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Synthesis, Structural Biological Studies and theoretical treatment of new chelating ligand with some transition metals complexes

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(بِسْمِ اللَّهِ الرَّحْمَنِ
الرَّحِيمِ)

﴿ يُؤتِي الْحِكْمَةَ مَن يَشَاءُ وَمَن يُؤْتَ الْحِكْمَةَ فَقَدْ أُوتِيَ خَيْراً كَثِيراً وَمَا يَذَّكَّرُ إِلاَّ أُوْلُواْ الأَلْبَابِ﴾

صدق الله العلي العظيم

سورة البقرة، الآية { 269 }

الإهداء

إلى شهيد جامعتي ومنبر العلم فيها.....

إلى من ستبقى نتائجه العلمية سراجا وهاجا ينير لنا درب العلم.....

إلى من يرقد بسلام في ارض السلام.....

إلى روح الأستاذ الدكتور الطاهرة

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إلى من جعل الجنة تحت أقدامها وتآنس روحي بقربها ويستنير دربي بدعائها وتغفو أحزاني بابتسامة عيناها

أمي حنان الدنيا كلها ورمز التضحية

إلى من شجعني على خوض التجربة وجعلني أمسك بدفة المركب وبموج هذه الحياة

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إلى من أحاطوني برعايتهم وشاركوني في فرحي وشجوني وقدموا لي الدعم المعنوي

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Abstract

A new ligand have been prepared in this work, which was chosen to synthesis a new set of transition metal complexes [Mn(II),Co (II), Ni (II),Cu(II),Zn(II),Hg (II),Cd (II),Pd(II), Cr(III) and Rh (III)].

The new ligand (Potassium (Benzothiozole-2-dithiocarbamato hydrzide)**)** was isolated and characterized by appropriate physical measurements, vibrational and uv- vis spectroscopy.

This dithiocarbamate derivative (L) has been used as ligand to prepare a number of new complexes with the selected metal ions, [Cr(III), Mn(II),Co (II), Ni (II),Cu(II),Zn(II),Hg (II),Cd (II),Pd(II) and Rh (III)]. These complexes were studied and characterized using FT.IR, UV-Vis Spectroscopy, molar conductivity, magnetic susceptibility melting points and atomic absorption measurements. It concluded that {$[CrL_3].3EtOH$, {$[CuL_2(H_2O)_2].H_2O$ and $[NiL_2(H_2O)_2].4EtOH$} have octahedral geometries ,{$[RhL_2]Cl$ and $[PdLCl].1.5EtOH$} have square planer geometries and {$[CoL(H_2O)Cl].3EtOH$, {$[ZnL_2].6EtOH$, $[MnL_2].1.5EtOH$ and $[CdLNO_3].3EtOH$,$[HgL_2].XH_2O$} have a tetrahedral geometry. Different bonding and structural behavior were revealed through the study of the coordination chemistry of the metal complexes of the new ligand.

The nature of bonding between the metal ion and the donar atoms of the ligand were demonstrated through the calculated of Racah parameter and the other ligand field parameters, which were calculated using the suitable Tanaba-Sugano diagrams.

A theoretical treatment of the formation of complex in the gas phase was studied; this was done using the hyperchem-6 program for the Molecular mechanics and semi- empirical calculations. The heat of

formation (ΔH°_{f}) and binding energy (ΔE_{b}) for the free ligand and its metal complexes were calculated by (PM3 and ZINDO/1) methods, at 298°K. Furthermore, the electrostatic potential of the free ligand was calculated to investigate the reactive sites of the molecule. PM3 was used to evaluate the vibrational spectra of the free ligand (L), and these obtained frequencies agreed well with those values experimentally found, in addition, the calculation helped to assign unambiguously the most diagnostic bands.

The antibacterial activity for the starting material, the ligand and its metal complexes were studied against two selected microorganisms (***Staphylococcus aureus***) and (***Pseudomonas aeruginosa***), using (10 mM) and (5mM) concentration in nutrient agar medium.

The results were showed a great enhancement of activity of some complexes relative to that of their respective ligand. These were attributed to the synergetic effect between the metal ion and the ligand, in addition to the differences in the structural varieties.

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Symbols and Abbreviations:

FT-IR	Fourier Transform Infrared
uv-vis	Ultraviole-Visible
DMSO	Dimethyl Sulfoxide
ETOH	Ethanol
Oh	Octahedral
Th	Tetrahedral
B.M	Bohr magneton
γ	Stretching
δ	Bending
nm	Nanometer
λ	Wave length
m.p	Melting point
B	Racah parameter
β	Nephelauxetic factor
ph	Phenyl
dec.	decomposition
DTC	dithiocarbamate

CHAPTER ONE

INTRODUCTION

INTRODUCTION

1.1 Bioinorganic Chemistry

From the clothes we wear to the diseases we battle, inorganic chemistry plays a central role in understanding our world and improving our lives.

Bioinorganic chemistry is a rapidly developing field and there is enormous potential for applications in medicine. On the other side a large number of metal containing therapeutically agents and other biologically active complexes have been prepared and proven to be of great effectiveness in this respect (1). Moreover, many enzymes require metal ions to achieve full catalytic activity has stimulated interest on the chemistry taking place at the active sites of the metalloenzymes (2).

The development of the field of bioinorganic chemistry has increased the interest in Schiff base and thiol derivatives complexes, since it has been recognized that many of these complexes may serve as models for biologically important species (3).

1.2 Coordination chemistry:

Coordination compound is a metal surrounded by neutral molecules or ions called ligands. Ligands are Lewis bases, they contain at least one unshared electrons. They are also called complexing agents. Metal ions have empty valance orbitals; they act as Lewis acids (4).

Coordination chemistry can be utilised in number of way in medicine. Coordination compounds can be employed in the treatment, management or diagnosis of disease, or coordination complexes can be formed in the body to handle dysfunction because of metal poisoning. There are four prime areas of the utilization of transition metal complexes in medicine. (5)

a) The use of chelating or complexing agents to treat metabolic dysfunction.

b) The use of coordination compound, or metal-base drugs, to treat disease.

c) The use of coordination complexes to transport metals to specific sites in the body tends to aid in imaging e.g. the use of these complexes in radio imaging.

d) The application of complexing or chelating agents to remove heavy metal poisons from the body, e.g. the excess of nickel, tin, lead, arsenic and mercury.

1.3 Interaction of Ligand with metal ion:

The study of the interaction of metal ions with different simple and complicated systems require, first of all, to be aware of the essential bases of coordination inorganic chemistry especially the structural and bonding aspects. Of the most important principle in this respect is the hard and soft acids and bases theory (HSAB) of Pearson, which shows the tendency of metal ions to coordinate with certain groups. Depending on the nature of the donating atom in these groups (6). Also to know the factors affecting the stability of the resulting complexes.

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

$Ba^{+2} < Sr^{+2} < Ca^{+2} < Mg^{+2} < Mn^{+2} < Fe^{+2} < Co^{+2} < Ni^{+2} < Cu^{+2} > Zn^{+2}$. This order arises in part from a decrease in size a cross the series and in part from ligand field effects. A second observation is that certain ligand form their most stable complexes with metal ions such as Ag^+ , Hg^{+2} and Pt^{+2} , but other ligand seem to prefer ions such as Al^{+3} , Ti^{+4} and Co^{+3} (7).

Ligands and metal ions are classified as either to type (a) or type (b) according to their preferential bonding. Class (a) metal ions include those of alkali metals, alkaline earth metals and lighter transition metals in higher oxidation states such as Ti^{+4} , Cr^{+3} , Fe^{+3} , Co^{+3} , and the hydrogen ion , H^+. Class (b) metal ions include those of the heavier transition metals, and those in lower oxidation states such as Cu^+ , Ag^+ , Hg^{+2} , Pd^{+2} and Pt^{+2} . According to their prefences toward either class (a) or class (b) metal ions, ligands may be classified as type (a) or (b) respectively. Stability of these complexes may be summarized as follows(8):

Table (1-1): Some ligands and their preferential bonding with different metals

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

For example, phosphines (R_3P) and thioethers (R_2S) have so much greater tendency to coordinate with Hg^{+2} , Pd^{+2} , and Pt^{+2} , but ammonia, amines (R_3N), water, and fluoride ion prefer Be^{+2} , Ti^{+4} , and Co^{+3} . Such a classification has proved very useful in accounting for and predicting the stability of coordination compounds (8).

One of the most important phenomena that control the stability of the oxidation states of a certain element and the stabilization of one state among another state is known as (symbiosis) (9).

Often metal complexes expand their coordination number by interaction with a Lewis base. This may take place by interaction association or by adduct formation with solvent or other available ligands. The physical properties of the resulting complex are often significantly different from those of the complex not having the expanded coordination number (10).

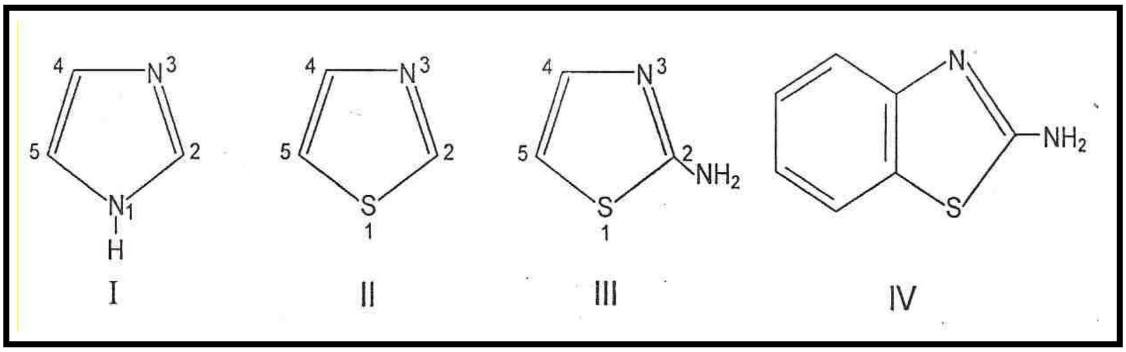
1.4 Metal complexes; chemistry of polydentate ligands:

Large molecules, which contain a number of donating atoms, have the ability to bind to the metal ion through more than one atom.(11) Polydentate ligand, especially those which have equivalent atoms with respect to their coordination ability, show different behavior with respect to the number of binding sites with the central metal, e.g. (ethylene-diamine tetraacetate may have coordination number between 2 and 6). The pH of the reaction mixture has also a large effect on the bonding properties of the polydentate ligands. In addition to that the type of solvent and the metal, concentration of the ligand and other factors which may affect the mechanism of the ligand exchange, have also important role in this respect (11).

The chemistry of metal complexes containing polydentate ligands which have delocalized π-orbitals like Schiff bases, triazole and porphyrins, have recently attracted the attention of many scientists due to their use in many biomodels, like respiratory pigments and vitamin B_{12} co-enzymes. In the case of Schiff base metal complexes, the works were carried out on cobalt (III) complexes because they are considered to be a reversal molecular oxygen carriers or vitamin B_{12} co-enzyme models. This interest extends to iron (II) and (III) complexes since iron is found in many living systems like hemoglobin. On the other hand, transition metal (especially vanadium) complexes of imine group are also used industrially as a catalyst in the co-polymerization of acetylene-propylene the method of Ziegler-Nata process (12).

1.5 Thiazole compounds and their derivatives:-

Thiazole is considered to be of a great biological importance and widely used as pharmaceuticals,(13) in which activity and potency of many enzymes depend on behavior of thiazole group when coordination with transition metal ions especially having double equivalence occurs (14). This group is a heterogeneous ring (structure II), fig (1-1), having two donating atom of sigma bonds for the metal (nitrogen, sulfur) which was derivated from imidazol (structure I), in which amine group is replaced by with one sulfur atom in position 1.



I. Imidazole.

II. Thiazole.

III. Thiazol-2-amine.

IV. Benzothiazol-2-amine (2-Mercaptobenzothiazoles).

Fig (1-1): Thiazole derivatives.

This makes thiazole group accepts (π) bond better than amidozol as a result of the existence of one empty (d) orbital on sulfur atom. Researches found that the overlapping of this group with metals showed a connection between metal ion and ligand was taking place through the nitrogen atom which is most possible than the connection by the sulfur atom, while the restoring of the hydrogen in position 2 with amine group (structure III), provides a third position for donating the bond to the metal ion (15).

One of the other derivative of the thiazole ring is 2-aminobenzothiazole which was preparated by Lane**(16)** from the reaction of thiocyanogen with o-aminothiophenol, consisting of a double ring system in which one benzene ring cohere with one thiazole ring in two position 4,5 (structure IV) .

1.5.1 Benzothiazoles:

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

(A) (B)

Fig (1-2):Benzothiazole and its derivative

2-Mercaptobenzothiazols are derivatives in which the position2 is linked to the sulfur atom like the structure (B).

The benzothiazoles are aromatic because they are cyclic, planer molecules, and have six pairs of delocalized **(π)** electrons, four of the pairs are shown as **(π)** bonds, and one pair is shown as a pair of nonbonding electrons on the sulfur atom and the other pair is shown as a pair of nonbonding electrons on the nitrogen atom **(17)**.

2-mercaptobenzothiazol was developed as a rubber vulcanization accelerators, thus the early impetus to the study of thiazole chemistry came from the practical importance of the benzothiazole **(18)**.

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

The biological importance of benzothiazole derivative was further emphasized during the period 1941-1945 The work on the structure of the antibiotic, penicillin, which has showed the presence of a thiazolidine ring in this important therapeutic agent **(19)**.

1.6 Synthesis of 2-Mercaptobenzothiazoles:

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

1.6.1 Reaction of aryl amine with carbon disulfide and sulfur:

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

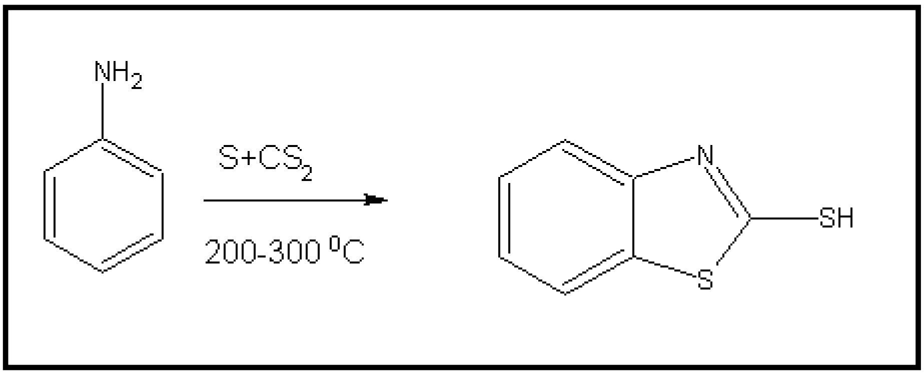


Fig (1-3):Preparation of 2-mercaptobenzothiozole

This method can be used with certain substituted aryl amines in place of aniline to yield mercaptobenzothiazol substituted in the benezenoid ring **(20)**.

1.6.2 Reaction of o-amino thiophenol with carbon disulfide:

A more versatile process and one that is more readily applicable in the laboratory involve the treatment of o-aminothiophenole with carbon disulfide in present of ethanol as solvent **(21)**.

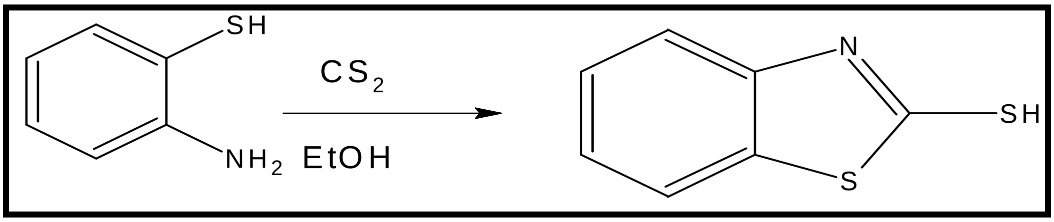


Fig (1-4):Preparation of 2-Mercaptobenzothiozole

A very useful modification of this procedure takes advantage of the reaction of an o-nitroaryl halide with a mixture of sodium hydrogen sulfide and carbon disulfide **(22)**.

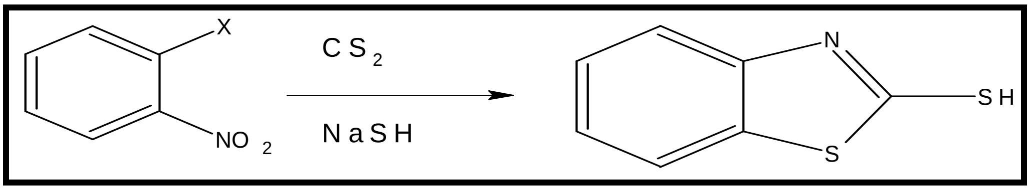


Fig (1-5): Preparation of 2-Mercaptobenzothiozole

1.6.3 Reaction of o-amino thiophenol with thiophosgen:

The synthesis of 2-Mercaptobenzothiazole by reaction of thiophosgen with ortho-aminophenol is of interest in connection with the independent existence of the two tautomeric form of the 2-Mercaptobenzothiazoles **(20)**.

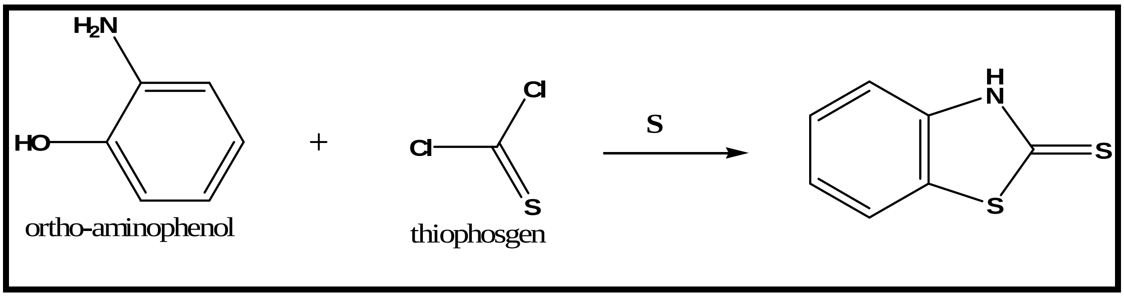


Fig (1-6):Preparation of 2-Mercaptobenzothiozole

1.6.4 Miscellaneous methods:

2-Mercaptobenzothiazoles are produced from N-aryldithiocarbamates, arylisothiocyanate and N,N-diphenylthioureas when these compounds heated with sulfur(23), as shown below.

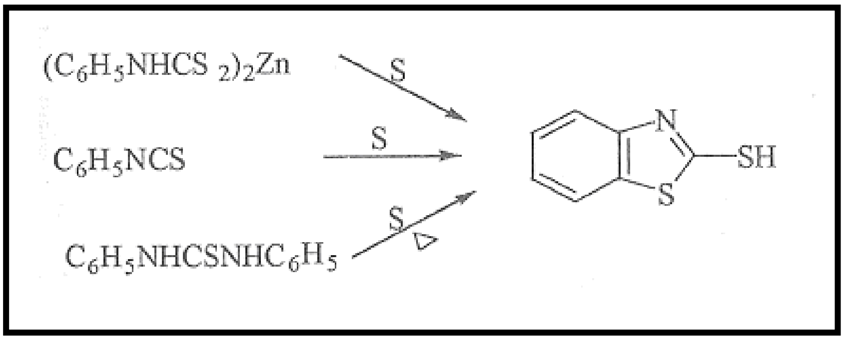


Fig (1-7): Type of 2-Mercaptobenzothiazole produced

1.7 Thiazole and its metal complexes:-

Many scientists studied the coordination behavior of thiazole and its derivatives with a number of transition metal ions **(24,25)**. Thiazole group contains two possible bonding locations (nitrogen, sulfur). **(26)**

After locating amine group at carbon 2 another bonding location appears because of the similarity between the nitrogen base and substituted amine. (27)

It has been found that most of metal ions bound with nitrogen atom (25,26), and when using soft atom like Au ,Cu it will tend to bound with sulfur rather than nitrogen with bidentate and this behavior with hard soft acid base (HSAB)(25,28). Formation of number of metal complexes for ligand 2-aminothiazol has been studied with transition metal ion in aqueous solution and those metals are Cu(II),Cd(II),Mn(II),Co(II), Ni(II) and has been suggested the connection with ions will depend on the nitrogen atom in thiazole ring except Copper ion which it may connect with sulfur atom(21) .

It has also been found that 2-aminothiazol suffer from rearrangement within the ring depending on pH-solution when it coordinates with Pt (II) and Pd (II) (29).

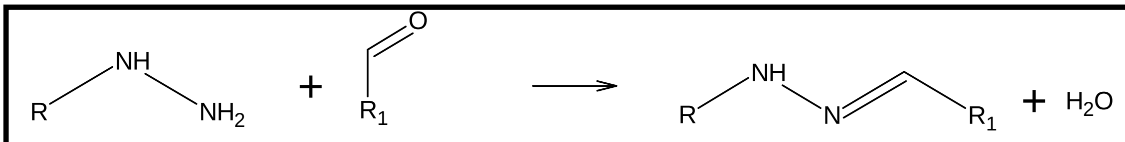
For the important of thiazole complexes and in order to know if this ring is working as a monodentate or bidentate ligand when adding NH_2 group in position 2 for benzothiazole molecule, A study has been made on the Fe (III) complex with 2-aminobenzothiazole using different spectral methods, and it has been noted that the ligand behave as a monodentate and also as a bridge group in polymer composition through the two sulfur and nitrogen ring atoms(30).

A study and preparation has also been made for this ligand with other transition elements included Zn(II), Cd(II), Hg(II)(30), Sb(IV) and Sn(II)(31), Cu(I), Ag(I)(32).

Connection of ligand with center ion by nitrogen ring. In a study made at the year 1980, which included the preparation of radium (I) complex with benzothiazole, It has been noted that the radium ion bond with benzothiazole through the (π) bond of the NCS group or the one distributed on the overall molecules. It has also been found that the prepared complexes own a catalyze properties in speeding up the polymerization of acetone to alkohldiacetone and Mesityl oxide and benzaldyhide polymerization (27).

1.8 Hydrazones:

Hydrazones are compounds derived from the condensation of Hydrazine or its derivatives with carbonyl compounds, namely aldehydes or ketones Fig (1-8).



R=aliphatic , aromatic or heterocyclic unit , etc

Fig (1-8): Preparation of Hydrazones.

Hydrozone compounds obtained by the reaction of aromatic and heterocyclic hydrazides with mono and di aldehydes or ketones have revealed very versatile behavior in the coordination with the metal ions (33).Many researches have synthesized a number of new hydrazones because of their ease of synthesis (34). Hydrazones are known to function as chelating agents.

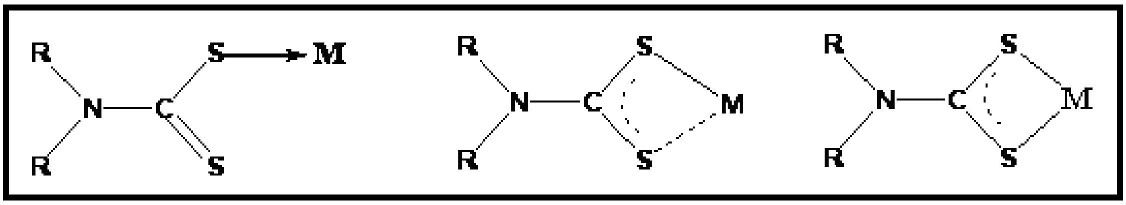
1.9 Ligands containing sulfur as a donar atom:

The sulfur atom can act either as terminal or bridging ligands. The dianion S^{2-} is also an effecting ligand, and chelating poly sulfides ($-S_n-$) are well established. These various sulfur ligands will be briefly considered before dealing with the broad rang of compounds in which sulfur act as the donar atom, e.g. H_2S, R_2S, and dithiocarbamates and related anions, 1,2-dithiolenes etc. ligands in which sulfur act as donar atom are usually classified as (soft) Lewis bases, in contrast to oxygen donar atom ligands which tends to be “hard” **(35)**.

The larger size of sulfur atom and the consequent greater deformability of its electron cloud give qualitative rationalization of this difference and the possible participation of dπ orbitals in bonding to sulfur has also been invoked **(35)**.

Hydrogen sulfide the simplest compound of sulfur, differ markedly from its homologue water in complex-forming ability; whereas aqua complexes are extremely numerous and frequently very stable, H_2S rarely forms simple adducts due to its ready oxidation to sulfur or its facile deprotonation to HS^- or S^{2-} $[Al\ Br_3(SH)]$ has long been known as stable compound of tetrahedral transition metal complexes having some degree of stability at room temperature are more recent vintage: $[Mn\ (\eta^5\text{-}C_5H_5)(CO)_2(SH_2)]$, and the tiragonal cluster complexes $[Ru_3(CO)_9(SH_2)]$ and $[Os_3(CO)_9(SH_2)]$ **(35)**.

Another large class of sulfur donar ligands comprises the dithiocarbamates $R_2NCS_2^{2-}$ related anions YCS_2, e.g. ditiocarboxylate RCS_2^-, Xanthates $ROCS_2^-$, thioxanthates $RSCS_2^-$, dithiocarbonates OCS_2^{2-}, trithiocarbonates SCS_2^{2-} and dithiophosphinates R_2PS_2. Dithiocarbamates can function as either unidentate or bidentate (chelating) ligands: **(35)**



1.9.1 Dithiocarbonates (Xanthates):

Dithiocarbonate (xanthate) group [O–C(–S)S–/O–C(–S)SH], which is chemically unstable, being readily oxidized to form a disulfide bond with subsequent loss of all biological activities. Dithiocarbonates can act as mono or bidentate ligands, and the complex forming ability of these sulfur donar ligands has invoked considerable attention**(36)**.

Cyclic thiocarbonates have received much attention in view of biological activity and material science. One of the most efficient methods for synthesizing cyclic thiocarbonates is performed by epoxide with carbon disulfide. Depending on the catalysts and reaction conditions five-membered cyclic dithiocarbonate, its region isomers, trithiocarbonate, and episulfide have been reported to be formed. Fig (1-9). **(37)**

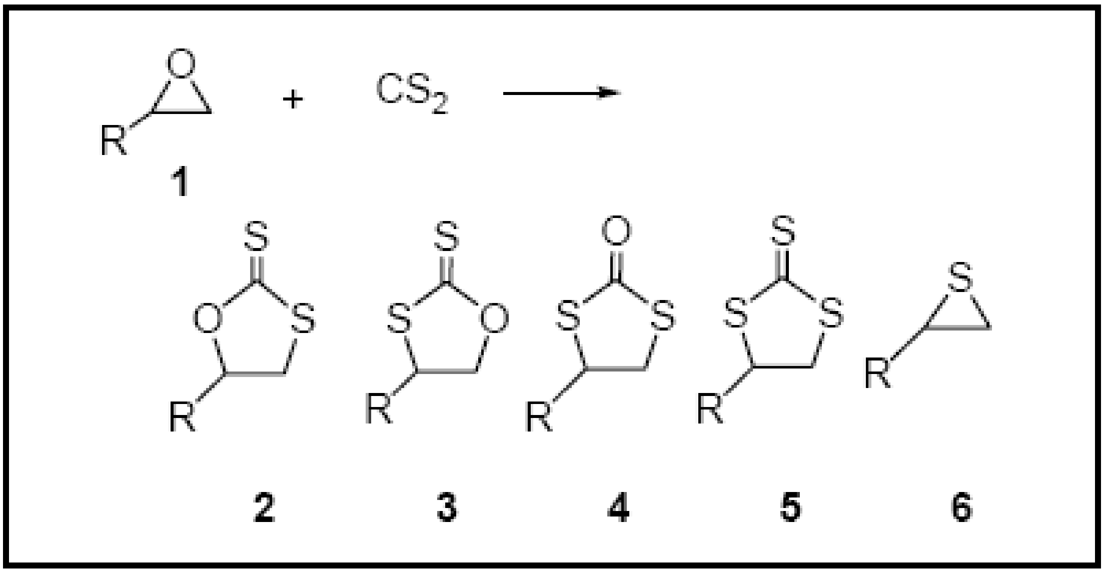


Fig (1-9): Isomers di and trithiocarbonate and it's episulfide

Metal xanthate complexes and their reaction products with a variety of Lewis bases have been extensively studied. The soluble alkali metal xanthates are widely used in extraction and separation of Hg, Ag, Cd, etc., Sodium and potassium ethyl xanthate have antidotal effects in acute mercurial poisoning. Transition metal xanthate complexes have been investigated for nonlinear optical applications and Cd xanthate was demonstrated to have nonlinear optical properties and generated a very strong second harmonic signal. To the best of our knowledge, the reaction products of Cd xanthate with Lewis bases have been much less extensively studied than other similar compounds (38).

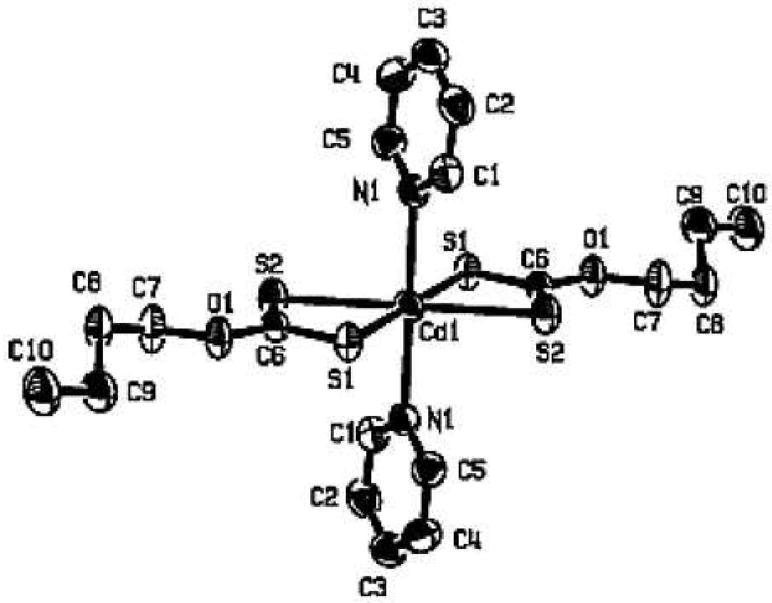


Fig (1-10): Proposed geometry of the Cd(II) complex with xanthate

1.9.2 Dithiocarbamates:

Sodium dithiocarbamate salt was prepared according to the reported procedure, using the reaction of commercially available 2-aminobenzothiazole and carbon disulfide in an alkaline medium (39).

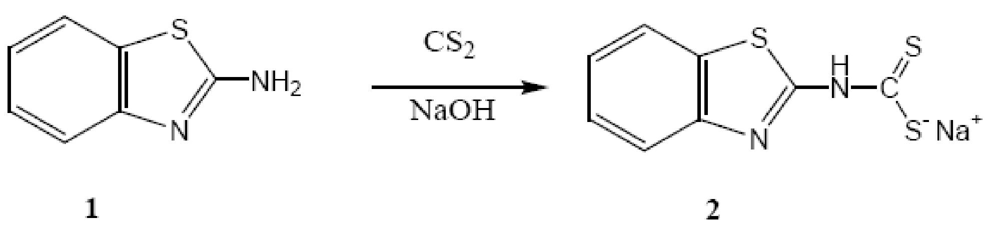


Fig (1-11): Preparation of derivative dithiocarbamate

Metal salts of heterocyclic dithiocarbamates (DTC) are of potential interest in applications such as pesticides and antioxidants. The reaction between amines and carbon disulfide involves catalysis by strong base. Some preliminary investigations were devoted to investigation of mechanism of the reaction and effect of solvent.

The main synthetic route to dithiocarbamates is based on the interaction between the corresponding amine and CS_2 in the presence of strong base (Fig (1-12)).

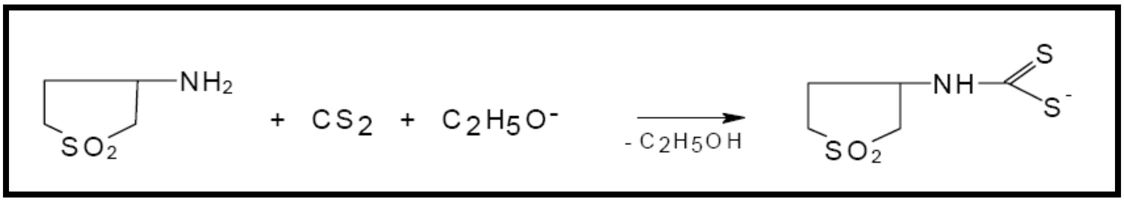


Fig (1-12): Preparation of derivative of dithiocarbamate

It was found that this method has some limitations. The solvent effect, upon decreasing of the protoning ability of the solvent, the rate of dithiocarbamate formation increases. In aprotic systems, the rate of the process increases with the increase of the dielectric permittivity of the solvent. Therefore, the problem of solvent selection is critical in the synthesis. Use of water-dioxane mixture did not provide satisfactory yields and purity of the product. Better results were obtained by carrying out the reaction in ethanol or its mixture with DMF.(40)

Figure(1-13) shows the molecular structure of $Zn_2[(n\text{-}Bu)_2NCSS]_4$. The molecular packing arrangement in the unit cell shows the crystal structure of the zinc (II) complex $Zn_2[(n\text{-}Bu)_2NCSS]_4$ is built up of centro-symmetric dimeric entities. The coordination sphere of two zinc ions is best described as a distorted octagon. Four sulfur atoms belonging to two dibutyldithiocarbamate ligands occupy the basal coordination positions. Therefore, each bridging sulfur simultaneous occupies an apical site of tetrahedron. The topology of the formed dimer is then viewed as an edge-sharing distorted octagon. Four bridging S atoms are strictly planar because the S(2)-C(1) bond distance is equal to $S(2)^{a}$-$C(1)^{a}$ (0.1725nm) and the S(1)-C(1) is equal to $S(1)^{a}$-$C(1)^{a}$ (0.1704nm).

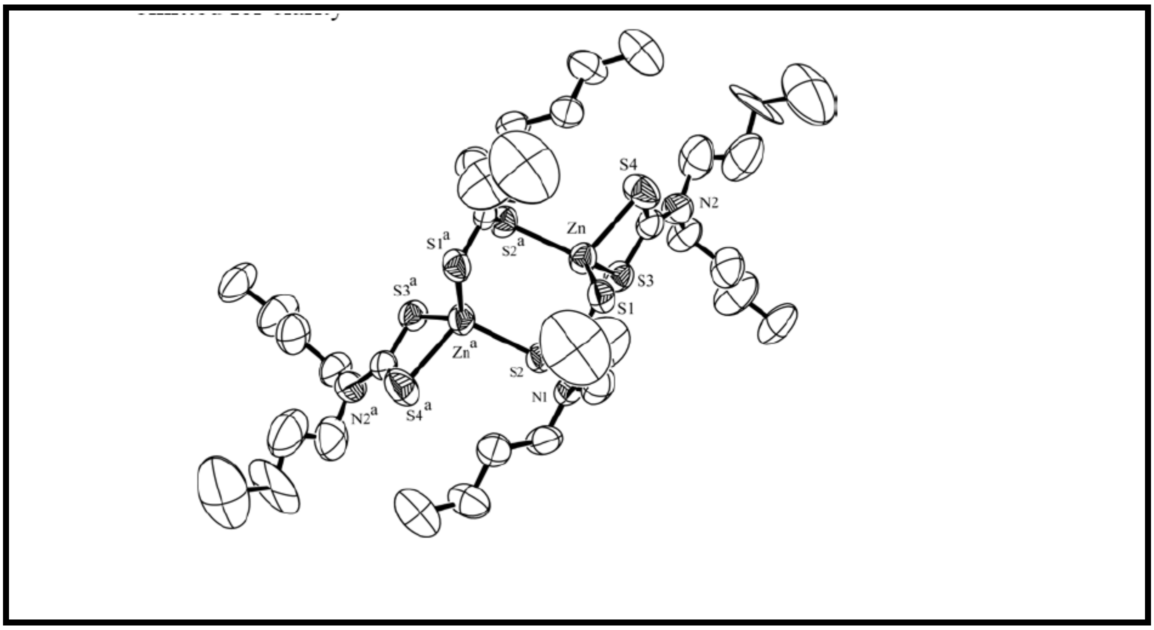
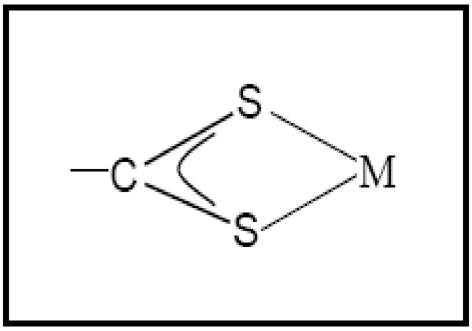
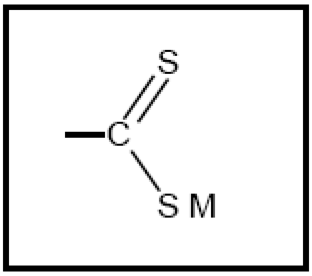


Fig (1-13): Molecular structure of $Zn_2[(n\text{-}Bu)_2NCSS]_4$ with hydrogen atoms.

The Zn(1)-C(1)-$Zn(1)^{a}$-$C(1)^{a}$ is strictly planar too, due to the inversion center. The carbon-sulfur bonds have an average length of 0.171 nm and the ligand "bite" angle S-C-S has a mean value of 117.8 deg. The N(1)-C(1) and N(2)-C(10) bond distances [0.131 nm, 0.133 nm] are shorter than the other N-C bond distances, and are indicative of considerable double-bond character. It is informative to examine the structure of the Zn complex. This is true for bidentate dithiocarbamate:





However, not for monodentate analogues:

One possible reason is that the enhancement of the Zn-S bond, which originates from reduction of a negative residual charge on the central ion, is partly compensated by the fact that one molecule of dithiocarbamate is replaced by two molecules of a monodentate ligand which results in less-stable crystal packing. On the other hand, the chelating mode of coordination of the bidentate ligand dibutyldithiocarbamate allows easy electron delocalization over a large conjugate system and the rigid plane permits a more stable crystal packing (41).

1.10 Application of dithiocarbamates:

1.10.1 Medical Application: (42,43)

- A withdrawal agent, used in the treatment of alcoholism.
- Effective against penicillin-resistant organisms using nontoxic penicillins containing a dithiocarbamatic acid.
- Used as antimycotics.
- Nickel-poisoning antidotes.
- Fungal infections of the skin can be treated with zinc ethylenebis(dithiocarbamate).
- Dithiocarbamic acid affects the biosynthesis of catecholamines and hepatosine.

- Dithiocarbamic acid reduce cholesterol production in rat liver.
- Lead in blood was determined by atomic absorption spectrometry (AAS) as described by the method of Hassel, using ammonium pyrrolidine dithiocarbamate solution to chelate the lead and the solution was then extracted with ketone.(43)

1.10.2 Radioprotective Agents (42)

Dithiocarbamic and other derivatives provide protection against γ-radiation. The metabolism of some of these agents in mice has been studied. Polymers, e.g., poly (vinyl chloride), that contain Dithiocarbamic acid substitutes are more radiation resistant than unsubstituted polymers.

1.10.3 Pesticides (42)

Dithiocarbamates are used as fungicides, nematocides and bactericides. These compounds liberate mustard oils or dialkyldithiocarbamic acids. Dithiocarbamate pesticides have been the subject of intensive metabolic and environmental investigation.

1.10.4 Vulcanization accelerators (42)

N,N-dialkyldithiocarbamic acids as Vulcanization accelerators for natural and synthetic rubber, water soluble derivatives are Used in low temperature processing of Latex. Sodium and Potassium dimethyldithiocarbamates used as modifiers in emission polumerization.

1.10.5 Imaging Technology (42)

Dithiocarbamates and derivatives have many applications in photographic and recording materials.

1.10.6 Other Uses (44-47)

- The formation of the semiconductor, such as alkyldiseleno- or alkyldithiocarbamato metal complexes .This method is particularly attractive when readily available air-stable precursors can be employed in a one-step process to obtain nanocrystalline materials; this has been clearly the case of the synthesis of several metal sulphides from dithiocarbamato or xantate complexes.(44)

- Other unique approaches using SAM(self-assembed monolayers) structures have been reported. It's developed supramolecular machines using SAM structures in which molecular configurations can be reversibly programmed using electrochemical stimuli [80]. The proposed machines addressed the chemistry of substrate surfaces for integrated microfluidic systems. SAM structures can be prepared on size-controlled nanoparticles, providing scaffolds for sensing target molecules. Sanchez-Cortes and co-workers reported the use of 25,27-diethyl-dithiocarbamic-26,28-dihydroxy-p-tert-butylcalix[4]arene in the functionalization of Ag nanoparticles for pyrene detection by surface-enhanced Raman scattering (SERS).(45),(46)

- ***Copper (II) thin-film microsensors:*** To confirm the possibility of realization of a future type thin-film microsensor, o-xylylene bis(N,Ndiisobutyl dithiocarbamate) has been used as electroactive material for Cu^2+ ions in an organic PVC (poly vinyl chloride) membrane. (47)

1.11 Theoretical Study:-

1.11.1 Computation Chemistry:-

Computational chemistry may be defined as the application of mathematical and theoretical principles to solve many chemical problems (48).

Molecular modeling, a subset of computational chemistry, concentrates on predicting the behaviour of individual molecules within a chemical system. The most accurate molecular models use ab initio or (first principles) electronic structure methods, based upon the principles of quantum mechanics, and are generally vary computer – intensive. However, due to advances in computer storage capacity and processor performance, molecular modeling has been rapidly evolving and expanding field, to the point that it is now possible to solve relevant problems in an acceptable amount of time

Electronic structure calculations provide useful estimates of the energetic properties of chemical systems, including molecular structures, spectroscopic features and probable reaction pathways (48).

1.11.2 Fields of Application:-

The types of prediction possible for molecules and reaction are (48):-

1- Heat of formation

2- Bond and reaction energies

3- Molecular energies and structures (thermochemical stability)

4- Vibrational frequencies (I.R and Raman spectra)

5- Electronic transitions (Uv. / Visible spectra)

6- Magnetic shielding effect (NMR spectra)

A prediction of these properties has many applications in energetic material research, including studies of synthesis pathways, reaction products and initiation mechanisms.

Heat of formation $\Delta H^{\circ}f$ (molecule): The heat of formation of the compound from its elements in their standard state is obtained when the energy is required to ionize the valence electrons of the atoms involved (calculated using semi – empirical parameters).

Binding energy ΔE_b (molecule): is the energy of the atoms separated by infinity minus the energy of the stable molecule at its equilibrium bond length(49).

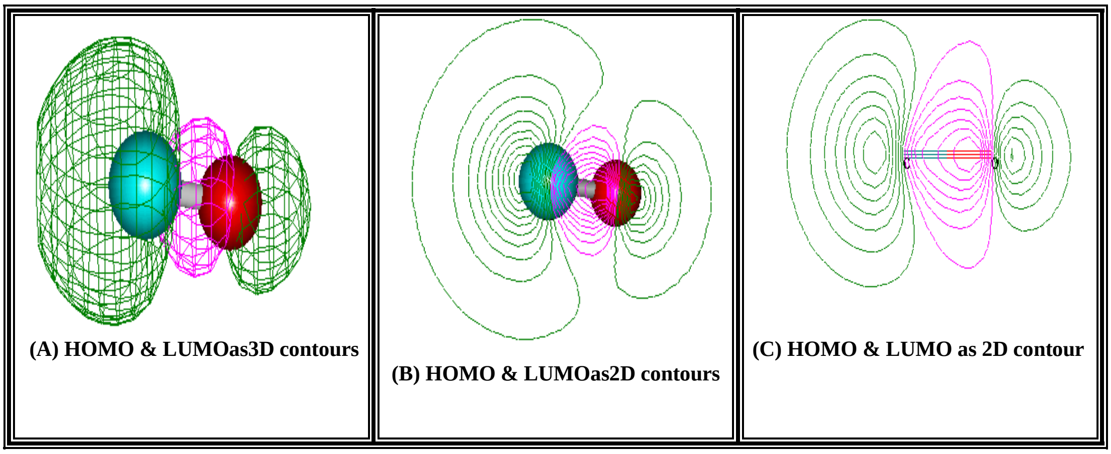
The elegant theory of (orbital symmetry) of Woodwark and Hoffmane(50). Enable; for the first time, the description of reactivity in trems of the size and detailed shapes of the molecular orbitals that comprise the valence manifold.

They have shown that how the inspection of the shape (symmetries) of only the highest – filled and lowest – empty molecular orbitals (HOMO and LUMO respectively) could often provide sufficient insight to determine whether or not two molecules would react.

Most applications(51) of qualitative molecular orbital theory have involved systems in which the valence orbital manifold is largely determined from symmetry considerations alone. Often, paralles in symmetries of key molecular orbitals suggest similarities in chemical reactivity.

Sometime the gross shape and location of the HOMO or LUMO, that is next to be occupied function, foreshadow a molecule's reactivity

Thus, the fact that the HOMO in carbon monoxide is a σ lone pair that protrudes mainly from carbon, and not from oxygen, implies that the molecule should be complex to electron deficient centers, for example, trasition as metals, shown in fig (1–14).



(A) HOMO & LUMOas3D contours

(B) HOMO & LUMOas2D contours

(C) HOMO & LUMO as 2D contour

Fig (1-14): Valence molecular orbital of CO

The noted polarizations of the corresponding CO π system, that is, the filled π orbital are directed mainly toward oxygen and the empty π* orbitals mainly toward carbon, easily of the coordinate linkage due to back bonding. It also serves to rationalize the observed decrease in CO stretching frequency with the increase in the coordinate bond strength; electrons are transferred into an orbital which is CO antibonding causing a weakening of the linkage.

1.11.3 Survey of Computational Chemistry Methods:-

All molecular modeling techniques can be classified under three major categories:-

(A) Ab initio Electronic structure Methods.

(B) Semi – Empirical Methods.

(C) Molecular Mechanics.

The general characteristics for each method are summarized in table (1-2).

Table (1-2): Synopsis of molecular modeling techniques.

Methods	Advantages	Disadvantages	Best for
Ab initio *Uses quantum physics *mathematically rigorous: no empirical parameters	*Useful for a broad range of systems *Does not depend on experimental data *Calculates transition states and excited states	*Computationally expensive	*Small systems (tens of atoms) *Electronic transition *Systems without experimental data *Systems requiring high accuracy
Semi – Empirical *Uses quantum physics *Uses experimental parameters *Uses extensive approximations	*Lees demanding computationally than ab initio methods *Calculates transition states and excited states	*Requires ab initio or experimental data for parameters *Less rigorous than ab initio methods	*Medium – sized systems (hundreds of atoms) *Electronic transitions
Molecular Mechanics *Uses classical physics *Relies on force field with embedded empirical parameters	*Computationally "cheap" fast and useful with limited computer resources *Can be used for large molecules like enzymes	*Does not calculate electronic properties * Requires ab initio or experimental data for parameters *Commercial software applicable to a limited range of molecules	*Large systems (thousands of atoms) *Systems or processes that do not involve bond breaking

(A) Ab Initio Electronic Structure Methods:-

Ab initio molecular orbital methods are the most accurate and have consistent predictions with high accuracy (± 20 KJ/mole) over a wide range of systems, because they provide the best mathematical approximation to the actual system.

The term ab initio implies that the computations are based on the laws of quantum mechanics, the masses and charges of electrons and the values of fundamental physical constants, such as the speed of light or planks constant and contain no approximations(52).

(B) Semi – Empirical Methods:-

The semi - empirical methods are used to compare the result to other studies. Semi - empirical methods increase the speed of computation by using approximations of ab initio techniques which have been fitted to experimental date. The size of many energetic molecules placed them beyond the scope of ab initio calculations, so preliminary theoretical studies were preformed using semi – empirical techniques(53). Semi - empirical methods have been calibrated to typical organic or biological systems and tend to be inaccurate for problems involving hydrogen bonding, chemical transitions or nitrated compounds (54).

(B.1) The Extended Hückel Method (EHM):-

Extended Hückal calculations neglect all electron – electron interactions, making them computationally fast but not very accurate. Extended Hückal models are good for chemical visualization and can be applied to (frontier orbital) treatments of chemical reactivity (55).

(B.2) Zerner's INDO Method (ZINDO/I and ZINDO/S):-

(ZINDO/I) method is the most suitable semi – empirical method for determining structures and energies of molecules with the first or second transition row metal(56).

(ZINDO/S) is parameterized to reporuce spectroscopic transitions, therefore it is not recommended for geometry optimization. Better results can be obtained by performing a single point calculation with ZINDO/S on optimized geometry (57).

(B.3) Parameterization Model, Version 3 (PM3):-

It is a recently developed semi – empirical method that may contain as yet undiscovered defects(58). The parameters for PM3 were derived by comparing a much larger number and wider variety of experimental versus computed molecular properties. PM3, which is primarily used for organic molecules, is also parameterized for many main groups and transition metal elements.

(C) Molecular Mechanics:-

Molecular Mechanics (MM) is often the only feasible means which to model very large and non – symmetric chemical systems such as proteins or polymers. Molecular mechanics (MM) is a purely empirical method that neglects explicit treatment of electrons, relying instead upon the laws of classical physics to predict the chemical properties of the system (59). The example of (MM) force field in commom use is **Assisted Model Builoting with Energy Refinement (AMBER):-**Primarily designed for the study of biomolecules such as proteins and nucleotides.

The aim of this work:

Dithiocarbamate derivative have been described as good chelating ligands, which have hard (N) besides soft (S) atoms. In the present work we synthesized new dithiocarbamate derivative from benzothiazole, in an attempt to introduce the dithiocarbamate moity in the structure of benzothiazole ring which is known to posses a pharmacologically important one, in a vast number of drug structures, and to investigate the coordination behavior of the new ligands toward some transition metal ions.

Potassium(benzothiazole-2-dithiocarbamato hydrizide) was to be prepared as new ligand, which was then to be treated with a number of ions such as: Mn(II), Co(II), Ni(II),Cu(II), Zn(II), Pd(II), Cd(II), Hg(II), Rh(III) and Cr(III),in order to prepare series of new complexes and to explore the ability of such derivatives to coordinate with the metal ions.

The prepared ligand and its metal complexes are to be isolated and characterized using the available conventional techniques, and by following different rules and as follows:

1. Isolating and studying the solid ligand and its metal complexes.
2. Studying theoretically in the gas phase by using semi – empirical method in order to:

- Show the most stable conformation through calculating the heat of formation and binding energy for all the probable geometries
- Find the most active sites of the Potassium(benzothiazole-2-dithiocarbamato hydrizide) by using the electrostatic potential calculations.
- Calculate the vibrational frequencies of the dithiocarbamate in order to compare the results with the experimental vibrational frequencies to make a certain assignment of the diagnostic bands.

3. Furthermore the new ligand and its complexes are to be tested for their antibacterial activities like (*staphylococcus aureus*) bacteria as a gram positive and (*Pseudomonas aeruginosa*) bacteria as a gram negative.

CHAPTER TWO

EXPERIMENTAL

2.1 Chemicals and Techniques:

2.1.1 Chemicals:

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

Table (2-1): Chemicals used in experimental part.

Compounds	Purity	Supplied from
Cadmium nitrate hexahydrate	98%	BDH
Chromium chloride hexahydrate	98%	Fluka
Cobalt chloride hexahydrate	99%	Fluka
Copper chloride dihydrate	99%	Fluka
Manganese acetate tetrahydrate	98%	BDH
Mercary chloride	99.5%	BRAND
Nickle nitrate hexahydrate	96%	BDH
Rhodium chloride hydrate	98%	BDH
Palladium chloride	60%	Ferak
Zinic chloride tetrahydrate	98%	BDH
Absolute ethanol	99%	Fluka
Acetone	99%	Fluka
diethelether	98%	BDH
Dimethyl sulphoxide	98%	BDH
Carbon disulfide	99%	Merck
Hydrazine hydrate	80%	Fluka
2-Mercaptobenzothiazole	98%	Fluka
Potassium hydroxide	85%	BDH
Hydrochloric acid	37%	BDH

2.1.2 Techniques :-

A- Fourier Transform Infrared Spectrophotometer (FT-IR)

The infrared spectra were recorded on a shimadzu 8400, single beam path laser. Thin film was performed by Central Organization of Standardization and Quality Control in the rang (400-4000) and a Shimadzu 8000 Fourier Transform Infrared Spectrophotometar (FT – IR) in the rang (200-4000) cm^{-1} samples used were in the form as CsI disc.

B- Electronic Absorption spectra

The electronic spectra of the complex were obtained using : (Shimadzu UV-Vis 160A) ultra violet spectrophotometer in ***(Al-Nahrain University)*** using the quartz cell in the range (1100-200)nm.

C- Magnatic Susceptibility Measurment

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

D-Melting Point Instrument

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

E- Metal Analysis

The metal content of the complexes was measured using atomic absorption technique of PERKIN-ELMER 5000 atomic absorption spectrophotometer for the determination of metal ion.

F- Conductivity Measurments

The conductivity measurments were obtained using Corning Conductivity Meter 220. Al-Nahrain University.

2.2 Methods of Preparation

2.2.1 Preparation of Ligands

A- Preparation of 2-hydrazino benzothiazole [1]

2-mercaptobenzothiazole (0.1mol,16.7gm) was refluxed for (6 hours) with hydrazine hydrate (75%, 0.1 mole) in presence of absolute ethanol.

The solution was filtered and recrystalization from ethanol, and the physical properties can be shown in table(3-1).

B-Preparation of Potassium (Benzothiozole-2-dithiocarbamato hydrazide)

To (0.1mol,16.5gm) of the above solution in ethanol an excess of carbon disufide in the present of KOH in ethanolic solution was added and the mixture was refluxed for an hour.

The excess of solvent and carbon disulfide was then distilled off, the resulting solid recrystallized from acetone(60), and the physical properties can be shown in table (3-1).

2.2.2Preparation of the complexes

1) Chromium (Ш) complex:

(0.01mol, 2.65g) of chromium salt dissolved in (2 ml) ethanol was added to (0.03mol, 8.37g) of the ligand dissolved in (10 ml) ethanol. The mixture was heated with stirring for 15 min. The resulting precipitate was filtered and washed with water then dried under vacuum. The prepared complex was soluble in DMSO, and the physical properties as shown in table (3-1).

2) Manganese (II) complex:

(0.01mol, 2.45g) of $Mn(CH_3COO)_2.4H_2O$ dissolved in (2 ml) ethanol was added to (0.02mol, 5.58g) of the ligand dissolved in (10 ml) ethanol The mixture was heated with stirring for 15 min.

The resulting precipitate was filtered and washed with water then dried under vacuum. The prepared complex was soluble in DMSO, and the physical properties as shown in table (3-1).

3) Rhodium (Ш) complex:

(0.01mol, 2.26g) of Rhodium salt dissolved in (2 ml) ethanol was added to (0.02mol, 5.58g) of the ligand dissolved in (10 ml) ethanol. The mixture was heated with stirring for 15 min. The resulting precipitate was filtered and washed with water then dried under vacuum. The prepared complex was soluble in DMSO, and the physical properties as shown in table(3-1).

4) Cobalt (II) complex:

(0.01mol, 1.65g) of $CoCl_2.2H_2O$ dissolved in (2 ml) ethanol was added to (0.01mol, 2.79g) of the ligand dissolved in (10 ml) ethanol. The mixture was heated with stirring for 15 min. The resulting precipitate was filtered and washed with water then dried under vacuum. The prepared complex was soluble in DMSO, and the physical properties as shown in table(3-1).

5) Nickel (П) complex:

(0.01mol, 2.91g) of Nickel salt dissolved in (2 ml) ethanol was added to (0.02mol, 5.58g) of the ligand dissolved in (10 ml) ethanol. The mixture was heated with stirring for 15 min. The resulting precipitate was filtered and washed with water then dried under vacuum. The prepared complex was soluble in DMSO, and the physical properties as shown in table(3-1).

6) Palladium (II) complex:

a- Preparation of Dichloro bis(benzonitrile) palladium (II) $PdCl_2(PhCN)_2$:

(0.4g) of palladium chloride was dissolved in (15 ml) of benzonitrile, the mixture was heated with continuous stirring on water bath until a large amount of $PdCl_2$ was dissolved. The product was filtered to remove the unreacted palladium chloride and the filtrate transferred to (100ml) of petroleum ether (60-80°C), the yellow precipitate was separated and dried under vacuum (61).

b- Palladium (II) complex:

(0.01mol, 3.84g) of Pd complex dissolved in (2 ml) ethanol was added to (0.01mol, 2.79g) of the ligand dissolved in (10 ml) ethanol. The mixture was heated with stirring for 15 min. The resulting precipitate was filtered and washed with water then dried under vacuum. The prepared complex was soluble in DMSO, and the physical properties as shown in table(3-1).

7) Copper (II) complex:

(0.01mol, 1.34g) of $CuCl_2$ dissolved in (2 ml) ethanol was added to (0.02mol, 5.58g) of the ligand dissolved in (10 ml) ethanol. The mixture was heated with stirring for 15 min. The resulting precipitate was filtered and washed with water then dried under vacuum. The prepared complex was soluble in DMSO, and the physical properties as shown in table(3-1).

8) Zinc (II) complex:

(0.01mol, 2.07g) of zinc salt dissolved in (2 ml) ethanol was added to (0.02mol,5.58g) of the ligand dissolved in (10 ml) ethanol. The mixture was heated with stirring for 15 min. The resulting precipitate was filtered and washed with water then dried under vacuum. The prepared complex was soluble in DMSO, and the physical properties as shown in table(3-1).

9) Cadmium (П) complex:

(0.01mol, 3.44g) of cadmium salt dissolved in (2 ml) ethanol was added to (0.01mol, 2.79g) of the ligand dissolved in (10 ml) ethanol. The mixture was heated with stirring for 15 min.

The resulting precipitate was filtered and washed with water then dried under vacuum. The prepared complex was soluble in DMSO, and the physical properties as shown in table (3-1).

10) Mercury (П) complex:

(0.01mol, 2.71g) of Mercury salt dissolved in (2 ml) ethanol was added to (0.02mol,2.79g) of the ligand dissolved in (10 ml) ethanol. The mixture was heated with stirring for 15 min. The resulting precipitate was filtered and washed with water then dried under vacuum. The prepared complex was soluble in DMSO, and the physical properties as shown in table(3-1).

2.3 Programs Used in Theoretical Calculation:-

2.3.1 Hyperchem 6:-

It is a sophisticated molecular modeler, editor and powerful computational package, that is known for its quality, flexibility and ease of use, uniting 3D visualization and animation with quantum chemical calculations, mechanic and dynamic.

Hyperchem can plot orbital ware functions resulting from semi empirical quantum mechanical calculation, as well as the electrostatic potential, the total charge density or the total spin density can also be determined during a semi – empirical calculation. This information is useful in determining reactivity and correlating calculation results with experimental data.

2.3.2 Types of Calculation:-

1. Single point calculation that determines the molecular energy and properties for a given fixed geometry.
2. Geometry optimization calculations employ energy minimization algorithms to locate stable structures.
3. Vibrational frequency calculations to find the normal vibrational modes of an optimized structure. The Vibrational spectrum can be displayed and the vibrational motions associated with specific transitions can be animated.

2.3.3 Computational Methods:-

Semi – empirical quantum mechanics:-

Hyperchem offers ten Semi – empirical molecular orbital methods, with options for organic and main group compounds, for transition metal complexes and spectral simulation.

Choose from Zerner's, INDO method (ZINDO/I) and parameterization model, version 3(PM3), [including transition metals]. PM3 were used for the calculation of heat of formation and binding energy for all metal complexes except Zn(II), Cr(III), Pd(II) and Rh(III) which (ZINDO/1) method was used for the calculation of the heat of formation and binding energy for them.

2.4 Biological activity:-

The biological activity of the prepared ligand and its respective complexes were studied against selected types of bacteria which included (*Staphylococcus aureus*) as Gram positive and (*Pseudomonas aeruginosa*) as a Gram negative to be cultivated in nutrient agar media, as shown in chapter four.

CHAPTER THREE

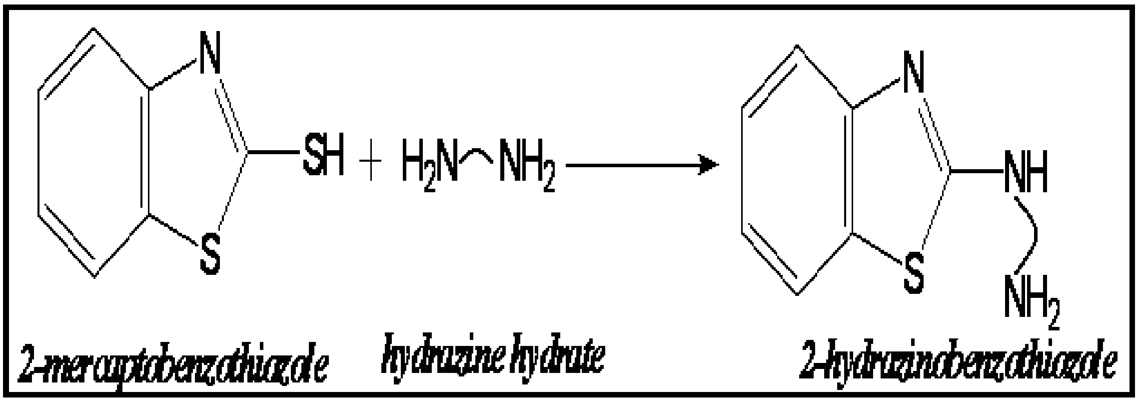
RESULTS AND DISCUSSION

Thiazole derivatives have been described as good chelating ligands, which have contained thioamide group. The present work describes the preparation of new thiocarbamato derivatives, in an attempt to introduce the dithiol hydrizde moiety in the structure of dithiocarbamate compound which is known to possess a theraptical and biological activity in addition to investigate the coordination behavior of the new ligand toward some transition metal ions and compare the biological activity of the ligand and its complexes.

3.1 Synthesis and Characterization of the ligand

1- Preparation and Characterization of 2-hydrazinobenzothiazole

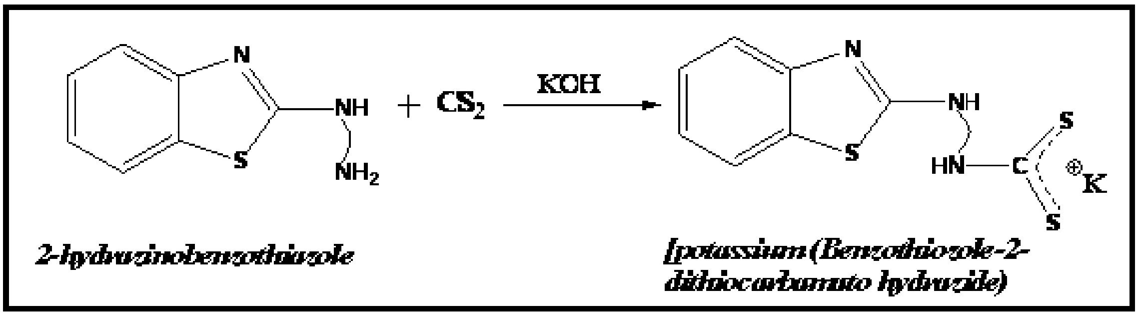
The Ligand (A) was prepared from starting material (2-mercaptobenzothiozole), as shown in the following scheme (3-1)



Scheme (3-1): ***Steps of 2-hydrazinobenzothiole formed***

2- Synthesis and Characterization of *[potassium (Benzothiozole-2-dithiocarbamato hydrazide)]:*

Ligand L was prepared from the reaction of A with CS_2 in the present of KOH in ethanolic solution. The following scheme(3-2) illustrates the structure of L:



Scheme (3-2): The preparation of Potassium (Benzothiozole-2-dithiocarbamato hydrazide)

The prepared dithiocarbamate derivative was characterized by their FT-IR and UV spectroscopic. The yellow crystalline product was formed to be highly soluble in DMF and DMSO, and they were to be stable towards air and moisture.

3.2 Reaction of ligand with some transition metal ions:

The interaction of dithiocarbamate derivative with the appropriate metal salt under study in ethanol. Crystalline products with different colors depending on metal ions. The physical and analytical data of all these complexes are given in table (3-1). The results obtained from metal analysis are in a satisfactory agreement with the calculated. The suggested molecular formula was also supported by spectra (FT-IR and uv-vis spectrophotometer) as well as magnetic susceptibility and conductivity measurements are described in the table (3-1).

Table (3-1): Physical properties of ligand and its metal complexes.

Symbol	Color	M.P.ºC	Yield%	Metal analysis found(calc.)	***Molecular formula***
A	yellow	210	75%	—	$C_7H_5NS_2$
L	Yellow	134 dec.	78%	—	$C_8H_6N_3S_3K$
CrL	Olive green	164 dec.	80%	4.6(5.71)	$[CrL_3]$. 3EtOH
MnL	Green	187 dec.	81%	9.20 (9.10)	$[MnL_2]$. 1.5EtOH
RhL	Brown	>300	80%	15.99(16.67)	$[RhL_2]Cl$
CoL	Dark green	>300	85%	11.72(12.04)	$[CoLCl(H_2O)]$.3EtOH
NiL	Light green	>300	77%	7.32 (7.62)	$[NiL_2(H_2O)_2]$.4EtOH
PdL	Red	177 dec.	81%	18.31(19.13)	[PdL(NCph)Cl].1.5EtOH
CuL	Brown	191	83%	11.72 (10.70)	$[CuL_2(H_2O)_2].H_2O$
ZnL	Light yellow	152	87%	6 86 (7.57)	$[ZnL_2]$.6EtOH
CdL	Light pink	170	79%	18.80(18.79)	$[CdLNO_3]$.4EtOH
HgL	Light yellow	181 dec.	89%	—	$[HgL_2]$. XH_2O

dec. = decomposion

Table (3-2): Molecular formula and names of the prepared ligand and its complexes.

symbol	*Molecular formula*	*Namenuclatures*
L	$C_8H_6N_3S_3K$	Potassium(Benzothiozole-2-dithiocarbamato hydrazide)
CrL	$[CrL_3]$. 3EtOH	Tris (Benzothiozole-2-dithiocarbamato hydrazide) Chromium(III). 3EtOH
MnL	$[MnL_2]$. 1.5EtOH	Bis (Benzothiozole-2-dithiocarbamato hydrazide) Magnesium (II).1.5EtOH
RhL	$[RhL_2]Cl$	bis (Benzothiozole-2-dithiocarbamato hydrazide) Rhodium(III). Chloride
CoL	$[CoLCl(H_2O)]$.3EtOH	[chloro-(Benzothiozole-2-dithiocarbamato hydrazide) aqua cobalt(II). 3EtOH
NiL	$[NiL_2(H_2O)_2]$.4EtOH	Bis (Benzothiozole-2-dithiocarbamato hydrazide) diaqua nickel(II).4EtOH
PdL	[PdL(NCph)Cl].1.5EtOH	Chloro-(Benzothiozole-2-dithiocarbamato hydrazide) benzonitrile palladium(II). 1.5EtOH
CuL	$[CuL_2(H_2O)_2].H_2O$	Bis[(Benzothiozole-2-dithiocarbamato hydrazide) diaqua copper(II)].hydrate
ZnL	$[ZnL_2]$.6EtOH	bis (Benzothiozole-2-dithiocarbamato hydrazide) zinc(II).6EtOH
CdL	$[CdLNO_3]$.4EtOH	Nitreto- (Benzothiozole-2-dithiocarbamato hydrazide) Cadmium (II).4EtOH
HgL	$[HgL_2]. XH_2O$	bis (Benzothiozole-2-dithiocarbamato hydrazide) Mercury (II).XH_2O

3.3 Spectroscopic studies

3.3-1 Infrared spectra

All the recorded spectra were in the solid state using CsI in the range200-4000 cm^{-1}.

Dithiocarbamate derivative is potential ligand, which may act a bidentate or tridentate chelating ligand as illustrated by their structures.

As expected FTIR gave good information about the complex behavior of the ligand with various metal ions. The characteristic frequencies of free ligand and its metal complexes were readily assigned in compassion with the literature values. (62)

The FT_IR spectrum of Potassium (Benzothiozole-2-dithiocarbamato hydrazide), table (3-3) shows, the main position and the most important vibration modes of the bands which can be presented by (νNH,, δNH, νN-N, νC-S and νC=s). The comparison of the spectrum for the free ligand with the prepared complexes, showed that their is two different coordination modes of the ligand i.e. one the ligand coordinate through (N,N,S) atoms. This main that the ligand behavior as a tridentate chelating, this type was confirmed by the ν(N-H), (δN-H), (N-N) and ν(C-S). which show splitting the peaks with shift in their values, this case Cd complex only. Others coordinate behavior took place as a bidentate chelating manner through (N,S) atoms only for the Co, Cu, Ni, Mn, Zn, Cr, Hg, Pd and Rh complexes. This coordination was conformed by the ν(N-H), (δN-H), (N-N) and ν(C-S).which show splitting in peaks with shift in their values. New bands appeared which supported by the appearance frequencies of ν(M-N), ν(M-S) and ν(M-O) respectively(1,63,64,65).

Table(3-3): The most diagnostic FT-IR bands of the ligand and its complexes

Symb	*νNH*	*δNH*	*νN-N*	*νC=S*	*νC-S*	*νM-N*	*νM-S*	*νM-O*	*other*
L	3382 3375	1650	995	1209	1072	-	-	-	-
CrL	2904 3053.11	1625 1699	925	1213	1054	480	450	-	-
MnL	3085.89 2997.42	1704	943	1205	1051	488	459	-	-
RhL	3011 3575	1620 1675	945	1211	1018	478	439	-	3485 νH_2O
CoL	3225 3201	1595 1620	925	1211	1018	486	420	516	3417 νH_2O 300.87 ν M-Cl
NiL	3341.23 3326.73	1616 1580	925	1218	1018	498	420	520	3485 νH_2O
PdL	3083.96 3029.96	1614	945	1215	1018	490	459	520	-
CuL	3379 3365	1622 1730	919	1215	1066	487	459	516	-
ZnL	3168.83 3119.87	1574 1618	942	1209	1051	486	424	-	3577 νEtOH 1332 νNO_3
CdL	3093.61 3073.25	1579 1622	945	1213	1049	498	472	-	-
HgL	3198 3090	1558 1610	933	1218	1018	498	424	-	3580 νH_2O

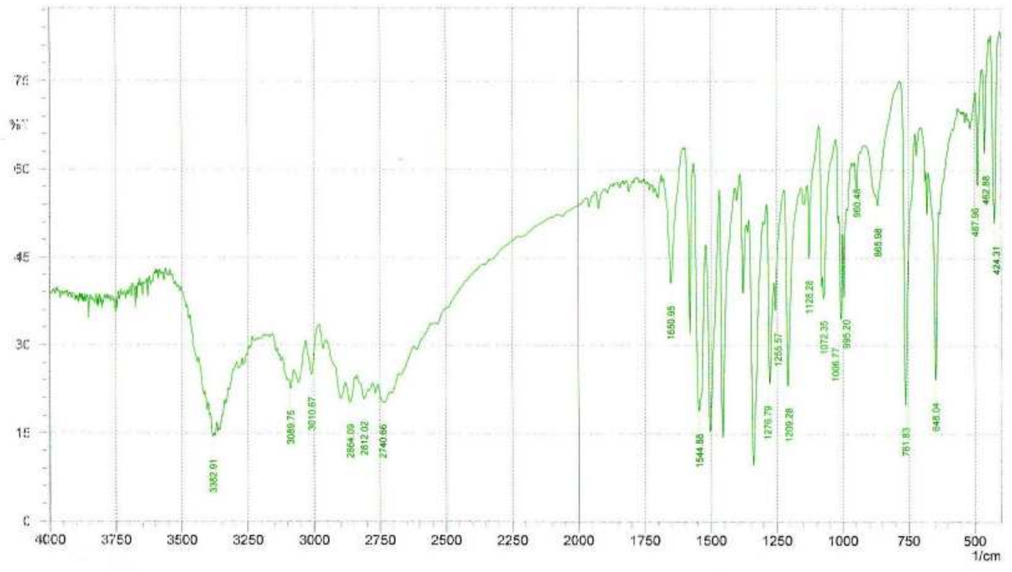


Figure (3-1): FTIR spectrum of L

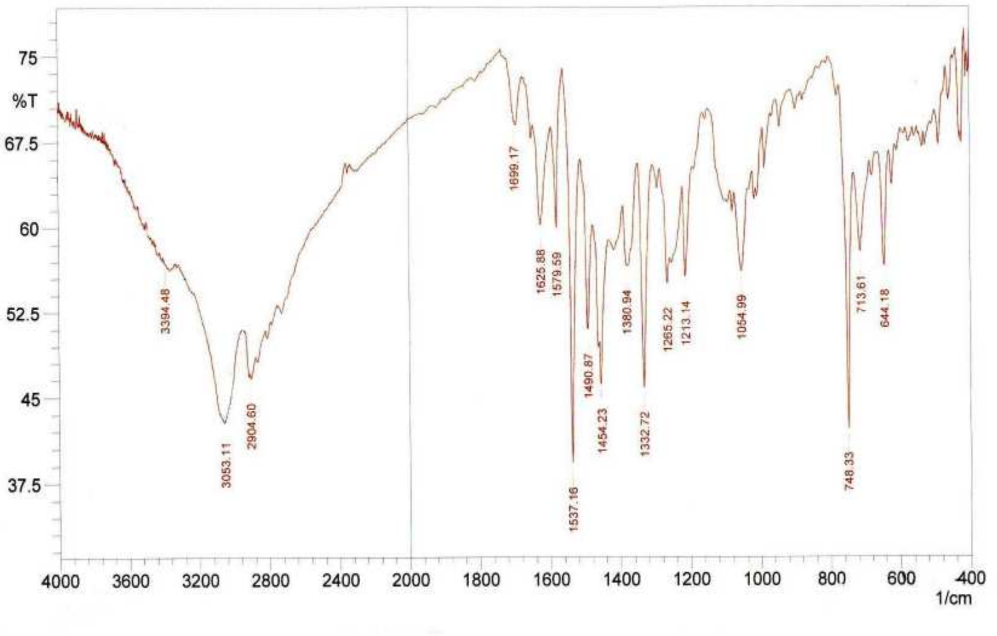


Figure (3-2): FTIR spectrum of [Cr(II)L]

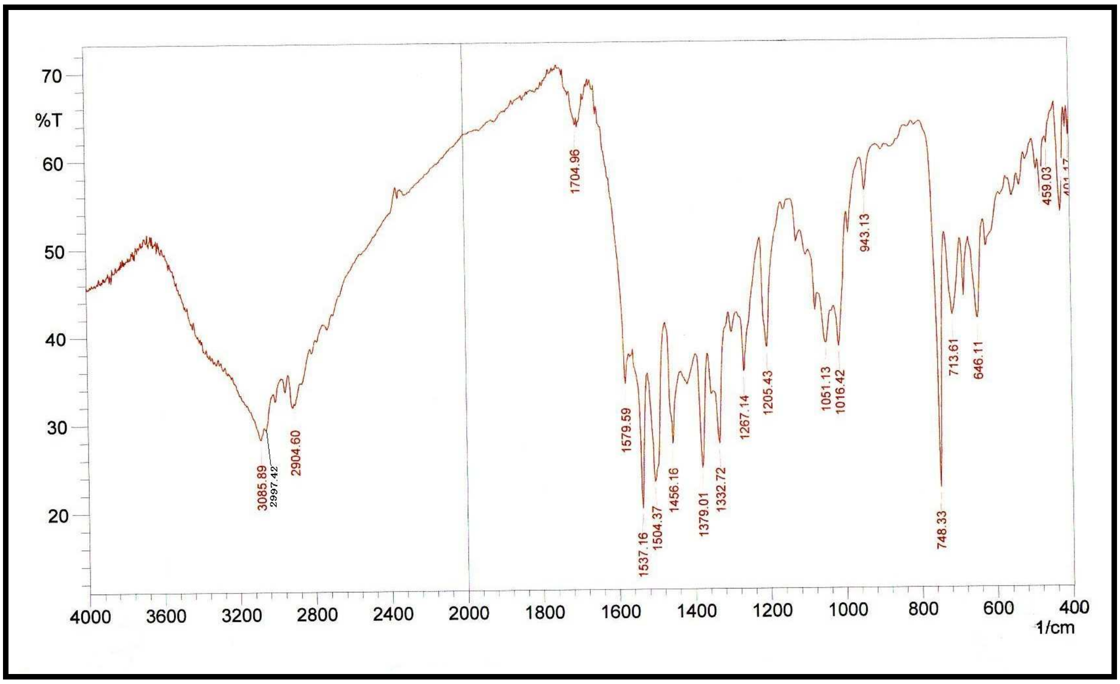


Figure (3-3): FTIR spectrum of [Mn(II)L]

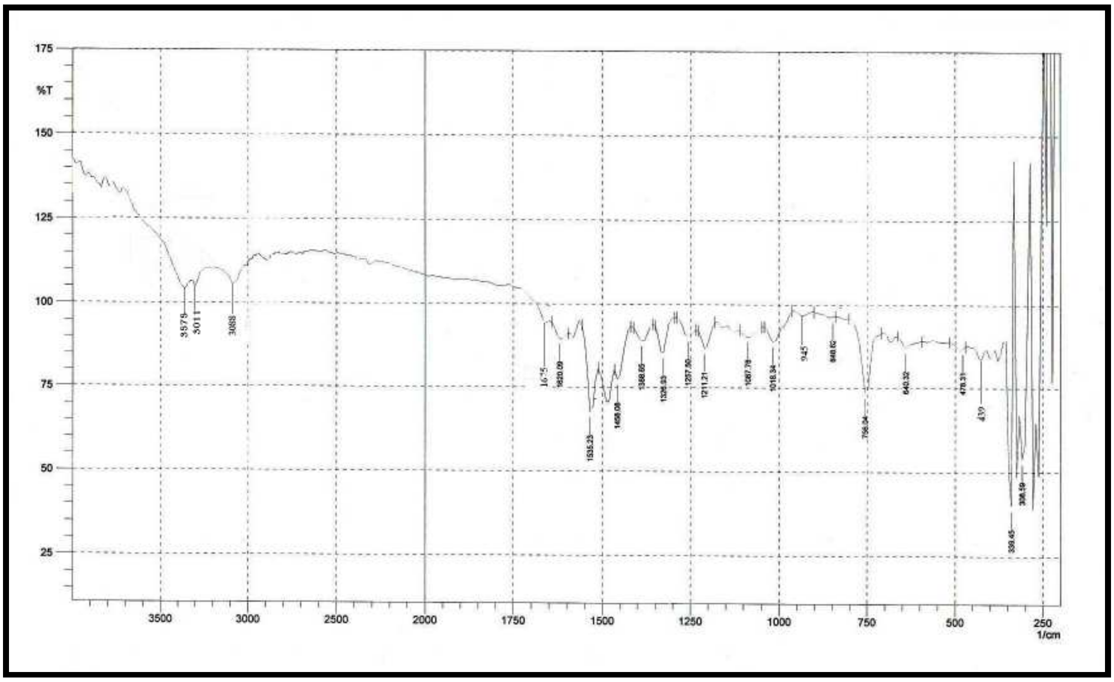


Figure (3-4): FTIR spectrum of [Rh(III)L]

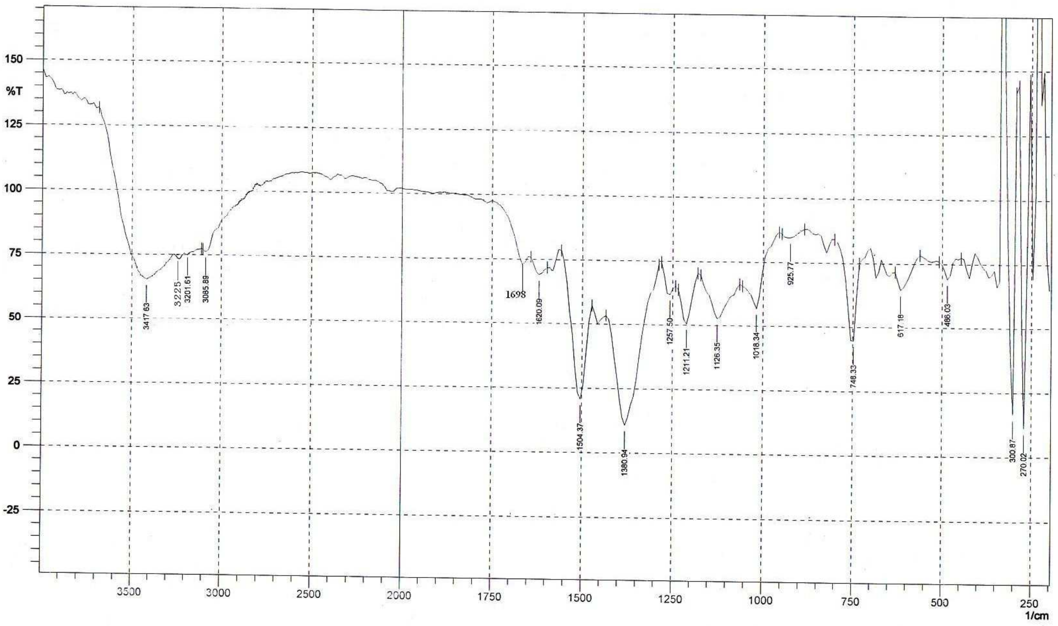


Figure (3-5): FTIR spectrum of [Co(III)L]

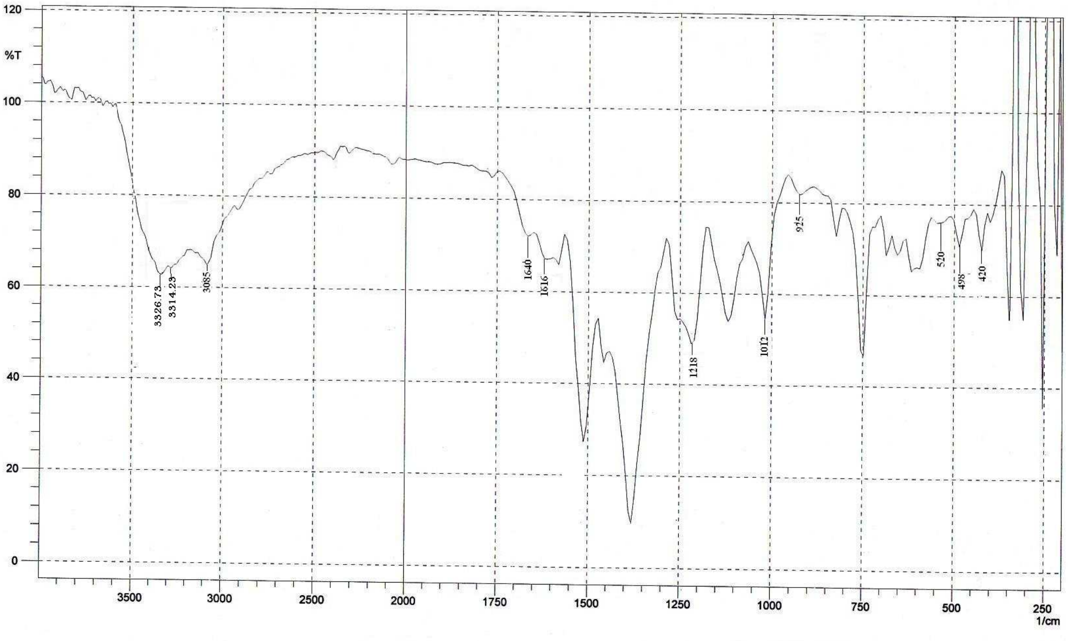


Figure (3-6): FTIR spectrum of [Ni(II)L]

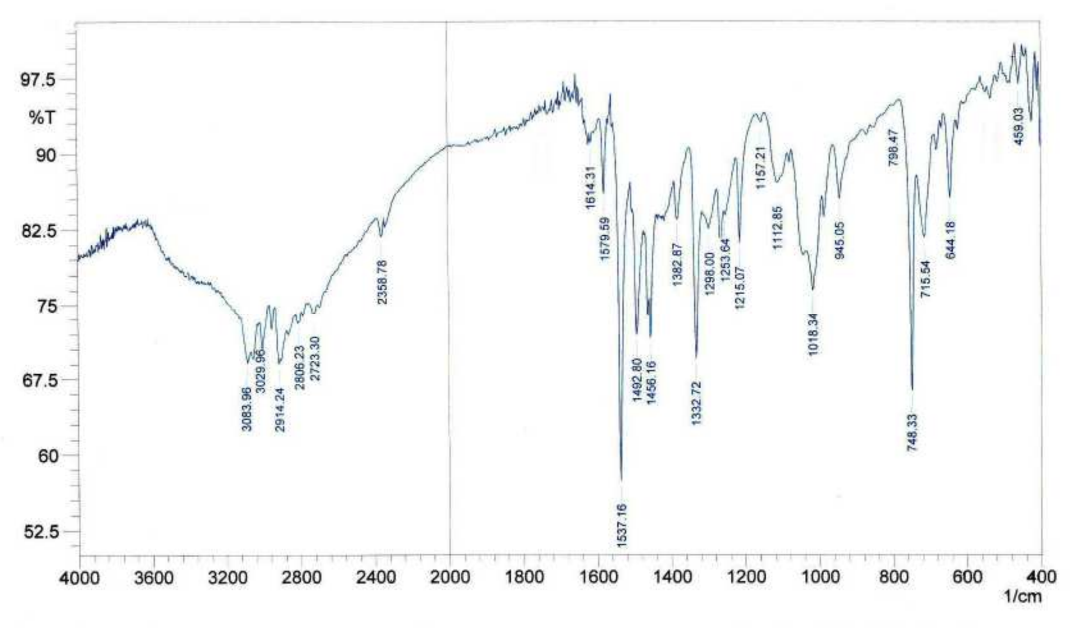


Figure (3-7): FTIR spectrum of [Pd(II)L]

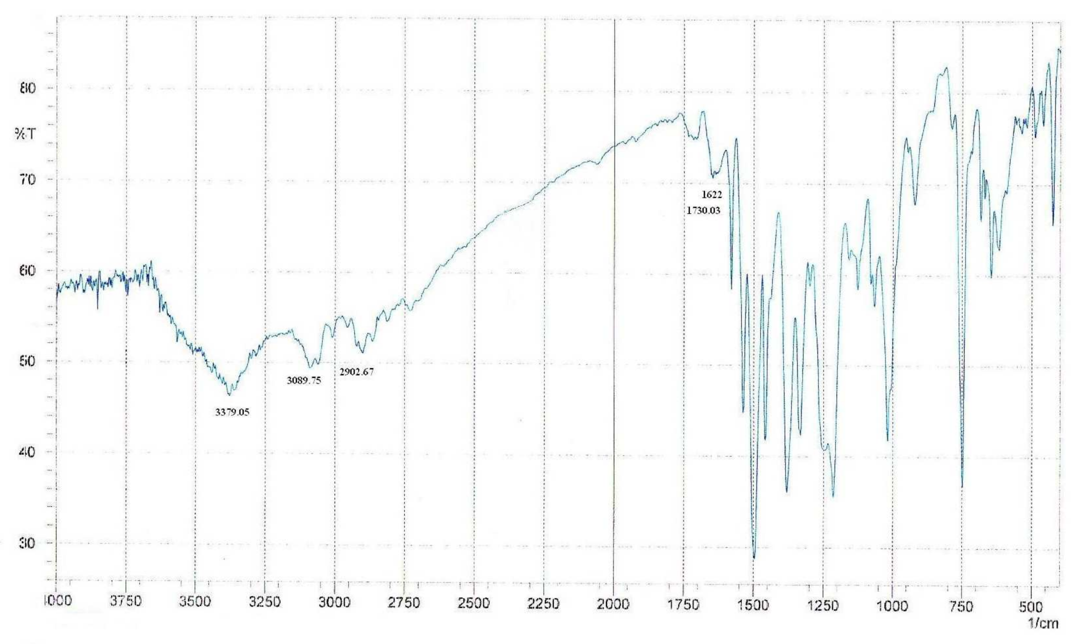


Figure (3-8): FTIR spectrum of [Cu(II)L]

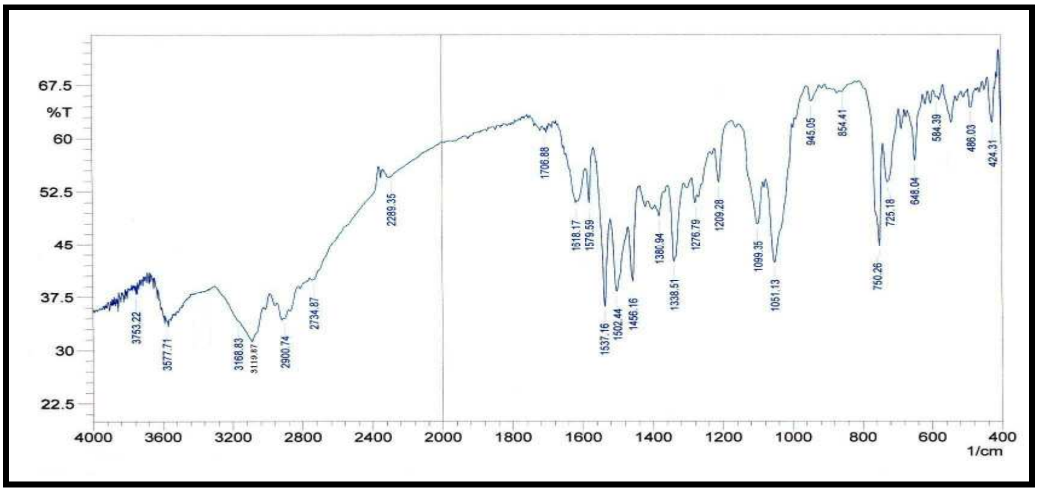


Figure (3-9): FTIR spectrum of [Zn(II)L]

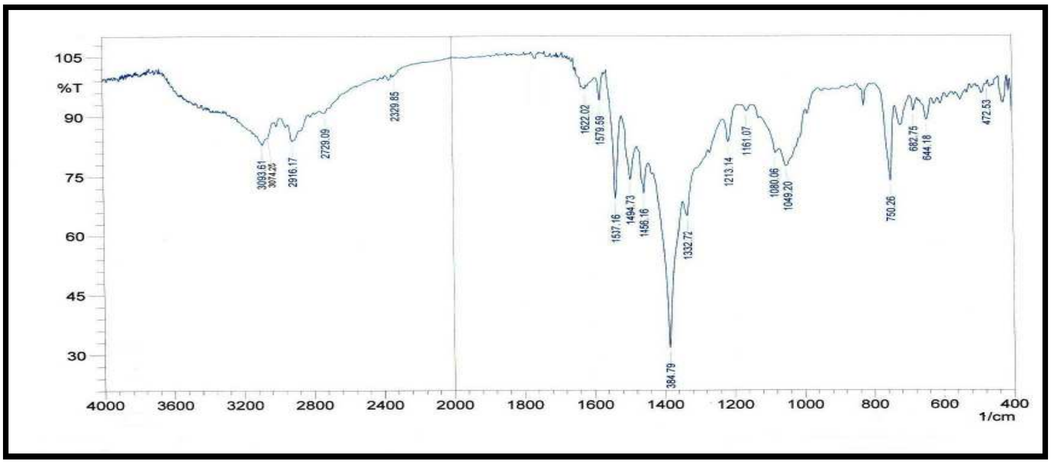


Figure (3-10): FTIR spectrum of [Cd(II)L]

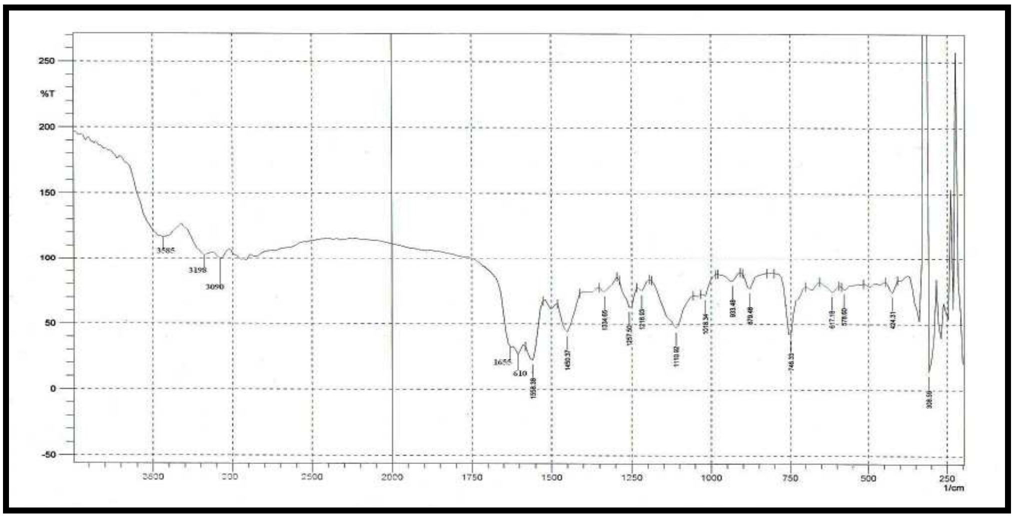


Figure (3-11): FTIR spectrum of [Hg(II)L]

3.3.2 Electronic spectra, magnetic properties and molar conductivity:

The Uv-Vis absorption spectra of the newly prepared complexes are of crucial importance besides the magnetic and conductivity measurements for the structural diagnosis in addition to the elucidation of the type and degree of bonding between the central metal and the ligands coordinated with it, taking in account the electronic within d-orbitals of the transition metal and the molecular orbitals formed between the metal and the ligands. There are four types of electronic spectra (66,67).

- ***a-*** ***Ligand spectra*:** This type of spectra is associated principally with the ligand only.
- ***b-*** ***Charge transfer spectra:*** This type involves electronic transitions between the metal and the ligand.
- ***c-*** ***d-d and f-f spectra:*** This type of spectra is associated principally with the metal due to the effects of the ligand.
- ***d-*** ***Counter-ion spectra:*** This type of spectra involves the spectra of ion and it’s associated with the complex.

In our work, the spectra were recorded in the range (200-1100) nm using dimethyl sulfoxide as a selected solvent.

Measuring magnetic susceptibility contributes to the determination of structure of the complexes. In addition, these measurements provide information about the type of bonding and strength of ligand field of complexes by giving the information about the number of unpaired electrons.

The effective magnetic spin of the complexes was measured using only a spin magnetic moment according to the following equation (68).

$$\mu_{S.O} = 2\sqrt{S(S+1)}$$

Where S = n / 2 (n=no. of unpaired electrons), the results obtained from this equation were compared to the actual values obtained through the magnetic measurements. Table (3-4).

These values were corrected for diamagnetic effects using the following relationship $^{(68,69)}$.

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

$X_A = X_M - D$

$X_M = X_g * M.Wt$

Where

T = Absolute temperature (298K)

X_A = Atomic susceptibility

X_M = Molar susceptibility

X_g = gram susceptibility

D = correction factor

The molar conductance values of all the complexes have been measured in DMSO as a solvent at concentration of 10^{-3}M at room temperature, for the determination of electrolytic or non-electrolytic nature of the complexes $^{(70,71)}$.

According to the results obtained from the electronic spectra, magnetic moment, conductivity measurement, in addition to the theoretical treatment, the stereochemistry around the metal ion were been suggested.

3.3.2.1 Electronic spectra of the complexes:

1- Chromium (III) complexes:

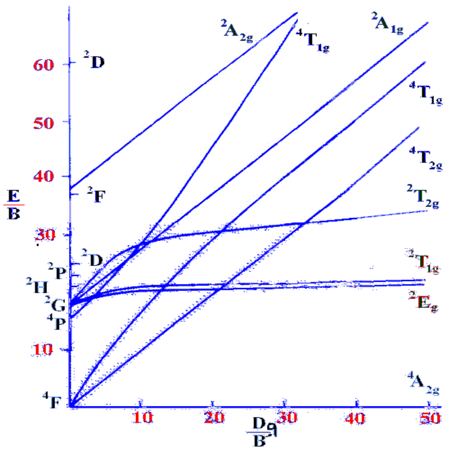
The electronic spectrum of octahedral Cr (III) consists of three bands reference to an Orgal diagram in d^3 system (7,72,73) and they can be assigned as:

$$v_1 = {}^4A_2g_{(F)} \longrightarrow {}^4T_2g_{(F)}$$

$$v_2 = {}^4A_2g_{(F)} \longrightarrow {}^4T_1g_{(F)}$$

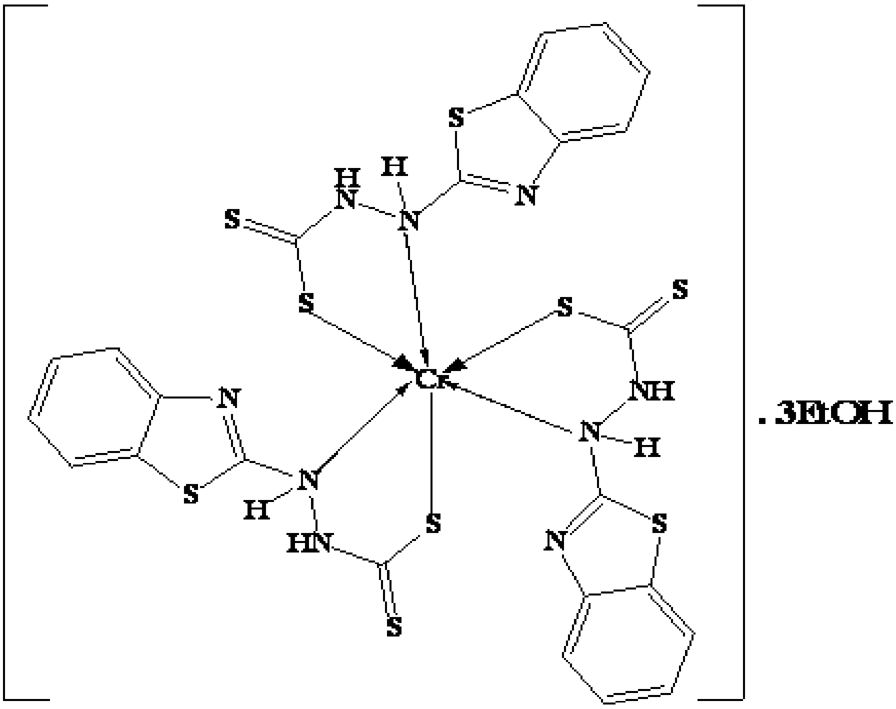
$$v_3 = {}^4A_2g_{(F)} \longrightarrow {}^4T_1g_{(P)}$$

Two bands are observed within the range of measurement. They have maxima at about 16.393 and 26.953 cm^{-1}. These are spin-allowed and laborite-forbidden d-d transition fig(3-13) ,table(3-4). The ligand field, v_3, nephelauxetic factor β and racha parameter B′ was calculated, reference to Tanaba-Sugano diagram for d^3 configuration.



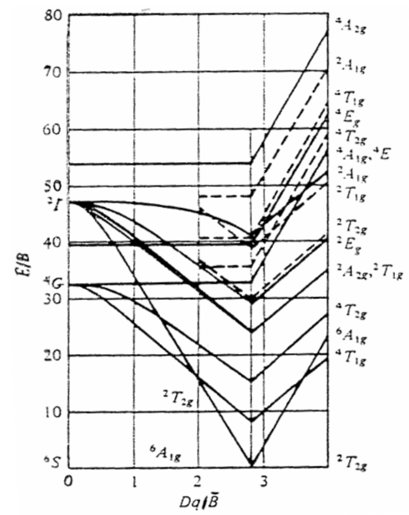
Tanabe-Sugano diagram for d^3 ion

The magnetic value (3.4) B.M., of chromium (III) observed, this agreement with octahedral geometry around Cr (III) ion(7, 74 , 75). The conductance measurements indicate the non-ionic behavior of this complex. According to these information and pervious analysis, the geometry of this complex can be suggested as illustrated below:



2- Mn (II) complexes:

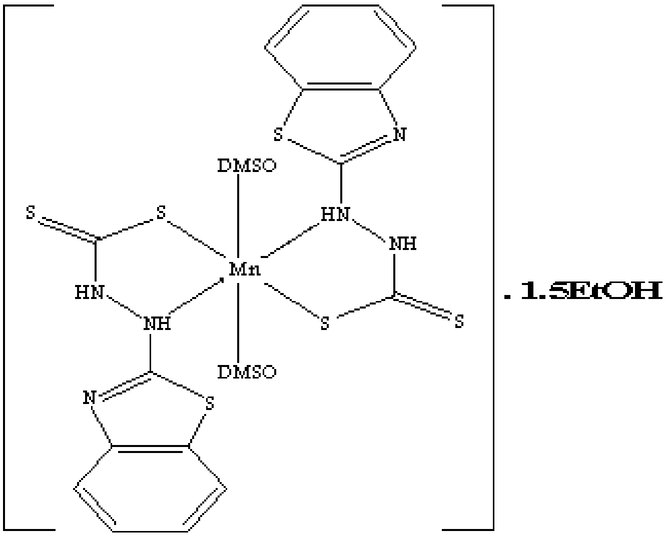
Tetrahedral Manganese (II) complexes are green or yellowish green (67,76). The color of the present work Mn(II) was green in the solid state, but color of the solution of this complex in DMSO was noticed to change from light green to Marconi during dissolution of solid compound, therefore it was postulated that two DMSO molecules coordinates with the compound to give distorted octahedral structure. The electronic spectra of our prepared complex was recorded and assignments were obtain by fitting the observed spectra to Tanaba-Sugano diagram for d^5



Tanabe-Sugano diagram for d^5 ion configuration

configuration, values of β, and 10Dq computed therefore(76), as shown in table (3-4), Fig(3-14).

Two observations to be pointed out: ***(1)*** a series of weak (some were narrow) bands have been observed in manganese spectra, this only expected because the only sextet term of the d^5 configuration in octahedral stereochemistry is the ^6A_1g, consequently, there can be no spin-allowed transition(76,77). Furthermore the energies of the $^4Eg_{(G)}$ and $^4A_1g_{(G)}$ terms do not change much relative to the ^6A_1g ground term as 10Dq change, as shown in Tanaba-Sugano diagram. Therefore the bands corresponding to transitions between ground term and these two terms are not appreciably broadened by vibronic coupling(76,77). ***(2)*** The value of the nephelauxetic ratio β, evaluated as the ratio of the term separation in the complex, B`, to that in the free ion , are high , as shown in table(3-4) this is in keeping with general opinion that manganese(II) complex was highly ionic(78). The electronic spectra coupled with magnetic (6.12 B.M.) showed a higher contribution and conductivity measurement showed that the complex was non-ionic consequently the octahedral geometric around Mn (II) ion can be suggested as illustrated below:



3- Rh(III) complex:

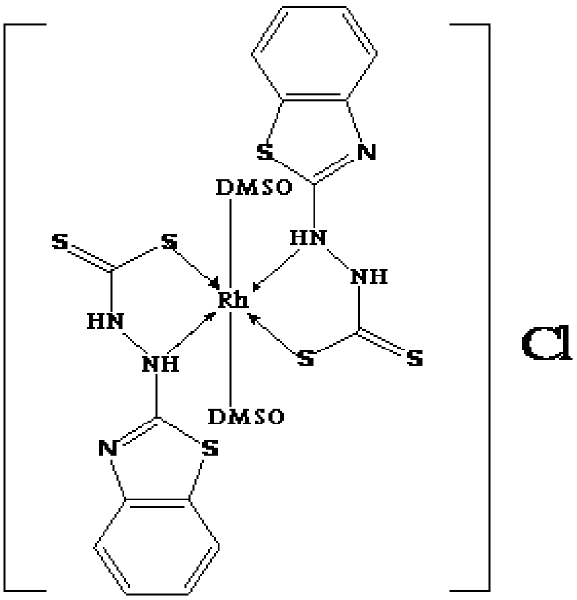
Square planer Rhodium (III) complex was commonly orange(66,67,79,80). The dark orange color of the present Rh (III) chelate was therefore not inconsistent of square planer structure. Furthermore, the color in DMSO solution of the complex was noticed to change from dark orange to brown during dissolution of the solid compound, therefore, it was postulated that two DMSO molecules coordinates through the axial positions of the square planer change it to distort octahedral. The electronic spectra data of this solution, table (3-4), provide further evidence in favor of distorted octahedral structure.

It is possible to observed spin-allowed *d-d* bands in the visible region of the spectra of low-spin Rh (III) complex. This means that the low-spin configuration occurs in complex with ligands, which do not cause the low energy (charge transfer) C.T. bands, which so often dominate the spectra of low-spin complex(8,35).

The electronic spectral bands of the prepared complex in the present work are presented in table (3-4) along with their assigned transitions, low-spin Rhodium (III) has the electronic configuration d^6, the ground term for which in octahedral stereochemistry is ^1A_1g, two bands are expected to appear in visible region due to the transition to the ^1T_1g and ^1T_2g states.

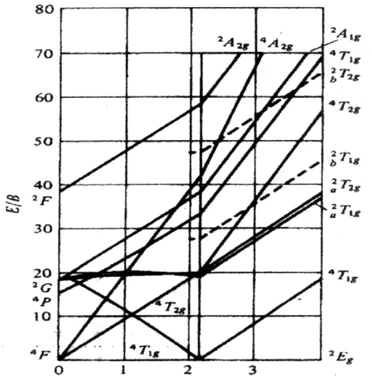
These transitions correspond to the electronic promotion $t_2g^6 \rightarrow t_2g^5eg^1$ with promoted electron maintaining its spin unaltered. The orbital multiplicity of $t_2g^5eg^1$ is 6 and so corresponds to two orbital triplet terms ^1T_1g and ^1T_2g(8,80,81). in the spectrum of our complex fig(3-15), a weak band was observed at 11.313 cm^{-1}, this weak band was attributed to the spin-forbidden $^1A_1g \rightarrow ^3T_1g$ transition which may occur when the promoted electron changes its spin and the two T terms be ^3T_1g and ^3T_2g.

The magnetic susceptibly and molar conductivity measurements indicated that the complex to be diamagnetic (0.6 B.M.), which is well with the range for square planer complexes$^{(76,81)}$ and conducting according to these finding results, the following structure for Rh (III) complex may be suggested.



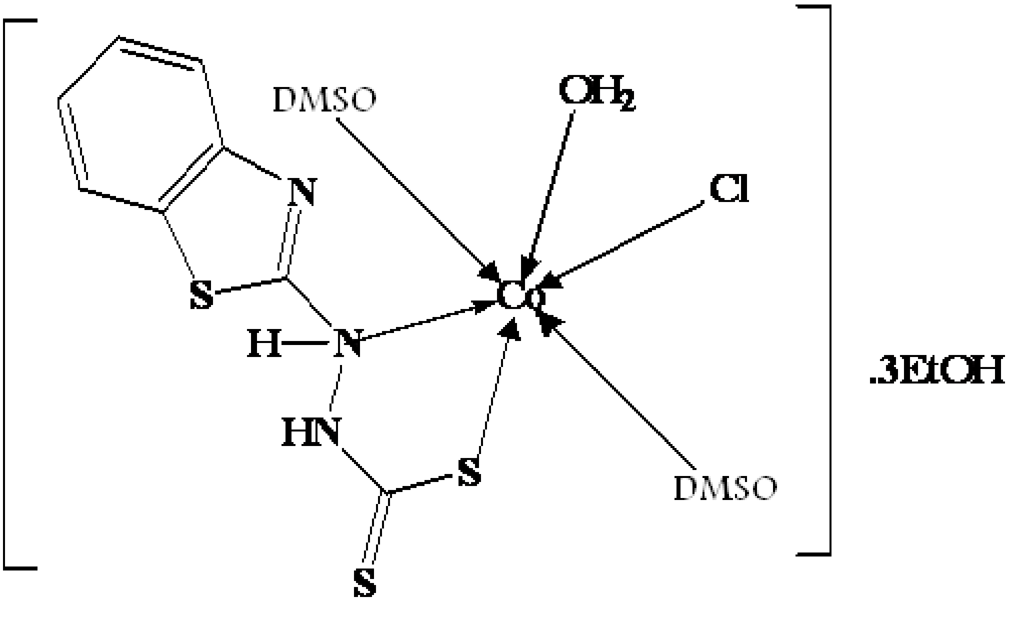
4-Co (II) complex

The value of the magnetic measurement (4.52B.M.), indicate that the greenish blue Co (II) complex to be paramagnetic and is characteristic of high spin tetrahedral cobalt ion species $^{(74,76)}$. The color of present Co (II) in DMSO was change from greenish blue to yellowish green during dissolution the solid compound, therefore, it was postulated that two DMSO molecules coordinate with the compound to give distorted octahedral structure.

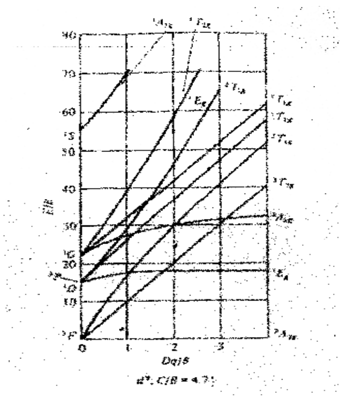


Tanabe-Sugano diagram for d^7 system.

The electronic spectrum of this complex showed three absorption bands at 10.121 , 14.084 and 23.529 cm^{-1},fig (3-16), these bands have been assigned to the transitions: $^4T_1g \rightarrow ^4T_2g$, $^4T_1g \rightarrow ^4A_2g$ and $^4T_1g \rightarrow ^4T_1g$, table (3-4), on the basis of these assignment it was possible to calculate the ligand field parameters β, B' and 10Dq by using Tanaba-Sugano diagram for d^7 configuration(74-76). The assigned values of transition d^7 and v_2 calculated as well as β, B' and 10Dq are all in good agreement with cobalt (II) octahedral complexes(73, 82). The molar conductivity measurements indicate that the complex was non-ionic. Table (3-4). In addition, these data obtained from atomic absorption analysis, infrared spectra, which made another prove for tetrahedral geometry of this complex and the following structure, can be proposed.

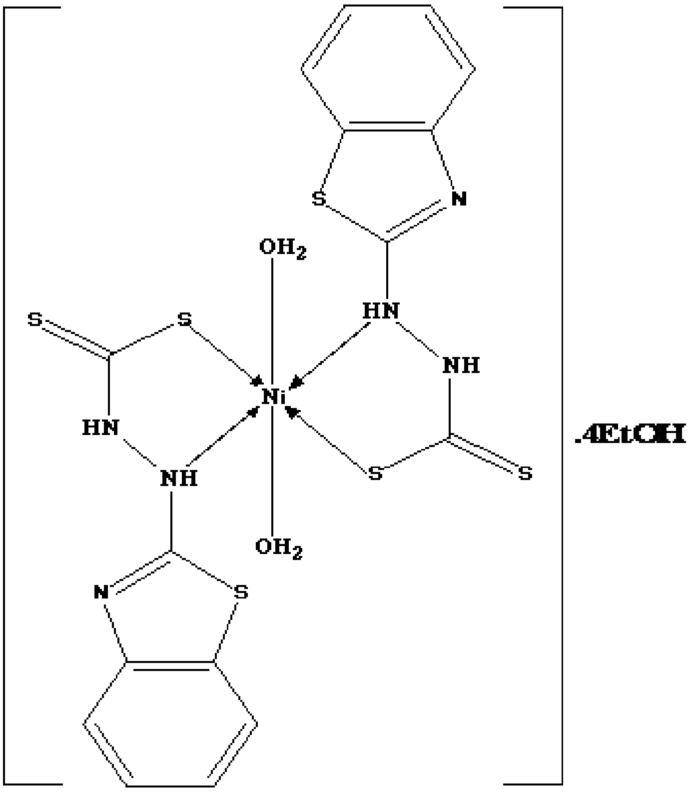


5- Ni (II) complex



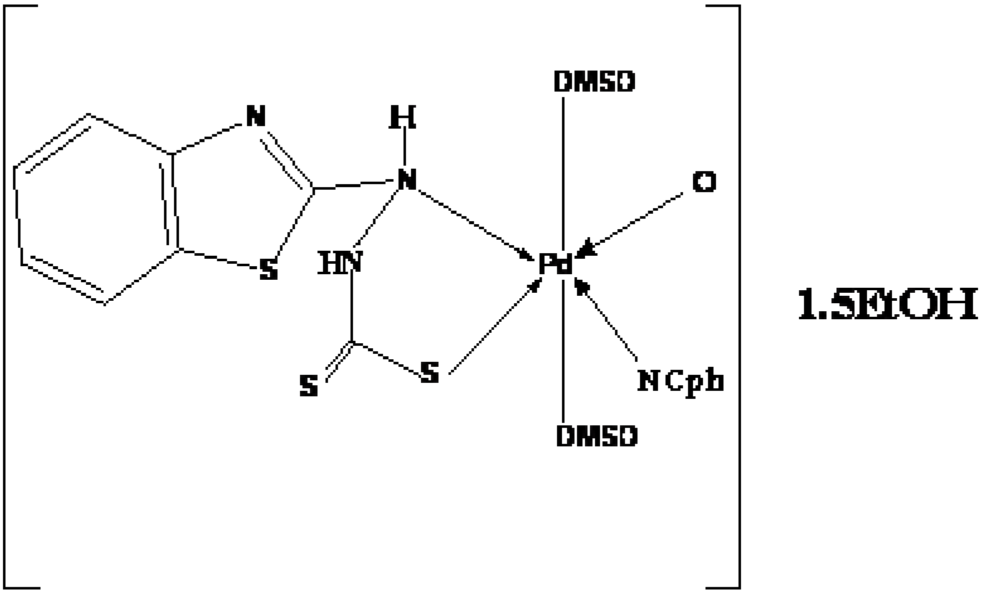
Tanabe-Sugano diagram for d^8 system

Square_planar nickel (II) complexes are orange-red, but green are known(76,83,84,85). The green color of the present Ni(II) was postulated to be distorted octahedral. The electronic spectral data of the solution complex, fig (3-17), table (3-4), provide further evidence in favor of distorted octahedral structure. The ground term for spin-free d^8 configuration is ^3F, in octahedral stereochemistry the triplet term of d^8 ion was the ^3A_2g, consequently, the possible spin-allowed transition can be assigned as shown in table (3-4) with their respective values. The values of v_1 (which is equal to 10Dq), the Racah interelectronic repulsion parameter B\` and the nephelauxetic factor β were calculated by fitting the ratio $v_3/v_2$ to the Tanaba-Sugano diagram for octahedral $d^8$ ion. The ratio $v_3/v_2=1.24$ fit the diagram at 1.9Dq/B\`, therefore from $v_2/B`=34.0$, B\` will be 550 cm^{-1} and β=0.53 (taking B for the free ion to be 1035 cm^{-1}), the value of the constant field splitting $10Dq=1.9\times550=10450\ cm^{-1}=v_1$. The transition observed at 13.245 cm^{-1} was assigned to the spin-forbidden transition $^3A_2g\rightarrow{}^1Eg$(86), the value of v_1 was reproduced using expression $15B`=v_3+v_2-v_1$ (75)and found to be 11.275 $cm^{-1}$. The assigned values of $v_2$ and $v_3$ and the calculated $v_1$ as well as B\`, β and 10Dq are all in a good agreement with nickel(II) complexes having similar donar atom groups(87,88). The quite low value of β suggests a considerable covalent bonding between metal and ligand atoms. Magnetic moment was (3.11 B.M.), and the conductivity measurement showed that the complex was to be non-electrolytic Table (3-4). Thus from these data and those obtained from infrared spectra and atomic absorption analysis studies, an octahedral geometry around Ni(II) ion can be suggested as illustrated below:



6- Palladium (II) complex

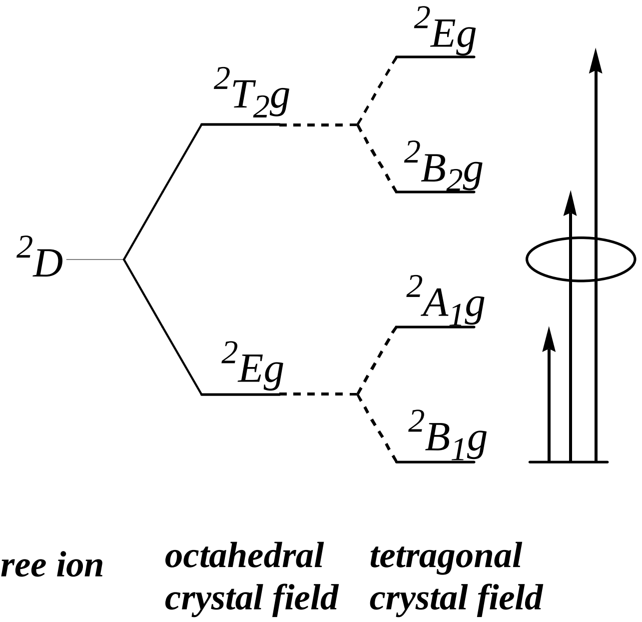
Square planer palladium (II) complexes are commonly orange(75,89). The red color of present palladium (II) chelate is therefore not consistent with our postulation of a square planer structure. Furthermore, the color of DMSO solution of the complex was noticed to change from red to brown during dissolution of the solid compound, therefore it was postulated that two DMSO molecules coordinates through the axial positions of the square planer change to distorted octahedral. The electronic spectral data of this solution, table (3-4), provide further evidence in favor of distorted octahedral structure. The ground term for spin-pairing d^8 configuration in octahedral stereochemistry is ^1A_1g state, consequently, the possible spin-allowed transition can be assigned as shown in table(3-4), with their respective values. Two bands are expected to appear in the visible region due to the transition ^1T_1g and ^1T_2g + ^1Eg states$^{(72,82)}$. In the spectrum of our complex fig (3-18), weak band was observed at 13.045 cm^{-1}, this weak band was attributed to the spin-forbidden $^1A_1g \rightarrow {}^3T_2g$ transition. The position of these bands are in agreement with that reported for octahedral geometry$^{(90)}$. In addition the measured magnetic moment in solid state for this complex was found to be zero Bohar magnetron, this value refer to low-spin d^8 complex. The conductance measurements indicate the non-conducting behavior of the complex, table(3-4), from infrared spectra, atomic absorption analysis make further evidence for square planer geometry of this complex and the following structure can be proposed



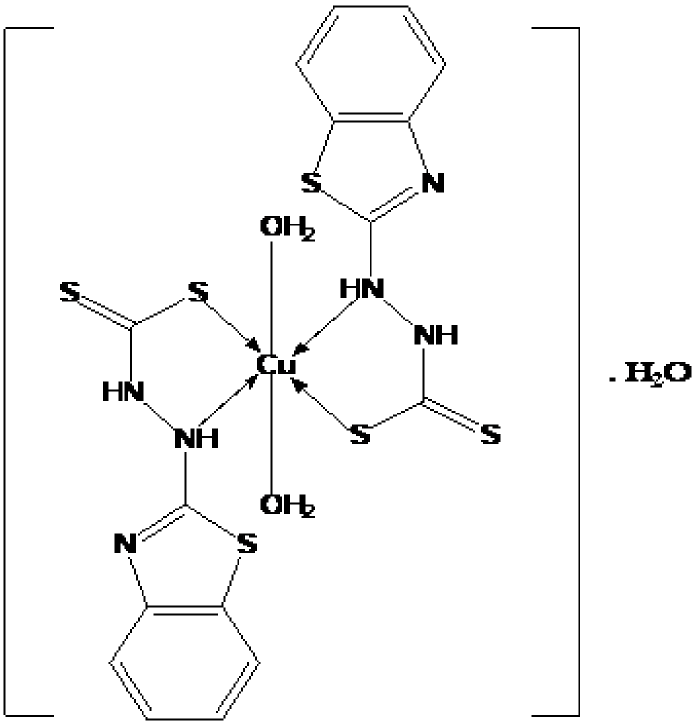
7- Cu(II) complex

The prepared complex was brown color in solution, and paramagnetic corresponding to one unpaired electron. The observed magnetic moment value of the complex was 2.17 B.M., higher than the spin only value (μeff =1.73B.M.), this can be attributed to spin free (monomeric) copper complex.

The free ion ground ^{2}D term is expected to split in crystal field according to the following scheme:



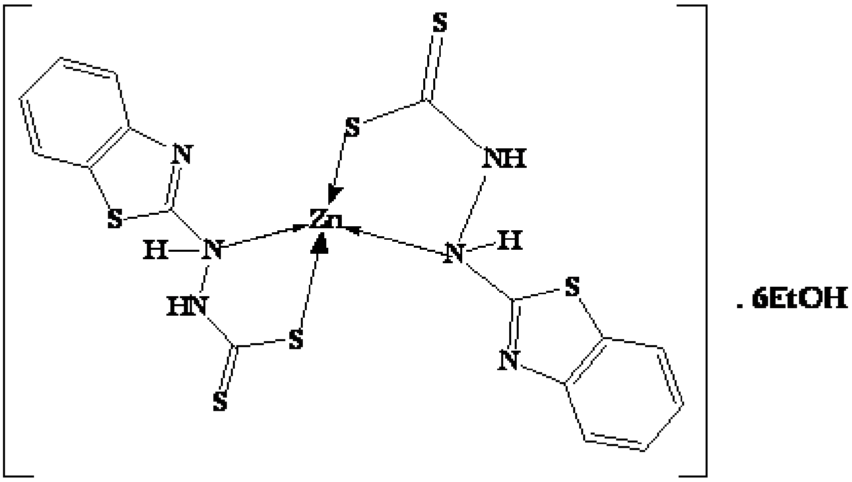
The spectra of prepared copper, show broad band in the visible region in (538-692) nm, as shows in table (3-4) and fig (3-19), the absorption band assign or pointed in 618 nm (16.181) cm^{-1}, which can be assigned to the transition $^2Eg\rightarrow{}^2T_2g$ in octahedral structure. According to the previous metal analysis, infrared spectra, magnetic measurements, uv-vis spectra and result of the conductivity measurement, which show, to be non-ionic, the following structure can be suggested.

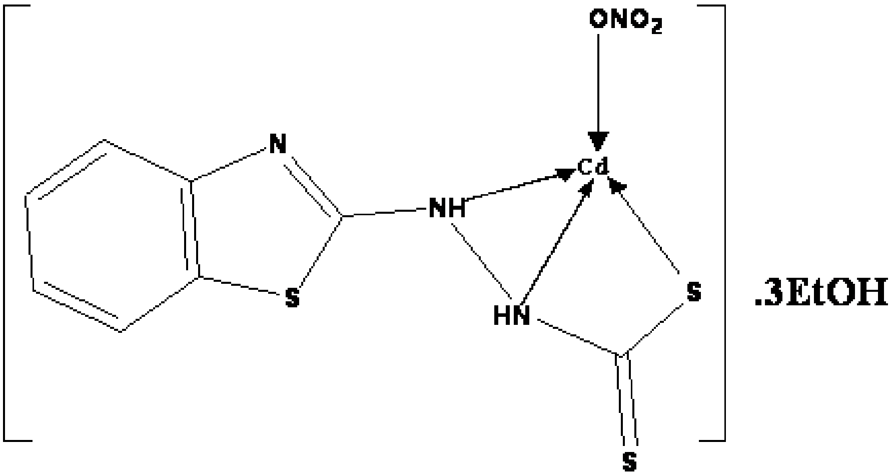


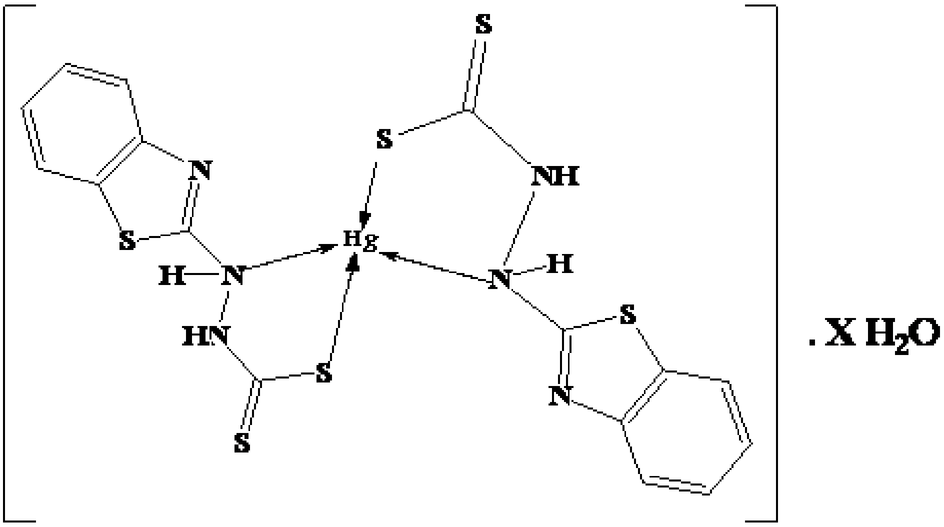
8- Zinc (II), Cadmium (II) and Mercury (II) complexes

Generally, zinc, cadmium and mercury ions behave similarly with respect to their coordination number: fig(3-20) ,fig(3-21) and fig (3-22); which may be 2,4,5 and 6, and the most probable is the 4 and 6 coordination number.

The prepared complexes are light yellow and diamagnetic which is expected for d^{10} ion. The uv-vis spectra of the compounds show relative change in the bands position compared to that of the free ligand, as listed in table (3-4). The effective magnetic moment for the prepared complexes shows these compounds to be diamagnetic as shown in table (3-4). The conductivity measurements for the prepared complexes in DMSO solvent at 25°C showed to be non-ionic depending on the above spectroscopic and analytical data; the proposed structure of the prepared complexes can be reported as follows:


S
S
NH
N
Zn
H—N
N
H
HN
S
S
S
N
S
. 6EtOH


ONO₂
N
Cd
NH
S
HN
S
S
.3EtOH


S
S
N
NH
S
Hg
H—N
N
H
HN
S
S
S
N
S
. X H₂O

Table(3-4): Electronic spectra, conductance in DMSO solvent and magnetic moment(B.M.) for the present prepared metal complexes.

Compound	Absorption Bands(cm^{-1})	Transition	B	B`	β	Dq/B`	10Dq	B.M.	15B`	µscm^{-1}	geometry
Cr(III)L	16.393 26.953 35.875	$^{4}A_{2}g \rightarrow {}^{4}T_{2}g$ $^{4}A_{2}g \rightarrow {}^{4}T_{1}g$ $^{4}A_{2}g \rightarrow {}^{4}T_{1}g_{(P)}$cal	1000	877	0.877	1.65	16120	3.40	14655	22	O.h
Mn(II)L	10.006 16.501 24.390	$^{6}A_{1}g_{(s)} \rightarrow {}^{4}T_{1}g_{(G)}$ $^{6}A_{1}g \rightarrow {}^{4}T_{2}g_{(G)}$ $^{6}A_{1}g \rightarrow {}^{4}A_{1}g + {}^{4}Eg$	860	756	0.88	1.5	11340	6.12	11340	29	O.h
Co(II)L	10.121 14.084 23.529	$^{4}T_{1}g \rightarrow {}^{4}T_{2}g$ $^{4}T_{1}g \rightarrow {}^{4}A_{2}g$ $^{4}T_{1}g \rightarrow {}^{4}T_{1}g_{(P)}$	1128	476	0.43	2.1	9982	4.52	7125	20	O.h
Ni(II)L	11.275 13.245 17.685 24.390	$^{3}A_{2}g \rightarrow {}^{3}T_{2}g$ $^{3}A_{2}g \rightarrow {}^{1}Eg$ $^{3}A_{2}g \rightarrow {}^{3}T_{1}g_{(F)}$ $^{3}A_{2}g \rightarrow {}^{3}T_{1}g_{(P)}$	1035	550	0.53	1.9	10450	3.11	8250	13	O.h
Cu(II)L	16.181	$^{2}Eg \rightarrow {}^{2}T_{2}g$						2.17		26	O.h
Zn(II)L	29.069 32.258	ILCT ILCT						0.00		18	T.h
Cd(II)L	28.735 33.735	ILCT ILCT						0.00		24	T.h
Hg(II)L	29.121 33.014	ILCT ILCT						0.00		20	T.h
Pd(II)L	13.054 18.726 26.041	$^{1}A_{1}g \rightarrow {}^{3}T_{2}g$ $^{1}A_{1}g \rightarrow {}^{1}T_{1}g$ $^{1}A_{1}g \rightarrow {}^{1}T_{2}g$						0.00		15	O.h
Rh(III)L	11.313 14.914 22.727	$^{1}A_{1}g \rightarrow {}^{3}T_{1}g$ $^{1}A_{1}g \rightarrow {}^{1}T_{1}g$ $^{1}A_{1}g \rightarrow {}^{1}T_{2}g$						0.60		34	O.h

ILCT=Internal ligand charge transfer.

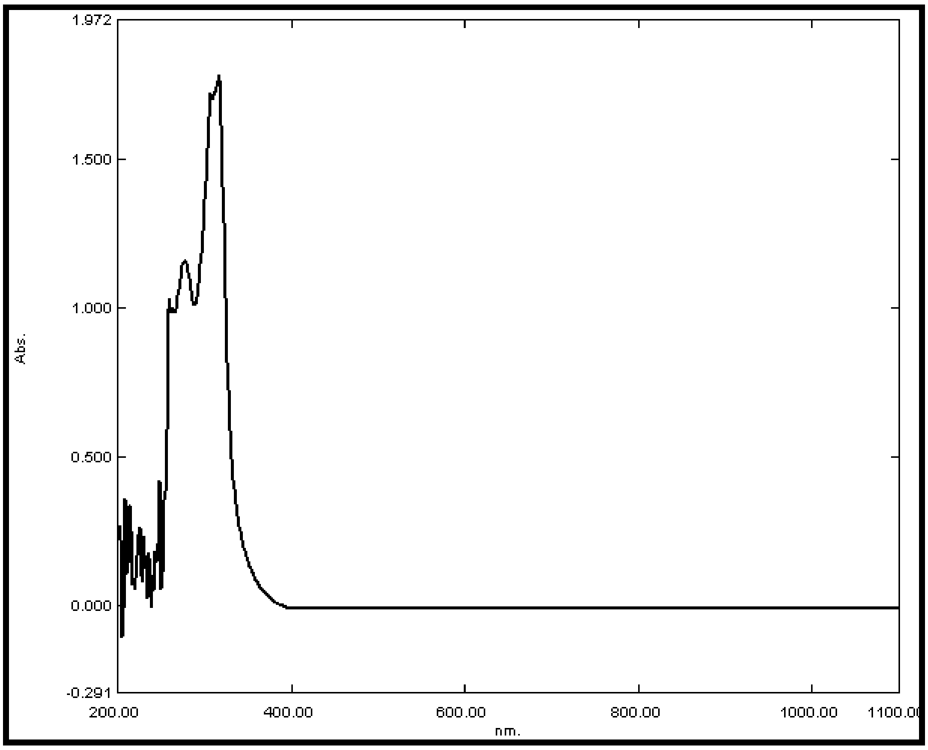


Figure (3-12): Electronic Spectrum of L

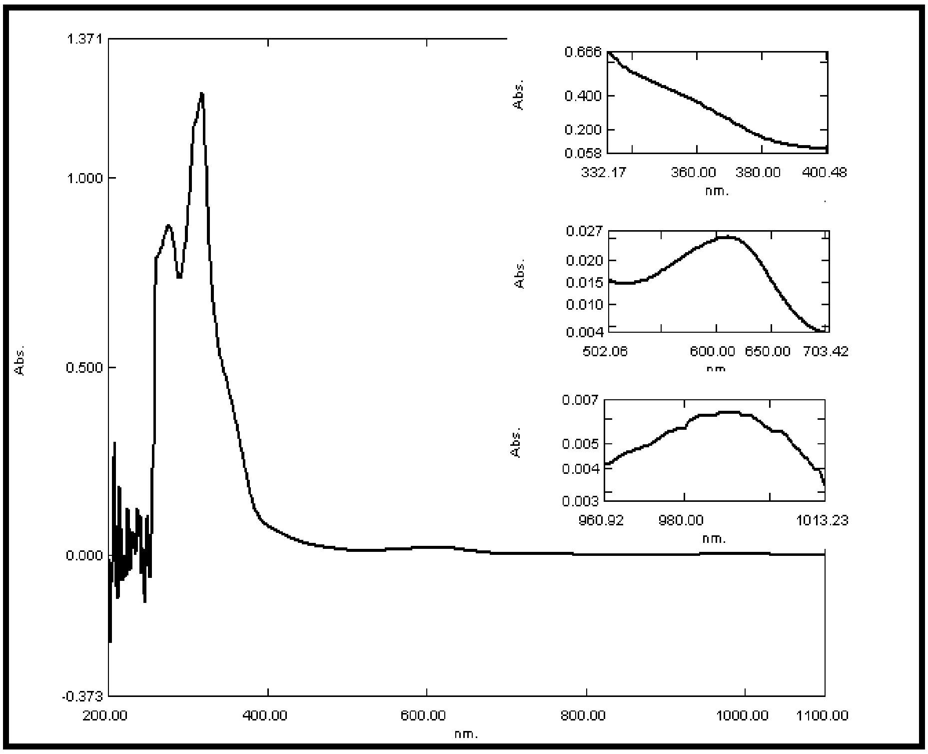


Figure (3-13): Electronic Spectrum of CrL

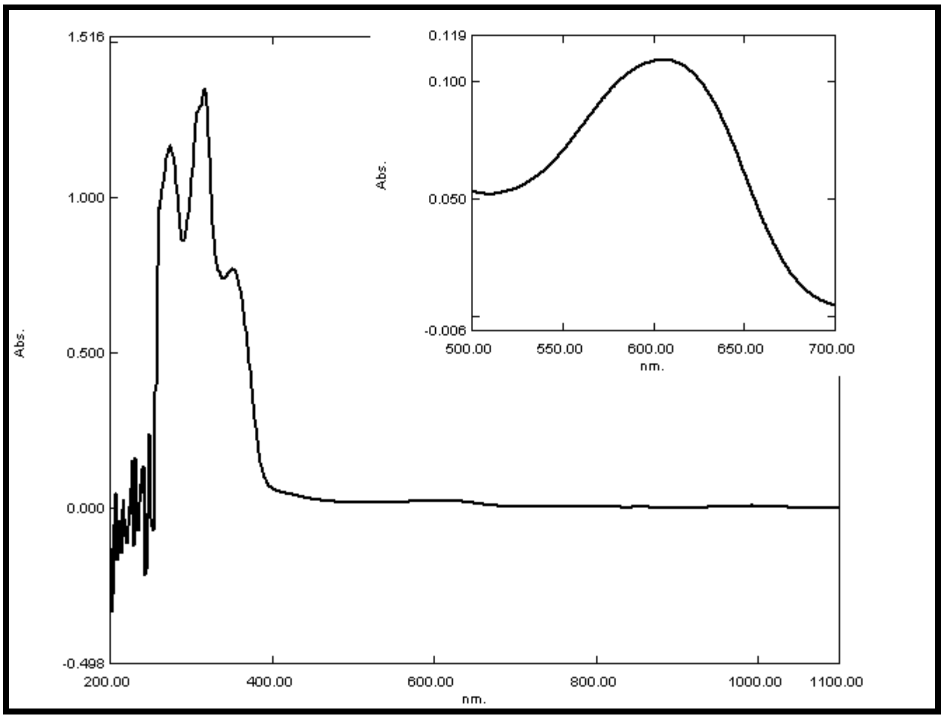


Figure (3-14): Electronic Spectrum of MnL

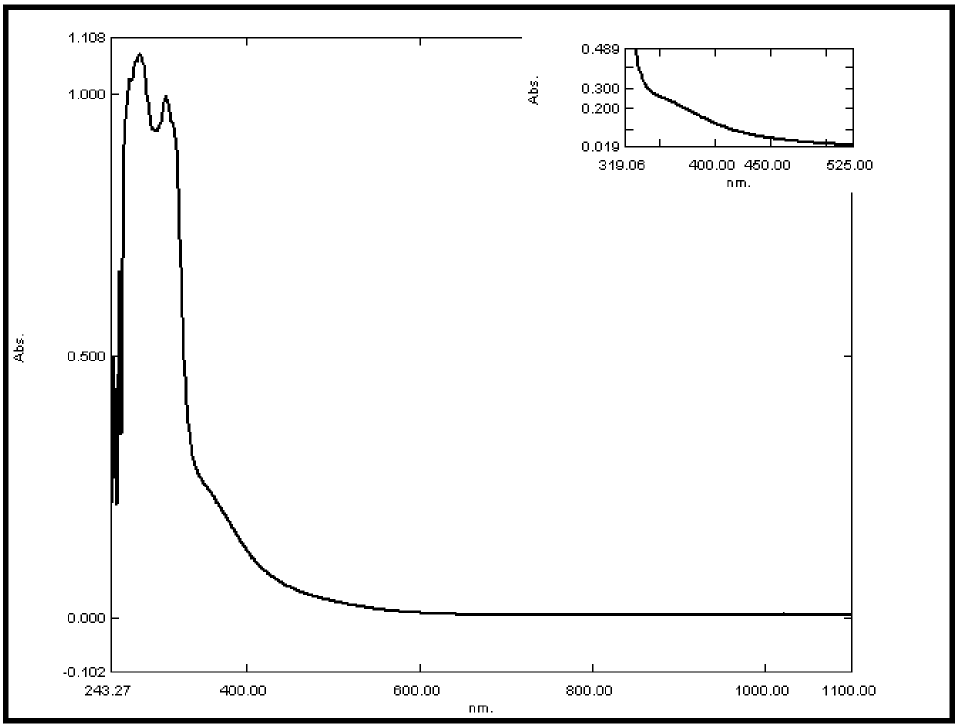


Figure (3-15): Electronic Spectrum of Rh

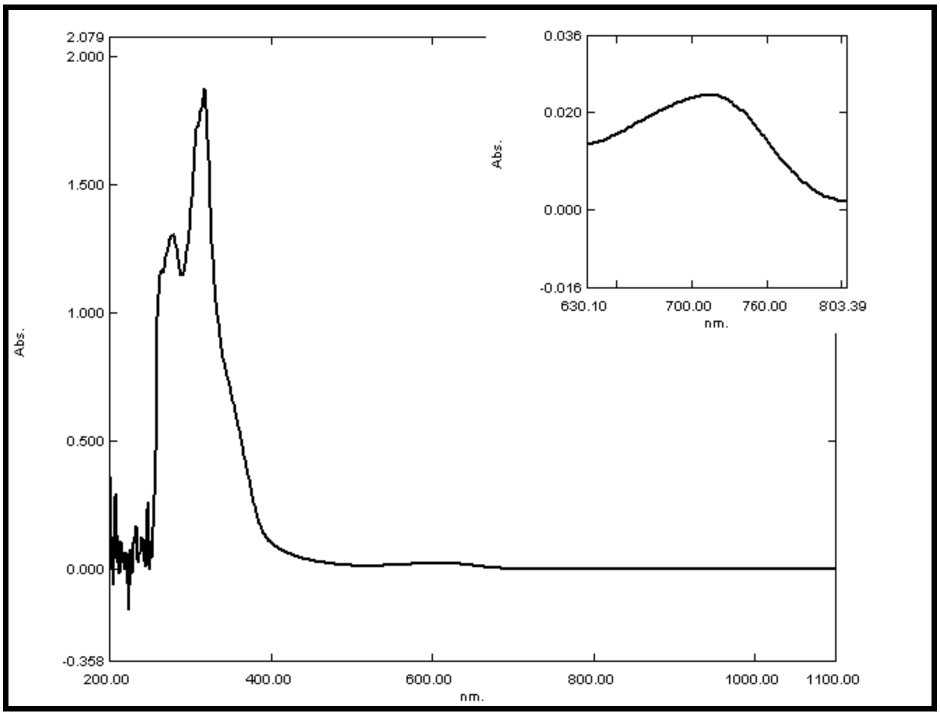


Figure (3-16): Electronic Spectrum of CoL

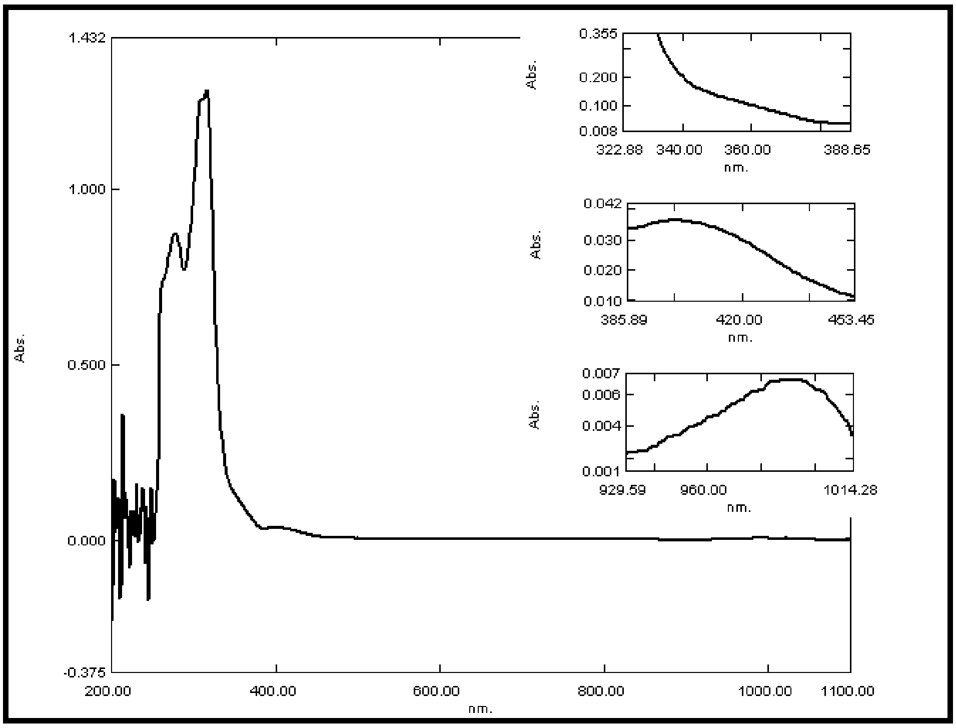


Figure (3-17): Electronic Spectrum of NiL

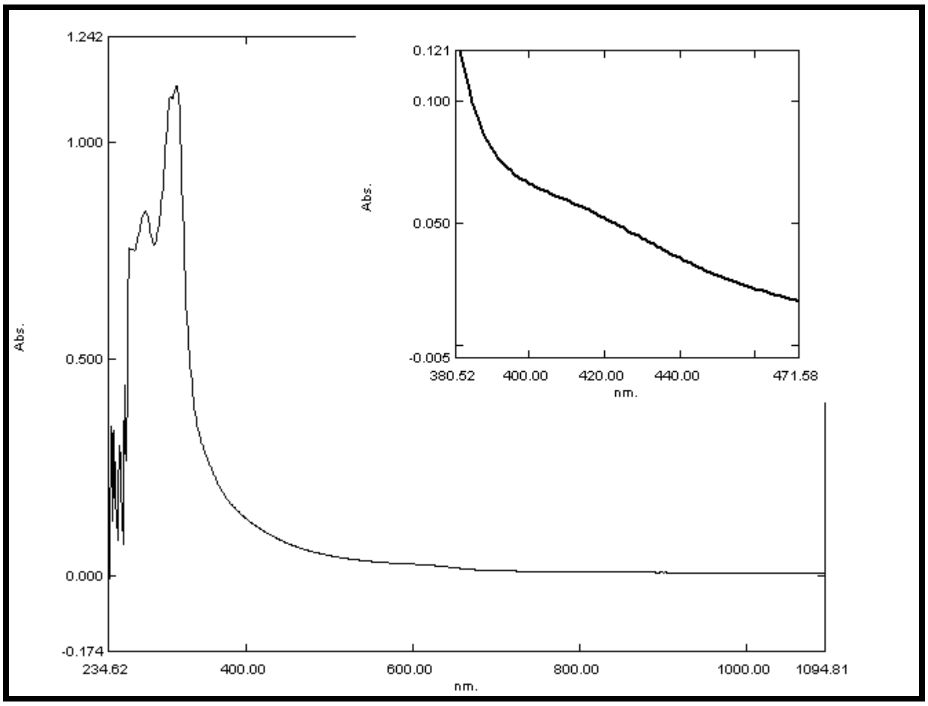


Figure (3-18): Electronic Spectrum of PdL

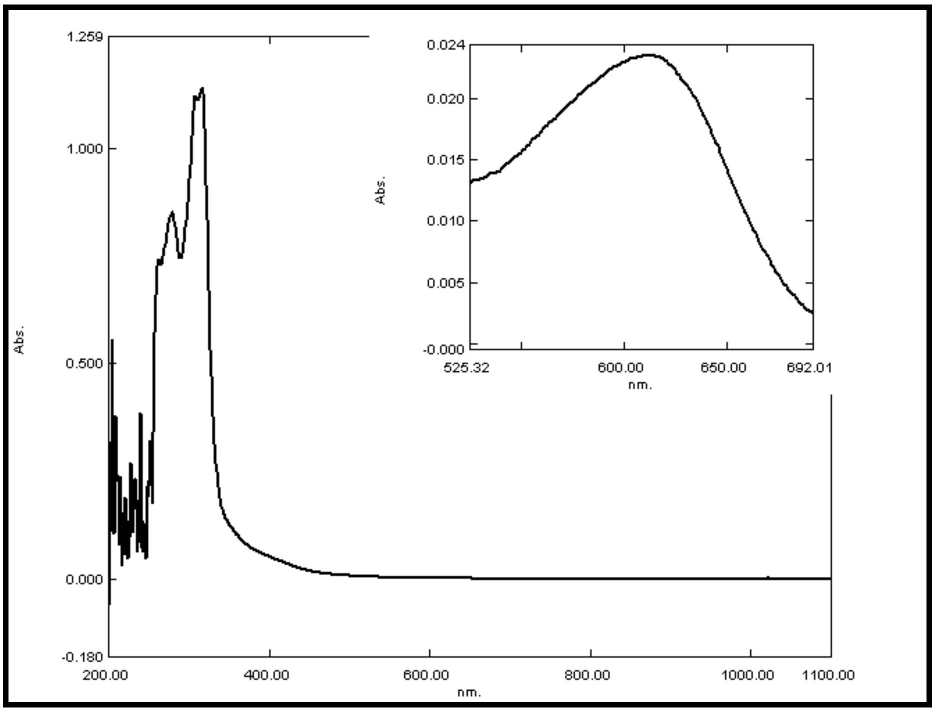


Figure (3-19): Electronic Spectrum of CuL

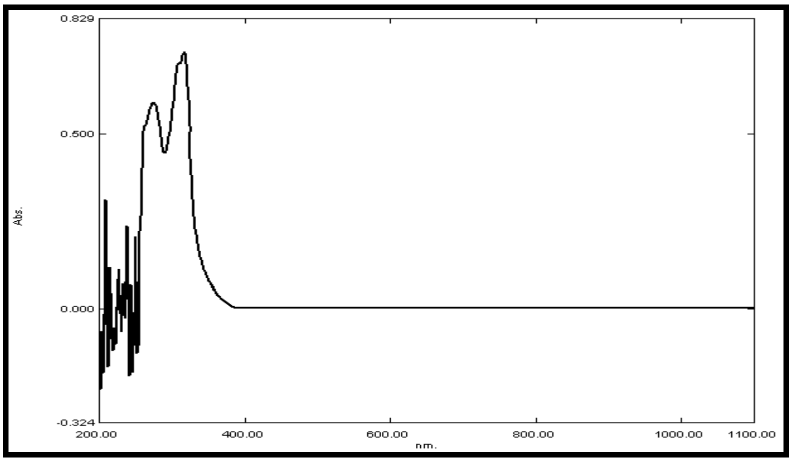


Figure (3-20): Electronic Spectrum of ZnL

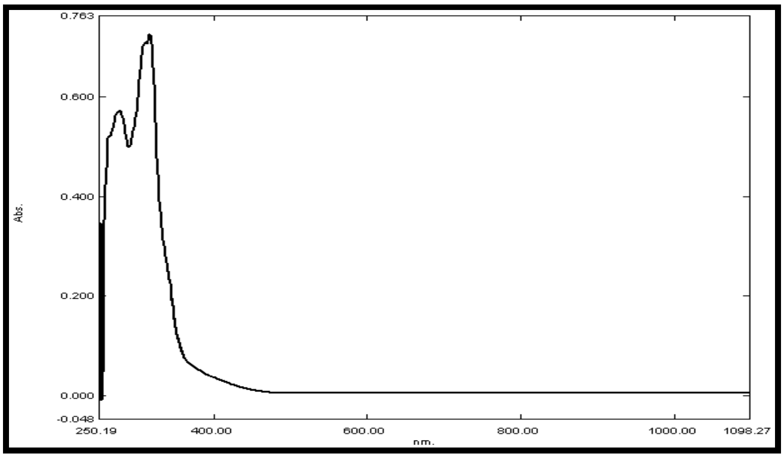


Figure (3-21): Electronic Spectrum of CdL

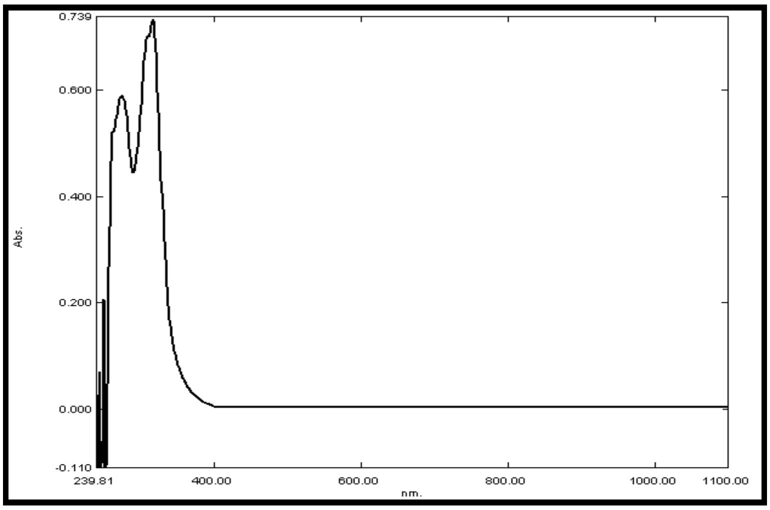


Figure (3-22): Electronic Spectrum of HgL

3.4 Theoretical studied:-

The program hyperchem6 was used for the semi-empirical and molecular mechanic calculations. The heat of formation (ΔH°_f) and binding energy (ΔE_b) for all free ligands and their metal complexes were calculated by PM3 and ZINDO/1, table (3-5) shows the calculated (ΔH°_f) and (ΔE_b). Also PM3 was used for evaluating (dithiocarbamate Ligand) table (3-6) compares the theoretically calculated wave numbers with the experimental values.

Table (3-5): Conformation Energetic (in KJ.Mol^{-1})for L and its metal complexes

Comp.	**PM3**		**ZINDO/1**	
	ΔH°_f	ΔE_b	ΔH°_f	ΔE_b
M	78.5397	-1887.5397		
L	68.1894	-2149.7425		
CoL	-397.3477	-4471.1347		
CuL	31.1348	-4812.9551		
CdL	86.6215	-2449.7074		
NiL	-42.9585	-4909.1485		
MnL	56.8426	-6007.4233		
ZnL			-9151.441	-13618.4749
CrL			-12802.4415	-19551.2375
HgL	236.7005	-4215.8534		
PdL			-16211.7940	-10744.430
RhL			-11963.4051	-18092.9711

3.4.1 Optimized geometries energies and vibrational for free ligand dithiocarbamate derivative (L):-

The results of PM3 method of calculation in gas phase for the heat of formation and binding energy of dithiocarbamate derivative were tabulated in table (3-5).

The vibrational spectra of the free ligands have been calculated, table (3-6). The theoretically calculated wave number for this ligand showed that some deviations from the experimental values, these deviations are generally acceptable in theoretical calculations.

The most diagnostic calculated vibrational frequencies were chosen for the assignment of ligand, which is included in table (3-6), fig (3-23), and their respective experimental vibrational modes are shown in table (3-3) , fig (3-1).

The results obtained for the theoretical calculations of the frequencies of υ (N-H), δ (N-H), υ (C=S) + υ (C–S) and υ (N-N) in agreed well with those obtained for the experimental values, table (3-6).

Table (3-6): Comparison of experimental and theoretical vibrational frequencies

Comp.	***vN-H(first)***	***δ(NH)first***	***N(C=S)***	***N(C-S)***	***vN-N***
Ligand	*(3382)** *(3338.3)*** *(1.29)****	*(1650)** *(1612)*** *(2.3)****	*(1209)** *(1283.37)*** *(-6.15)***	*(1072)** *(974.98)*** *(9.05)****	*(995)** *(975.89)*** *(1.92)****

Where:
*: Experimental frequency
**: Theoretical frequency
***: Error percentage due to main difference in the experimental measurements and theoretical treatments of vibrational spectrum

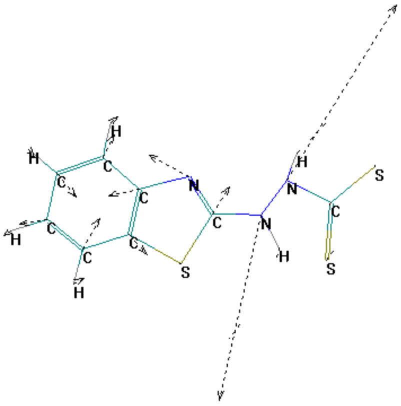
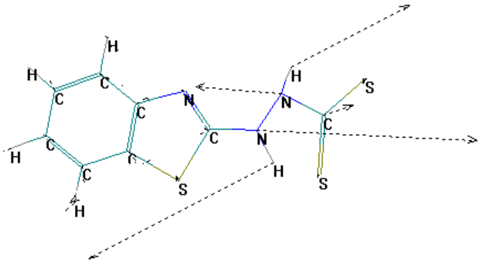
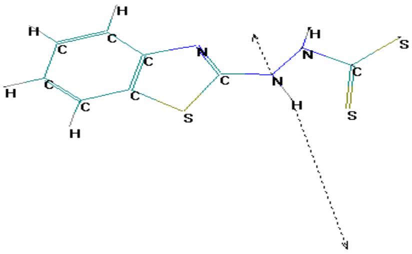
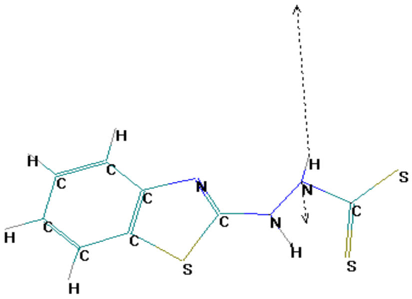
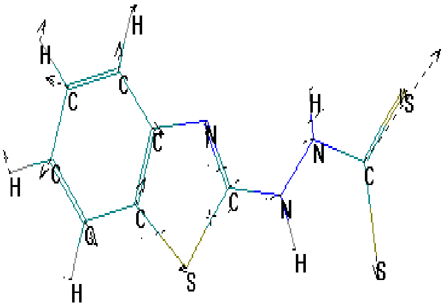
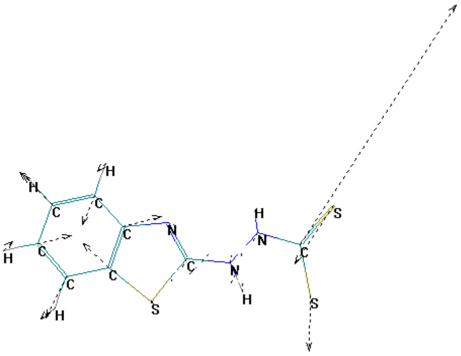
	
νN-N(975.89)	δN-H(1612)
	
νN-H (3151.5)	νN-H(3338.3)
	
νC=S(1283.37)	νC-S(974.98)

Fig. (3-23): The Calculated Vibrational Frequencies of L

3.4.2 Electrostatic potential:

Electrostatic potential of the ligand was calculated and plotted as 2D contour to investigate the reactive sites of the molecules fig (3-24). Also one can interpret the stereochemistry and rates of many reactions involving soft electrophiles and nuclephiles in terms of the properties of frontier orbitals (HOMO and LUMO).

Overlap between the HOMO and LUMO is a govering factor in many reactions. The HOMO and LUMO values were plotted as 2D contour to get more information about these molecules.

The results of calculation showed that the LUMO of transition metal ion prefer to react with the HOMO of sulfur and nitrogen atoms of dithiocarbamate derivatives compound.

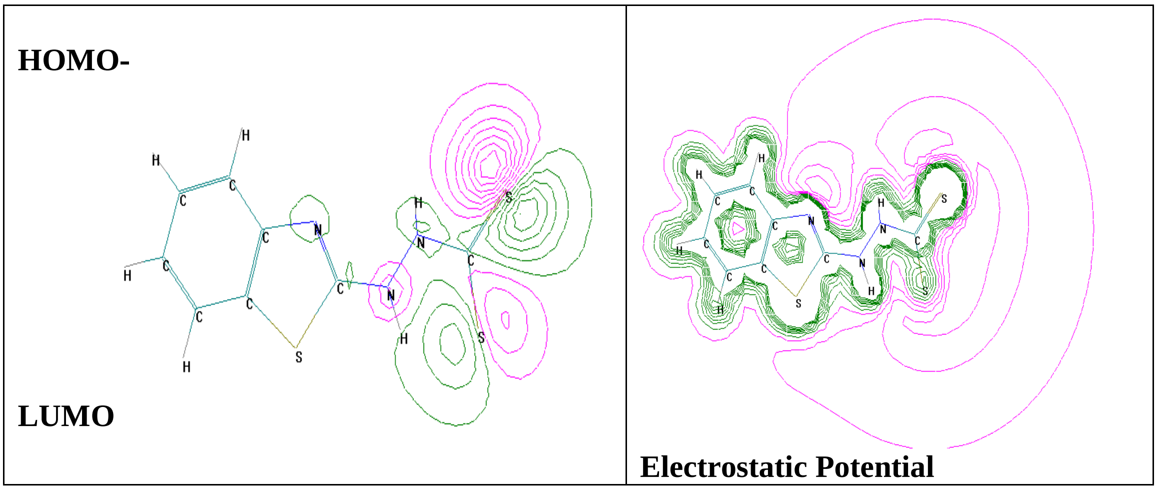


Fig. (3-24): HOMO and Electrostatic Potential as 2D Contours for L

3.5.3 Optimized geometries energy of metal complexes for dithiocarbamate derivative:-

All theoretically probable structures of metal complexes with dithiocarbamate derivative has been calculated to search for the most probable model building stable structure, fig (3-25).

The results of PM3 method calculation in gas phase for the binding energies and heat of formation of Mn(II), Co(II), Ni(II), Cu(II),Cd(II) and Hg(II),while ZINDO/1 method has been used for Cr(III), Rh(III), Pd(II) and Zn(II), these can be shown in table (3-5). The result reflected that the complexes of dithiocarbamate derivative (L) exhibited to be more stable than the donor base (L), this difference in stability of complexes might be related to the chelating effect.

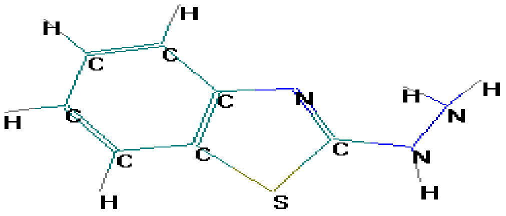
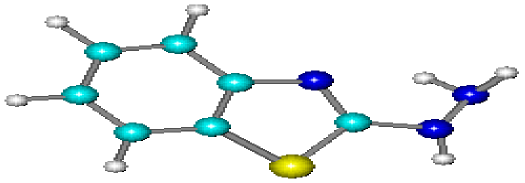
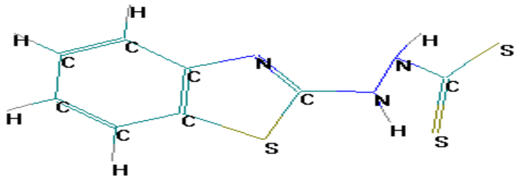
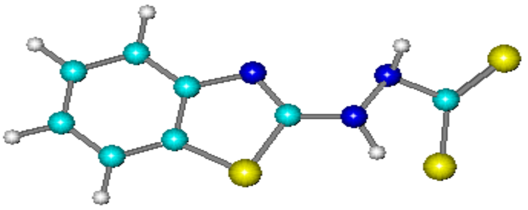
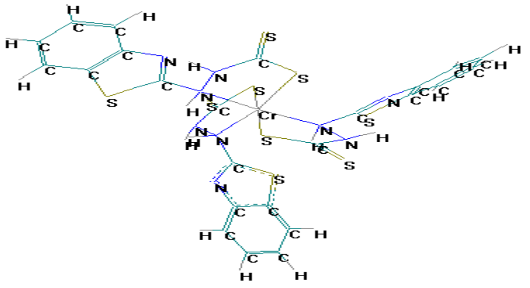
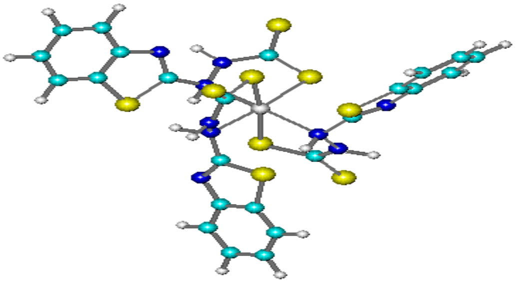
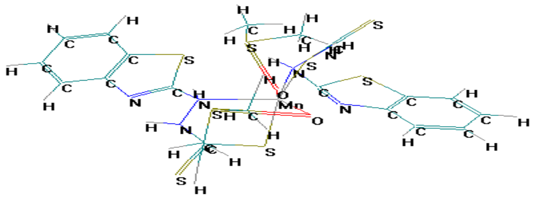
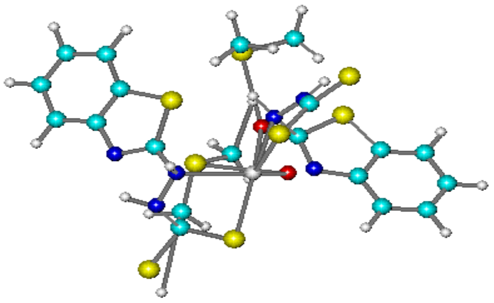
 **A**	
 Ligand	
 CrL	
 MnL	

Fig. (3-25): Conformational Structure of A and L and its Complexes

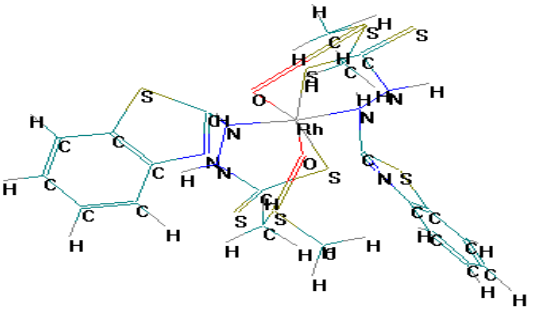
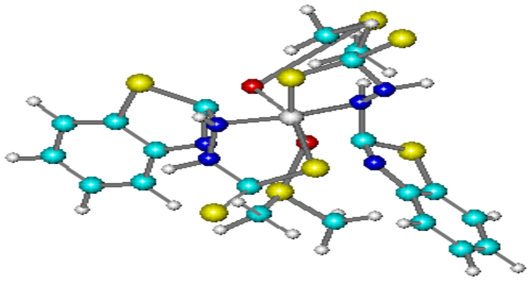
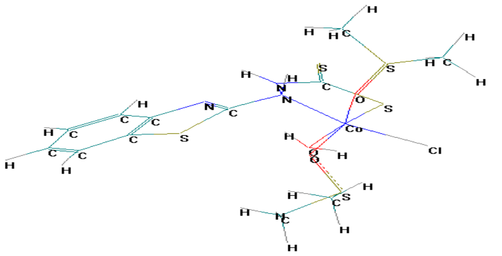
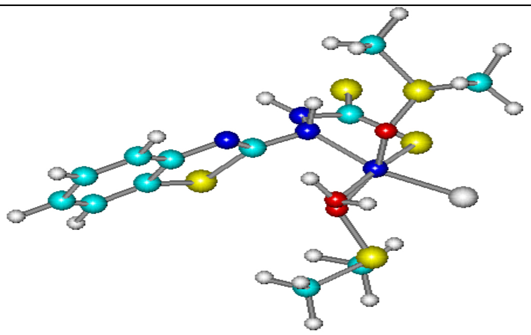
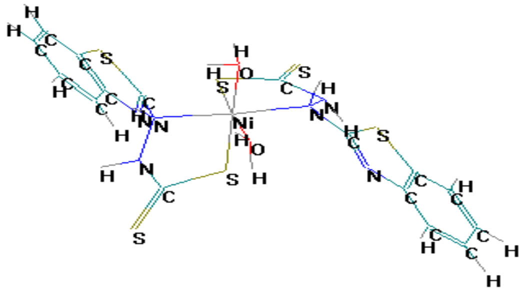
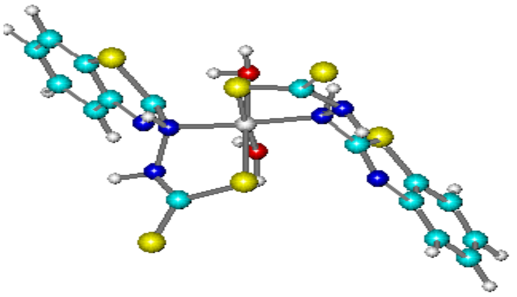
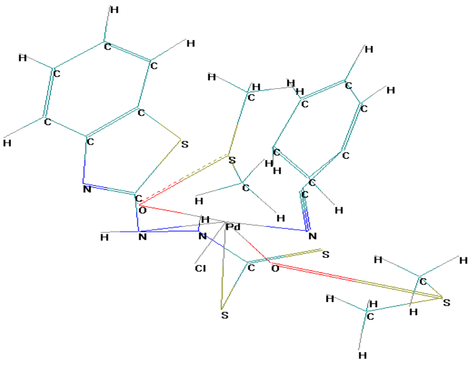
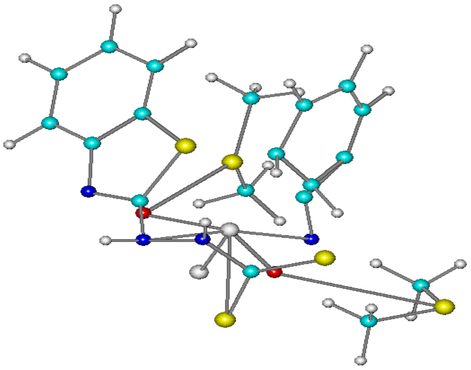
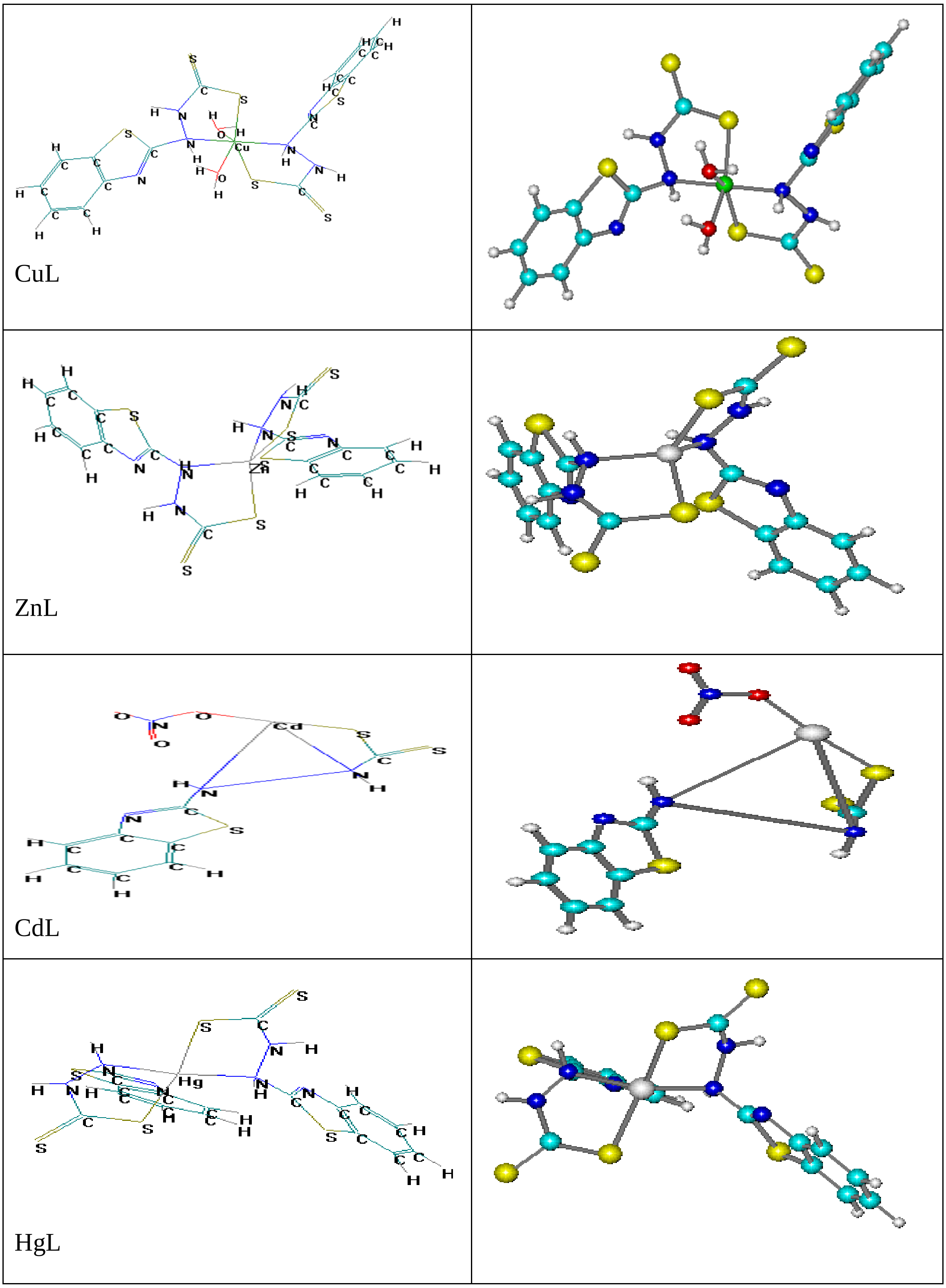
 RhL	
 CoL	
 NiL	
 PdL	

Fig. (3-25): Conformational Structure of A and L and its Complexes



CuL

ZnL

CdL

HgL

Fig. (3-25): Conformational Structure of A and L and its Complexes

CHAPTER FOUR

BIOLOGICAL ACTIVITY Study

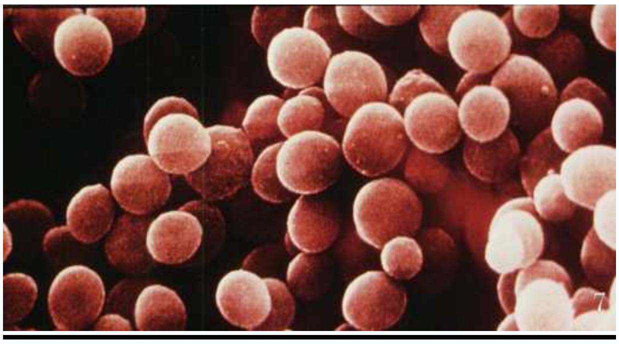
4.1.0 Introduction:

Micro organism causes different kinds of diseases to humans and animals. Discovery 0f chemotherapeutic agents played a very important role in controlling and preventing such diseases.

Chemotherapeutic agents are isolated either from living organisms known as anti-biotic like penicillin and tetracycline or they are chemical compounds prepared by chemists such as the sulfa drugs (91,92).

Micro organisms have the ability to develop resistance to these chemotherapeutic agents and such strains which are resistance cause major problems in the treatment of microbial infections. For this reason, searching for new anti-microbial agent is continuous process and great efforts have been employed to find new anti-biotic or new chemical compounds with good anti-microbial activity which might be suitable to be used as chemotherapeutic agents.

4.1.1 *Staphylococcus aureus*:



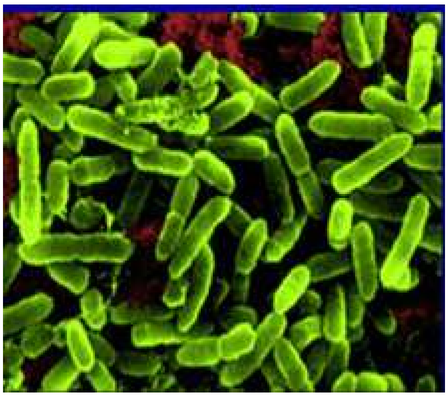
The sphereical-shaped bacterium called staphylococcs aureus is the causative agent of a wide variety of human infections. Many stains, with varying degree of virulence, exist and are frequently carried on the skin, in the nose, and around the rectum of healthy persons. These bacterial cells are about 1µm in diameter, and usually occur in grapelike, a characteristic that provided the basis for their name (Greek staphyle= bunch of grapes) **(93)**. *Staphylococcus* is Gram-positive spherical bacteria **(94)**.

Staphylococci are perhaps the best examples of the parasites that have great pathogenic potential, yet are able to live in symbiotic balance with their hosts. In spite of their ability to produce serious, life-threatening disease, pathogenic staphylococci are present on the skin or mucous membranes of all humans. S. aureas produce cause some case of food poisoning(95). Generally they act as opportunists, causing infections only on damaged tissues. These inflections may be serious, and hospital-acquired staphylococcal disease are recognized as a major problem. The prevention and control of these inflections depend on the combined efforts of all hospital personnel[96].

4.1.2 Pseudomonas aeruginosa:

Pseudomonas (in Greek *pseudo* means *false unit* and *monas* means *a single unit*). The species name *aeruginosa* is derived from the Greek prefix "*ae*" meaning 'old' or 'aged' and the suffix "*ruginosa*" means 'wrinkled or bumpy' **(97)**.[10]

*P.*aeruginosa is an opportunistic gram-negative bacterium that is a frequent, deadly pathogen of patients with cysticfibrosis, severe burns, or neutropenia.



P.aeruginosa secrets iron-containing compounds that are extremely toxic to endothelial cells and so may cause the vascular lesions characteristic of the infection.[98]

P.aeruginosa infections are often malignant and very resistant to therapy. The remarkable metabolic capabilities and diverse plasmids associated with these organisms have resulted in the development of a high level of resistance to a broad range of antimicrobials. A number of a new antibiotics have been specifically designed for treatment of pseudomonas infections. As yet, the ideal antipesudomonal compound has not been discovered.

4.2 Biological activity of the synthesized compounds:-

The dithiocarbamate as one of the thiole moieties are of considerable interest due to the wide range of therapeutic properties associated with them(99). Furthermore, the reported importance of biological properties of thiole stimulated our interest in synthesizing the structure (dithiocarbamate). The test was performed according to the disk diffusion method(100). The prepared compounds were tested against one strain of Gram-positive bacteria (*Staphylococcus aureus*) and Gram-negative bacteria (*Pseudomonas aeruginosa),* prepared agar and petridishes were sterilized by autoclaving for (15 min) at 121˚C. the agar plates were surface inoculated uniformly from the broth culture of the lested microorganisms. In the solidified medium suitable spaced apart holes were made all (6 mm) in diameter compounds (0.02mg of the compounds dissolved in 1ml of DMSO solvent).

These plates were incubated at (37˚C) for (24hrs), the inhibition zones caused by the various compounds on the bacteria were examined. The results of the preliminary screening test are listed in table (4-1).

4.3 Bactericidal activity

As results from the study of antimicrobial of prepared compound and its metal complexes, Table (4-1) and fig (4-1), the following points were concluded:

1. The result reflected that the starting material (A) exhibition toward Gram-positive and Gram negative, at higher and lower concentrations.
2. The results of antibacterial activity study for the Potassium (Benzothiozole-2-dithiocarbamato hydrzide) indicated that the new compound exhibited less antibacterial activity against the *Pseudomonas aeruginosa* bacteria at high and low concentrations; this indicates that introductions of dithiol hydrzide group on benzothiazole derivative raised the killing zone.
3. Biological evaluations of considerable number of these compounds have been maintained, and they were found to exhibit the expected synergic effect of activity, this attributed to the impact of the compound and the metal present in these complexes.
4. Generally, the results of the prepared complexes exhibited greater activity toward *Pseudomonas aeruginosa* and *Staphylococcus aureus* bacteria when we use higher than lower concentrations.
5. The study of antibacterial activities revealed that the d^{10} configuration (Zn, Cd and Hg) complexes, exhibited highly significant activity against the studied bacteria rather than that observed for any of the remainder complexes, especially for mercury complex, when we use high and low concentrations.

6. The result of antibacterial activities of chromium (III) and nickel (II) complexes showed that there is inhibition toward Gram-positive and Gram-negative bacteria, when we use only high concentration.

7. The inhibition that is exhibited from cobalt (II) complex toward the bacteria used in this study, at high and low concentration is similar to that inhibition for copper (II) complex at the same species of bacteria and concentration.

8. The results of the prepared palladium (II)complex, exhibited antibacterial activity toward the bacteria used in this study is similar inhibition, and also Rhodium (III) complex at two concentration, except, Rhodium (III) complex has been more inhibition than palladium complex because of the Rhodium (III) has high oxidation state.

Table (4-1): Antibacterial activities for dithiocarbamate and its metal complexes.

Comp. No.	*comp*	*Staphylococcus aureus*		*Pseudomonas aeruginosa*	
		10mM	*5mM*	*10mM*	*5mM*
1	*2-mercapto-benzothiozle*	–	–	–	–
2	Ligand	–	–	+	+
3	*CrL*	+	–	++	–
4	*MnL*	–	–	++	+
5	*CoL*	+	+	+	–
6	*NiL*	+	–	++	+
7	*CuL*	+	+	+	–
8	*ZnL*	+	++++	++	+++
9	*CdL*	++++	+	++	++
10	*HgL*	+++	+++	++++	++++
11	*RhL*	++	++	++	++
12	*PdL*	+	+	+	+

(-) = No inhibition = inactive

(+) = (1-4) mm = slightly active

(++) = (4-8) mm = moderately active

(+++) = (8-12) = active

(++++) =(12 and more) = highly active

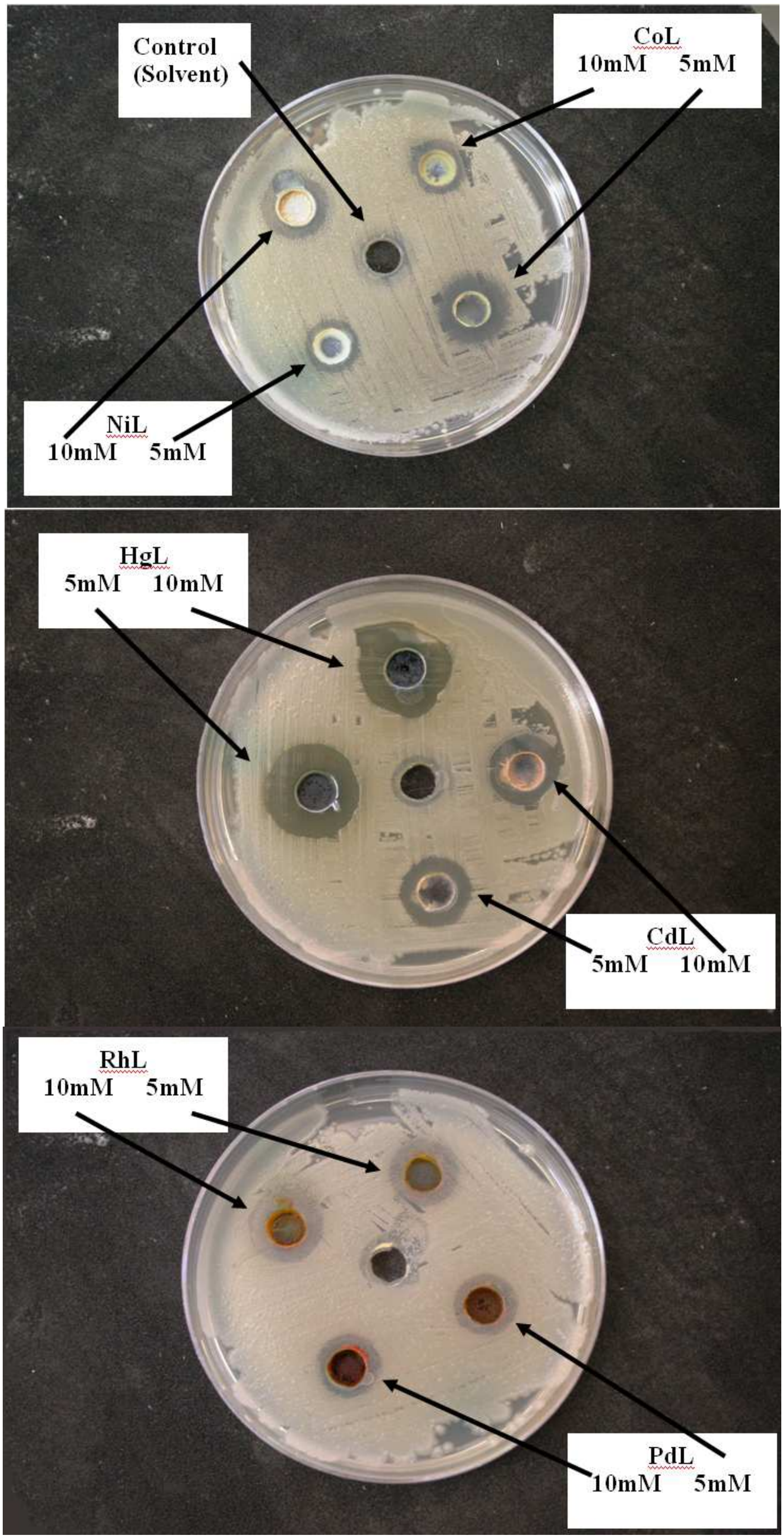


Fig (4-1): The antibacterial activity for dithiocarbamate metal complexes toward ***Staphylococcus aureus***

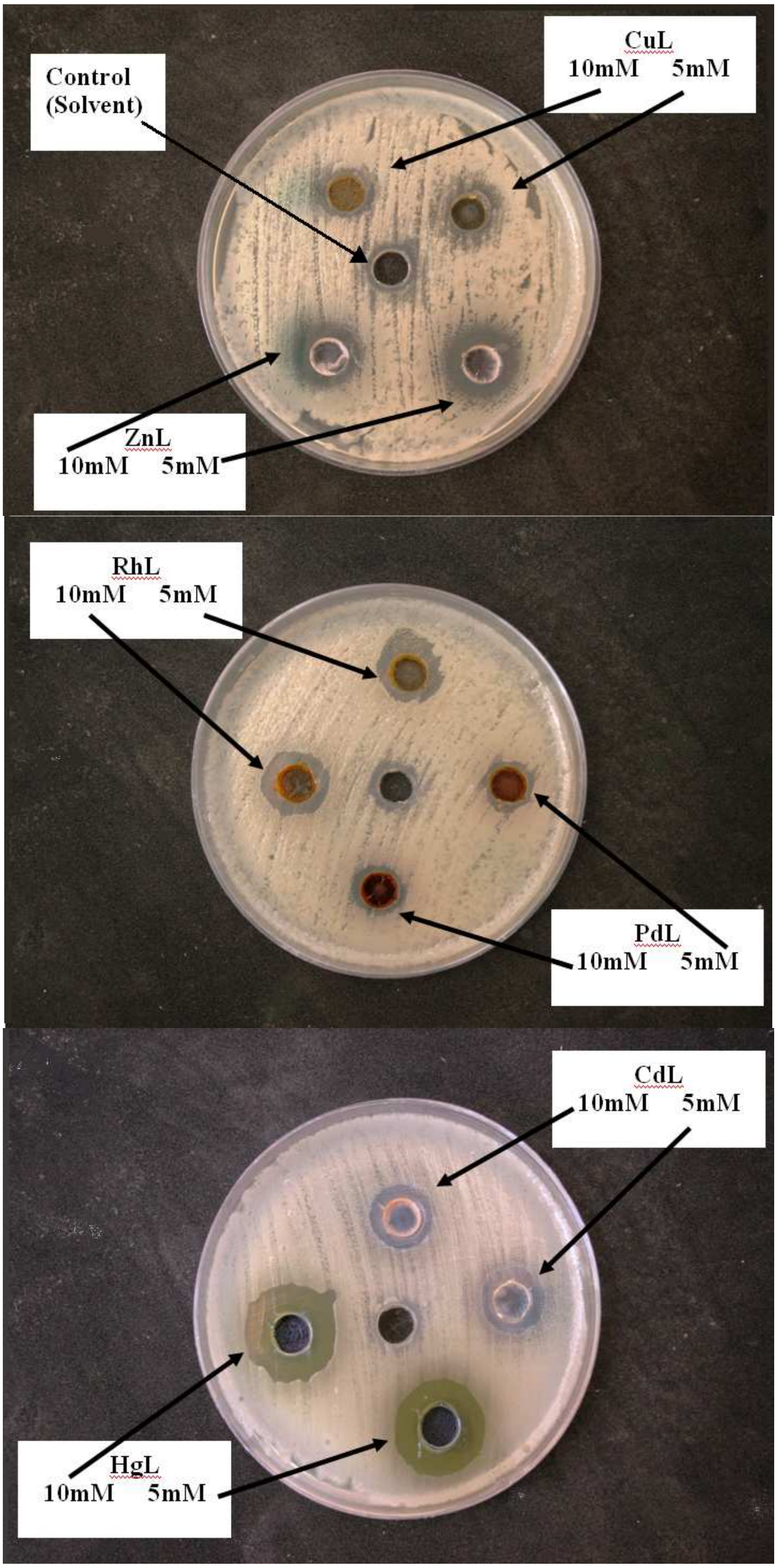


Fig (4-2): The antibacterial activity for dithiocarbamate metal complexes toward Pseudomonas aeruginosa

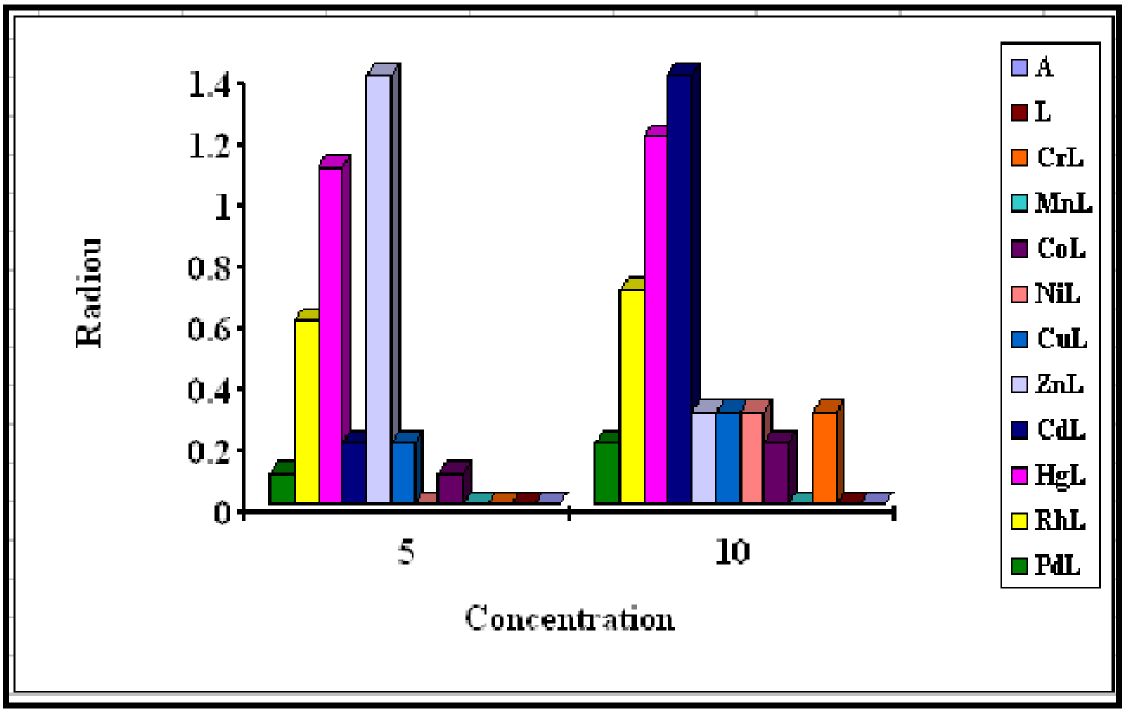


Fig (4-3): Shows the effect of Staphylococcus aureus bacterial toward complexes of L.

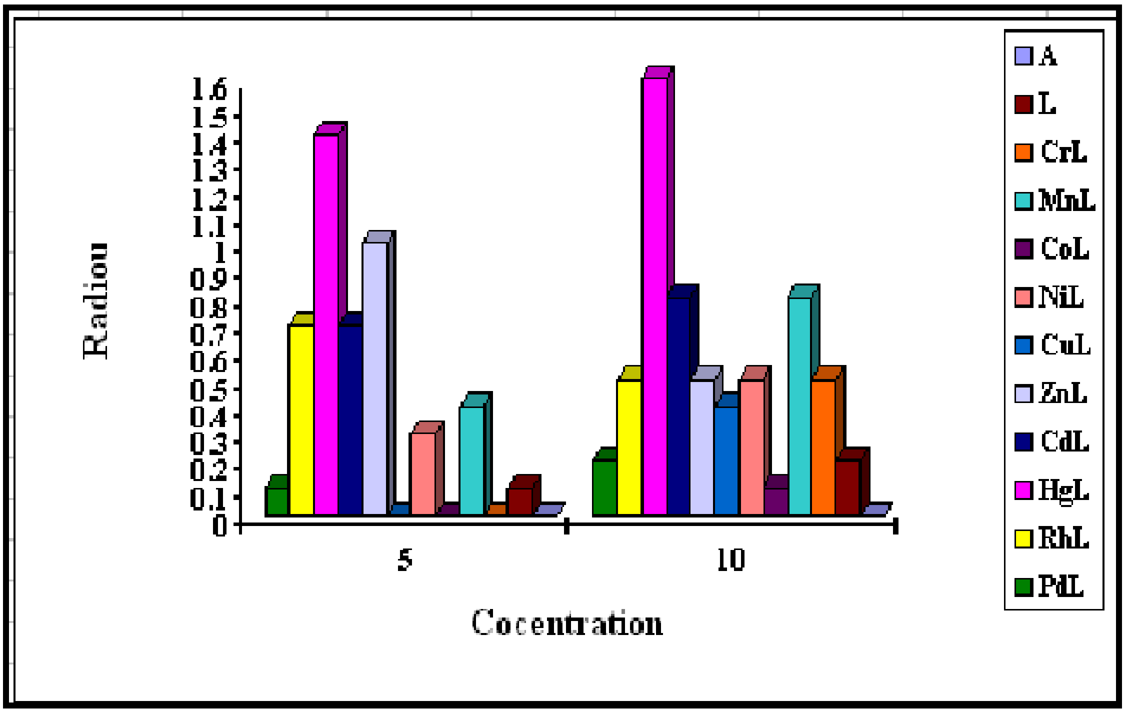


Fig (4-4): Shows the effect of Pseudomonas aeruginosa bacterial toward complexes of L.

Suggestions for future work:-

We hope to continue our extensive program directed towards the synthesis of novel biheterocycles of potential biological applications. On the bases of the experience gained during this work, one can suggest the following as projects for future work:-

1. Synthesizing and isolating new organic compounds by using different substitution thiazole to study the effect of these substituants on the thiazole along with their metal complexes and compare their chemical and biological activities with our new compounds.
2. Synthesizing new complexes using other sets of metal ions.
3. Performing stability of constant studies for the new complexes at different temperatures.
4. Continuing further theoretical studies on the new compounds, such as the evaluation of electronic spectra.
5. Making a screening antifungal activity of the dithiocarbamate ligand and all the metal complexes, to explore their activity and the synergic effect between the metal and the ligand.
6. Using C.H.N. microanalysis and NMR techniques to complete the identification of the structures of the prepared dithiocarbamate ligand and its metal complexes.
7. Studying the nature of the prepared complexes in solution in different solvent following the molar ratio or Job method.

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الخلاصة

تم في هذا البحث تحضير ليكند مخلبي جديد والذي أختبر لتحضير سلسله من معقدات بعض العناصر الانتقالية {Mn(II),Co (II), Ni (II),Cu(II),Zn(II),Hg (II),Cd (II),Pd(II)} {Cr(III), Rh (III)}

تم عزل الليكند الجديد [بوتاسيوم (بنزوثايوزل-2-دايثايوكاربميت هيدرازايد)] ثم تم تشخيصه بواسطة القياسات الفيزياوية المناسبة وكذلك باستخدام الأشعة تحت الحمراء والأشعة فوق البنفسجية-المرئية.

الدايثايوكاربميت هيدرازايد(L) أستخدم كمركب مانح لتحضير سلسلة من المعقدات الجديدة مع أيونات فلزيه مختارة وتم دراسة وتشخيص المعقدات بواسطة الأشعة تحت الحمراء والأشعة فوق البنفسجية-المرئية والتوصيلية الكهربائية والقياسات المغناطيسية بدرجة حرارة الغرفة بالأضافه إلى الامتصاص الذري أللهبي، بهذا أتضح عدد من الخصائص التركيبية والسلوكية عند دراسة معقدات الدايثايوكاربميت هيدرازايد المحضرة في هذا البحث، كذلك تم حساب معامل راكاح والمجال الليكاندي باستخدام مخططات تانابا-سوكانو المناسبة التي ساعدت على إيضاح طبيعة التأصر بين الفلز المركزي و ذرات الليكاند المانحة.

وقد أستنتج أن {$[CrL_3].3EtOH,[CuL_2(H_2O)_2].H_2O, [NiL_2(H_2O)_2].4EtOH$} لها الشكل الهندسي ثماني السطوح ومعقدات {$[RhL_2]Cl, [PdLCl].1.5EtOH$} لها الشكل الهندسي مربع مستوي ومعقدات {$[CoL(H_2O)Cl].3EtOH, [ZnL_2].3EtOH, [MnL_2].1.5EtOH,[CdLNO_3].3EtOH , [HgL_2].XH_2O$} لها الشكل الهندسي رباعي السطوح.

كذلك تم معالجة تكوين المعقدات نظريا في الطور الغازي. وباستخدام برنامج Hyperchem6 وباستخدام الدوال ZINDO\1-PM3 لحساب حرارة تكوين (ΔH°_f) لليكند والمعقدات فضلا عن طاقة الترابط (ΔE_b) وبدرجة 298 كلفن. وكذلك تم حساب الجهد الألكتروستاتيكي لبيان المواقع الفعالة فيه. وتم حساب التردد الاهتزازي لليكند نظريا وباستخدام

طريقة PM3 ، ووجد بأن هناك توافق كبير بين القيم العملية والمحسوبة نظريا مع أمكانية تشخيص الحزم بشكل أدق.

جرى دراسة الفعالية البايولوجيه للمركب البدائي وجميع المركبات المحضرة واختير نوعان من البكتيريا(***Staphylococcus aureus***) موجبة الصبغة و (***Pseudomonas aeruginosa***) السالبة الصبغة وباستخدام تركيزيين (10 ملي مولاري و5 ملي مولاري) في وسط زراعي متعادل. وقد أظهرت النتائج زيادة في فعالية بعض المعقدات بالمقارنة مع الليكند المحضرة منها. تم تفسير الفعالية المضاده للبكتيريا ألى حصول التأثير المتداوب للفعالية بين الفلز والليكند بسبب اختلاف في تراكيب الهندسية المركبات المحضرة.

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

تحضير والدراسة التركيبيه والفعالية البايولوجية والمعالجة النظرية لبعض معقدات الليكاند المخلبي الجديد

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

من قِبَلْ
سمر عدنان أحمد
بكالوريوس علوم في الكيمياء
كلية العلوم–جامعة النهرين
2005

بأشرف
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