochloric acid	
H_2SO_4	Sulfuric acid	
DCM	*Dichloromethane*	
L1	9,10phenanthrenequinone	
L2	2,5-dihydroxy-1,4-benzoquinon	

جمهورية العراق
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العنوان

تحضير وتشخيص معقدات فلزيه جديدة مع قاعدتي شف المشتقة من الكوينونات والكوينونات المعوضة

رساله

مقدمه الى مجلس كلية العلوم للبنات-جامعه بابل كجزء

من متطلبات نيل شهادة الماجستير في الكيمياء

للطالب

سلام عبد الستار عاشج

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إشراف

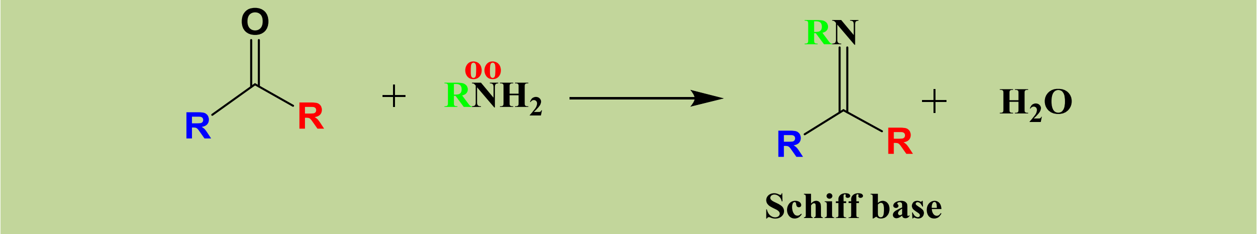
أ.م.د (سعاد طه سعد)

2022 م 1444هـ

1.General Introduction to Schiff Bases

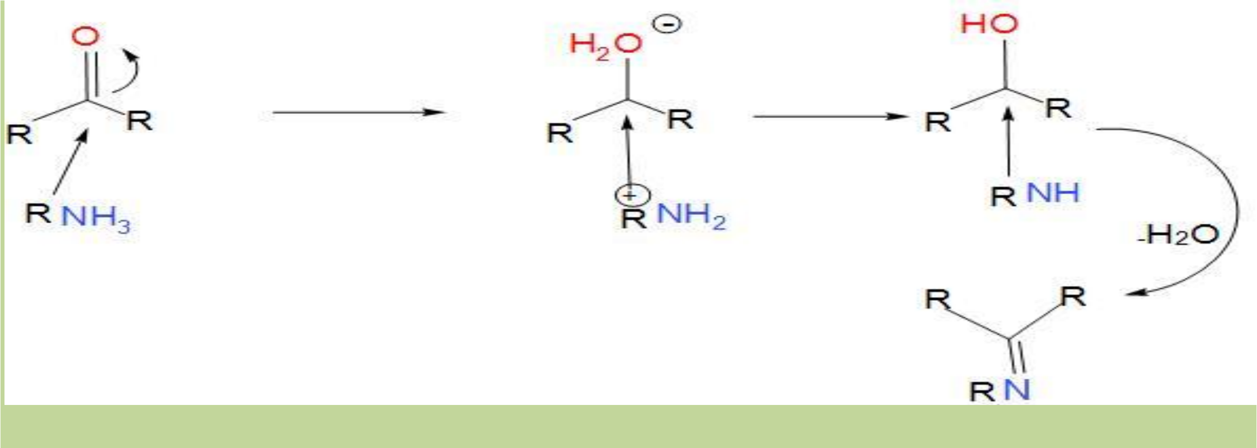
According to the reaction conditions, a primary amine can combine with an aldehyde or a ketone to produce a Schiff base, which a German chemist bear hugo joseph named schiffs described these compounds at first in 1864**[1-3]**.These compounds (Schiff bases) are also known with other different names, such as anils, imines or azomethines**[4]**.

In Schiff base synthesis analdehyde or ketone whose carbonyl group (C=O) has been replaced by -C=N group to give aldimines or ketimines respectively with the elimination of water molecule **[5,6]**. The general reaction of Schiff bases synthesis is shown in the following Figure(1.1)**[7]**.



scheme(1.1) General reaction for Schiff base synthesis

Where R groups can be alkyl or aryl and amines act as nucleophile, while aldehydes or a ketones are electrophiles**[8]**.Schiff bases which are substituted with aryl groups are significantly stable and easy to synthesize. While Schiff bases with alkyl substituents are unstable. The Schemi below shows the synthesis mechanism of Schiff bases by the reaction between the carbonyl compound and amines.



Scheme (1.2) Schiff base mechanism synthesis.

The use of Schiff bases in different fields is due to the presence of the lone pair of electrons in an sp^2 hybridized orbital of nitrogen atom of the azomethine group (–C=N)**[9]**.There fore, Schiff bases can be found as catalysts in the organic synthesis and can be used as pigments and dyes**[10,11]**.

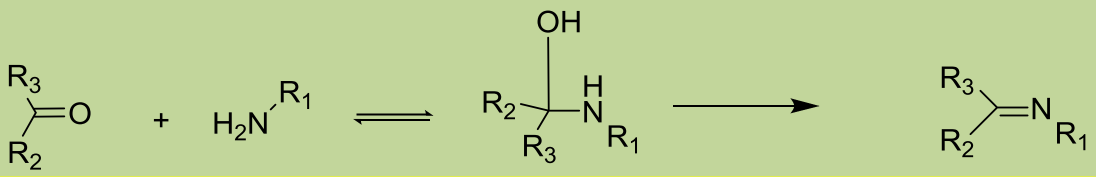
In addition, Schiff bases poses a biological importance, therefore, they can be used also as antifungal, antibacterial, antimalarial, anti-inflammatory, antiviral, and antipyretic effects**[12-16]**.

In coordination chemistry , Schiff bases form complexes with different metal ions by binding these metal ions with the azomethine nitrogen**[17]**.

1.1 Methods to prepare Schiff bases

1.1.2 Reactions of primary amines with aldehydes or ketones

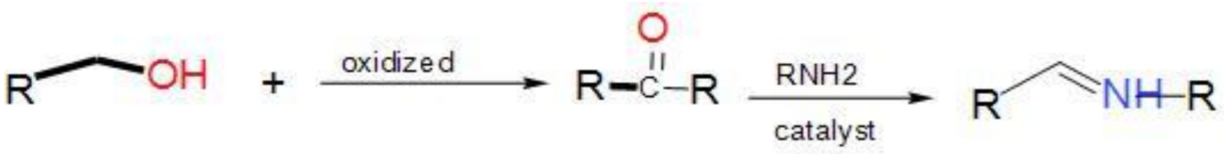
This method can be considered as the most often used method to prepare Schiff bases. This method relies on the reaction between aldehydes or ketones with primary amines to produce a Schiff base compound with the characteristic asomethine group with the releasing of water molecule. The presence of acids in this reaction can improve the reaction and make it faster. Such as hydrochloric acid, sulphuric acid and glacial acetic acid**[2, 18,19]**.Scheme(1.3)



Scheme (1.3) Schiff base synthesis from primary amines with aldehydes or ketones

1.1.3 Reaction of amines with oxidized alcohols

Hence the synthesis of aldehydes and ketones relies on the oxidation of alcohols , therefore, in this method alcohols are used and oxidized to produce aldehydes and ketones. Then the latest compounds are reacted with amines to give Schiff bases as shown in Scheme 1.4 **[20-27]**.



Scheme (1.4) Schiff base synthesis from amines with oxidized alcohols

1.1.4Reaction of organometallic compounds with cyanides

In this method (figure. 1.5) a grignard reagent is added to aryl cyanides or aliphatic cyanide to produce ketimines which converted to the related ketone by hydrolysis of the intermediate compound of metallo imine**[28]**.

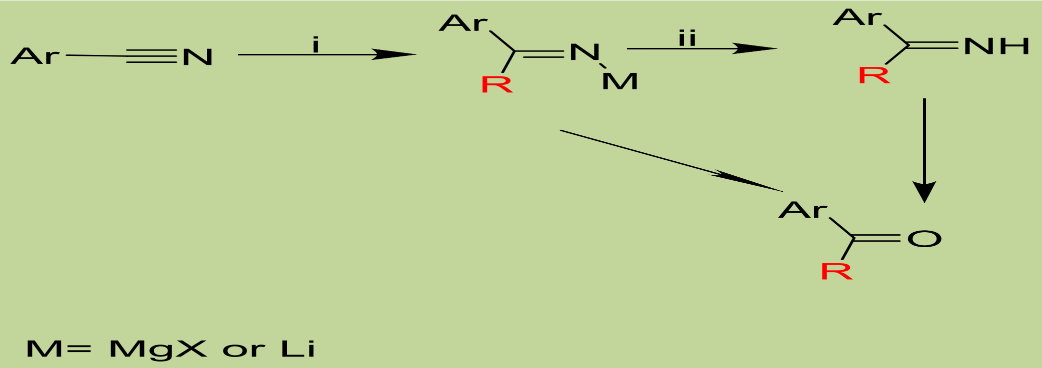


Figure (1.5) Schiff base synthesis from organometallic compounds with cyanides

1.1.5 Reaction of phenols and phenol-ethers and nitriles

Nitriles compounds can react with phenols and their phenol ethers to give ketimines. this reaction can be accelerated by an acid**[29-31]**.. This reaction can be explained by figure **(1.6)**

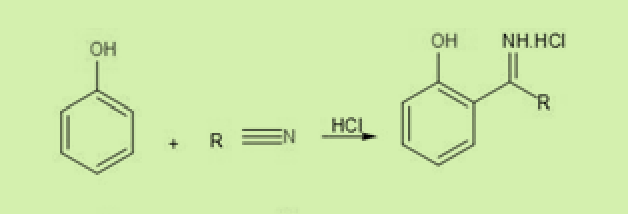


Figure (1.6) Schiff base synthesis from phenols and nitriles

1.1.6 Metal amides reaction

In this method an alkali metal or its amine salt are added to ketones to give the Ketimine inorder to give Schiff base compound.

1.2Classification of Schiff bases according to the number of donation groups

Schiff base can be classified according to the number of coordination sites in Schiff ligand to:

1.2.1Monodentate Schiff bases: In these ligands the metal ion coordinates with a Schiff base ligand through the azomethine group (one coordination site) an example of such Schiff bases is shown in figure(1.7)**[32]**.

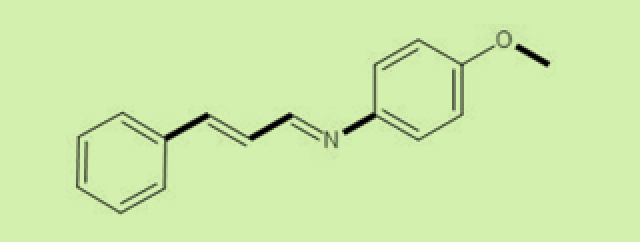


Figure (1.7)Monodentate Schiff base ligand

1.2.2Bidentate Schiff bases[33]: These ligands linked with the metal ion by two chelate sites in the Schiff base ligand as given in figure(1.8)

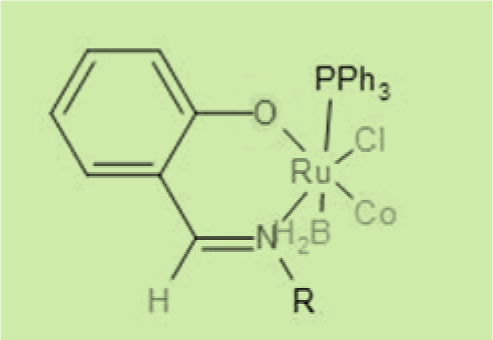


Figure (1.8)Ru(II) complex with bidentate Schiff base ligand

1.2.3 Tridentate Schiff bases: Three coordination sites are available in the Schiff base ligand to coordinate with the metal**[34]**. ionas given in figure(1.9)

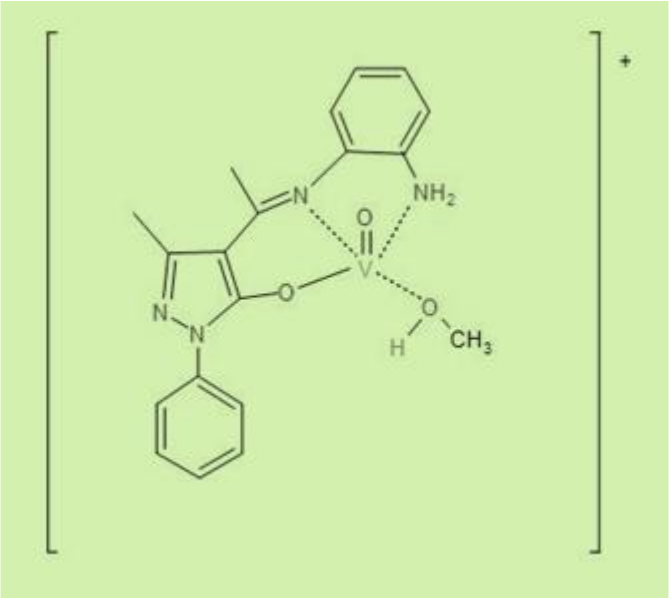


Figure (1.9) V(II) complex with tridentate Schiff base ligand

1.2.4 Tetradentate Schiff base ligands: These ligands coordinate with metal ions through four coordination sites**[35].** as shown in figure (1.10)

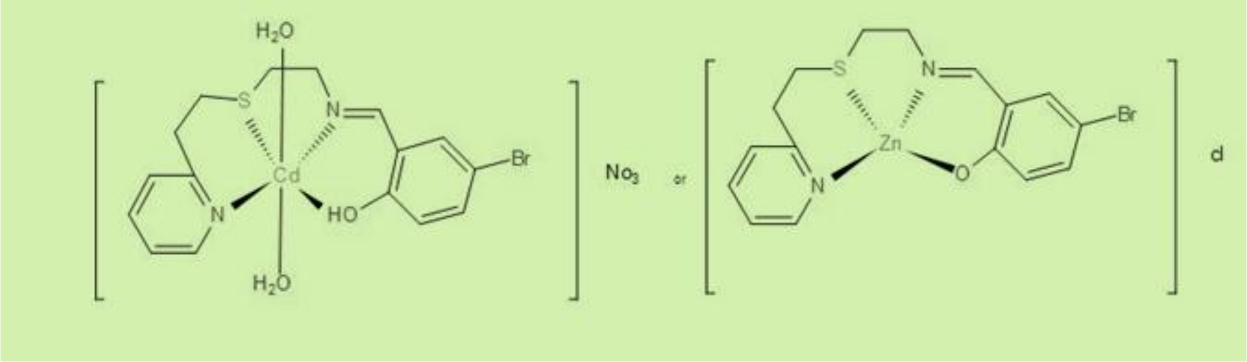


Figure (1.10) Metal complexes with tetradentate Schiff base ligand

1.2.5Polydentate Schiff bases: These ligands contain more than four coordination sites**[36]**.Figure (1.11) shows such Schiff bases[**37]**.

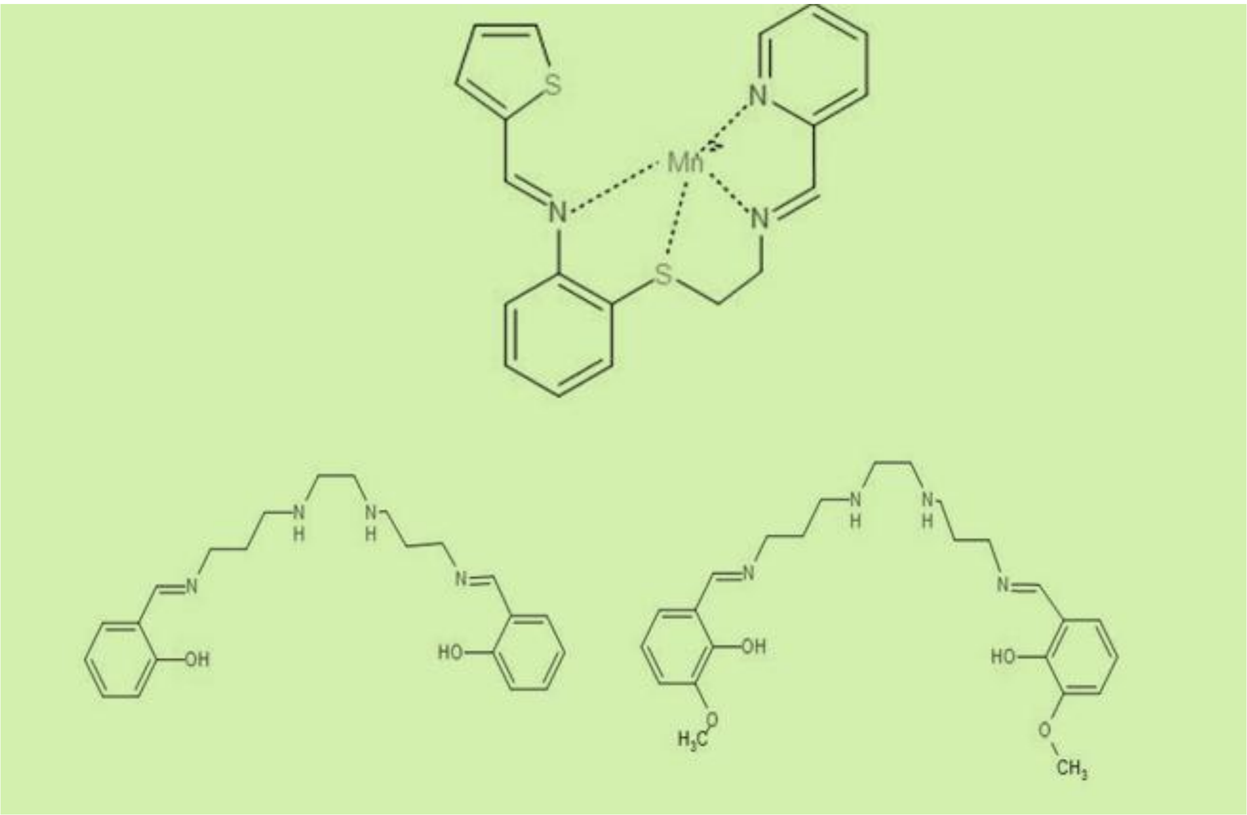


Figure (1.11) Examples of polydentate Schiff bases

1.3Metal Complexes with Schiff Bases

In the last twenty years, there has been a lot of interest in Schiff base complexes of some transition metal ions, specially the first row of transition metals in the periodic table. The interest comes from the importance of these complexes in a wide range of applications, including biological, clinical, analytical, industrial, and catalytic activity in organic chemistry **[38]**.

Schiff base compounds are acting as good chelating agents by the coordination with the metal ion through the azomethine group nitrogen atom. In addition, the presence of special coordinating sites in the skeleton of Schiff base ligands such as, hydroxyl and thiol groups can enrich the properties of the produced Schiff base ligand as well as the formation of stable six or five membered ring**[39-41]**. As a result these Schiff base ligands find their way in various applications as mentioned above**[42,43]**.

1.3.1 Cobalt chemistry

Cobalt as an element has been isolated firstly in 1735 by the Swedish chemist Georg Brand. In nature , cobalt can be found with other metals such as Fe, Ni, Cu, Ag and As**[44]**.

Cobalt has the electronic configuration$[Ar]^{18}4s^{2}3d^{7}$.In cobalt compounds, the common oxidation states are 1, 0, +1, +2, and +3. Divalent and trivalent states are the common cobalt oxidation states.table(1-1)

Table (1-1) shows some of cobalt properties[45].

Cobalt general properties					
Atomic number	electronic configuration	Melting point °C	Ionization energy	oxidation states	Atomic mass
27	$[Ar]^{18}4s^{2}3d^{7}$	1495	757.6kJ/mol	1, 0, +1, +2, and +3	58.93

Cobalt with +2 oxidation state gives different types of complexes with different structures such as, blue tetrahedral and pink octahedral complexes. Co(II) octahedral complexes are either high spin or low spin with the electronic configurations $t_{2g}^{5}e_{g}^{2}$ and $t_{2g}^{6}e_{g}^{1}$ respectively**[46]**. While the high spin tetrahedral complexes have the electronic configuration $e^{4}t_{2}^{3}$.

Cobalt with +3 oxidation state gives also complexes with four or six coordination numbers. The frequent ones are the octahedral complexes with (six coordinating ligands). In such complexes Co^{3+} is found as low spin with the electronic configurations $t_{2g}^{6}e_{g}^{0}$ and its hybridization is $d^{2}sp^{3}$**[47,48]**.

An example of tetrahedral Co(II) complexes are those which have been reported by Tunçel*et.al.*,(Figure. 1.12).In these complexes the ligands 4-(3-methoxysalicylidene)-5-hydroxy-6-(2-hydroxyphenylazo)-2,7-naphthalene disulfonic acid disodium salt and 4-(3-methoxysalicylidene)-5-hydroxy-6-(2-hydroxy-4-cholorophenylazo)-2,7-naphthalenedisulfonic acid disodium salt form tetrahedral Co(II) complexes. These complexes were prepared by the addition of cobalt chloride dissolved in ethanol to an aqueous solution of the ligand at pH 5 and the mixture was heated in a water bath for four hours**[49]**.

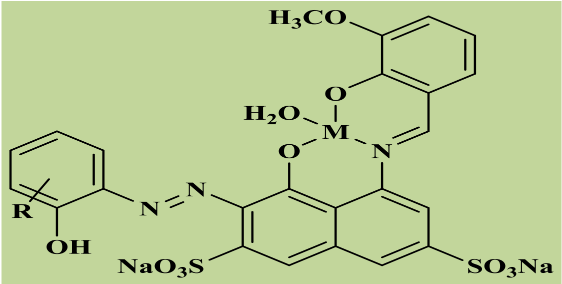


Figure (1.12) An example of tetrahedral Co(II) complexes

On the other hand, an example of octahedral Co(II) complexes, is its complex with {2,2'-(((2-aminophenyl)imino) methylphenol(Figure 1.13). The Schiff base ligand was prepared by the refluxing o-phenyldiamine with salicylaldehyde in ethanol and glacial acetic acid for three hrurs. These ligands were reacted with $CoCl_2.6H_2O$ in methanol for six hr. to give the Co(II) complex**[50]**.

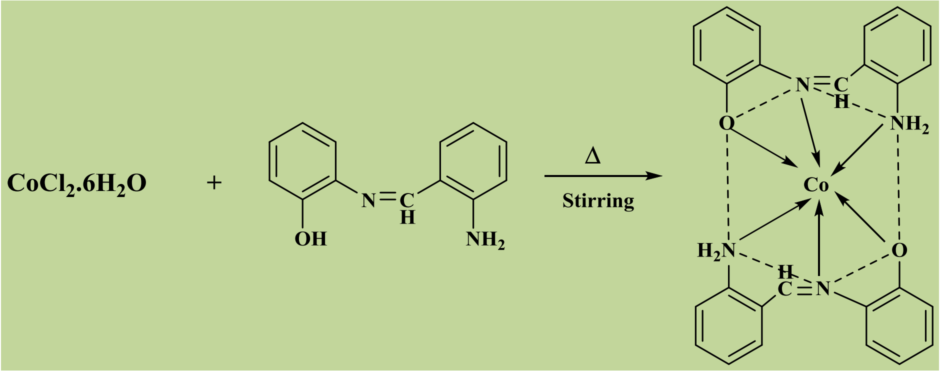


Figure (1.13) Example of octahedral Co(II) complexes

1.3.2 Nickel chemistry

In the first transition row, nickel (Ni) is found with the valence shell configuration $3d^8 4s^2$. It is found a ssilver white crystals and in nature combined with other elements. Oxide and silicate are the common ores of nickel**[51]**. The common oxidation states of nickel are 0 and +2.

Table (1-2) Shows some of nickel properties

Nickel general properties					
Atomic number	electronic configuration	Melting point °C	Ionization energy	oxidation states	Atomic mass
28	$[Ar]^{18}4s^{2}3d^{8}$	1453	737	0, +4, +2, and +3	58.71

Ni^{2+}possess different coordination numbers and geometries, therefore, square-planar, octahedral, and tetrahedral structures are the most available**[52-54]**.Ni^{2+} tetrahedral complexes as well as square planar geometry with the maximum of four coordination number have the electronic configuration d^8**[55-57]**. In the latest complexes type eight electrons are fitted into four d orbitals while one empty orbital is left.

In addition, benzyl -2-[phenyl(pyridin-3-yl)methylidene]hydrazinecarbodithioate Schiff base ligand was reacted with nickel(II) acetate in ethanol to form Ni^{2+} square planar complex(Fig. 1.14)**[58]**.

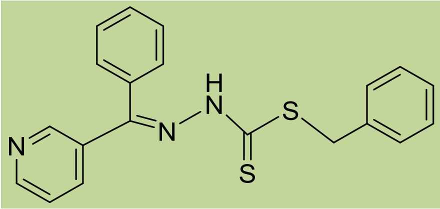


Figure (1.14) Ni^{2+} square planar complex with benzyl -2-[phenyl(pyridin-3-yl)methylidene]hydrazinecarbodithioate Schiff base ligand

Singh and coworkers have prepared octahedral Nickel(II) complex with Schiff base ligand of 2,4-Furyliminobenzylacetophenone(Figure. 1.15). This complex was prepared by the reaction between this Schiff base and nickel chloride hexahydrate in methanol for 3 hour.**[59]**.

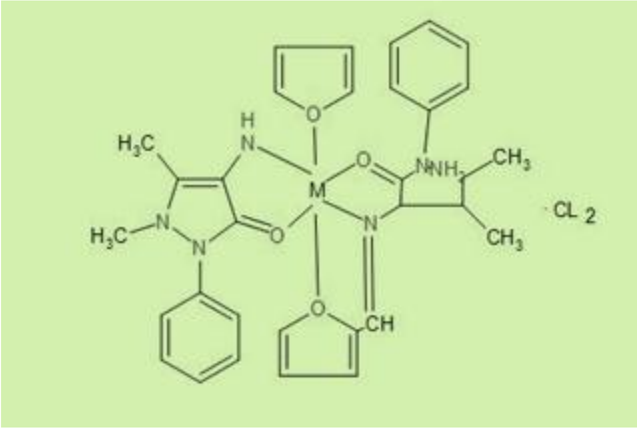


Figure (1.15) Ni^{2+}octahedral complex with2,4-Furyliminobenzylacetophenone Schiff base ligand

Another octahedral Nickel(II) complex was reported by AL-Jibouri *et.al.*,(Fig. 1.16)where (E)-2-(((3-mercapto-5-(3,4,5-trimethoxyphenyl)-4H-1,2,4-triazol-4-yl)imino)methyl)phenol was reacted with $NiCl_2.4H_2O$ in ethanol and for (10-12) hours**[60]**.

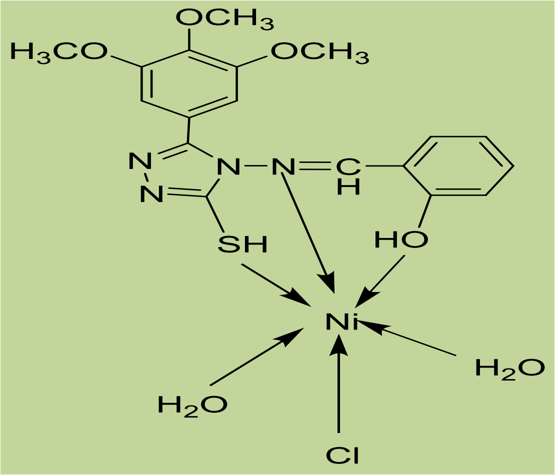


Figure (1.16)Octahedral Nickel(II) complex with(E)-2-(((3-mercapto-5-(3,4,5-trimethoxyphenyl)-4H-1,2,4-triazol-4- yl)imino)methyl)phenol

1.3.3 Copper Chemistry

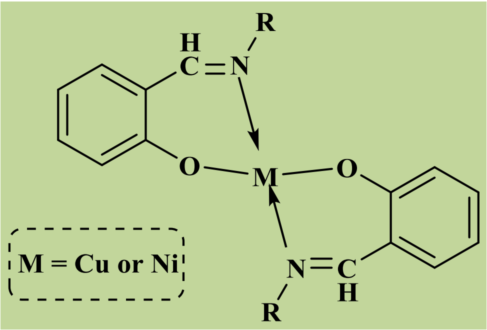
Copper is also found in the first transition row with the electronic configuration $3d^{10}4s^{1}$. It was firstly discovered in 1776 and it is found as two ores, sulfides and oxides. As a metal it appears as a soft red .The most common oxidation states for copper is +2**[61]**.as im table (1-3)

Table (1-3) shows some of copper properties

Copper general properties					
Atomic number	electronic configuration	Melting point °C	Ionization energy	oxidation states	Atomic mass
29	$[Ar]^{18}3d^{10}4s^{1}$	1083	745.5	+1 and +2,	63.54

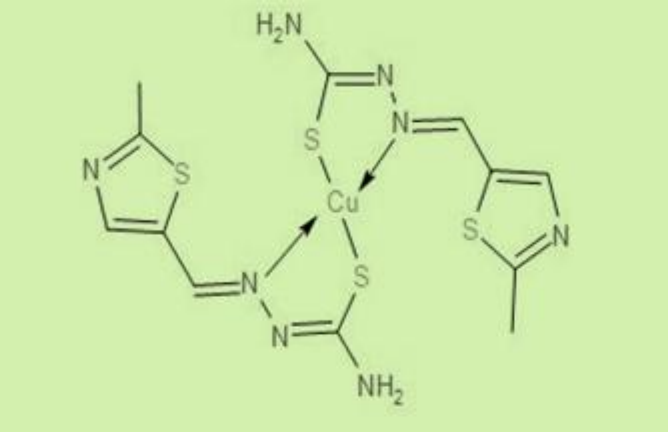
Most Cu^{2+} compounds have four, five and six coordination numbers**[62-64]**.Complexes of copper (II) show blue or green color with d-d electronic transitions , charge transfer transitions (from metal to ligand and ligand to metal). Tetra coordinated copper is preferred a square planar geometry**[65-67]**.

For example, Cu(II) complex with N-alkylsalicyladimines(Fig. 1.17)) adopts square planar structure. This complex was prepared by the reaction between a Schiff base formed from salicyldehdye and primary amine with copper salt in the presence of a base**[68]**.



Figure(1.17) Cu(II) square planar complex with N-alkylsalicyladimines

Another example of Cu(II) square planar complexes is its complex with [(E)-[(2-methyl-1,3-thiazol-5-yl)methylidene]amino]thiourea which was prepared by Yallur and co-workers (Fig. 1.18). The Schiff base ligand was prepared by refluxing an alcoholic solution of 2-methyl-1,3-thiazole-5-carbaldehyde with thiosemicarbazide in the presence of 5% aqueous acetic acid. This ligand was mixed with copper (II) chloride dihydrate in ethanol for two hour.**[69]**.



Figure(1.18) Cu(II) square planar complex with[(E)-[(2-methyl-1,3-thiazol-5-yl)methylidene]amino]thiourea

Bakare has prepared octahedral Cu(II) complex with a Schiff base ligand derived from4-amino-3-hydroxynaphthalene-1-sulfonic acid and 2-hydroxy-1-naphthaldehyde in methanol(Figure. 1.19). This ligand was reacted with copper (II) chloride dehydrate in a basic solution for an hour and half using methanol as a solvent**[70]**.

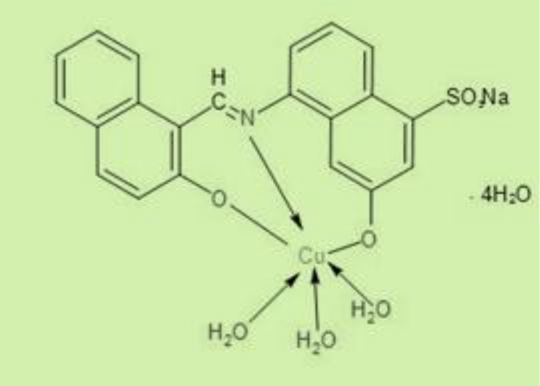


Figure (1.19) Octahedral Cu(II) complex with a Schiff base ligand derived from 4-amino-3-hydroxynaphthalene-1-sulfonic acid and 2-hydroxy-1-naphthaldehyde

1.4Applications of Schiff base metal complexes

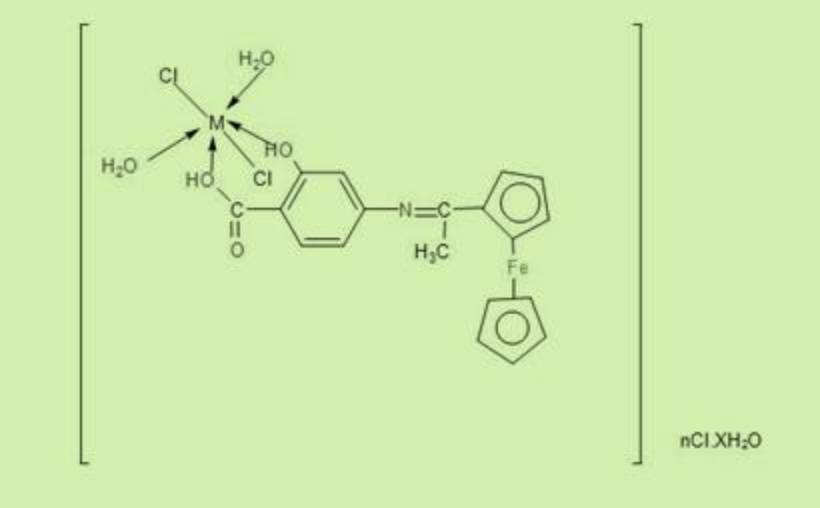
As it is well known that Schiff base ligands have been studied widely, because they are easy to prepare. Therefore, these ligands play an important roles in the both coordination chemistry and bioinorganic chemistry. Due to the presence of the azomethine group with the one pair of electrons as mentioned before.Therefore, they have a potential use chemistry and biology. The activity of the azomethine group is due to the sp^{2}hybridization of its nitrogen atom. For example, this atom can form a hydrogen bond with the active centres in the cell.In addition Schiff-bases can be used for inflammation, microbial, cancer treatments in addition to their use in industry**[71-73]**.Some of Schiff bases applications are listed below.

1.4.1 Anticancer application of Schiff bases

Cancer, is a kind of disorder of cells whi chleads to non-controlled development of those cells in some circumstances**[74]**. For Cancer treatment, Surgery and chemotherapy are the available solutions**[7]**. However, chemotherapy drawback is the undesirable side effects.Therefore, many Schiff-bases metal complexes have been prepared and investigated against different types of cancer.

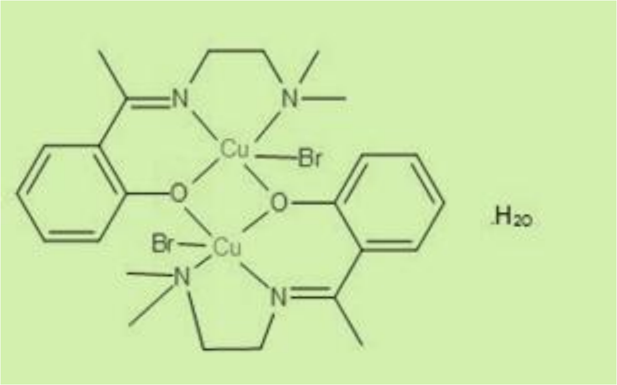
Kaur*et.al.,* have prepared di and Triorganotincomplexes with 2-{[(E)-(2-hydroxy-3-methox yphenyl)methylidene]amino}-2-methylpropanoic acid and used to investigate their activity against MCF-7 breast cancer cells. These two complexes show a good anticancer activity in comparison with the ligand**[75]**.

Deghadi and co-workers have prepared Schiff base Cu(II), Co(II), and Zn(II) complexes and tested against the MCF-7 breast cancer cell. The Schiff base ligand was prepared by the reflux reaction between 4-aminosalicylic acid and 2-acetylferrocene for three hours(Fig. 1.20).Then the metal complexes were prepared by mixing the ligand (dissolved in DMF) with these metal chlorides (dissolved in hot ethanol) in 1:1 molar ratio for one hour**[76]**.



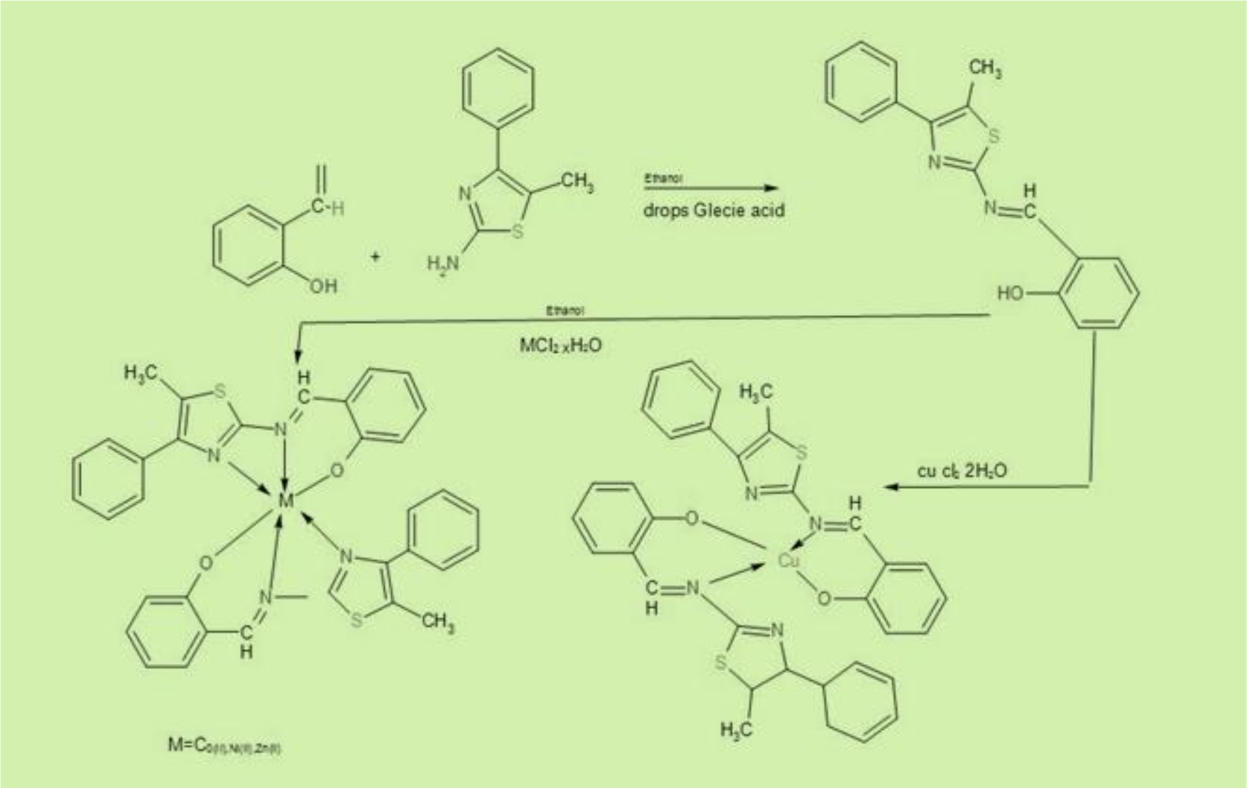
Figure(1.20) Different anti-breast cancer metal ion complexes with Schiff base derived from 4-aminosalicylic acid and 2-acetylferrocene

Abdulla *et.al.,* have tested the effect of Schiff-base complex Cu(Br-HAP) on Ht-29 colon cancer cells (Figure. 1.21) and the data suggest that Cu(Br-HAP) could be a suitable candidate for treating colon cancer**[77]**.



Figure(1.21) Cu(Br-HAP) complex used to treat colon cancer

Abd-Elzaher*et.al.*, have tested the anticancer activity of Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} complexes with a Schiff base prepared by refluxing 2-amino-4-phenyl-5-methyl thiazole and salicyladehyde in ethanol with drops of glacial acetic acid for four hours(Fig. 1.22). The metal complexes were prepared by dissolving the related metal chlorides in ethanol and adding them to an ethanolic solution of the ligand. This reaction was carried out for three hours. These complexes were tested against breast cancer cell line MCF-7, liver cancer cell line HepG2, lung carcinoma A549 and colorectal cancer HCT116 where they showed a good inhibition activity**[78]**.



Figure(1.22) Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}anticancer complexes with Schiff base derived from 2-amino-4-phenyl-5-methyl thiazole and salicyladehyde

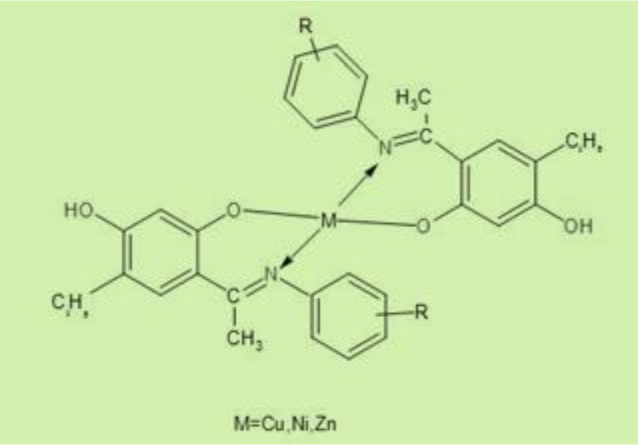
Hathout and co- workers have prepared Co(II), Ni(II), Cu(II) and Pd(II) Co(II) complexes withSchiff base ligands, which were produced from aminneocryptolpine and salicyladehyde. according to research conducted on colorectal adnocrcinoma (HT-29) cells .The ligand was prepared by reacting 11-chloro-6Hindolo[2,3-b]quinolone dissolved (in hot DMF) with 1,2-diaminobenzen in the same solvent for 24hrs and in the presence of trimethylamine**[79]**.

Pour and co-workers have synthesized Cu(II) complex with Schiff base derived from gabapentin and 2- hydroxy1-naphthaldehydeand tested its anticancer activityagainstleukemic T cell line, human ovarian cancer cell lineand human glioblastoma cell line**[74]**

1.4.2 Antimicrobial applications of Schiff bases

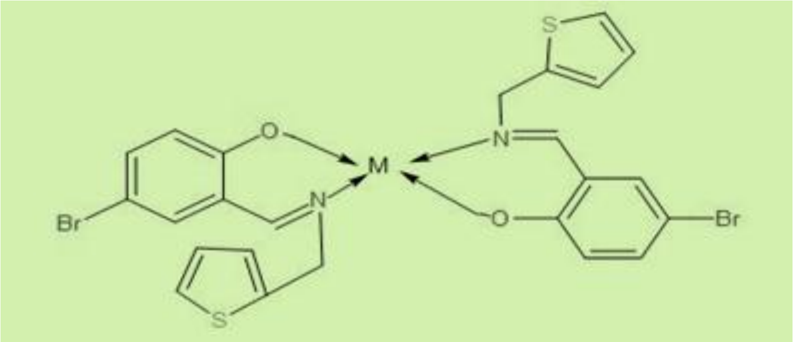
The relationship between the human health and the prepared metal complexes have been studied widely. As these complexes have potential effect on human health and life. For example, these metal complexes can be used to treat different diseases even using them in industry**[81]**.

Chanda and co-workers have prepared two Schiff base ligands from raceacetophenone, 4-ethyl-6-{(E)-1-[(3-nitrophenyl)imino]ethyl}benzene-1,3-diol and 4-ethyl-6-{(E)-1-[(2-nitrophenyl)imino]ethyl}benzene-1,3-diol(Fig. 1.23).Then prepared their metal complexes with iron, copper, nickel and zinc by reacting the related metal salt with the ligands in 1,4-dioxane and distilled water and only 1,4-dioxane at appropriate pH. These complexes were obtained upon reflux for 4-6hours. These complexes with their ligands were tested against *Pseudomonas aeruginosa, Proteus vulgaris, Proteus mirabilis, Klebsiellapneumoniae and Staphylococcus aureus*. The results show the high antibacterial activity of the ligands in comparison with their metal complexes**[82]**.



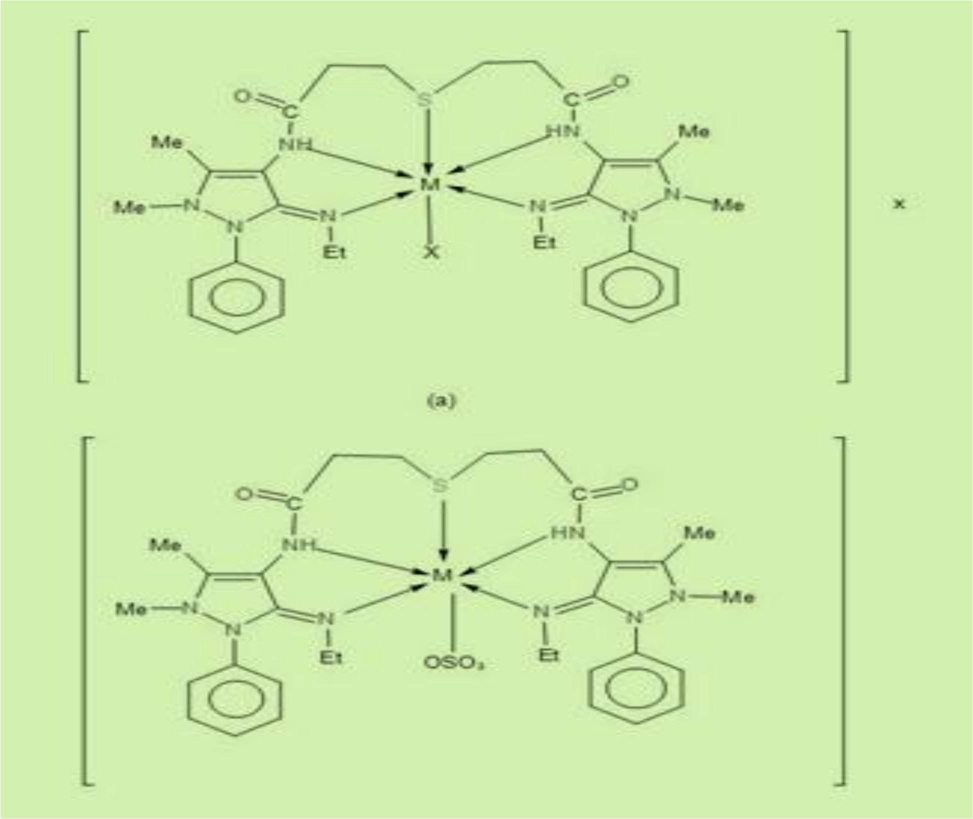
Figure(1.23)Antibacterialmetal complexes with Schiff base ligands 4-ethyl-6-{(E)-1-[(3-nitrophenyl)imino]ethyl}benzene-1,3-diol and 4-ethyl-6-{(E)-1-[(2-nitrophenyl)imino]ethyl}benzene-1,3-diol

El-Sherif *et. al.,* have synthesized the metal complexes of Cu^{2+}, Zn^{2+}, and Ni^{2+} with Schiff base ligand (E)-4-bromo-2-(((thiophen-2-lmethyl)imino)methy)phenolby refluxing 5-bromo-2-hydroxybenzaldehyde and 2-aminomethylthiophen for one hour (Fig. 1.24). Then the metal complexes were prepared by reacting hydrated copper chloride, hydrated nickel and zinc nitrate with the Schiff base ligand for two hours. These complexes proved to be good antimicrobial activity against different bacteria like *E. coli, P. aeruginosa, S. aureus, and B. subtilis*bacteria**[83]**.



Figure(1.24)Antibacterial Cu^{2+}, Zn^{2+}, and Ni^{2+} complexes with Schiff base ligand (E)-4-bromo-2-(((thiophen-2-ylmethyl)imino)methy)phenol

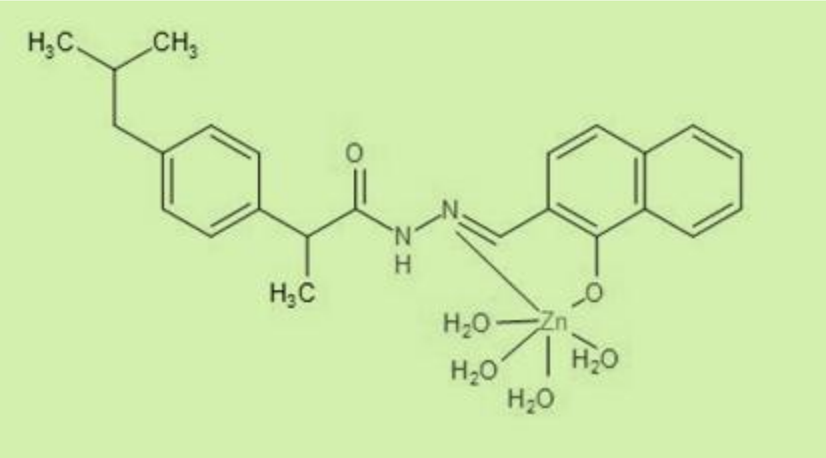
Cobalt (II), nickel (II) and copper(II) Schiff base complexes with 3,3'-thiodipropionic acid bis(4-amino-5-ethylimino-2,3-dimethyl-1-phenyl-3-pyrazoline) have been prepared by Chandra and co-workers (Figure. 1.25). All these compounds were tested against *Alternariabrassicae, Aspergillusniger and Fusariumoxysporum* fungi types. And they showed a good antifungal activity if compared with the ligand**[84]**.



M= Co(II), Ni(II) and Cu(II), X = NO_3^- , Cl^- and OAc

Figure(1.25)Antifungial metalcomplexes with Schiff base ligand (E)-4-bromo-2-(((thiophen-2-ylmethyl)imino)methy)phenol

Abdel-Hameed *et.al.*, were prepared zinc (II) complexes with two Schiff bases derived from Ibuprofen hydrazide with bromosalicylaldehyde and 2-hydroxy-1-naphthaldhyde (Fig. 1.26). Zinc (II) complexes were prepared by reacting hydrated zinc nitate with the two ligands in ethanol. The ligands and the complexes were examined against two fungi types, *C. albicans and A. fumigatus*. The results showed also the high antifungal activity of the complexes if compared with ligands**[85]**.

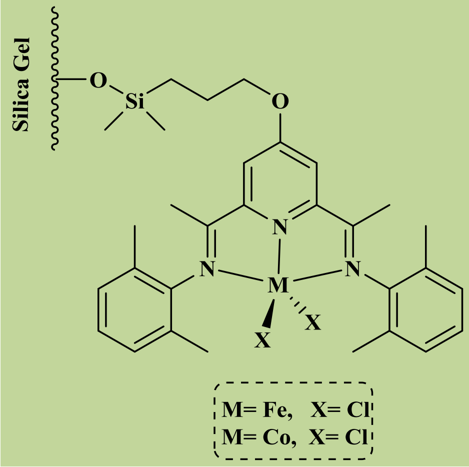


Figure(1.26)Antifungial Zn(II)complexes with two Schiff bases derived from Ibuprofen hydrazide with bromosalicylaldehyde and 2-hydroxy-1-naphthaldhyd

1.4.3 Catalysts

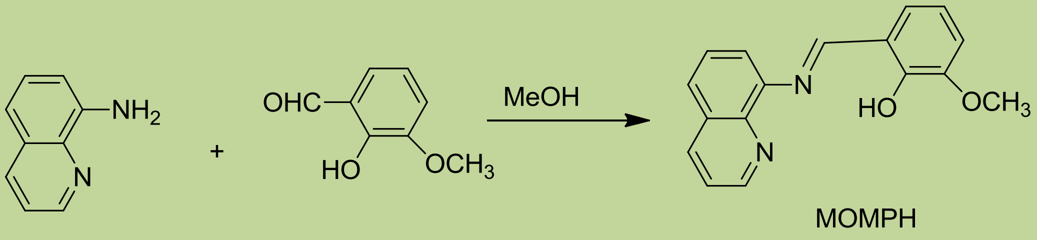
The use of Schiff base complexes in different reactions has been investigated widely. Such complexes can be used in industry in oxidation reaction, hydroxylation, polymerization of alkenes, aldol condensation and epoxidation**[86]**.

In polymerization of olefins, Schiff base complexes have been used in polymerizationre action. For example Co(II) and Fe(II) Schiff base complexes with pyridylbis(imide) have been used to produce polyethylene as shown in figure(1.27)**[7]**.



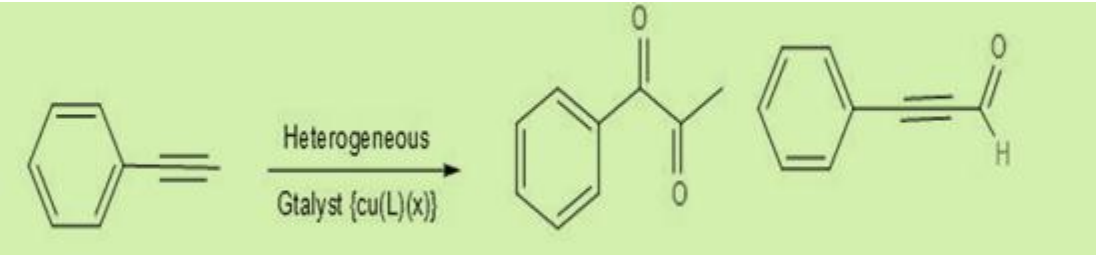
Figure(1.27) Co(II) and Fe(II) Schiff base complexes with pyridylbis(imide)

Nayak and co-workers have prepared iron(III), cobalt(II) and copper(II)complexes with the Schiff base ligand 2-methoxy-6-((quinolin-8-ylimino) methyl)phenol (Figure.1.28) . These complexes were used as catalysts for the oxidation of alkanes and alkenes in the presence of oxygen and H_2O_2 as oxidizing agent at 50°C . The resulted oxidation process compounds are alcohols and ketones**[87,88]**.



Figure(1.28) 2-methoxy-6-((quinolin-8-ylimino) methyl)phenol ligand used to coordinate with iron(III), cobalt(II) and copper(II) .

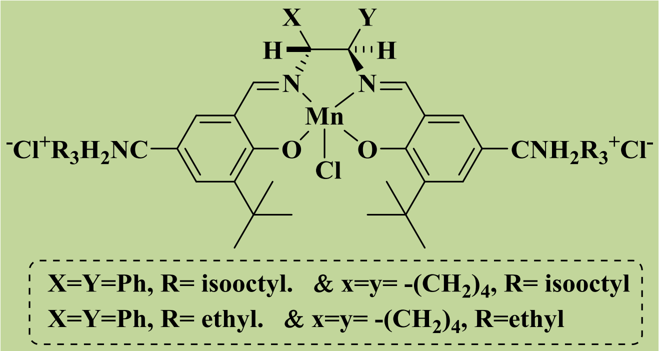
Copper(II) complex with Schiff base ligand containing N-substituted benzimidazolyl has been used as catalyst to oxidize 1-phenylpropyne with the presence of an oxidant in both basic and acidic media as reported by Kumar and Mathur(Fig. 1.29). The products of this reaction were diketone, aldehyde and benzoic acid**[89]**.



Figure(1.29) Schiff base ligand containing N-substituted benzimidazolyl used to form copper(II) complex

On the other hand, Decinti *et.al.*, have reported the use of Cu(II) Schiff base complex as a catalyst for styrene epoxidation with iodosylbenzene**[90]**.

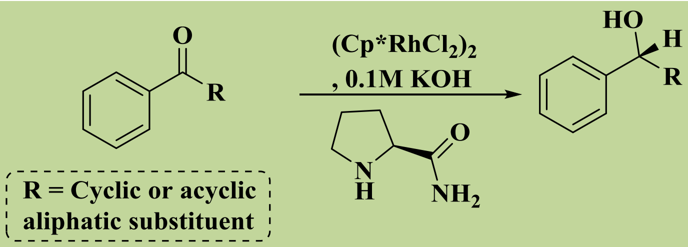
Two Mn^{2+} complexes with Schiff bases derived from 1,3-diamino-2-hydroxypropane andsalicylaldehyde, 2- hydroxynaphthaldehyde or 2-hydroxyacetophenone were used in the epoxidation of olefins in the presence of idosylbenzene as an oxidizing agent(Fig. 1.30)**[91]**.



Figure(1.30)Mn^{2+} complexes with Schiff bases derived from 1,3-diamino-2-hydroxypropane and salicylaldehyde, 2- hydroxynaphthaldehyde or 2-hydroxyacetophenone

The transformation of alcohols to aldehydes was also investigated using Schiff base complexes. for example, Gao and co-workers have used dioxomolybdenum(VI) complex to oxidize benzyl alcohol to benzaldehyde in the presence of O_2 at ordinary pressure at 90°C for 10 h.**[88]**.

The reduction of ketones was also reported by using different metal Schiff base complexes. For example, Rh and Ru complexes ($(pCymeneRuCl_2)_2$ or $(Cp^*RhCl_2)_2$with L-prolinamide) have been reported byFaller and Lavoie (Fig. 1.31) to reduce aryl ketones to the respective (R)-alcohols**[92,93]**.



Figure(1.31) Reduce aryl ketones to the respective (R)-alcohols by Rh complexes

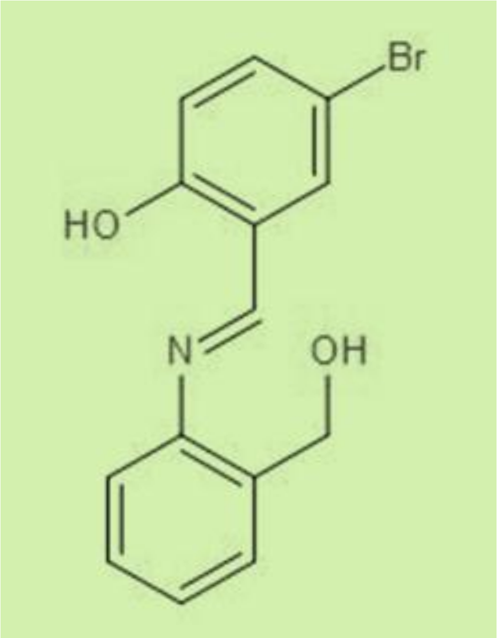
inAldol reaction of 1,3- dibenzoylmethanes with formaldehyde was carried out using tetradentatehydroxycobalt(III) Schiff base complexes under neutral condition **[94]**.

Aluminium(III) Schiff base complexes were used also to catalyse the reaction between 5-methoxyoxazoles and benzaldehydes to giveecis-oxazoline adducts **[95]**.

1.4.4 Dyes

Schiff base complexes with different metal ions give Schiff bases the good advantages to be used in dyes synthesis**[96]**. These dyes can be classified according to their chemical structure or the type of chromophors in its structure**[97]**. Dyes consist of metal complex can be considered as a combination of the dyes itself and the metal ion. Where this metal complex is used to improve the dye properties. The effectiveness of these dyes can be tested using many techniques.

Topal*et.al.,* have reported the use of 2-[(2-hydroxymethylphenylimino) methyl]-5-bromo-phenol dye to monitorcarbon dioxide levels**[98]**. Figure(1.32)shows the structure of this Schiff base.

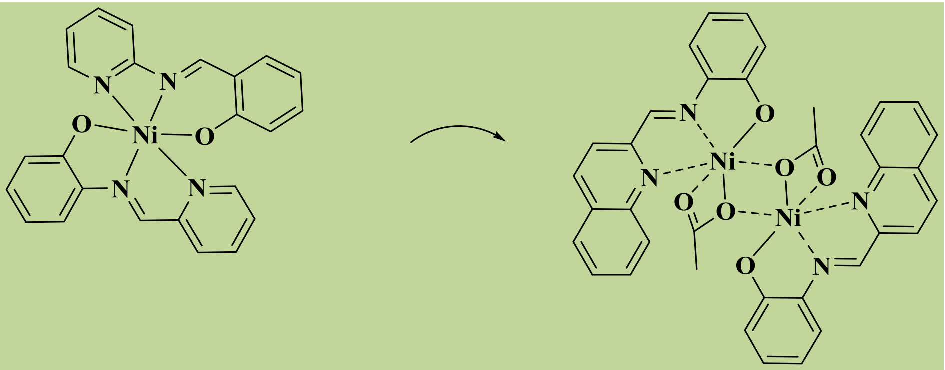


Figure(1.32)2-[(2-hydroxymethylphenylimino)methyl]-5-bromo-phenol dye

Etorki*et.al.,* have reported the use of two Schiff bases prepared by the reaction between 2-aminophenol and 2-aminobenzyl alcohol with salicylaldehyde. The two reactions were carried out by refluxing the starting materials in ethanol and using ammonium hydroxide as a catalyst. Nickel, chromium , copper….etc. complexes with these Schiff bases were prepared. The produced complexes were used to dye wool and goat hair**[96]**.

Grabaric*et.al.,* have also prepared two nickel(II) complexes with two Schiff bases and investigated them as dyes. The first Schiff base was prepared by reacting 2-pyridinecarbaldehyde)and 2-hydroxyaniline, while the second was prepared by reacting o-aminophenol and 2-quinolinecarbaldehyde). The nickel(II) complexes were prepared by the addition of Ni(I1) acetate tetrahydrate to the ligands in methanol at room temperature and for 10 and six h. to give(Ni-PMAP and (Ni-QMAP complexesrespectively (Fig 1.33). The two complexes were applied on

Polyamide 66 Fiber and the results showed that(Ni-PMAP) complex showed good dyeing properties**[99]**.



Figure(1.33) Ni-PMAP and Ni-QMAP complexes which were used as dyes

Aim of work

1- Synthesis of two Schiff base ligands by the reaction between two ketones and amine.

2- Synthesis of these ligands metal complexes with different ions, such as Co(II), Ni(II) and Cu(II).

3- Characterization of all the prepared compounds using various techniques, such as ^{1}H NMR, FTIR, Uv.-visible, magnetic susceptibility, molar conductivity and thermal analysis.

4- Study the biological activity of these compounds against the bacteria.

2. Experiments and methods

2.1. Chemicals

The following chemicals were used to prepare the ligands and their metal complexes and their suppliers as listed in the following table(2-1).

Table (2-1): Chemicals and their suppliers

Chemicals	suppliers	Purity
2-Aminothiophenol	Shanghai Macklin biochemical	95%
9,10-phenathrenquinon	Shanghai Macklin biochemical	95%
2,5-dihydroxy-1,4-benzoquinon	Shanghai Macklin biochemical	98%
Absolute Ethanol	ECHOCHEM	99%
HCl	Thomas Baker	35%-38%
H_2SO_4	Sigma aldrich	95-97%
NaOH	B.D.H	97%
DCM	CHEM-SUPPLY-PTY.LTD	98%
DMSO	Thomas Baker	98%
$NiCl_2.6H_2O$	C.D.H	98%
$CoCl_2.6H_2O$	Merck	99%
$CuCl_2.2H_2O$	B.D.H	98%

2.2 Apparatuses

The following apparatuses were used to characterize the prepared ligands and their metal complexes:

2.2.1 UV-Visible spectrophotometer

The UV-Visible spectra of the two ligands and their complexes was measured using UV-Visible spectrophotometer (UV – 1700) manufactured by the Japanese company (Shimadzu)and this spectrophotometer is available at the College of science for women / University of Babylon.

2.2.2 FT-IR Spectrophotometer

The infrared spectra has been measured to the all prepared compounds by using FT-IR – 8400S in the range (4000-400) cm^{-1} using KBr disc. Also this device has been supplied by Shimadzu companyand it is also available at the College of sciencefor women / University of Babylon.

2.2.3^{1}H-NMR Spectroscopy

The spectra of nuclear magnetic resonance has been measured for the prepared ligands by using NMRInnova 5 Concole with an oxford 500, , Magnet device using DMSO as a solvent. In Iran

2.2.4Melting point apparatus

The melting points of all prepared compounds were measured by the melting point / SMP30 Stuart apparatus . University of Babylon

2.2.5 Balance magnetic susceptibility apparatus

The magnetic susceptibility for the metal complexes was measured using Auto Balance Magnetic Susceptibility Balance Sherwood Scientificatthe College of Sciences / Al-Mustansiriyah University .

2.2.6 Conductivity meter

The molar conductivity of the complexes was measured at the University of Babylon, College of science for women using conductivity device WTW SERIES, cond 722.

2.2.7 Thermal analysis

Thermal analysis for all compounds was measured by differential thermal gravimeter (DTG-160-FC-60A) at the University of Babylon, College of science for women .

2.3 **Syntheses** of Ligands

2.3.1 Synthesis of Schiffbase ligand (L1)

9,10-phenathrenquinon (1g, 4.803 mmol) was dissolved in absolute ethanol (20 ml).2-aminothiopenol(1.20gm, 9.61 mmol) and three drops of hydrochloric acid were added to 9,10-phenathrenquinon solution. The reaction mixture was refluxed for 4 hours. A green precipitate of L1 was collected by filtration, washed with water and recrystallized from ethanol.

2.3.2 Synthesis of Schiff base ligand (L2)

2,5-dihydroxy-1,4-benzoquinon (1g, 7.138mmol) in ethanol (20ml) was mixed with 2-Aminothiopenol (1.773g, 14.277mmol).The mixture was refluxed for six hours.The brown precipitate of L2 was filtrated, washed with water and recrystallized from ethanol.

2.4 Synthesis of L1 metal complexes

2.4.1 Synthesis of cobalt (II), nickel (II) and copper(II) complexes

All metal complexes were prepared by dissolving L1 (0.4gm, 0.95mmol)) in 20ml ethanol and mixing it with $CoCl_2.6H_2O$, $NiCl_2.6H_2O$ and $CuCl_2.2H_2O$ in(1:1) ligand: metal ratio. The mixture was refluxed for (6) hours. Blue complexes were formed which were filtered , washed with water and ethanol. Table (2-2) illustrates the used amounts of L1 and the metal chloride salts.table(2-2)

Table (2-2) Summarizes the amount used of L1 and the metal salts to prepare the metal complexes

Complexes	Weight of metal salt	Weight of ligand
$[Co(L1)]Cl_2.3H_2O$	0.2252gm,0.95mmol	0.4gm, 0.95mmol
$[Ni(L1)]Cl_2.3H_2O$	0.225gm, 0.95mmol	0.4gm, 0.95mmol
$[Cu(L1)] Cl_2.2H_2O$	0.1614gm, 0.95mmol	0.4gm, 0.95mmol

2.5 Synthesis of L2 metal complexes

2.5.1 Synthesis of cobalt (II) , nickel and copper complexes

The metal complexes with L2 were synthesized by reacting (0.4g, 1.13mmol) of L2 with $CoCl_2.6H_2O$, $NiCl_2.6H_2O$in 1:2 ligand: metal ratio in (20ml) of ethanol in the presence of NaOH (3.75 M, 1ml). The reaction mixture was refluxed for six hours until a dark brown precipitate of these complexes was formed. These complexes were filtered , washed with water and ethanol. Table (2-3) shows the amounts used of L2 and the metal chloride salts.

Table (2-3) Summarizes the amount used of L2 and the metal salts to prepare its complexes

Complexes	Weight of metal salt	Weight of ligand
$[Co_2(L2)] Cl_2.3H_2O$	0.5371gm,2.261mmol	0.4gm,1.13mmol
$[Ni_2(L2) Cl_2].4H_2O$	0.5365gm,2.261mmol	0.4gm,1.13mmol

2.6Biological activity

The biological activity of the prepared ligands and their metal complexes has been investigated. Two types of bacteria (*Escherichia coli* and *Staphylococcus aureus*) as an example of gram negative and gram positive bacteria respectively have been isolated and diagnosed using biochemical and microscopic tests.

2.6.1 Preparation of the culture medium

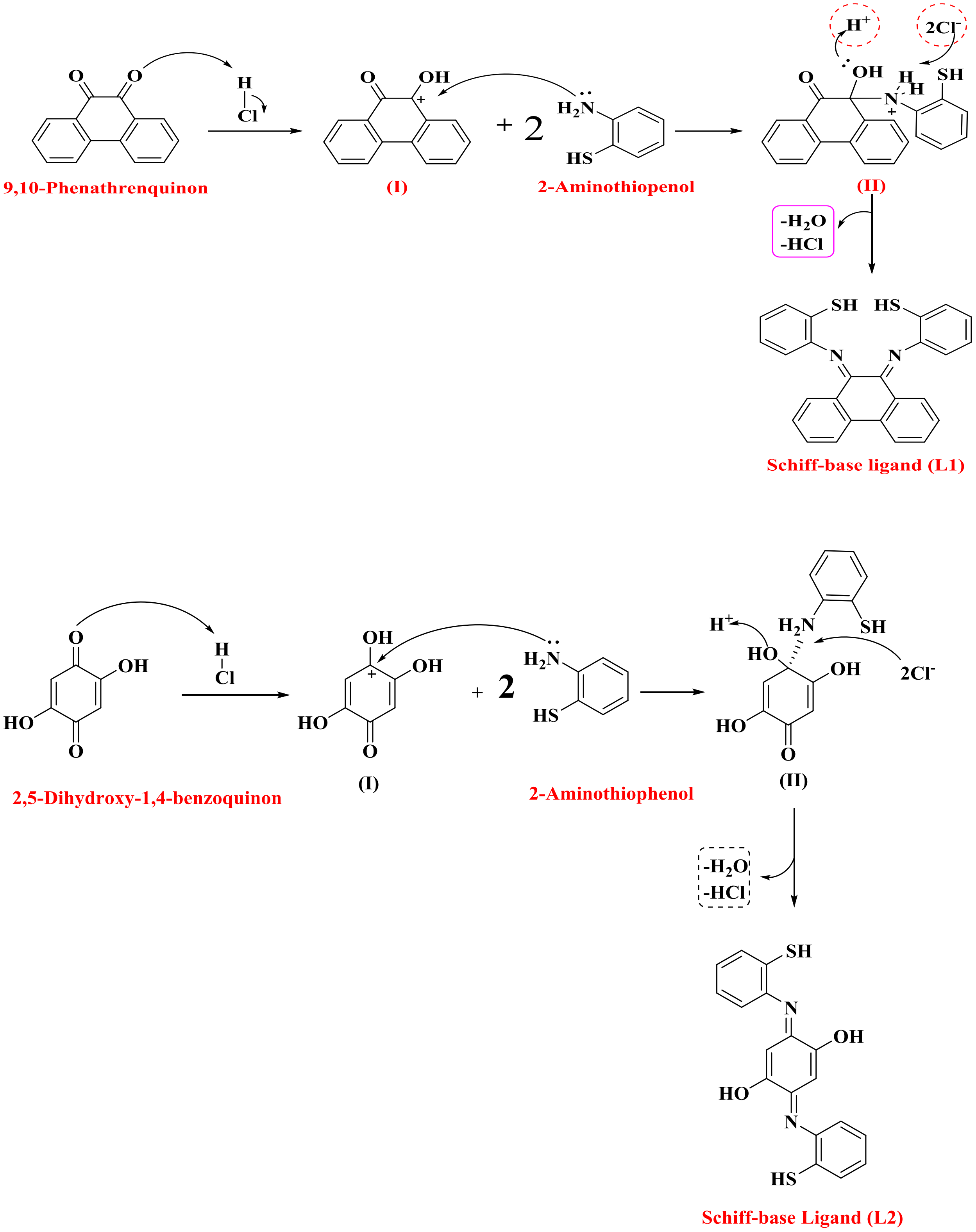
All the prepared compounds have been used with the weigh(0.006 g) and dissolved in 10 ml of DMSO. The two bacteria types were cultured on the plates, each type in a separate plate. Samples were taken from each ligand and its complexes and placed inside the plates cultured with bacteria with numbering for each complex. It was left for 48 hours and then results were read.

3.1 Synthesis of Schiff Base ligands L1 and L2

The synthesis of Schiff base ligands L1 and L2 was carried out by reacting commercially available ketones, namely 9,10-phenanthrenequinone and 2,5-dihydroxy-1,4-benzoquinon with 2-aminothiopenol respectively. The two reactions involved the addition of hydrochloric acid and sulphuric acid to the mixture between the amine and the ketones to produce a green precipitate of L1 and a brown precipitate of L2 .

The two used acids efficiently catalysed the reaction of both ketones with 2-aminothiophenol where the latest acts as a nucleophile attacking the electrophiles 9,10-phenanthrenequinone and 2,5-dihydroxy-1,4-benzoquinon, resulting in the formation of the Schiff base (L1) and L2 and release of water molecule.

The mechanism of the reaction begins with the protonation process to an oxygen atom in the carbonyl group, resulting in the hydroxyl group and the carbonium ion (electrophile). Due to the low steric hindrance effect in the synthesis of the intermediate compound (I), the attack of nucleophile (represented by the primary amine group in the 2-Aminothiophenol molecule) favours this geometry of intermediate compound (I) to attack it more than the 9,10-phenanthrenequinone molecule. The protonation process caused by the addition of excessive amounts of hydrochloric acid releases the water molecules from the intermediate compound (II)**[110-101].** The final process is the deprotonation of amine protons to form an imine group (N=C) and give the target compound its final structure of a Schiff base (L1)based on the following mechanism (scheme 3.1).

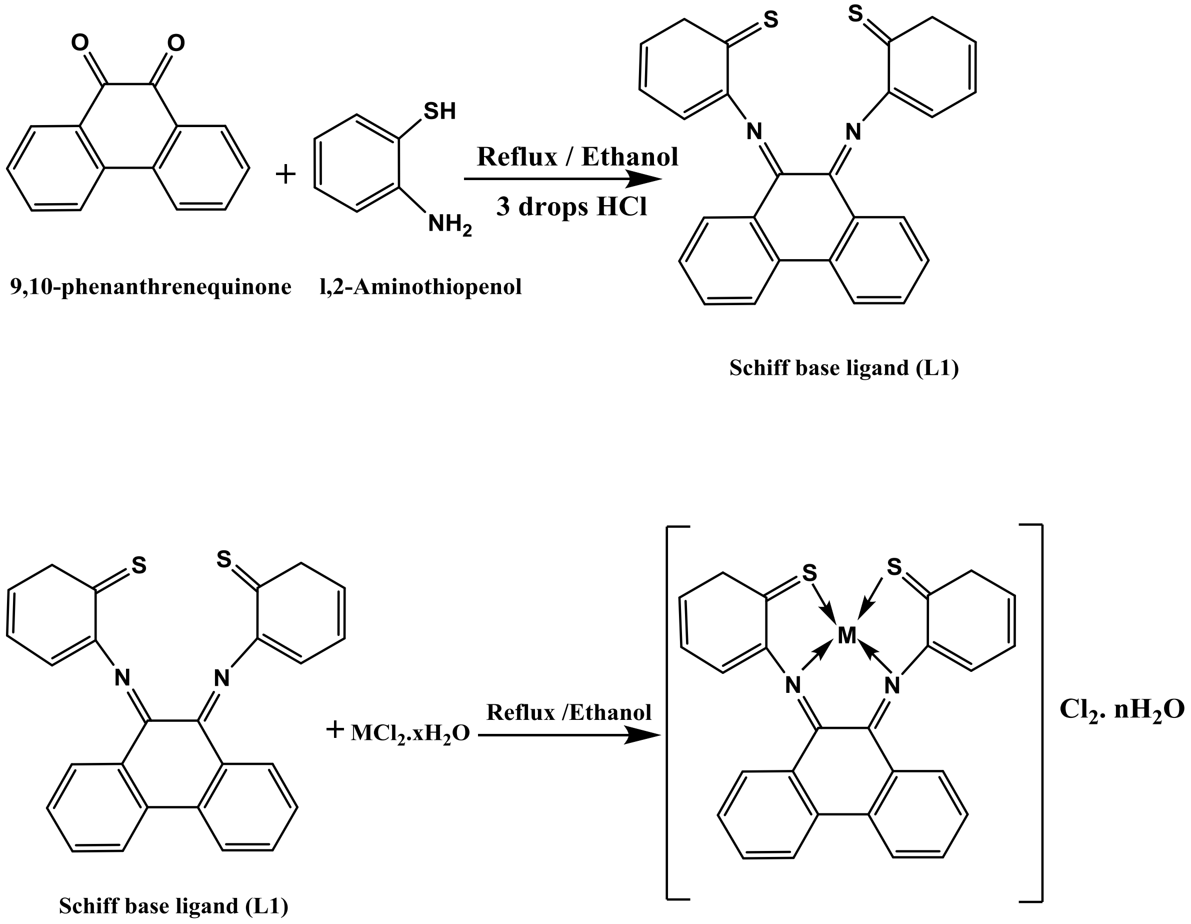


Scheme 3.1 Possible mechanism for the synthesis of both Schiff base ligands

3.2 Synthesis of metal complexes

3.2.2 Synthesis of cobalt (II), nickel(II) and copper (II) complexes with L1

Metal complexes were produced by reacting L1 with Co(II), Ni(II) and Cu(II) chloride salts in 1:1 metal: ligand molar ratio. Scheme 3.2 shows the metal complexes synthesis with L1.



M= Co^{2+}, Ni^{2+} and Cu^{2+}

Scheme 3.2 shows the metal complexes synthesis with L1

In detail, Schiff base ligand (L1)is reacting with these metal salts through the imine and the thiol groups and forming four coordination bonds with these four chelate sites. The nitrogen of the imine group and sulfur atom of the thiolgroup attackthe metal ion and form strong covalent-coordination bonds. It is worth mentioning that the thiol groups in both ligands are converted to the thione group according to the keto-enol tautomerism as shown in figure (3.1).

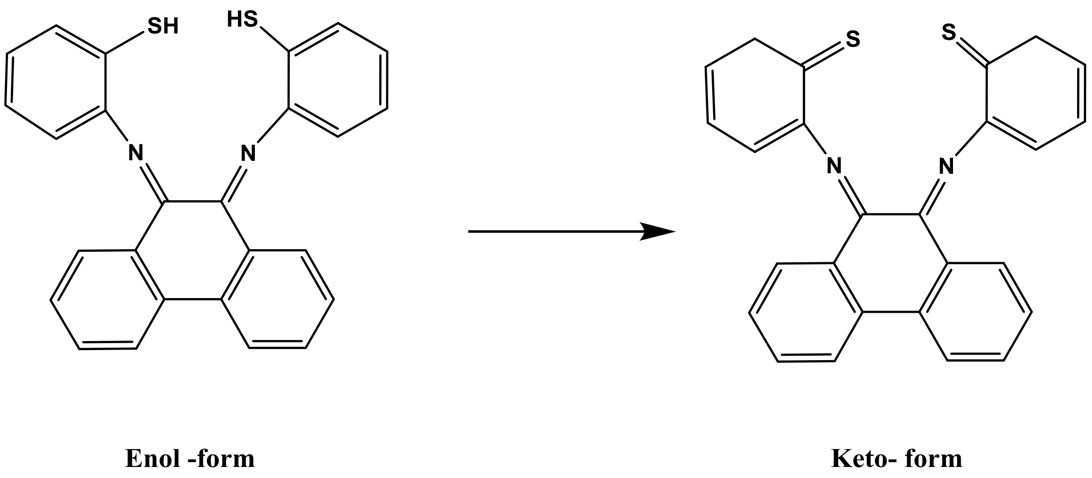
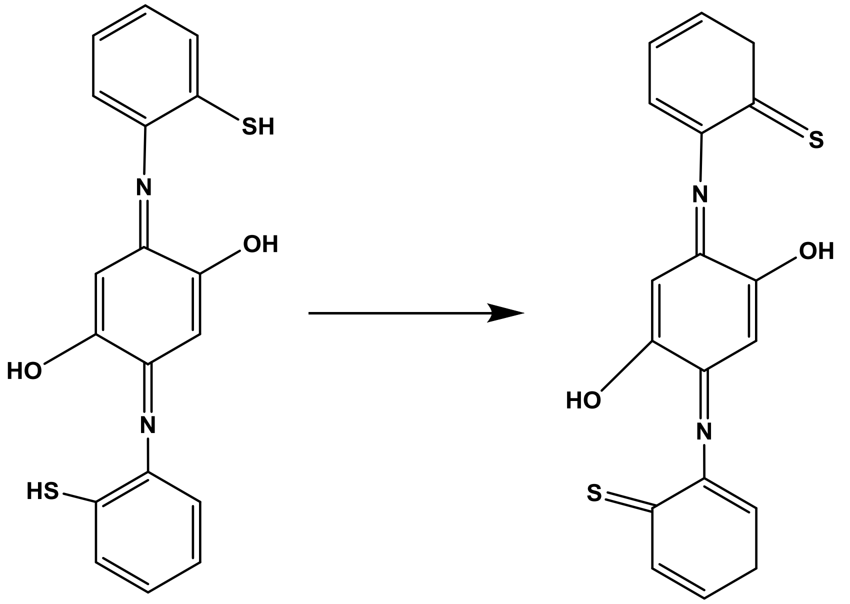


Figure (3.1) keto-enoltautomerism for L1 ligand

3.2.3 Synthesis cobalt (II) and nickel(II) complexes with L2

By reacting second Schiff base ligand (L2) with metal chloride salts, the equivalent ratio was 1:2 for L:M respectively in the presence of sodium hydroxide.The synthesis reaction of metal-L2 complexes is depicted in Scheme 3.3. The metal-L2 complexes are bound to the ligand by three bonds, two of which are coordination bonds with imine group nitrogen atom and sulfur atoms of the thione group. Where the thiol group is also converted to the thione group in L2 as shownin figure (3.2),while the third is acovalent bond with the deprotonated hydroxyl group. In this ligand synthesis procedure sodium hydroxide was used to ensure the deprotonation of the hydroxyl group in the ligand structure and finally offer a third coordination site in the ligand structure.

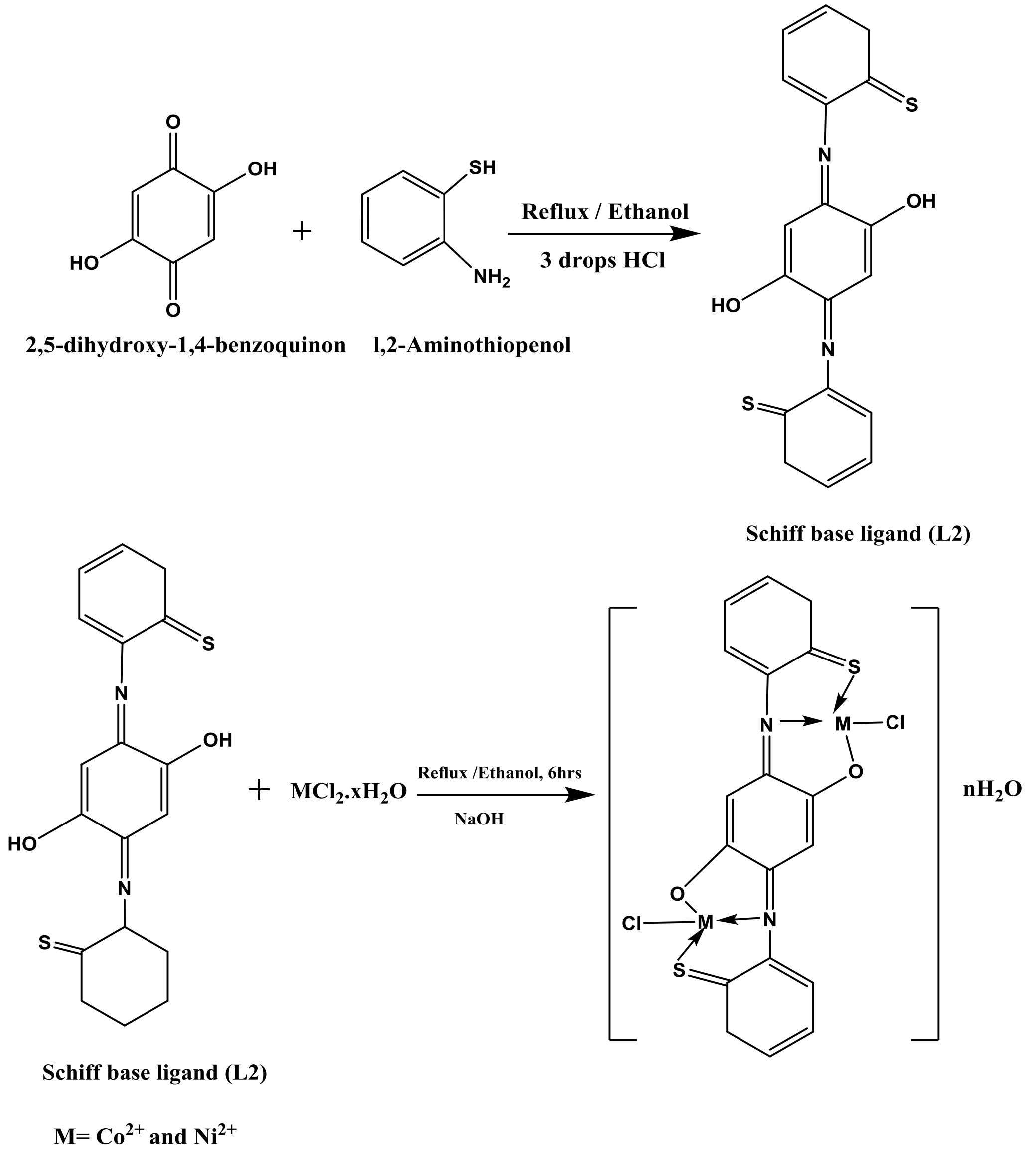


Thioenol - form

Thioketo- form

Figure (3.2) keto-enoltautomerism for L2 ligand

Metal-L1 and metal-L2 complexes are prepared in the same way, but the reaction time is different, taking four hours for metal-L1 complexes and six hours for metal-L2 complexes. This difference is due to the fact that the L2 ligand has two triple chelating sites and has a higher steric hindrance than the L1 ligand.



Scheme 3.3Synthesis of metal-L2 complexes

All the synthesised compounds are insoluble in water and soluble in most organic solvents. Ligands and their complexes synthesis was confirmed by using methods of analysis such as^{1}HNMR, FTIR and UV-Vis spectroscopies and thermalanalysis.

Table (3-1) Some physical properties of the prepared ligands and their metal complexes

Compound	Color	m.p °C	Yield %	M.Wt g/mol
Ligand (L1)	Green	210-212	49	422.56
[Co(L1)]Cl_2.3H_2O	Blue	>350	78	606.44
[Ni(L1)]Cl_2.3H_2O	Blue	>350	67	606.20
[Cu(L1)]Cl_2.2H_2O	Blue	>350	54	593.04
Ligand (L2)	Brown	96-98	67	354.44
[Co_2(L2)Cl_2].3H_2O	Brown	236-238	80	594.22
[Ni_2(L2)Cl_2].4H_2O	Brown	>350	78	612.77

3.3 ^{1}H NMR spectroscopy

^{1}H NMR spectroscopy was used to determine the presence of protons in the two Schiff base ligands using DMSO-d_6 as a solvent which can be detected at δ 2.50 ppm signal. This spectrum shows signals in the range δ 6.5-9 ppm which are related to the aromatic protons. And signal between δ 3-4 ppm which was identified to S-H bond in the ligand structure as shown in figure (3.3)**[102-103]**.

signals are in the ^{1}H NMR spectrum for the L2 have been identified. The proton signals for each -SH, -OH groups appeared at δ 3.4/9.5 ppm respectively, where–OH signals observed as a broad peak. While multiple signals in the range δ 7-9 ppm are related to the aromatic protons as shown in figure (3.4).

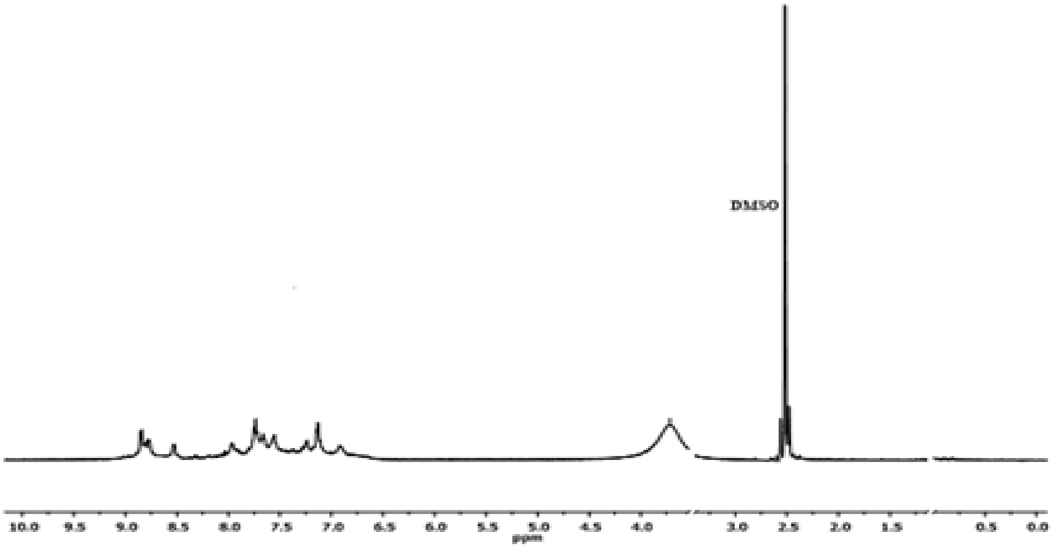


Figure (3.3)^{1}H NMR for L1

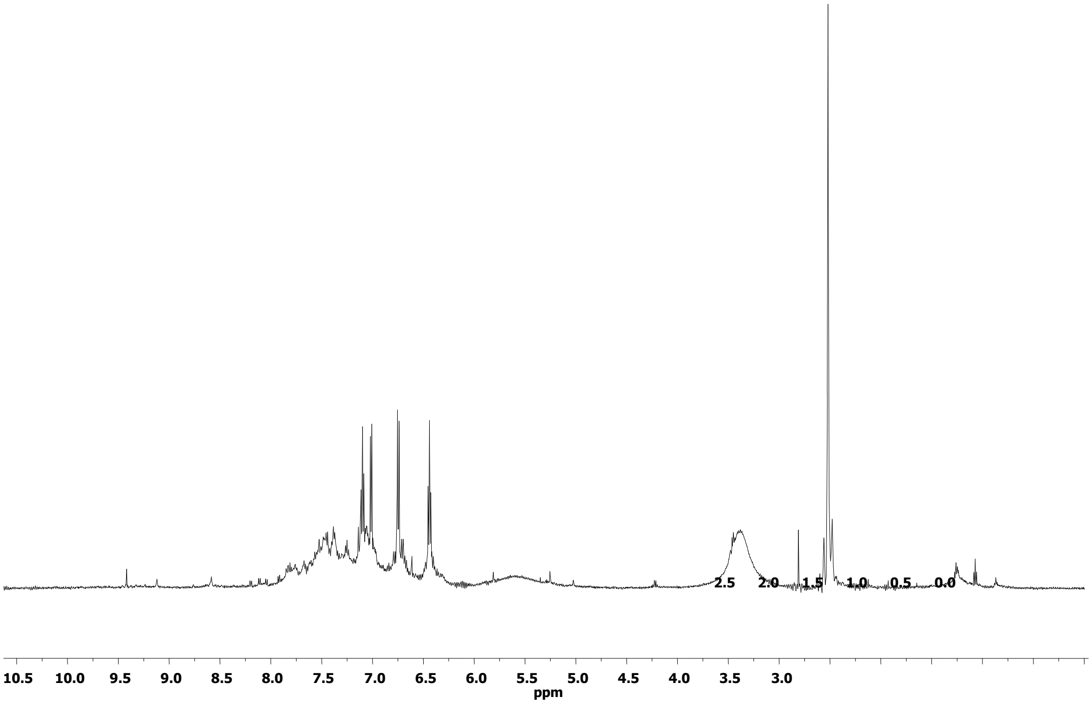


Figure (3.4)^{1}H NMR for L2

3.4 FT-IR Spectroscopy

The chemical structure of the ligands and their metal complexes have been identified by determination the presence of functional groups such as C=N, S-H, O-H, using Fourier transform infrared spectroscopy analysis and vibration modes in the specified compound.

3.4.1 FT-IR Spectra of L1 and its metal complexes

The FT-IR spectra of Schiff base ligand (L1) (Fig.3.5) shows a new band at 1610 cm^{-1} which is assigned to imino group (C=N) with the absence of an adsorption band of the NH_2- in the free 2-aminothiopenol at 3446-3356 $cm^{-1}$and the absence of υ (C=O) group in 9,10-phenathrenquinon adsorption band which appears at 1674$cm^{-1.}$

The characteristic υ (S–H) vibration frequency in 2-Aminothiophenol which appears at 2522 cm^{-1} as a single band was also disappeared upon the ligand formation which suggests its conversion to the thione form (C=S) which appears at 1325cm^{-1}**[104]**.

These two bands (C=N) and (C=S) were changed when the metal complexes are formed as shown in figures(3.6-3.8). The υ (C=N) frequency in all metal complexes was shifted to 1608 cm^{-1} which suggests the metal coordination with L1 through the lone pair of nitrogen of imino group**[105]**. While the υ (C=S) was shifted to 1338 cm^{-1} in Co^{2+}, Cu^{2+} complexes and to 1336 cm^{-1} in Ni^{2+} complex which suggests the metal coordination with the ligand through the second coordination site (the thione group)**[106]**.

New bands appear at 400-600 cm^{-1} refer to υ (M-N) and υ (M-S) bonds. While a broad band at 3200-3600 cm^{-1} suggests the presence of hydrated water molecules outer the coordination sphere. **[107-108]**.Figures illustrate the FT-IR spectra of Schiff base ligand (L1) and its Co(II), Ni(II) and Cu(II) complexes

Table (3-2) gives a summary of the characteristic bands in the FTIR spectrum of L1 and how they were shifted upon complexes formation.

Table (3-2) FT-IR data in cm^{-1} of L1 and its complexes

Compound	H_2O	C=N	C=S	M-N	M-S
L1	----	1604	1325	----	----
$[Co(L1)]Cl_2.3H_2O$	3200-3600	1608	1338	549	480
$[Ni(L1)]Cl_2.3H_2O$	3200-3600	1610	1336	559	472
$[Cu(L1)]Cl_2.2H_2O$	3200-3600	1618	1338	507	451

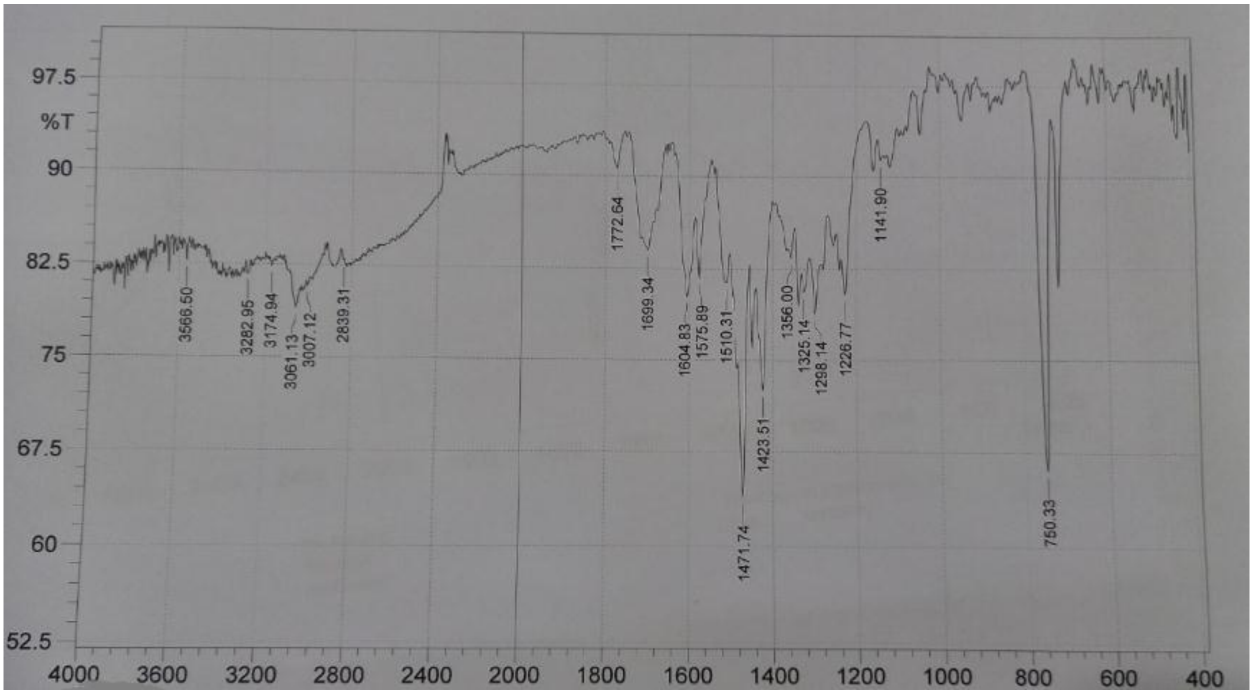


Figure (3.5) FT-IR spectrum of L1 Schiff base ligand

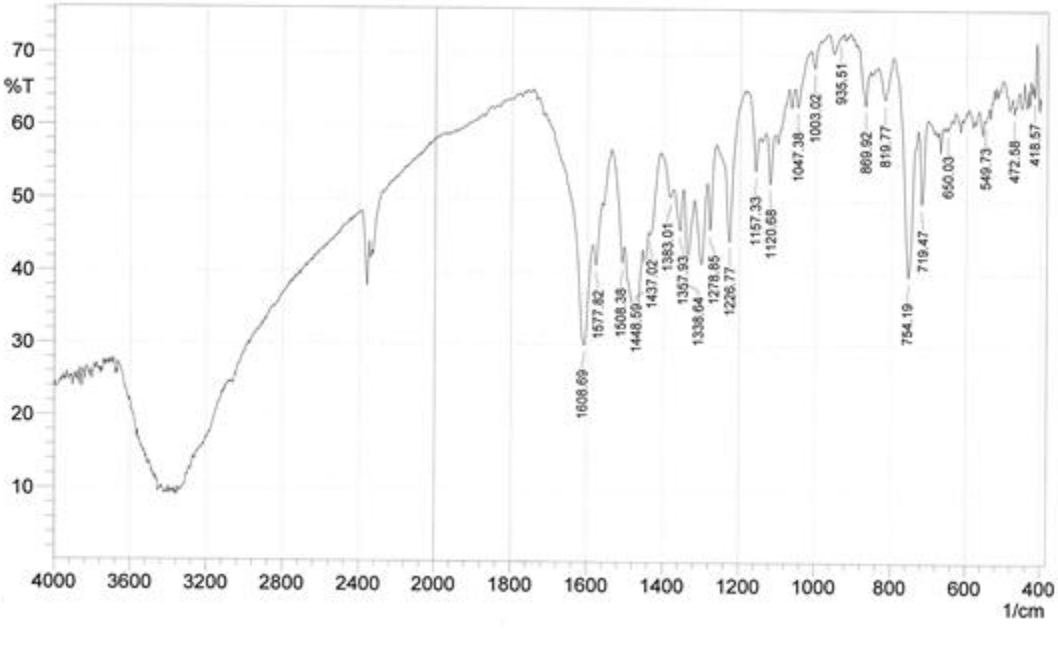


Figure (3.6) FT-IR spectrum of Co-L1 complex

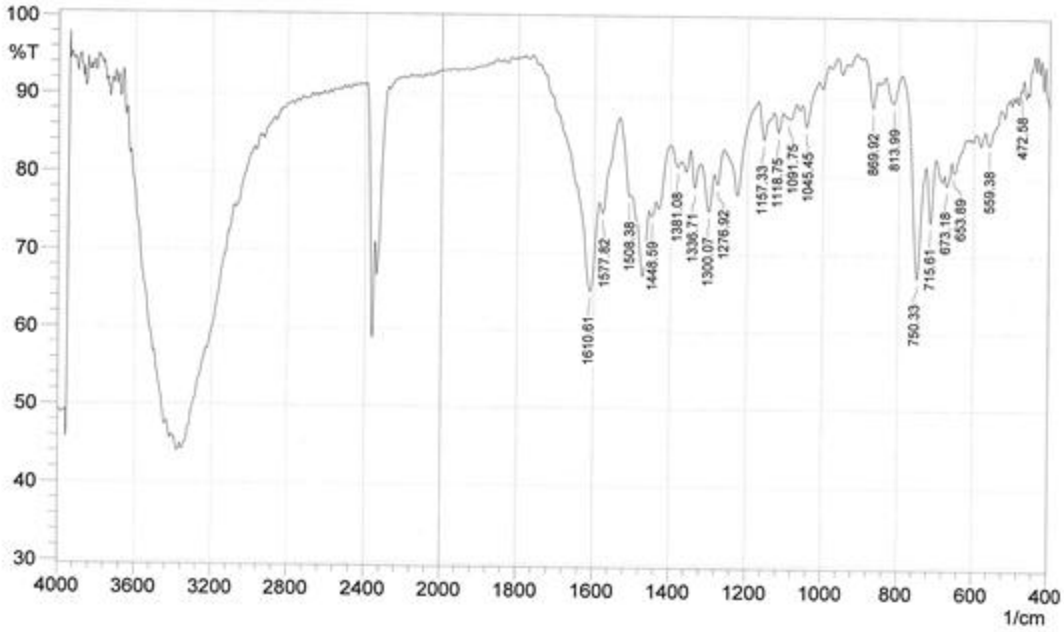


Figure (3.7) FT-IR spectrum of Ni-L1 complex

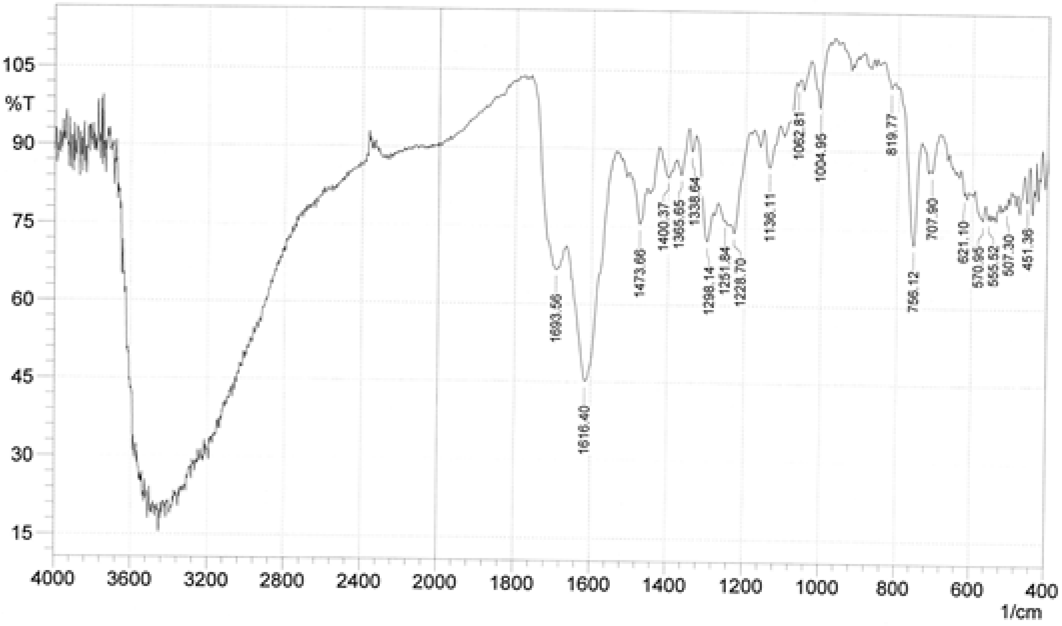


Figure (3.8) FT-IR spectrum of Cu-L1 complexes

3.4.2 FT-IR Spectra of L2 and its metal complexes

The FT-IR spectra of L2 (Fig.3.9) also shows the characteristic imine group band which is seen around 1558 cm^{-1}. The formation of this band was supported with the absence of both adsorption bands of the amino group in 2-aminothiophenol and the carbonyl group in 2,5-dihydroxy-1,4-benzoquinon which is found at 1647 cm^{-1}.

v(S–H) vibration frequency which should appear as a single band at 2528 cm^{-1} is also disappeared in L2 FT-IR spectra, which suggests its conversion to the thione group.While the v(O-H) frequency is seen around 3358 cm^{-1} as a single band in L2 spectra.

Upon complexation these characteristic bands are changed and shifted(Fig 3.10 and 3.11). For example, the imine group frequency is shifted to a lower wavelength (from 1588 cm^{-1} in the free ligand to 1579 cm^{-1})in both $[Co_2(L2)Cl_2].3H_2O$ and $[Ni_2\ (L2)Cl_2].4H_2O$ complexes which confirms the metal coordination with L2 through the imine group .

The thione groups frequencies were also shifted upon the metal coordination. It appeared at 1230 cm^{-1} in L2 spectra and shifted to 1224 cm^{-1} and 1226 cm^{-1} in $[Co_2(L2)Cl_2].3H_2O$ and $[Ni_2\ (L2)Cl_2].4H_2O$ respectively**[109]**.

While the hydroxyl group is deprotonated and coordinates with the metal ions through the oxygen atom to form (M-O) bonds which appears at 688 cm^{-1} and 659 cm^{-1} in $[Co_2(L2)Cl_2].3H_2O$ and $[Ni_2\ (L2)Cl_2].4H_2O$ respectively[**110-111]**.

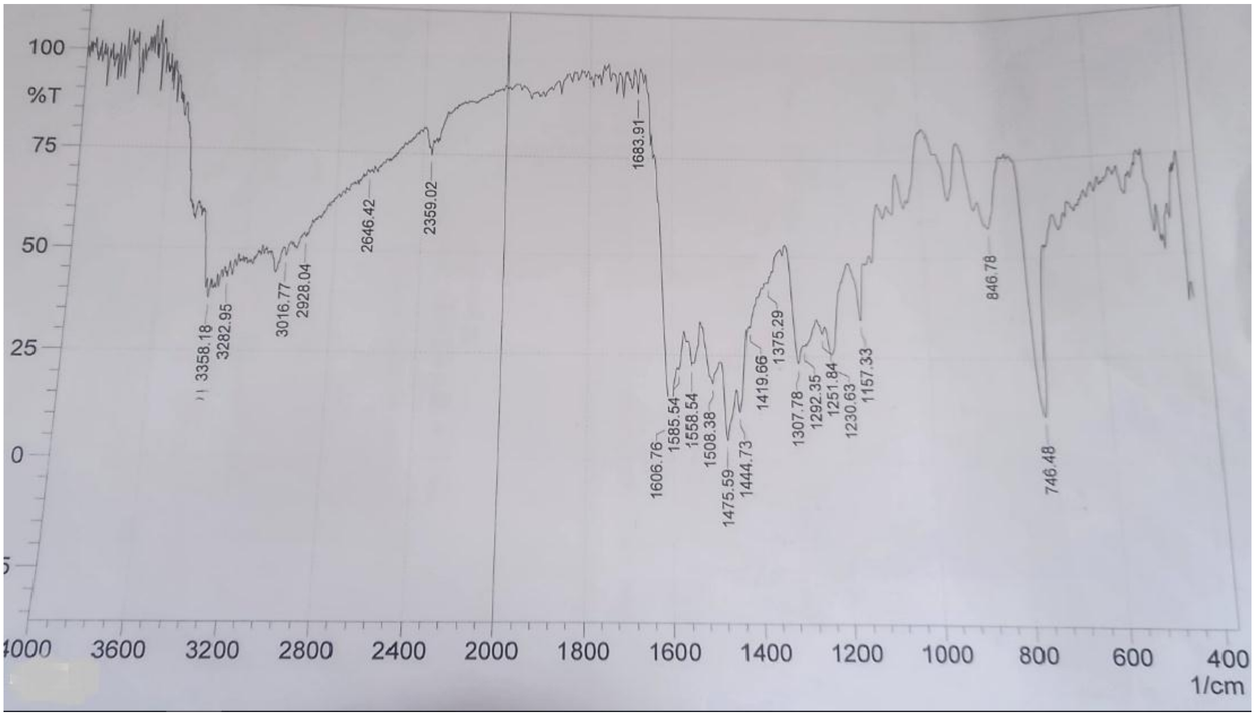
An extra new bands in the metal complexes FT-IR spectra also appeared between 400-600cm^{-1} which are attributed to the v(M–N) and v(M–S). In $[Co_2(L2)Cl_2].3H_2O$ complex both bands appear at 669 cm^{-1} and 457 cm^{-1}

respectively. While the two bands appear at 586 cm^{-1} and 493 cm^{-1} respectively in $[Ni_2 (L2)Cl_2].4H_2O$ complex**[112]**.

In addition, the appearance of new bands at a lower frequency at a range of 3300 $cm^{-1}$and 3400 in complexes may be assigned to the presence of water molecules in the complexes chemical structure**[113]**. Table (3-3) shows all the mentioned above bands and the shift in them.

Table (3-3) FT-IR data in $cm^{-1}$of L2 and its complexes

Symbol of	-OH	H_2O	C=N	C=S	M-O	M-N	M-S
L2	3358	----	1558	1230	----	----	----
$[Co_2(L2)Cl_2].3H_2O$	---	3200-3600	1588	1224	688	669	457
$[Ni_2 (L2)Cl_2].4H_2O$	---	3200-3600	1579	1226	659	586	493



(Fig.3.9) FT-IR spectrum of L2 Schiff base ligand

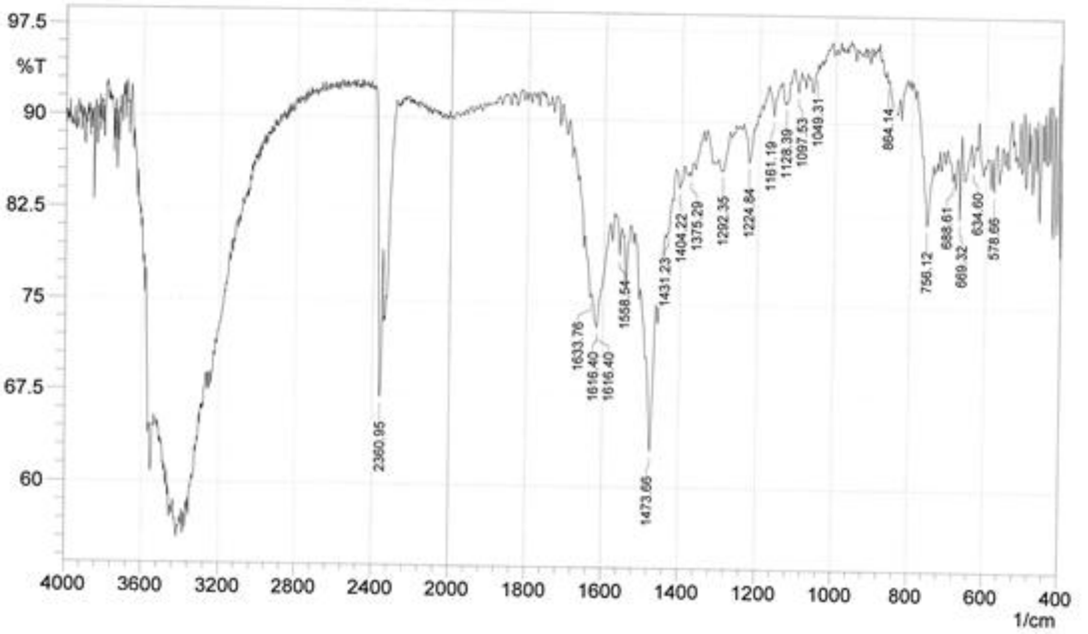


Figure (3.10) FT-IR spectrum of Co-L2 complex

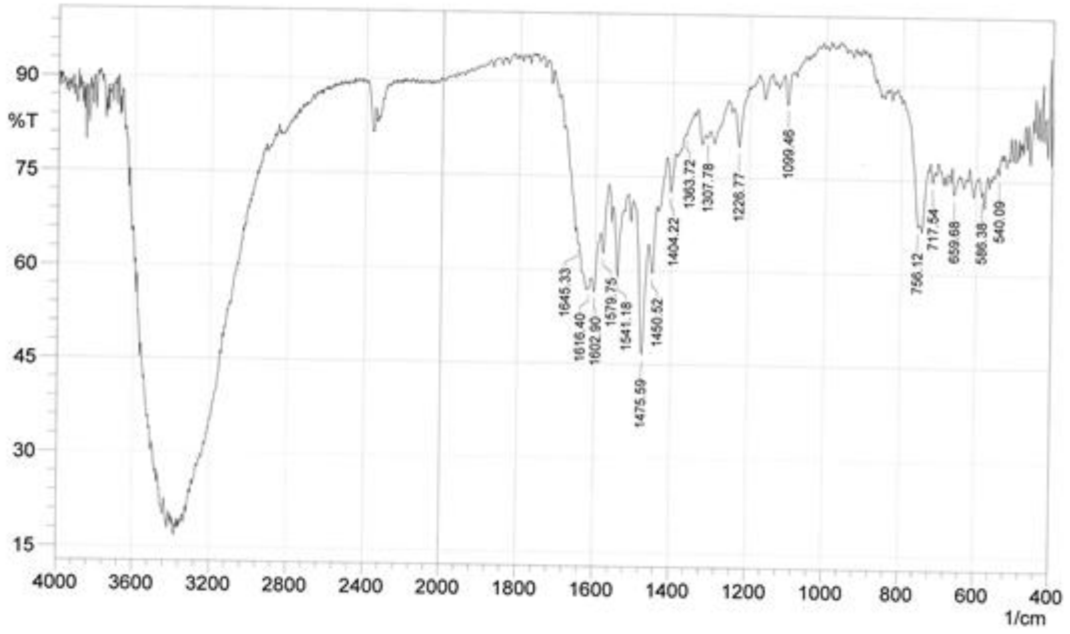


Figure (3.11) FT-IR spectrum of Ni-L2 complex

3.5UV-Visible Electronic Spectra

3.5.1 UV-Visible electronic spectra of L1 and Co(II), Ni(II) and Cu(II) complexes

UV-Vis absorption spectra (Fig.3.12) of L1 ligand and its metal complexes has been recorded in DCM solution as a solvent and at room temperature.Table(3-4) gives a summery for electronic transitions in L1 and its complexes.

The L1 spectra shows electronic transitions in the range 227-392nm and electronic transitions in the range 598-788nm which are related to π-$\pi*$and n-$\pi*$transitions respectively. The three metal complexes with L1 (Co (II), Ni(II) and Cu (II)UV-Visible spectra are either blue or red shifted which confirm the complexes formation.

In Co (II) complex the absorption spectraum shows a peak at 360nm which is related to INCT (intraligand charge transfer). While the four bands at (560, 602, 702 and 779) are related to the charge transfer and $^2A_{1g} \rightarrow {}^2B_{1g}$and $E_g \rightarrow {}^2A_{1g}$transitions in a complex with a square planar geometry **[114-116]**.

The absorption spectra of the nickel(II) complex shows also four bands. Two bands at 559 and 601 nm which are related to the $^1A_1g \rightarrow {}^1B_1g$ and $^1A_1g \rightarrow {}^1A_2g$ transitions. These transitions are characteristic for Ni^{2+} in square planar environment. While peaks at high energy (299 and 359) are related to INCT **[117]**.

In addition, the absorption spectrum of the copper(II) complex also exhibits four bands. Two bands at (551 and 594) nm which are assigned to the $^2B_{1g} \rightarrow {}^2B_{2g}$ and

$^{2}B_{1g} \rightarrow {}^{2}E_{g}$ transitions which are related to square planar Cu^{2+} complexes. While peaks at 293 and 308 are related to INCT **[118]**.

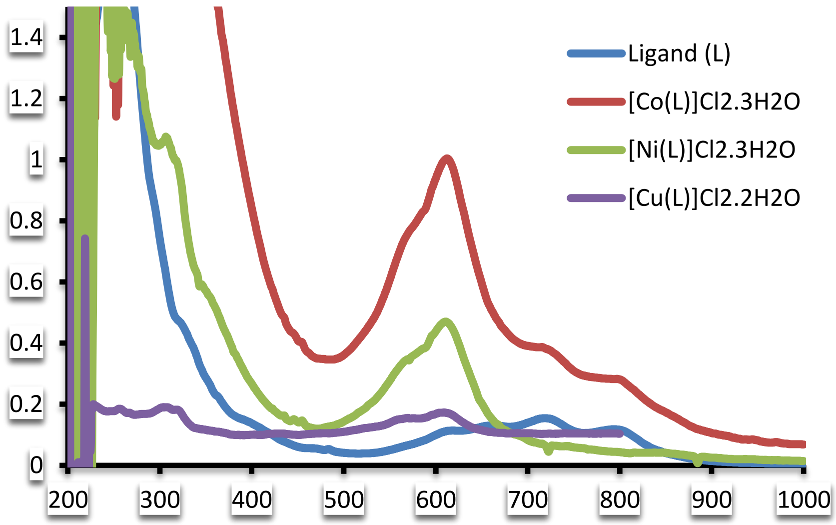


Figure (3.12) UV. visible spectra of L1, Co (II), Ni (II) and Cu (II) complexes

Table (3-4) Electronic transitions with their wavelengths of L1, Co(II), Ni(II) and Cu(II) complexes

compound	λ_{max}(nm)	Type of Transition
Ligand (L1)	227,250,314,392 598,650,712, 788	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$
$[Co(L1)]Cl_2.3H_2O$	360 560,602 702, 779	INCT Charge transfer $^2A1g \rightarrow {}^2B1g$ $E_g \rightarrow {}^2A_{1g}$
$[Ni(L1)]Cl_2.3H_2O$	299, 359 559, 601	INCT $^2A1g \rightarrow {}^2B1g$ $^1A_{1g} \rightarrow {}^1A_{2g}$
$[Cu(L1)]Cl_2.2H_2O$	293, 308 559, 601	INCT $^2B_{1g} \rightarrow {}^1B_{1g}$ $^2B_{1g} \rightarrow {}^2E_g$

3.5.2 UV-Visible electronic spectra of L2 and its Co(II) and Ni(II) complexes

The UV-Visible Electronic Spectra of L2 (Fig. 3.13) also shows peaks in the ultraviolet and the visible region which are assigned to π-$\pi*$and n-$\pi*$transitions respectively. In L2 electronic spectra, peaks appear at 259 and 326nm are related to π-$\pi*$transitions, while peaks at 419 and 461nm are related to n-$\pi*$transitions.

These peaks are also shifted when the Co(II) and Ni(II) complexes are formed (Fig. 3.13). For example, Co(II) complex with L2 shows five bands one at 311nm which is INCT band type. While the other four ones appear at (476, 499, 540 and 659)nm. The first one is assigned to charge transfer, while the other represent $^4A_2 \rightarrow {}^4T_2$, $^4A_2 \rightarrow {}^4T_1$(P) and $^4A_2 \rightarrow {}^4T_1$(F) respectively in the tetrahedral Co(II) complexes**[119]**.

In Ni(II) complex electronic spectra there is also a band at 320nm which is INCT peak and peaks at(480,506,543 and 667)nm. The first band is related to charge transfer,$^3T_1 \rightarrow {}^3T_2$, $^3T_1 \rightarrow {}^3A_2$and $^3T_1 \rightarrow {}^3T_1$(P) respectively in the tetrahedral Ni(II) complexes**[120]**.Table **(**3-5)gives a summary of these described above electronic transitions.

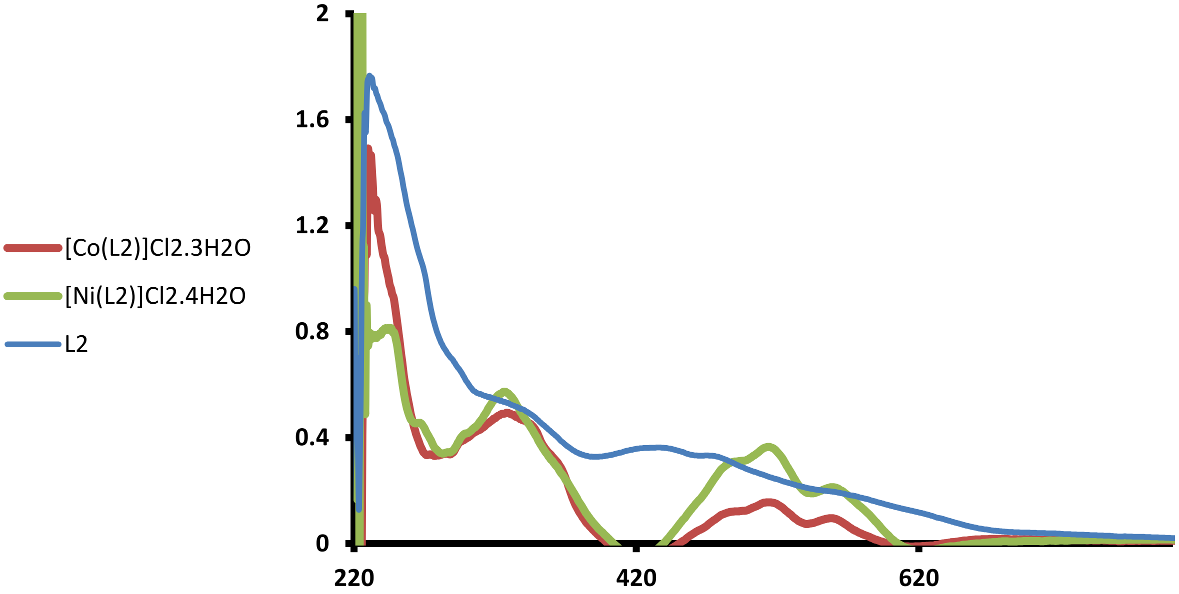


Figure (3.13) UV. visible spectra of L2, Co (II) and Ni (II) complexes

Table (3-5) Electronic transitions with their wavelengths of the L2 and its Co(II) and Ni(II) complexes

Compound	**λ_{max}(nm)**	**Type of Transition**
Ligand (L2)	259, 326 419, 461	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$
$[Co_2(L2)]Cl_2.3H_2O$	311 476 499 540 659	INCT Charge transfer $^4A_2 \rightarrow {}^4T_2$ $^4A_2 \rightarrow {}^4T_1(F)$ $^4A_2 \rightarrow {}^4T_1(P)$
$[Ni_2(L2)]Cl_2.3H_2O$	320 480 506 543 667	INCT Charge transfer $^3T_1 \rightarrow {}^3T_2$ $^3T_1 \rightarrow {}^3A_2$ $^3T_1 \rightarrow {}^3T_1(P)$

3.6 Molar conductivity measurements

The ionic formulas of compound in solution can be investigated using the molar conductivity measurements. This kind of measurements can be considered as an useful tool in coordination chemistry to know the ionic nature of compounds in solution. Where these compounds are found in solution either as neutral or ionic. The more ions released in solution, the greater conductivity values give**[121]**.

In such measurements water is not using as a solvent to measure the molar conductivity for compounds. Due to low solubility of these compounds in it, while organic solvents such as ethanol, nitromethane and methyl cyanide are often used as solvent for this purpose. Due to their high electrical constant and a low viscosity**[122]**. Table (3-6) shows molar conductivity of different electrolytes in different solvents.

Table (3-6) Molar conductivity values of electrolytes at ($1*10^{-3}$) M in different solvents

solvent	non electrolyte	Electrolyte type			
		1:1	2:1	3:1	4:1
water	0	120	240	360	480
Ethanol	0 – 20	35 – 45	70 – 90	120	160
nitromethane	0 – 20	75 – 95	150 – 180	220 –260	290 – 330
methyl cyanide	0 – 30	120 – 160	220 – 300	340 – 420	500
Dimethylformamide	0 – 30	65 – 90	130 – 170	220 – 240	300
Dimethyl sulfoxide	0 – 20	30 – 40	70 – 80	--------	-------

As it is shown in table (3-7) the conductivity of all the prepared complexes with the concentration 1x10^{-3} M was recorded in DMSO as a solvent. It's obvious from the conductance measurements for $[Co(L1)]Cl_2.3H_2O$, $[Ni(L1)]Cl_2.3H_2O$ and$[Cu(L1)]Cl_2.2H_2O$ are in range (70-80)Ohm^{-1} cm^2 mol^{-1} which indicate that all three complexes are electrolytes and the complexes are considered to be 1:2 in DMSO electrolyte type

While the conductivity values for $[Co_2(L2)Cl_2].3H_2O$ and $[Ni_2(L2)Cl_2].4H_2O$ in the same solvent are suggested the non-electrolyte nature of both complexes.

Table (3-7): The values of molar conductivity of complexes at (1*10^{-3}) M in DMSO

Molecularformula of complexes	Molar conductivity ($Ohm^{-1}.mol^{-1}.cm^{-1}$) of metal complexes at (1X10^{-3}) M in DMSO
$[Co(L1)]Cl_2.3H_2O$	79
$[Ni(L1)]Cl_2.3H_2O$	79
$[Cu(L1)]Cl_2.2H_2O$	78
$[Co_2(L2)Cl_2].3H_2O$	29
$[Ni_2(L_2)Cl_2].4H_2O$	29

3.7 Magnetic Susceptibility

This technique is usually used to detect the presence of single electrons in metal complexes. This technique also helps to suggest the hybridization of the central ions in their complexes, their magnetic properties if they are paramagnetic or diamagnetic and finally the structure of the metal complexes**[123-124]**.

The calculated magnetic susceptibility of the prepared metal complexes was measured at (298 °K) using the following equations .

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

$X_A=XM-D$

$X_M=Xg\times M.wt$

$X_g= CL/109m \text{ x } (R-RO)$

They represent:

T = absolute temperature = 289K

X_A = atomic sensitivity.

X_M = molar sensitivity.

X_g = Gram's (weight) sensitivity.

D = diamagnetic correction factor.

μ_{eff} = effective magnetic moment.

wt. M = gram molecular weight.

M.B = 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 tube with material - weight of tube empty.

Based on the obtained results of magnetic susceptibility measurement, it was found that the $[Co(L1)]Cl_{2.}$ $3H_2O$ and $[Cu\ (L1)]Cl_{2.}$ $2H_2O$ are paramagnetic, while $[Ni\ (L1)]Cl_{2.}$ $3H_2O$ is diamagnetic and all adopt the square planar geometry. While, $[Co_2(L2)Cl_2].3H_2O$ and $[Ni_2(L2)Cl_2].4H_2O$ complexes are paramagnetic and the complexes have the tetrahedral shape**[125]**. The results magnetic susceptibility measurement, magnetic properties and the suggested structure for L2-metal complexes are listed in the table (3-8).

Table (3-8) Magnetic measurements, magnetic properties and the proposed complexes structure

Compounds	μeff (B.M)	Magnetic properties	Suggested structure
$[Co(L1)]\ Cl_{2.}\ 3H_2O$	1.51	Paramagnetic	Square planar
$[Ni(L1)]\ Cl_{2.}\ 3H_2O$	0.0	Diamagnetic	Square planar
$[Cu(L1)]Cl_{2.}\ 2H_2O$	1.48	Paramagnetic	Square planar
$[Ni_2(L2)Cl_2].4H_2O$	2.051	Paramagnetic	Tetrahedral
$[Co_2(L2)Cl_2].3H_2O$	2.051	Paramagnetic	Tetrahedral

2.7.1 $[Co(L1)_2]Cl_2.3H_2O$ and $[Co(L2)Cl_2].3H_2O$ complexes

The first Co^{2+} complex with L1 ligand gives a magnetic susceptibility value equal to 1.51 BM. This value agrees with the low spin electronic configuration for Co^{2+}

in [Co(L1)] $Cl_2.3H_2O$ complex. In addition, this μ_{eff} value suggested the presence of one unpaired electron. The hybridization for Co^{2+} in [Co(L1)]$Cl_2.3H_2O$ will be dsp^2 and finally the complex structure is suggested to be square planar. On the other hand, the complex [Co(L2)Cl_2].$3H_2O$ gives a μ_{eff}= 2. 1 BM which indicates the paramagnetic nature of this complex also and this value agrees with the high spin tetrahedral for Co^{2+} **[12 6]**.

2.7.2[Ni(L1)] $Cl_2.3H_2O$ and [Ni(L2)Cl_2].$2H_2O$cofo $Co^{2+}$and the presence of one unpaired elecmplexes

The magnetic susceptibility measurement for Ni^{2+} in [Ni(L1)]$Cl_2.3H_2O$ suggests the low spin electronic configuration for Ni^{2+} where both electrons are paired. As a result the complex is diamagnetic with μ_{eff}= 0. 0 BM and the nickel central ion adopts the dsp^2 hybridization and the complex structure suggests to be square planar. While for [Ni_2(L2)Cl_2].$4H_2O$ the magnetic susceptibility measurements shows its paramagnetic with μ_{eff}= 2.1 B.M for which suggested the high spin electronic configuration for Ni^{2+} in [Ni_2(L2)Cl_2].$4H_2O$ complex and the complex structure is tetrahedral **[127-128].**

2.7.3[Cu(L1)] $Cl_2.2H_2O$

This complex also gives a magnetic susceptibility value equal to 1.48 BM which agrees with the presence of one single electron and this is correct for Cu^{2+} **[129]**. This value reflects the paramegnetism of Cu^{2+} and the suggested complex structure is also square planar.

3.8Thermal analysis

3.8.1 Thermal analysis for L1 and its complexes

The thermal analysis was carried out under air atmosphere with a temperature range 0-700°C.and 0-800 Figure (3.14) shows the TG curves for the ligand and the metal complexes. And table (3-9) gives a summary for the decomposition temperature range and the mass loss from all the studied compounds. In Figure (3.14) the early stage of ligand decomposition shows the loss of moisture and the other volatile species in the temperature range 43-170°C and 170-305°C. While the other two decomposition steps show the loss of some of the ligand moiety, which are the thione groups, nitrogen of imine group and two benzene rings.

In Co (II) complex the TG curve shows the loss of one lattice water molecule in the temperature range 64-198°C with a mass loss of 2.890%. The other two lattice water molecules and the two chloride ions from the outer sphere were lost in the temperature range 198-333 °C and 333-502 °C with a mass loss of 6.313% and 11.762% respectively. The final decomposition step leads to more of Co (II) complex decomposition when the temperature is between 502°C and 639°C and this shows the loss of some of the organic ligand molecule with a mass loss of 40.114%. While the thermal decomposition for Ni (II)complex shows also the loss of one lattice water molecule in the temperature range 60-269°C with a mass loss of 2.551%. And two water molecules in the range 269-410 °C with a mass lose 5.096%. Both chloride ions are lost at 410-544 with a mass loss of 11.828 %. The final decomposition step in Ni (II)complex involves the loss of thione groups, nitrogen of imine groups and two phenyl groups at 544-633°Cwith a mass loss of

37.464 %. The thermal decomposition of [Cu(L1)]Cl_2.2H_2O can be explained in the same way and is summarized in table(3-9) .

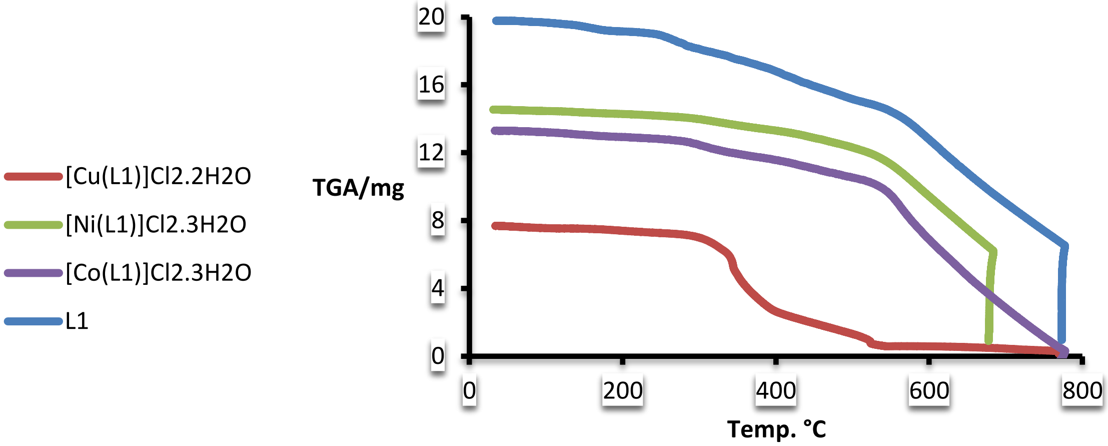


Figure (3.14) TG curves for L1 , [Co(L_1)] $Cl_{2.}$ 3H_2O, [Ni(L_1)] $Cl_{2.}$ 3H_2O and [Cu(L_1)]$Cl_{2.}$2H_2O complexes

Table(3-9) Thermal decomposition data for L1, $[Co(L_1)]$ $Cl_{2.}$ $3H_2O$, $[Ni(L_1)]$ $Cl_{2.}$ $3H_2O$ and $[Cu(L_1)]Cl_{2.}$ $2H_2O$

Compound	**Steps of Degradation**	**Decomposition Temperature ° C**	**Mass Loss%**	**Type of Lost Species**
Ligand (L1)	**1**	43-170	2.332	Moisture
	2	170-305	5.664	CN
	3	305-506	15.116	-2S
	4	506-771	42.300	-N , -2(C_6H_6)
$[Co(L1)]Cl_2.3H_2O$	**1**	64-198	2.890	$-H_2O$
	2	198-333	6.313	$-2H_2O$
	3	333-502	11.762	$-2Cl^-$
	4	502-639	40.114	-2(C_6H_5S + N)
$[Ni(L1)]Cl_2.3H_2O$	**1**	60-269	2.551	$-H_2O$
	2	269-410	5.096	$-2H_2O$
	3	410-544	11.828	$-2Cl^-$
	4	544-633	37.464	- 2(C_6H_5S + N)

$[Cu(L1)]Cl_2.2H_2O$	**1**	38-178	2.105	$-H_2O$
	2	178-376	52	$-H_2O$,- $2Cl^-$, - 2 (C_6H_5S)
	3	376-526	39	- $(C_{14}H_8N_2)$

3.8.2 Thermal analysis for L2 and its complexes

The thermal analysis was also carried out under air with a temperature range 0-800°C. Figure (3.15) shows the TG curves for the ligand and the two metal complexes. And table (3-10) gives a summary for the decomposition temperature range and the mass lose for L2 and its metal complexes. In this figure the first stage of L2 decomposition process shows the loss of moisture and the other volatile species in the temperature range 44-160°C with a mass loss of 1.161% mass loss of 18.104% and 55.895% respectively

The other two decomposition steps indicate the loss of some of the ligand molecule. In Co (II) complex the TG curve shows the loss of one lattice water molecule in the temperature range 45-118°C with a mass loss of 2.841 %. The other two lattice water molecules, two chloride ions and some of the ligand fragment were lost in the temperature range 118-368 °C and 368-494 °C with a mass loss of 27.048 % and 33.012 % respectively

In Ni(II) complex the TG curve shows also the loss of one lattice water molecule in the temperature range 44-243°C with a mass loss of 3.033 %. The rest three water molecules, two chloride ions and some of the ligand fragment were lost in the temperature range 243-344°C and 344-483°C with a mass loss of 30.966% and 31.304%.

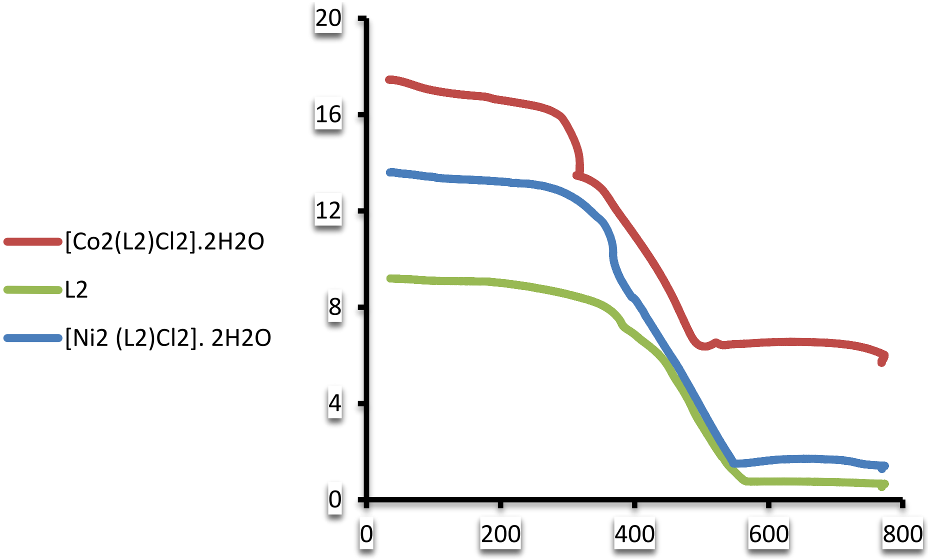


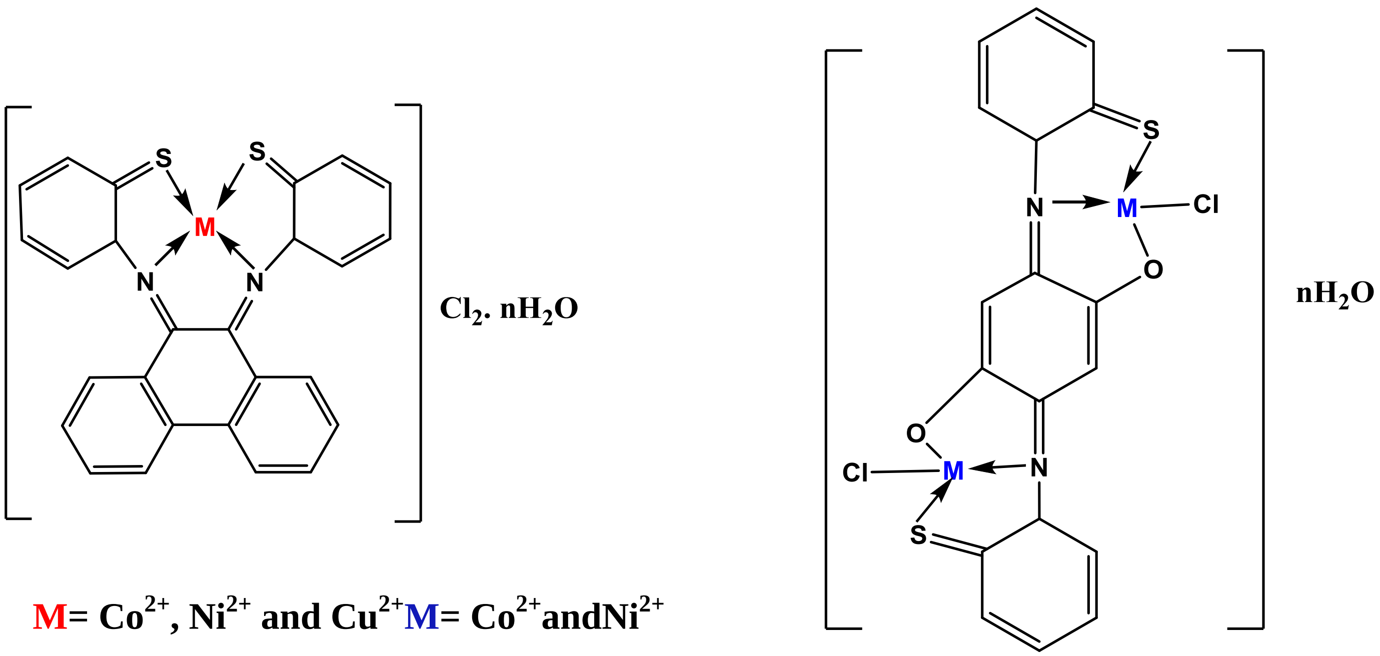
Figure (3.15) TG curves for L2 , $[Co_2(L2)]\ Cl_2.\ 3H_2O$ and $[Ni_2(L2)]\ Cl_2.\ 3H_2O$complexes

Table(3-10) Thermal decomposition data for L2 , $[Co_2(L2)]\ Cl_{2.}\ 3H_2O$ and $[Ni_2(L2)]\ Cl_{2.}\ 3H_2O$complexes

Compound	Steps of Degradation	Decomposition Temperature ° C	Mass Loss%	Type of Lost Species
Ligand (L2)	**1**	44-160	1.161	Moisture
	2	160-379	18.104	-2S
	3	379 -520	55.895	$-(C_{12}H_{10}NO_2)$
$[Co_2(L2)]Cl_2.3H_2O$	**1**	45-118	2.841	$-H_2O$
	2	118-368	27.048	$-2H_2O + 2Cl^-+$ -2S
	3	368-494	33.012	$-(C_{12}H_{10}NO_2)$
$[Ni_2(L2)]Cl_2.4H_2O$	**1**	44-243	3.033	$-H_2O$
	2	243-344	30.966	$-3H_2O + 2Cl^-+$ -2S
	3	344-483	31.304	$-(C_{12}H_{10}NO_2)$

3.9. Suggested structures for metal complexes

According to the available and mentioned data in this work, it is obvious that L1 behave as tetea dentate ligand coordinates with the studied metal ions through the free lone pairs of electrons in both isomethine and thione groups. This ligand binds with the metal ion in the molar ratio 1:1 metal: ligand. While, the chloride counter ions are found outer the coordination sphere as this was confirmed by the mentioned previously conductivity results. Therefore, metal complexes with L1 are electrolytes.and their structre with L1suggested to be square planar While Co(II) and Ni(II) metal complexes coordinate with L2 in 1:2 L:M molar ratio through three binding sites, namely imine, thione and the deprotonated hydroxyl groups. The chloride ions are available inside the coordination sphere and this was also confirmed by the conductivity results. The complexes structure with L2 is suggested to be tetrahedral. Figure (3.16) shows the general formula of metal complexes with L1 and L2.



M= Co^{2+}, Ni^{2+} and Cu^{2+}M= Co^{2+}andNi^{2+}

Figure (3.16) General structure of metal complexes with L1 and L2

3.10. Biological activity study

The resistance to different types of bacteriahave developed concern about the drug activity against such microorganisms. This resistance include the resistance against gram Negative Bacteria**[130]** .

In this work the biological activity of the two Schiff base ligands (L1, L2) and their metal complexes with Co^{2+}, Ni^{2+} and Cu^{2+} have been tested against two kinds of bacteria, namely *Escherichia coli* and *Staphylococcus aureus*. As examples of gram negative and gram positive bacteria respectively. The drilling method (wells) was used for this purpose. By making two holes and then measuring the diameter by a ruler. When the bacterial grows this appears in the middle of the (Mueller-Hinton ager). The inhibition zone is shown in table(3-11) and figure (3.17).

It is clear that some of the prepared metal complexes effect both kinds of bacteria when compared with the L1 and L2.As shown figure (3.17) the metal complexes$[Co(L_1)]\ Cl_2.\ 3H_2O[Ni(L_1)]\ Cl_2.\ 3H_2O$ and $[Cu(L_1)]Cl_2.2H_2O$ have an effect against the two bacteria. While the rest complexes gave negative results indicating that the bacteria have overcome the complexes. The positive results of some complexes can be explained according to the chelation theory. In this theory, the polarity of the metal ion is reduced due to the chelation by the partial sharing of the metal positive charge with donor groups within the chelate ring. As a result the lipophilic nature of the central metal atom will be increase and finally it can penetrate the lipoid layer of the bacterial membrane and inhibit growth of organisms**[131-132].**

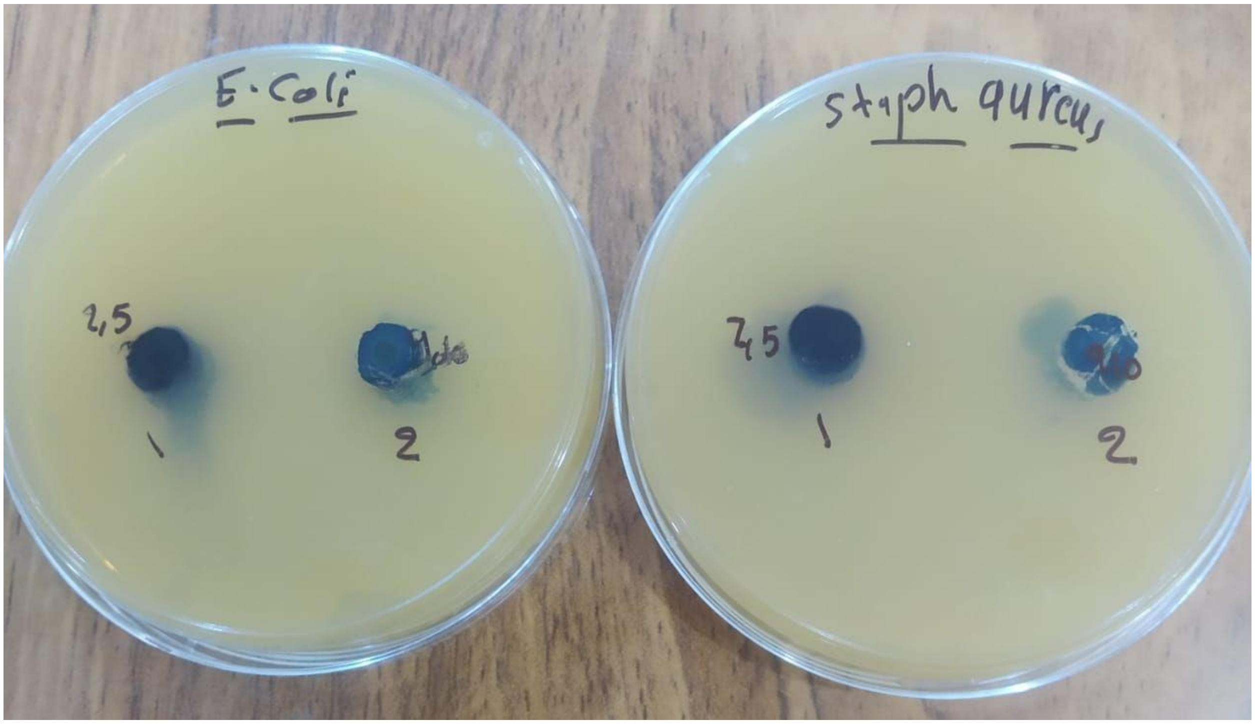
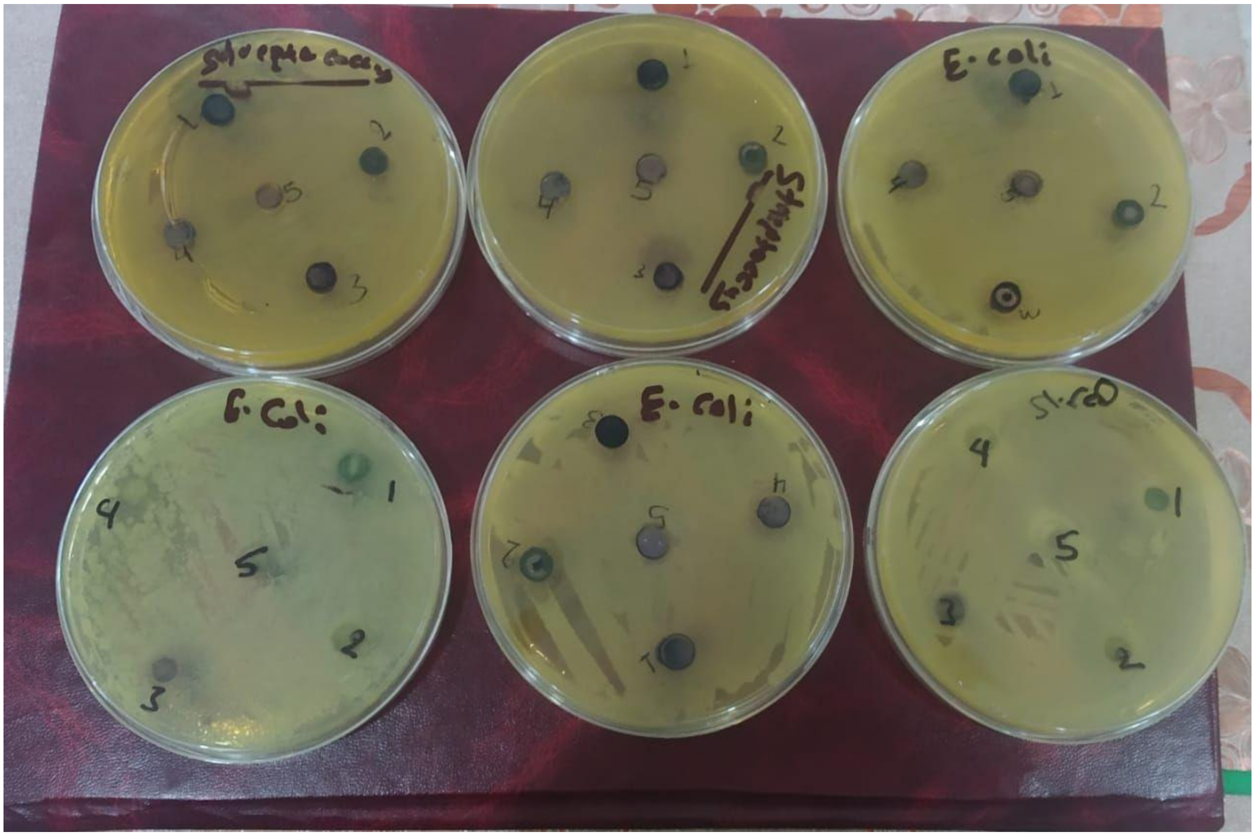


Figure.(3.17) .*Coli*and *Staphylococcus aureus* effect on the L1and L2



Figure(3.17) *E.Coli*and *Staphylococcus aureus* effect on the prepared compounds

Table (3-11):Inhibition effect of Schiff base ligands and their complexes on *E.Coli*and *Staphylococcus aureus*

Compound	***E.Coli***	***S.aureus***
L1	--	--
$[Co(L_1)] Cl_{2.} 3H_2O$	+	+
$[Ni(L_1)] Cl_{2.} 3H_2O$	+	+
$[Cu(L_1)]Cl_{2.}2H_2O$	+	+
L2	--	--
$Co_2(L2)] Cl_{2.} 3H_2O$	--	--
$[Ni_2(L2)] Cl_{2.} 3H_2O$	--	--

3.11. Conclusions:

1-The Schiff base ligands were prepared by the condensation methods between two ketones and amine(9,10-phenanthrenequinone and 2,5-dihydroxy-1,4-benzoquinon with 2-aminothiophenol)in 1:2 molar ratio ketones: amine respectively.

2-The structure of both ligands was confirmed by^{1}HNMR and infrared spectroscopy.

3-Co(II), Ni(II) and Cu(II) complexes were prepared with L1 and Co(II) and Ni(II) complexes were prepared with L2.

4-By the obtained results the ratio between the metals and L1 was suggested to be (1:1) M:L1 and 2:1M:L2 molar ratio.

5- The conductivity values show the electrolytic nature for metal complexes with L1. While for metal complexes with L2 it was found that all the complexes are non- electrolyte.

6- The proposed structure for the prepared complexes with L1, which showed that the prepared ligands behaved as a tetradentate ligand , where the coordination occurs through the azomethine group and the thione group. And the complexes are square planar. While the structure for The prepared lignd L2showed it s behave as polydentate Ligand and the metal complexes with L2 are tetrahedrl and the coordination between L2 and these ions occurs through also the azomethine group, the thione group and the oxygen atom .

3.12. Future work

1- L1 can be used to prepare metal ion complexes with the molar ratio 1:1 ketone: amine.

2- Other new metal complexes using diffrernt metal ions can be prepared with L1 using both molar ratios, 1:2 ketone: amine and 1:1 ketone: amine.

3- The synthesis of other metal ion complexes with L2 Schiff base ligands can be investigated also.

4- Mononuclear complexes with L2 can be prepared instead of dinuclear complexes.

5- Hetrodinuclear and homodinuclear complexes can be also prepared with L2.

6-The use of the prepared complexes in different fields, such as in industry and in biology.

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الخلاصة:

تضمنت الدراسة تحضير نوعين من قواعد شف الأول (L1) حضر من مفاعله 2-aminothiophenol مع 9,10-phenathrenquinon والثاني (L2) حضرمن مفاعله 2-aminothiophenol مع 2,5-dihydroxy1,4-benzoquinon . حيث تناسق الليكاند الأول مع ايونات الكوبلت و النيكل والنحاس (ثنائية التكافؤ) بنسبة موليه (M:L)(1:1) فيما تناسق الليكاند الثاني مع ايوني الكوبلت و النيكل(ثنائية التكافؤ) بنسبه موليه (M:L)(2:1). جرى تشخيص الليكاندين المحضرين بتقنية (الرنين النووي المغناطيسي، الاشعة فوق البنفسجية المرئية، الاشعة تحت الحمراء والتحاليل الحرارية)فيما شخصت معقدات الليكاندين المحضرين بتقنيات (الاشعة فوق البنفسجية المرئيه، الاشعة تحت الحمراء، التوصيليةالمولارية، الحساسية المغناطيسية والتحاليل الحرارية). تم اقتراح الشكل الهندسي المربع المستوي لمعقدات الليكاند الأول فيما أظهر معقدي الليكاند الثاني الشكل رباعي السطوح. كذلك تم اختبار الفعالية البايلوجية للمركبات المحضرة جميعها باستخدام نوعين من البكتريا (*Escherichia coli* و *Staphylococcus aureus*). حيث اظهرت معقدات الليكاند الاول فعالية بايلوجية مقارنة بالليكاندين المحضرين و معقدات الليكاند الثاني.