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AL-Nahrain University
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Chemistry Department



*Synthesis, Structural ,And Anti bacterial Activity
Studies of Some Transition Metal Complexes of New
Some Trithiocarbonate Derivatives*

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for the Degree of Master in Chemistry*

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محمد المصطفى (صلى الله عليه وسلم)

إلى من منحني نعمة الانتماء واسقني من ماء فرائده إلى من رعاني وضمني إليه إلى من أدين له بكل هذا.

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إلى استاذي القدير الذي شجعني على خوض التجربة وجعلني امسك بدفة المركب وبموج هذه الحياة

رحمه الله الدكتور اياذ حمزة

إلى الذي بذل جهد السنين سخياً وصاغ الأيام سلماً لارتقي به إلى طريق الحياة من أحمل اسمه

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والذي العزيز.

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Symbols and abbreviations

FT-IR	Fourier transformer Infrared
Uv-Vis	Ultraviolet-Visible
DMSO	Dimethyl sulfoxide
EtOH	Ethanol
oh	Octahedral
B.M	Bohr magneton
nm	Nanometer
B	Racha parameter
β	Nephalaxetic factor
dec	Decomposition
(OAc)	Acetate group

Abstract

The new ligands have been prepared in this work (potassium 2-carbomethoxy amino 5-5trithiocarbonate 1,3,4-thiadiazole) (LI) was prepared from 2-carbomethoxy amino-5-mercapto 1,3,4-thiadiazole with CS₂ in alkali media , while the second ligand was prepared from 2-N(4-N,N-dimethylamino benzyliden)-5-mercapto 1,3,4-thiadiazole with CS₂ and in alkali media to obtain potassium 2-N(4-N,N-dimethylaminobenzyliden)4-trithiocarbonate 1,3,4-thiadiazole (LII).The products were isolated and characterized by appropriate physical measurement , vibrational and electronic spectroscopy .

The new ligands have been used to prepare a number of new complexes with the selected metal ions Cd(II), Cu(II) , Ni(II) , Co(II) , Fe(III) , and Mn(II) . These complexes were studied and characterized using FT,IR, UV-Vis. spectra, molar conductivity, magnetic susceptibility , melting point , and atomic absorption measurement. We concluded that the [Cu₂L₂Cl₂(H₂O)₂]. 3C₂H₅OH, [Ni L₂ Cl₂].2H₂O, [Fe₂L₂(OH) ₂ Cl₄] .4H₂O and [Mn L₂ (H₂O)₂] . 2H₂O have octahedral geometry while [Cd L₂]. 3C₂H₅OH and [Co L H₂O Cl] .3H₂O have tetrahedral geometry for the complexes of LI.

While octahedral geometry for the complexes of LII for the [Cu L₂ (H₂O)₄ Cl₂].2H₂O , [Mn L₂ (H₂O) (OAc)].3 H₂O [Ni L₂ (H₂O)₂ Cl₂].C₂H₅OH , [Fe₂ L₄ (OH) ₂].5H₂O and [Co₂L₂(H₂O)₄Cl₂]. 2.5 C₂H₅OH ,But [Cd L₂]. 4C₂H₅OH have tetrahedral geometry

Different bonding and structural behavior were revealed through the study of the coordination chemistry of the metal complexes of the new ligands.

The nature of bonding between the metal ion and the donor atom of the ligands were demonstrated through the calculated Racah parameter and the other ligand field parameters,which were calculated using the suitable Tanaba-sugano diagram.

The antibacterial activity for the ligands and their metal complexes were studied against two selected microorganisms *pseudomonas earuginsa* and *staphylococcus aureus* using (10mM) 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 ligands , these were attributed to the synergetic effect between the metal ion and the ligand , in addition to the difference in the structural varieties .

Chapter one

Introduction

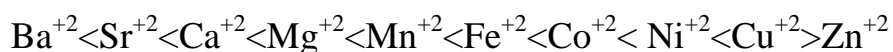
Chapter one

Introduction

(1-1) Interaction of ligand with metal ion

The study of the interaction of metal ions with different simple and complicated systems requires, first of all, to be aware of the essential bases of coordination inorganic chemistry especially the structure and bonding aspects of the most important theories in this respect is the hard and soft acids and bases Concept (HSAB) of Pearson⁽¹⁾, which show the tendency of metal ions to coordinate with certain groups in the structure of the ligand depending on the nature of the donating atom in this group⁽¹⁾, also to know the factors affecting the stability of the resulting complexes.

One of the earliest correlations was the Irving – Williams's series of stability. For a given ligand the stability of complexes with divalent metal ions follows the order



This order arises in part from a decrease in size across the series and in part from ligand field effects^(1,2). A second observation is that certain ligands form their most stable complexes with metal ions such as Ag^+ , Hg^{+2} and Pt^{+2} , but other ligands seem to prefer ions such as Al^{+3} , Ti^{+4} and Co^{+3} . Ligands and metal ions were classified as belonging to type (a) or (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 state 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 state such as Cu^+ , Ag^+ , Hg^{+2} , Pt^{+2} , and Pd^{+2} . According to their preferences toward either class (a) or class (b) metal ions, ligands may be classified as type (a) or (b)

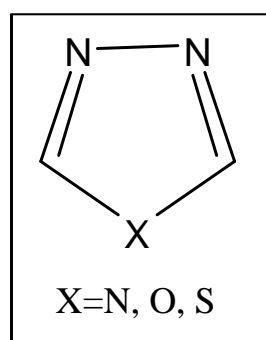
Tendency to complex with Class (a) metal ions	Tendency to complex with Class (b) metal ions
N>>P>As> Sb	N<<P>>As>Sb
O>>S>Se>Te	O<<S<Se_ Te
F>Cl>Br>I	F<Cl<Br<I

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

One of the most important phenomena that control the stability of oxidation state of a certain element and the stabilization of one state among another state is known as (symbiosis)⁽⁴⁾, often metal complexes expand their coordination number by interaction with Lewis bases. This may take place by interaction association or by adduct formation with solvent or other available ligand⁽²⁾, The physical properties of the resulting complex often are significantly different from those of the complex not having the expand coordination number.⁽⁵⁾

(1-2) Thiadiazole compounds

The most important heterocyclic compounds containing two nitrogen atoms and another heteroatom, have the following structure:-



compounds
heteroatom,

oxadiazole

The central ring is called 1,3,4-oxadiazole when $X=O$, 1,3,4-triazole when $X=N$, and 1,3,4-thiadiazole when $X=S$ ⁽⁶⁻⁸⁾ when thiol group is substituted at position 5, the thioamide group is formed. This

group is included many common pharmaceutical structures ⁽⁶⁻¹⁰⁾, the presence of this group within a biologically active structure increase its activity too.

It can be found as part of an open series (aliphatic) like thioisocyanate or thiocarbamate or thiosemicarbazide, these structures have biological important⁽⁹⁾

Thiadiazole derivatives have been prepared by substitution on the 2-and 5 position with different functional groups, A large number of 1, 3, 4 - thiadiazole derivatives have been prepared using certain substituents, and then screened for their activity as anti-bacteria or anti-fungal, These substituents include amino group or derivatives like acetamide or any other amide, thioalkyl, thioalkynyl radicals, disulfide or another heterocyclic ring ^(11,12), e.g. 5-(sub)-2-(amino derivative) 1, 3, 4-thiadiazole.

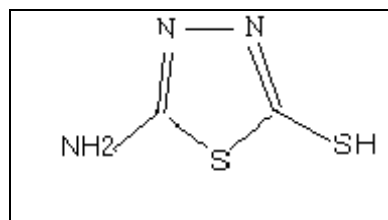
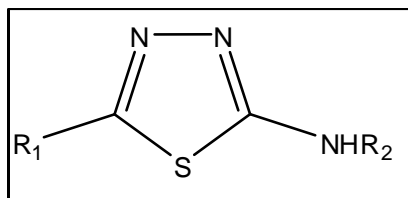
R₁= phenyl, or substituted phenyl, halogen

, alkyl, furanyl, benzyl, amine

R₂= H, alkyl, cycloalkyl, phenyl, substituted phenyl and alkyl. Many ways were used to

prepare the derivatives of this ring.

V. Petrow ⁽¹³⁾ has prepared the compound

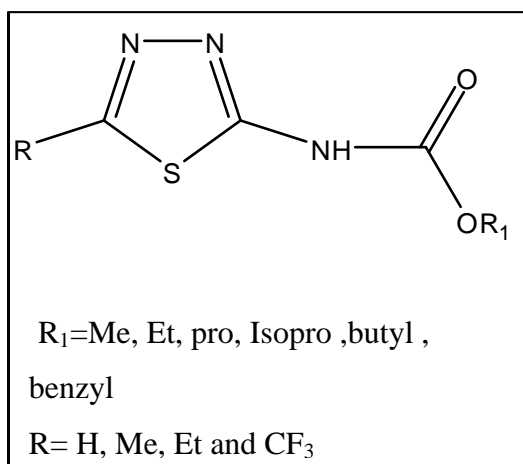


potassium thiosemicarbazide dicarboxylate in alcoholic solution under pressure.

Another method, gave high percentage, was used to prepare the same compound (previous structure where R,R₁= -SH) by heating thiosemicarbazide, carbon disulfide and potassium hydroxide or potassium ethyl xanthate in alcohol or ethylene glycol.

Another series of some derivatives include 2,5-dimercapto-1,3,4-thiadiazole by hydrolysis of thiosemicarbazide to hydrazine that reacted with carbon disulfide⁽¹³⁾

A glance at the standard references show that most of the studies has been carried out on 1,3,4-thiadiazole containing compound which synthesized and tested for their antimicrobial activity against *E-coli*, *Bacillus anthracis* and *staphylococcus aureus* and found to



are

inhibit the growth of *Bacillus* -anthracis such as derivatives of thiadiazole containing Me, CF_3 , propyl Groups.

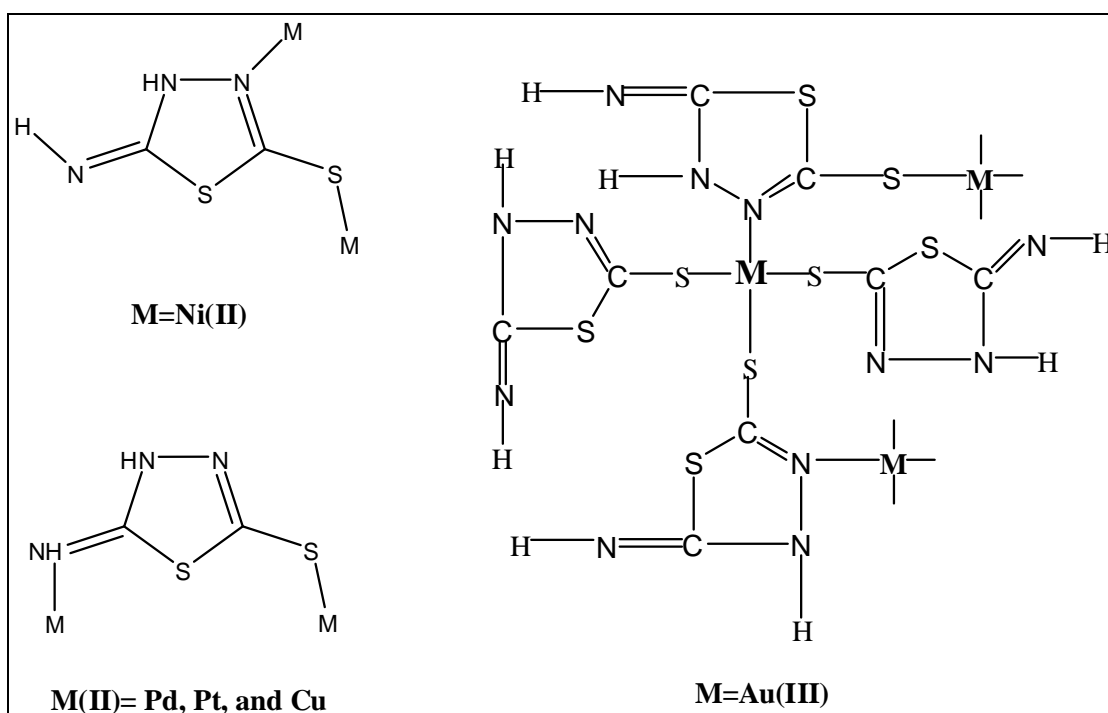
(1-3)Metal complexes of thiadiazole and its derivatives

The thiadiazole ring and its derivatives possess good coordination behavior, since they have sulfur atom and two nitrogen atoms in addition the substituents having donating group in the structure, therefore the study of its metallic complexes is of structural important in addition to many important applications⁽¹¹⁾.

In 1975 some complexes of 5-amino-2-thiol-1,3,4-thiadiazole with some transition metals were prepared and characterized. It was found that the metals: ligand ratio was 1:1 in case of Cu^{+2} , Ag^+ , and Tl^+ and 1:2 in the case of Zn^{+2} and Cd^{+2} in addition to the two complexes $\text{Pt}(\text{pph}_3)_2 \text{L}_2$ and

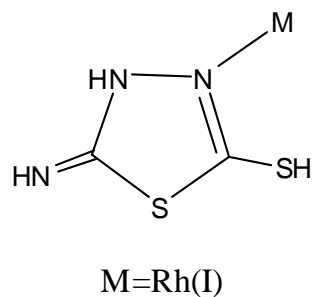
$\text{Pd}(\text{pph}_3)_3 \text{L}_3$, the expected structures for these complexes were suggested on the basis of element analysis, spectroscopy study and results from magnetic measurement⁽¹⁴⁾.

In the same year the complexes of Ni(II), Rh(I), Pd(II), Au(III), and Cu(II) with the same derivatives have been prepared. The probable structures have proposed for the complexes on the basis of visible and infrared spectral data, magnetic susceptibility data and on the results of chemical analysis⁽¹⁵⁾. The following were the proposed structures



In a subsequent work a series of Ru(I), Rh(I), and Ir(I) complexes of some derivatives were prepared by John and Arora and then characterized by their thermal behavior and they were found to be stable up to 200°C then decomposed above this point giving the free element in its solid state⁽¹⁶⁾.

Introducing the acetylenic group in the the ring of mercaptoamino Thiadiazole contribute to the change of coordination behavior of this ring due to the ability of this moiety to coordinate with metal ion through sigma or pi bond .



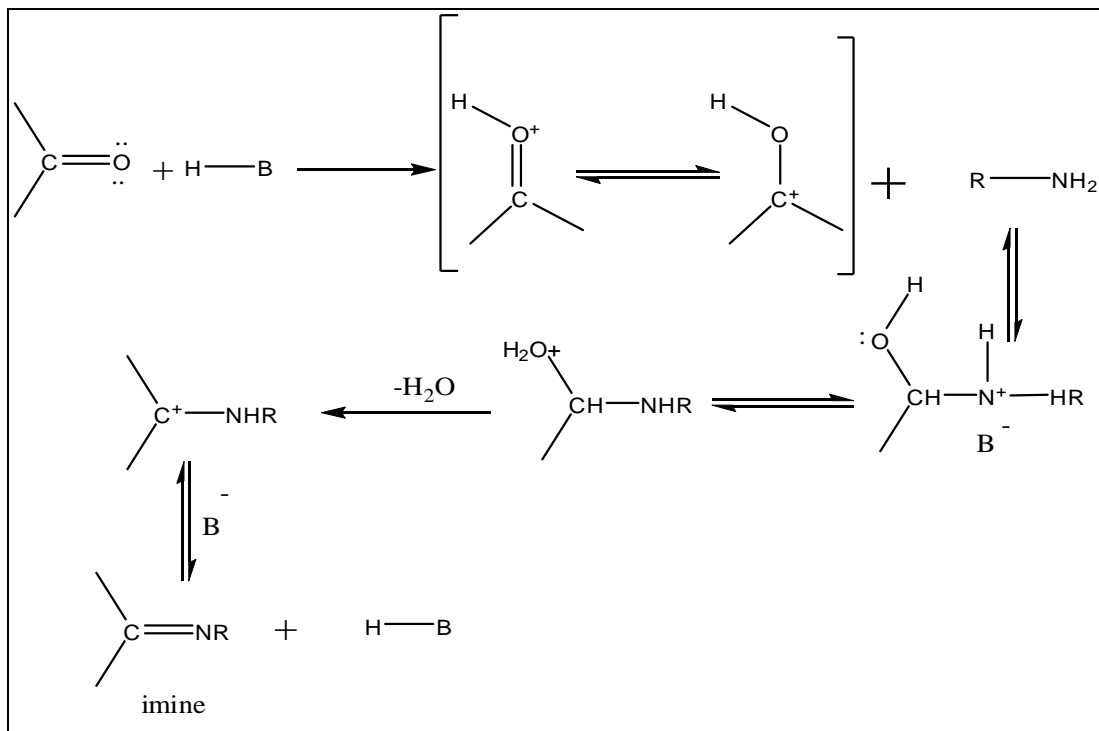
structure of many

(1-4) Schiff bases

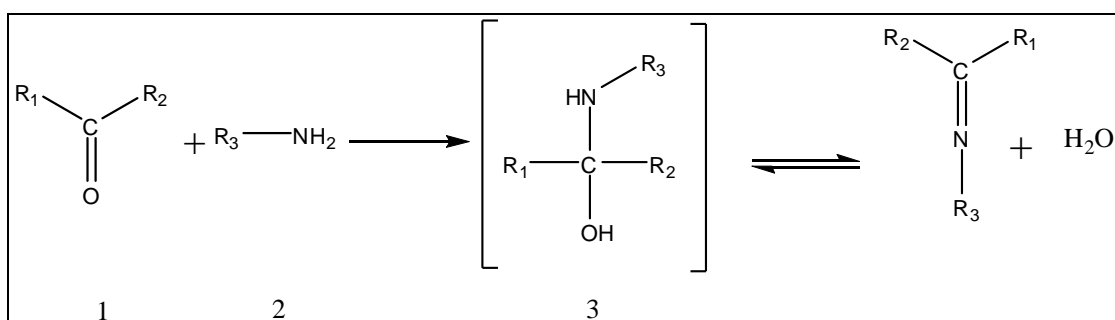
This term "Schiff bases" used to define those organic compounds which contain the functional group (C=N). Schiff bases were firstly prepared by Schiff in (1864)⁽¹⁷⁾, from condensation reaction of aldehydes or ketones with primary amines . Imines have several nomenclature such as anils, imines ,azomethine ,benzanils and benzylideneanilines .⁽¹⁸⁾ Imines, and other (C=N) compound can be reduced with LiAlH₄, NaBH₄, Na-EtOH, Hydrogen, and catalyst as well as with other reducing agents ⁽¹⁹⁾ Schiff bases can be rapidly decompose in aqueous acidic media , but they are very stable basic solution ⁽²⁰⁾ . (SB) can be obtained by condensation reaction between carbonyl compound (1) and amine (2) with the formation of amino alcohol as intermediate (3).

The experimental conditions depend on the nature of amines and especially of the carbonyl compound which determine the position of the equilibrium.

The addition of proton to the carbonyl group yields the conjugated acid in which the carbon of the carbonyl group is more electrophelic, thus facilitating the attack of the amine on the carbonyl group . The added acid with enhance elimination of water molecule to give final product (SB) that suggested by Hammett as follow⁽²¹⁾ ;



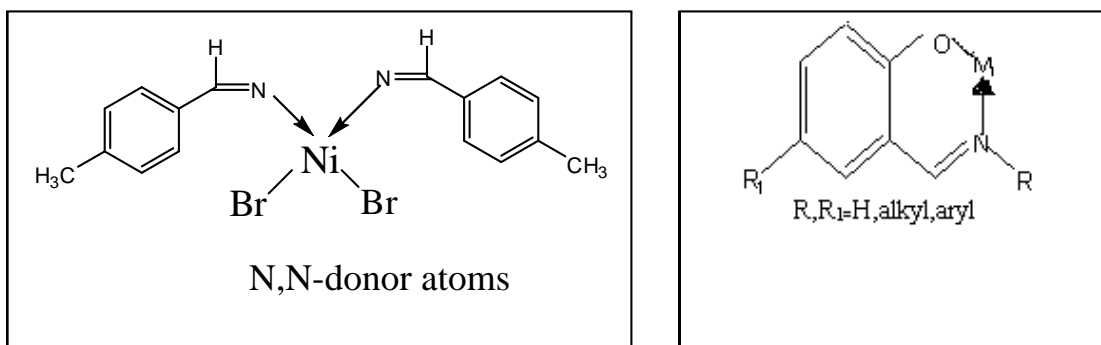
The general mechanism of the Schiff bases formation reaction can be depicted as follow



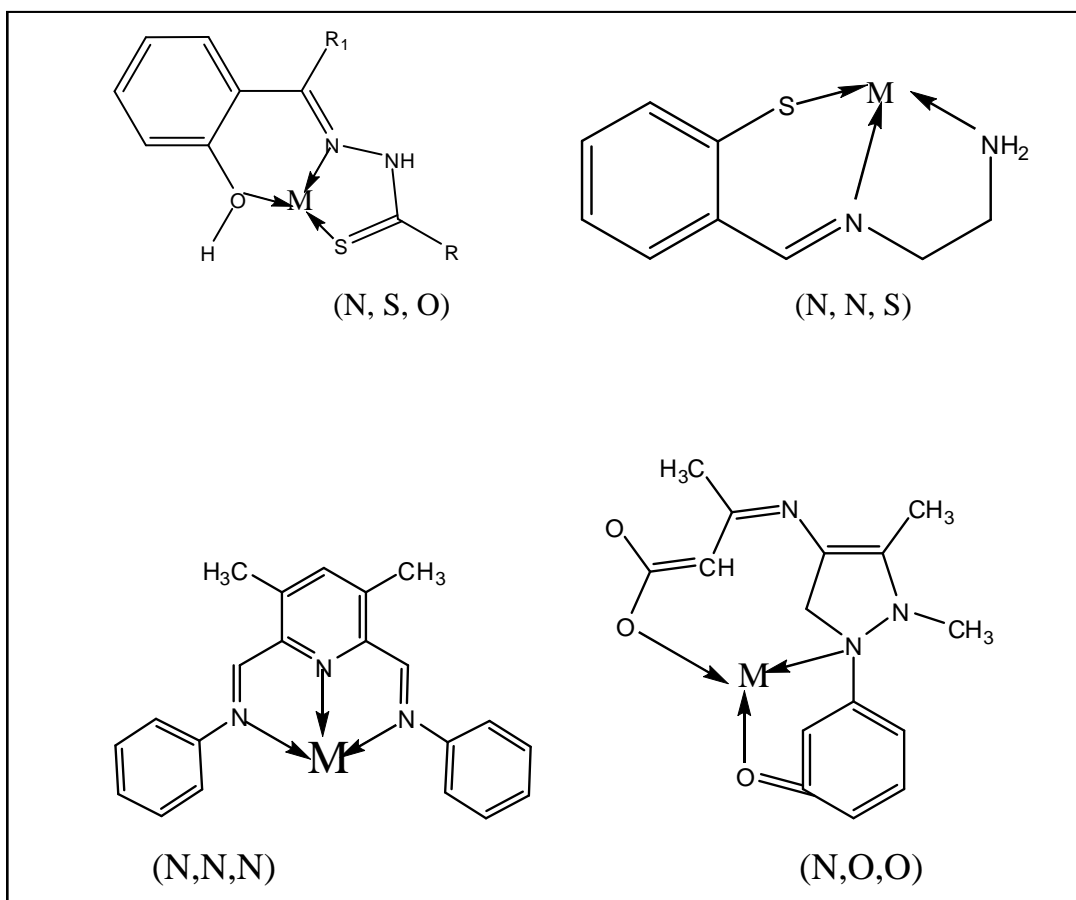
These bases can also be prepared by refluxing of equimolar quantities of aldehyde or ketone with amine by slow melting for minute and then isolating and purifying the product by recrystallization or sublimation under reduced pressure^(18,22).

Staab⁽²³⁾ prepared Schiff bases by removing water which was formed by condensation of aldehyde with amine and by reflux in benzene. This was done by mixing the amine and the aldehyde in benzene and then the residual solution

Bidentate Schiff bases have among ligands that are extensively used for preparing metal complexes. These ligands are described according to their donor set N,N^(24,25)-donor and N,O-donor Schiff bases⁽²⁶⁾ for example .



Tridentate Schiff bases may be generally considered as derived from the bidentate analogs by adding another donor group, These have been utilized as an ionic ligand having (N, N, O) , (N, N, S) , (N,O,O) , and (N,S,O) donor set^(27,28) as shown below :-



Schiff bases exhibit good antimicrobial activity and pharmacological applications, these compounds show good fungicidal activity and antiviral, inflammatory activities and play as antioxidant, anticancer. Artificial receptors for biologically active molecules have attracted attention from the viewpoint of molecule recognition⁽²⁹⁾.

(1-5) Metal complexes of Schiff bases as biologically important compounds:

Schiff bases and their metal complexes have received a great deal of attention during the last decade by many workers to prepare new sets of these bases and their transition metal complexes.⁽³⁰⁾ These complexes have been proven to be antitumor and have carcinostatic activities^(30,31) They show leukaemic activity, Schiff bases on other side, have greater importance in biological reactions like (visual process)⁽³²⁾ and in the reaction that involve removing the amine group by enzymic effect (enzymatic transition reaction) and some B₆-catalysed reaction⁽³³⁾.

The biological activity of Schiff bases is attributed to the formation of stable chelates with transition metal ions present in cell.⁽³⁴⁾

Schiff bases derived from sulfa drugs have been successfully used for the bacteriostatic activities and complexes⁽³⁵⁾. A great deal of work concentrated on the cobalt (III) complexes, that they are used as reversible oxygen carriers or model for vitamin B₁₂ co-enzyme. The attention was also extended to Fe(II) and Fe(III). Complexes which are included in the hemoglobin found in some biological system⁽³⁶⁾

It has been noticed that the number of papers regarding the preparation of palladium and platinum complexes with Schiff bases increase

The discovery of cis- platinum complexes cis-[Pt(NH₃)₂Cl₂] as an antitumor agent by Recabarren⁽³⁷⁾, led to development of platinum complexes chemistry designed for wide biological applications⁽³⁸⁾

Palladium and platinum are regarded as soft metals, so they react with soft ligand that contain an electron-donating group like S and P, they also can form complexes with hard ligand⁽³⁹⁾ like oxygenating molecules or molecule which contain nitrogen.

The research work⁽⁴⁰⁾ appeared which deal with the study of palladium interaction with Schiff bases through cyclometalation reaction (this include metal containing cyclic in which the metal is bonded to carbon atom). This reaction plays an important role in preparation of some organometalic compounds in which these complexes are used as starting materials to improve the stereochemistry of these compound also these complexes were used in the photochemical reactions.

(1-6) Ligands containing sulfur as a donor atom

The sulfur atom can act either as terminal or bridging ligands, The dianion S²⁻ is also an effecting ligand, and chelating poly sulfides (-S_n-) are well established⁽⁴¹⁾, These various sulfur ligand will be briefly considered before dealing with the broad range of compounds in which sulfur act as the donor atom e.g. H₂S R₂S and dithiocarbamate and related anions, 1,2-dithionlenes etc. ligands in which sulfur acts as donor atom are usually classified as (soft) Lewis bases, in contrast to oxygen donor atom ligands which tends to be hard⁽⁴¹⁾

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, H₂S really form simple adducts due to its ready oxidation to sulfur or its facile

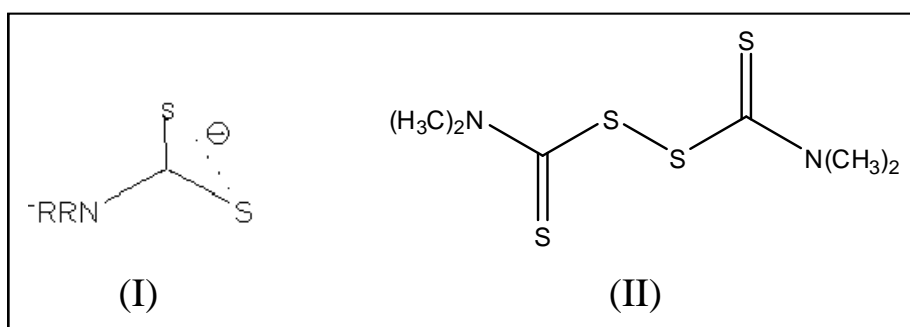
deprotonation to H_2S or HS^- , $[\text{AlBr}_3(\text{SH})]$ has long been known as stable compound of tetrahedral transition metal complexes having some degree of stability at room temperature are more recent vintage; $[\text{Mn}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{SH}_2)]$ and the trigonal cluster complexes $[\text{Ru}_3(\text{CO})_9(\text{SH}_2)]$.

Another large class of sulfur donor ligands comprises the dithiocarbamate $\text{R}_2\text{NCS}_2^{2-}$ related anions YCS_2 , e.g. dithiocarboxylate RCS_2^- , trithiocarbonates SCS_2^{2-} , xanthates ROCS_2^- , and dithiocarbonate OCS_2^{2-} .

(1-6-1) Dithiocarbamate derivatives as active ligand

Dithiocarbamate are normally prepared by alkali metal salt by action of primary or secondary amines on CS_2 in presence of NaOH .⁽²⁾

Dithiocarbamate are used to stabilize a wide range of oxidation state of different metal ion⁽⁴¹⁾. Dithiocarbamate structure (I) was known as fungicides therefore many research projects were extended and directed to prepare another type of fungicides of this type. The N,N-dimethyl derivatives were found to be the most active compound in vitro and vivo compound to large number of compounds that have been screened for their activity, and the oxidation product for this compound (II) was used as commercial fungicide.⁽⁴²⁾

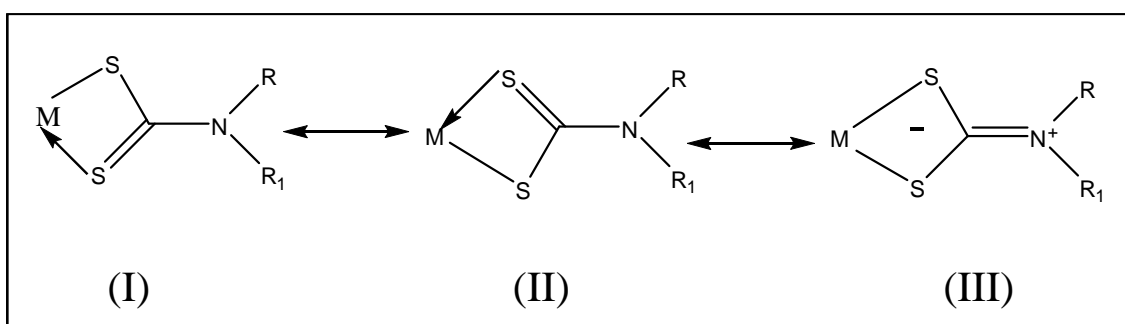


On other side strong amino bases derivatives of dithiocarbamate show an anti-oxidation activity against ionization radiation in experiment done

using mice . These types of compound also have an ability to be used as accelerators for vulcanization process in rubber industry ⁽⁴³⁾ and in imaging technology.

(1-6-1-1) Structure of metal complexes of dithiocarbamate linkage

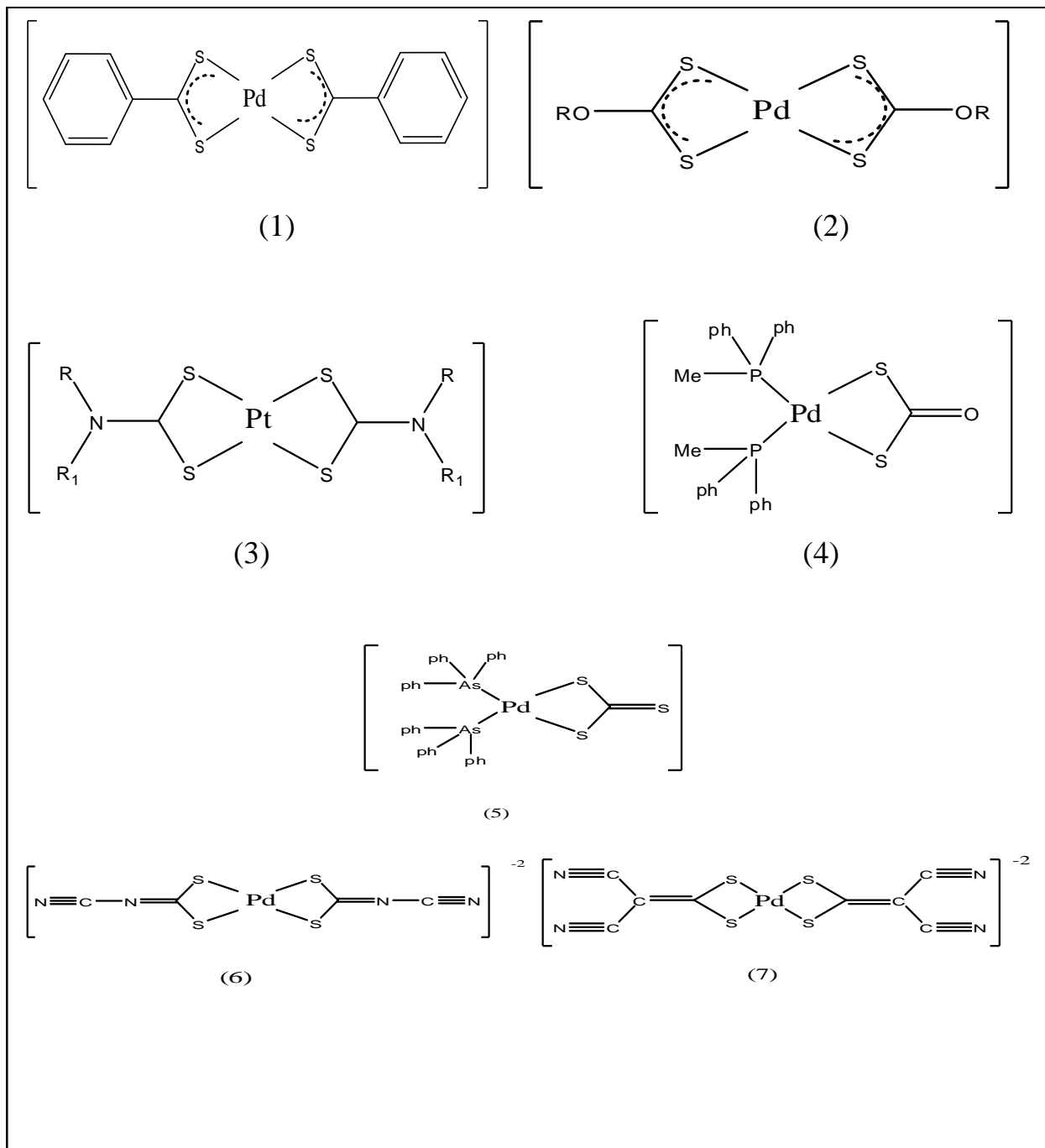
The metal complex, especially the transition metals of dithiocarbamate have been extensively studied due to their important and uses in many aspects . Therefore the structure of these complexes where a subject of numerous studies ⁽⁴⁴⁾



There is very strong evidence that the canonical form (III) is an important contributor to the structure for a variety of transition metal ions (Ni(II) , Cu(II) , Fe(III) , etc.) both from infrared spectroscopy^(44,45) which show a C-N bond intermediate between a single and double bond and from X-ray diffraction data⁽⁴⁶⁾ , which show C-S and C-N bonds of intermediate character . This structure affects the physical and chemical properties of the complexes, The contribution of structure (III) was greatest for the corresponding dialkyl complexes , lower for more complex aliphatic chain and it is relatively small for heterocyclic derivatives ⁽⁴⁶⁾. Perhaps because of the rigid heterocyclic ring system, which shows fewer tendencies to release the electrons to the nitrogen –carbon bond and as consequence, this bond has a less double-bond

Four – membered chelate ring were formed by palladium (II) with Dithiobenzoate (1) , alkylxanthates (2) , dialkyldithiocarbamate (3) dithiocarbamate (3,where R=H), dithiocarbonate (4)

Trithiocarbonate (5) ,N- cyndithiocarbamate (6).1,1-dicynoethylene-2,2-dithilae

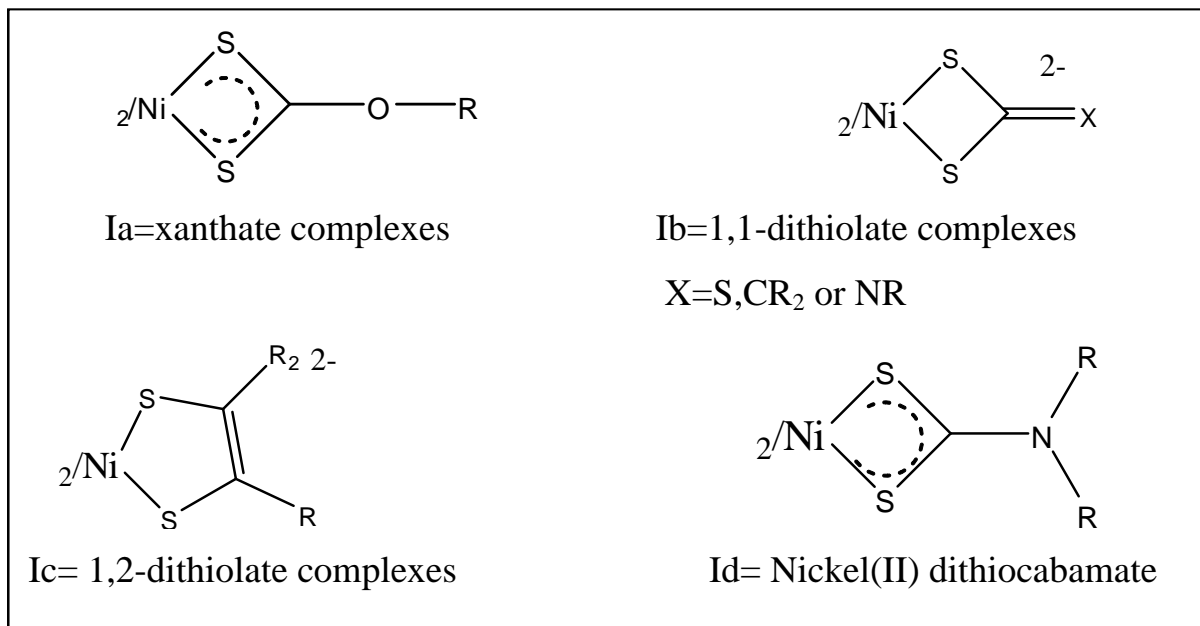


The xanthate complexes are generally less stable than Dithiocarbamate complexes. A comparison of the infrared spectra of these two complexes has suggested that there is considerable double bond character in the C-N bond of coordinated⁽⁴⁶⁾ dithiocarbamate (8), but little double bond character in C-O bond of coordinated xanthate (9)

This is lead to mesomeric drift of electrons to the sulfur in the dithiocarbamate complex so increasing the donor ability of the sulfur atom of the dithiocarbamate ligand over that of the sulfur atom of xanthate ligand so that the dithiocarbamate form the more stable complexes⁽⁴⁸⁾. It was well documented that the ability to interact with bases seems to be related closely to the electronic properties of the ligand as a whole, not just the atoms bonded to the metal. Thus xanthate complexes (Ia)^(49,50) of nickel (II) strongly interact with Lewis bases while the electronic spectra of 1,1-dithiolate complexes⁽⁵¹⁾ (Ib, X=S, CR₂ or NR) or 1,2-dithiolate complexes⁽⁵²⁾ (Ic) are unperturbed even by dissolution in solvents which are good bases. The complexes of dithiocarbamate have many applications⁽⁵³⁾ such as zinc dialkyl dithiocarbamates are antioxidants. Nickel dithiocarbamate inhibits the photodegradation of

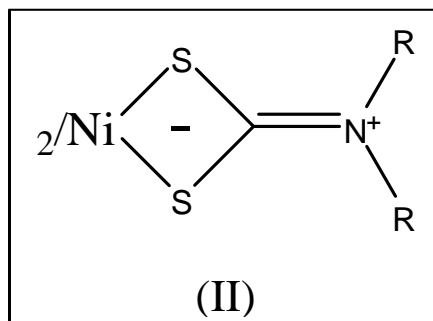
The Fe (II) , Fe (III) ,dithiocabamate have been studied for their spin-crossover phenomenon ,Cu (II) dithiocarbamate was successfully used as single source precursor for growth of semiconducting copper sulfide thin film .

The nickel (II) dithiocarbamates^(54,55) (Id) display a behavior toward adduct



on which is intermediate to the extremes mentioned above for the xanthates and dithiolates.

In fact the tendency for adduct formation appears to be related to the degree to which a canonical structure of type (II) is important ⁽⁵⁶⁾ in describing these complexes .

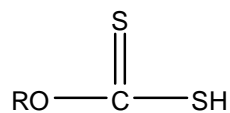


(1-6-2) Thiocarbonte and thioxanthate compounds

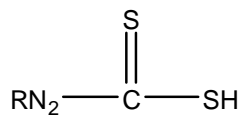
Xanthate , dithiocarbamates and organotrithiocarbonates are the salts of the corresponding xanthic [I] , dithiocarbamic [II] ,

and trithiocarbonic (or thioxanthic) [III] acids respectively . All characterized by

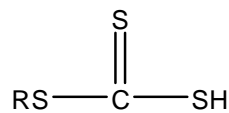
the presence of the $\text{—}\overset{\text{S}}{\parallel}{\text{C}}\text{—S}$ group ⁽⁵⁷⁾



[I]



[II]



[III]

(R= alkyl or aryl group)

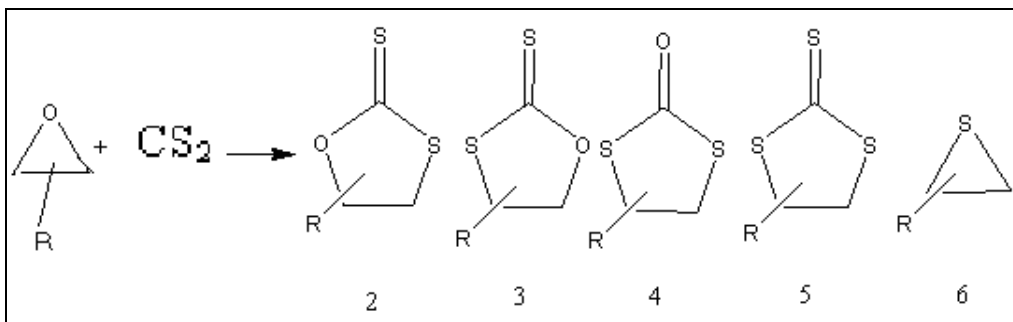
Thioxanthic acid like xanthic and dithiocarbamic analogues can't themselves be isolated , but from complex of the type $\text{M}(\text{S}_2\text{CSR})_n$ which are known for a limited number of alkyl substituents R ⁽⁵⁸⁾

The related planer trithiocarbonate ion CS_3^{2-} forms numerous yellow salts , which are formed by the action of SH on CS_2 in alkaline solution ;



The free acid of CS_3^{2-} ion can be obtained as red oil stable at low temperature ⁽³⁾

Cyclic thiocarbonate have received much attention in view of biological activity and material science ⁽⁵⁹⁾ . One of the most efficient methods for synthesizing of cyclic thiocarbonates was performed by reaction of epoxide with carbon disulfide . Depending on the catalysts and reaction conditions five-membered cyclic dithiocarbonates (2) , its regioisomers (3) , and (4) trithiocarbonate (5) , and episulfide (6) have been reported to formed



Trithiocarbonate are used as antiwear and antioxidant additives to extreme pressure lubricant oil and greases ⁽⁶⁰⁾. The activity of the thioicarbonate and thiocarbamate against human tumor ,xenograft in vivo suggests consideration of these two series of derivatives of DM-PEN (DM= 4 dimethyl pendomeding) . (PEN= pinclomedine) for clinical development Dithioacid ligand X-CS₂ (X=OR , SR , NR₂) have a rich coordination and organometalic chemistry⁽⁶¹⁾. These ligands are obtained easily by the addition of the nucleophilies (OR⁻,SR⁻ R₂NH) to carbon disulfide . Dithioacid ligand and their metal complexes have received continuous attraction due to their interesting structural and chemical properties as well as their wide rang of application in biological system.

(1-6-2-1) Metal complexes of thiocarbonates and their applications

Trithiocarbonate complexes have received attention because of the dual nature of metal –CS₃ moiety as an electrophelic and nucleophilic reagents , which makes them versatile intermediates for the synthesis of other thio species by their participation in (i) alkylation at the exocyclic sulfur atom , (ii) displacement of weakly bound ligand from metal complexes (iii) sulfur extraction to give CS₂ complexes or (v) sulfur addition to give CS₄²⁻ complexes .Gold(I) complexes with S-donor ligand are interested because of their potential use in medicine⁽⁶⁰⁾

Although the main application is treatment of a variety of rheumatic disease , some of these compounds have been shown to have anti-leishmanial activity in vitro inhibitory effect on HIV or activity tumor cell .Transition metal

complexes with dithioacid ligand are very common in literatures ⁽⁶¹⁾, they have been generally prepared by metatheses reaction of transition metal halide with the free ligand. In most cases the ligand is bonded to the metal in chelate fashion through the two S atoms, however, several complexes in which made of coordination of the dithioacid ligand is monodentate were obtained

A variety of complexes containing dithioacid ligand with cyclopentadienyl iron system has been reported. Treatment of iron chloride complexes $\text{CpFe}(\text{CO})_2\text{Cl}$, with sodium dialkyldithiocarbamate in acetone give $\text{CpFe}(\text{CO})_2(\text{KS}_2\text{CNR}_2)$ where R= Me or Et which contain a unidentate dialkyldithiocarbamate group.

Organic trithiocarbonates have found many applications in a various fields such as in analysis, organic synthesis, medicine, industry and agriculture of these application are flotation agents, vulcanization accelerators, pesticides, plant defoliant, rust inhibitor, lubricating oil additives, and some have recently been reported to possess activity as anti-radiation drugs ^(58,62).

Chapter two

Experimental part

Chapter two

(2-1) Chemicals

All chemicals used were of the highest purity available, the employed chemicals and their suppliers companies were listed in table (2-1)

Table (2-1): Employed chemicals and their supplier

Compounds	Purity	Supplier
Nickel chloride hexahydrate	99%	BDH
Cadmium chloride dehydrate	98%	BDH
Cobalt chloride hexahydrate	99%	Fluka
Copper chloride dehydrate	95%	Fluka
Magnesium acetate tetrahydrate	95%	Fluka
Ferrous chloride tetrahydrate	98%	Fluka
Dimethyl sulfoxide	95%	BDH
Ethanol absolute	99%	Fluka
Hydrochloric acid	37%	BDH
Methylchloroformate	98%	Fluka
Carbon disulfide	98%	Fluka
Thiosemicarbazide	95%	Merck
Potassium hydroxide	85%	BDH
N,N-dimethyl aminobenzaldehyde	98%	BDH

(2-2) Instrumentation

1- Fourier transform infrared spectrophotometer (FT-IR)

The infrared spectra were recorded on a shimadzo 8400 Fourier transform spectrophotometer (FT-IR) by using the CsI in the wave number range (4000-200) cm^{-1} in College of Science/ Baghdad University .

2- Electronic absorption spectra

The electronic spectra of the complexes were obtained using (shimadzu UV-Vis 1600A) ultra violet spectrophotometer and using the quartz cell in the rang at wave length rang (1100-200)nm in College of Science/ Baghdad university .

3- Magnetic susptibility measurement

The magnetic susptibility values for the prepared complexes were obtained at room temperature using Magnetic susptibility balance of Johnson matting catalytic system division ,(England) in ,College of Science/ AL-Nahrain University

4- Melting point instrument

Gallencamp M.F.B 600.01 of melting apparatus was used to measure the melting point of all the prepared complexes in College of Science/ AL-Nahrain University

5- Metal analysis

The metal content of the complexes was measure by using atomic absorption spectrometric technique by perkin elmer 5000 atomic absorption spectrometer for the determination of metal ion in College of Science/ Baghdad University .

6- Conductivity measurement

The conductivity measurements were obtained by using coring conductivity meter 220 at room temperature in DMSO as a solvent in College of Science/ AL-Nahrain University

(2-3) Preparation of the ligands

(2-3-1) Preparation of 2-amino-5-mercapto -1, 3, 4-thiadiazole (A):

This compound (A) was prepared by the method adopted by petrow and co-workers⁽⁶³⁾ as follow

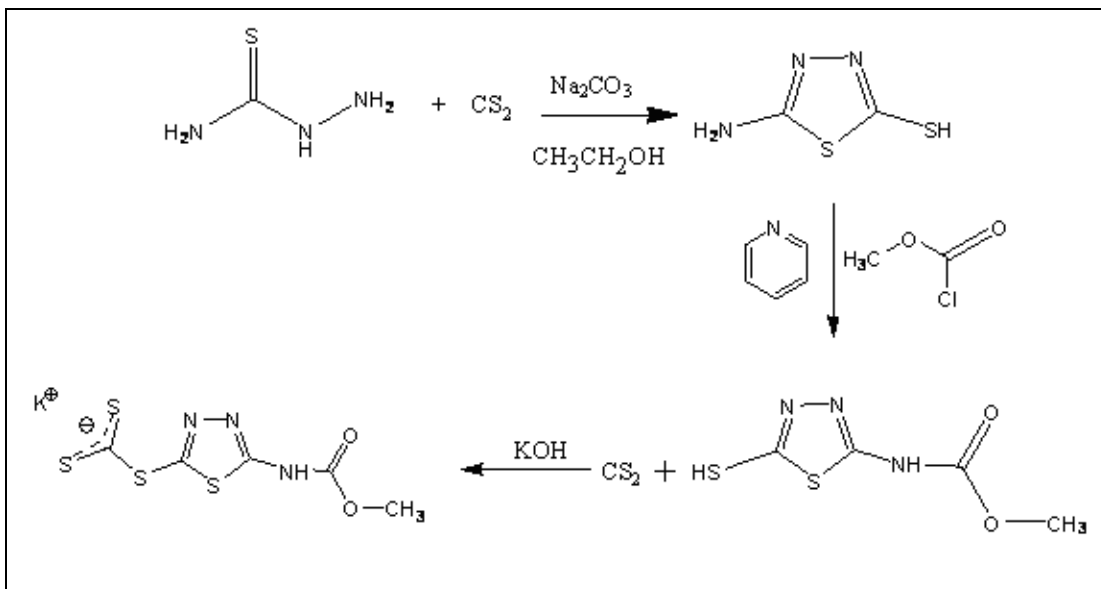
Thiosemicarbazide (3.380g,0.04mole) was suspended in absolute ethanol (20ml) , anhydrous sodium carbonate (2.24)g and carbon disulfide (3.62ml, 4.5g, 0,06mole) were added then the mixture was refluxed with stirring for 6hrs ,The reaction mixture was then allowed to cool at room temperature and filtrated . The filtrate was evaporated to dryness under reduced pressure and residue was dissolved in distilled water (15ml) and carefully acidified with concentrated HCl (3.5 ml) to give orange precipitate .The crude product was filtrated, washed excessively with distilled water and recrystallized from the hot ethanol to give the product as pale yellow needles and other physical properties can be shown in table (3-1).

(2-3-2) Preparation 2-carbomethoxy amino-5-mercapto1, 3, 4-thiadiazole (B):

This compound was prepared by the reaction of methyl chloroformate with compound in section 2-3-1 in pyridine⁽⁶⁴⁾ .Methyl chloroformate 1.16ml was added dropwise to solution of compound (1) (2g,15.03mmole) in pyridine (5.42ml) with continuous stirring at room temperature for 1hr , the mixture was diluted with cold distilled water (24.63ml) with dilute hydrochloric acid to pH =3 . A pale precipitate was formed and collected by filtration washed excessively with cold distilled water and dried in oven at 70°C .This compound is obtained as yellow crystals .The physical properties can be show in table (3-1).

(2-3-3) Preparation of potassium 2- carbomethoxy amino-5-trithiocarbonate mercapto 1, 3, 4-thiadiazole (LI):

This compound was prepared by dissolving (2g,0.01mole)of compound in section (2-3-2) in ethanol (20ml) then (1.5ml) of carbon disulfide was added alkali media potassium hydroxide (0.58g, 0.01mole) . The mixture was refluxed for (3hrs) then the solvent was evaporated and the precipitate was filtrated , then recrystallized from ethanol , the physical properties can shown in table (3-1).

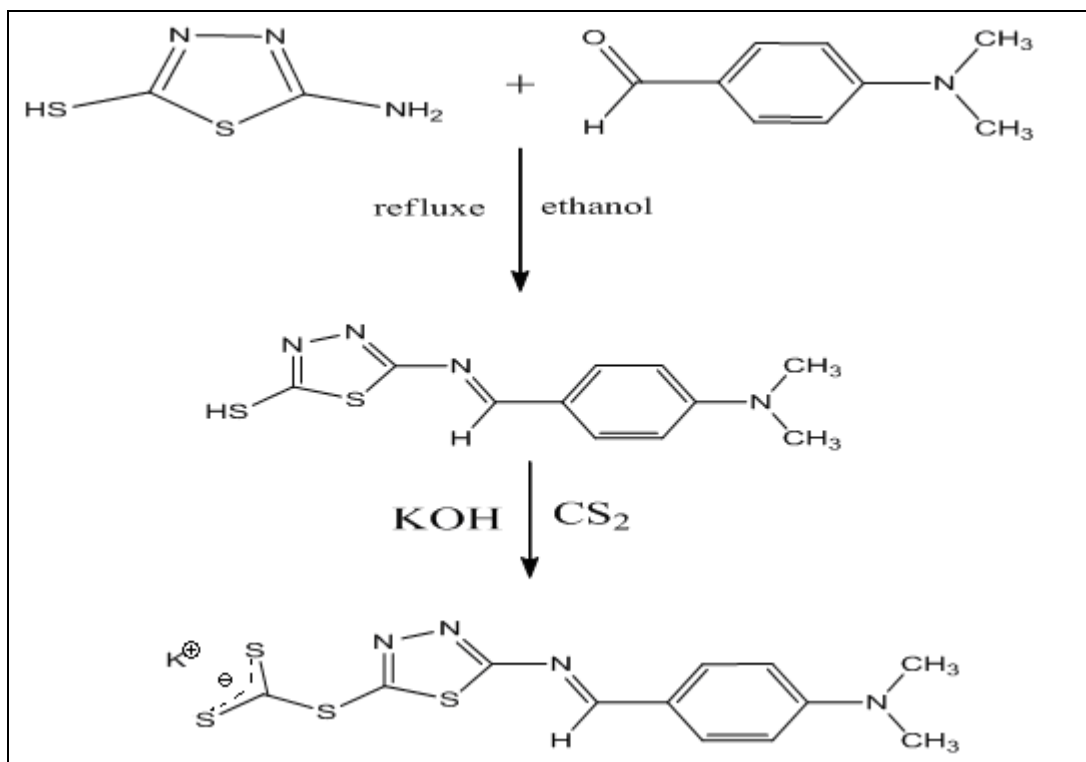


(2-3-4) Preparation of 2-N (4, 4-dimethylamino benzyliden)-5-mercapto 1, 3, 4-thiadiazole (C):

To prepare this compound according to synthesis of Schiff bases ⁽⁶⁵⁾ by using compound in section (2-3-1) (2g, 0.015mole) and (3.07g, 0.015mole) of 4-N, N-dimethylaminobenzaldehyde in (10ml) in absolute ethanol and one drop of glacial acetic acid in continuous stirring and heated in water bath at (60-70) °C and reflux for one hour, then left to cool in ice-water bath where orange precipitate was obtained. The physical properties can be shown in table (3-2).

(2-3-5) Preparation of potassium 2-N(4-N,N-dimethylamino benzyliden)-4-trithiocarbonate 1,3,4-thiadiazole (LII):

To prepare this compound using of (2g, 0.0075mole) from compound in section (2-3-4), In absolute ethanol (20ml) was added to carbon disulfide (1.5ml) and potassium hydroxide (0.42g, 0.0075mole). The mixture was refluxed for 3hrs and then the solvent was evaporated. The precipitate crystal was filtrated and recrystallized from ethanol to obtain orange precipitate. The physical properties can be shown in table (3-2).



2-4 Preparation of complexes

2-4-1 Preparation of metal complexes of the LI

1- Preparation of copper (II) complex (Cu LI)

A solution of (0.12g, 1mmole) CuCl₂ · 2H₂O dissolved in (5ml) of absolute ethanol was added to (0.33g, 2mmole) of (LI) dissolved in (10ml) of absolute ethanol. The mixture was refluxed with stirring for one hour. The resulting green precipitate was filtrated and washed with hot ethanol. The physical properties can be obtained in table (3-1).

2- Preparation of Cobalt (II) complex (Co LI)

A solution of (0.03g, 1mmole) of CoCl₂ · 6H₂O dissolved in (5ml) ethanol was added to (0.21g, 2mmole) of LI dissolved in (10ml) ethanol. The mixture was refluxed with stirring for one hour; the resulting precipitate was filtrated and washed with hot ethanol. The physical properties can be shown in table (3-1).

3- Preparation of Nickel(II) complex (Ni LI)

A solution of (0.145g, 1mmole) of NiCl₂ · 6H₂O dissolved in (5ml) ethanol was added (0.335g, 2mmole) of (LI) dissolved in (10ml) ethanol. The mixture was refluxed with stirring for one hour, The resulting precipitate was filtrated and washed with hot ethanol. The physical properties can be shown in table (3-1)

4- Preparation of Cadmium (II) complex (Cd LI)

A solution of (0.14g, 1mmole) of CdCl₂ · 2H₂O dissolved in (5ml) ethanol was added to (0.43g, 2mmole) of (LI) dissolved in (10ml) ethanol. The mixture was refluxed with stirring for one hour, The resulting precipitate was filtrated

and washed with hot ethanol , The physical properties can be shown in table (3-1) .

5- Preparation of Iron Fe(II) complex (Fe LI)

A solution of (0.12g , 1mmole) of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ dissolved in (5ml) ethanol was added to (0.33g,2mmole) of (LI) dissolved in (10ml) ethanol .The mixture was refluxed with stirring for one hour ,The resulting precipitate was filtrated and washed with hot ethanol , The physical properties can be shown in table (3-1) .

6- Preparation of Manganese Mn(II)complex (Mn LI)

A solution of (0.145g , 1mmole) of $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ dissolved in (5ml) ethanol was added to (0.335g , 2mmole) of (LI) dissolved in (10ml) ethanol .The mixture was refluxed with stirring for one hour ,The resulting precipitate was filtrated and washed with hot ethanol , The physical properties can be shown in table (3-1) .

2-4-2Preparation of the metal complexes of ligand (LII)

1- Preparation of Cobalt (II) complex (Co LII)

A solution of (0.24g,2mmole) of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ dissolved in (5ml) ethanol was added to (0.43g, 2mmole) of(LII)dissolved in (10ml) ethanol. The mixture was refluxed with stirring for one hour ; the resulting precipitate was filtrated and washed with hot ethanol . The physical properties can be shown in table (3-2).

2- Preparation of Copper (II) complex (Cu LII)

A solution of (0.24g, 2mmole) of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ dissolved in (5ml) ethanol was added to (0.43g ,2mmole) of(LII) dissolved in (10ml) ethanol. The mixture was refluxed with stirring for one hour; the resulting precipitate was filtrated and washed with hot ethanol . the physical properties can be shown in table (3-2).

3-Preparation of Nickel (II) complex (Ni LII)

A solution of (0.145 g, 1mmole) of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ dissolved in (5ml) ethanol was added to (0.335g, 2mmole) of (LII)dissolved in (10ml) ethanol. The mixture was refluxed with stirring for one hour; the resulting precipitate was filtrated and washed with hot ethanol . The physical properties can be shown in table (3-2).

4- Preparation of Cadmium (II) complex (Cd LII)

A solution of (0.19 g,1mmole) of $\text{CdCl}_2 \cdot 4\text{H}_2\text{O}$ dissolved in (5ml) ethanol was added to (0.15g,1mmole) of(LII) dissolved in (10ml) ethanol. The mixture was refluxed with stirring for one hour; the resulting precipitate was

filtrated and washed with hot ethanol . the physical properties can be shown in table (3-2).

5- Preparation of Iron Fe(II) complex (Fe LII)

A solution of (0.12g , 1mmole) of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ dissolved in (5ml) ethanol was added to (0.335g, 2mmole) of (LII) dissolved in (10ml) ethanol .The mixture was refluxed with stirring for one hour ,The resulting precipitate was filtrated and washed with hot ethanol .The physical properties can be shown in table (3-2)

6- Preparation of Manganese Mn(II)complex (Mn LII)

A solution of (0.17g ,1mmole) of $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ dissolved in (5ml) ethanol was added to (0.33g, 2mmole) of (LII) dissolved in (10ml) ethanol .The mixture was refluxed with stirring for one hour , The resulting precipitate was filtrated and washed with hot ethanol , The physical properties can be shown in table (3-2) .

Chapter three

Results and discussion

Chapter three

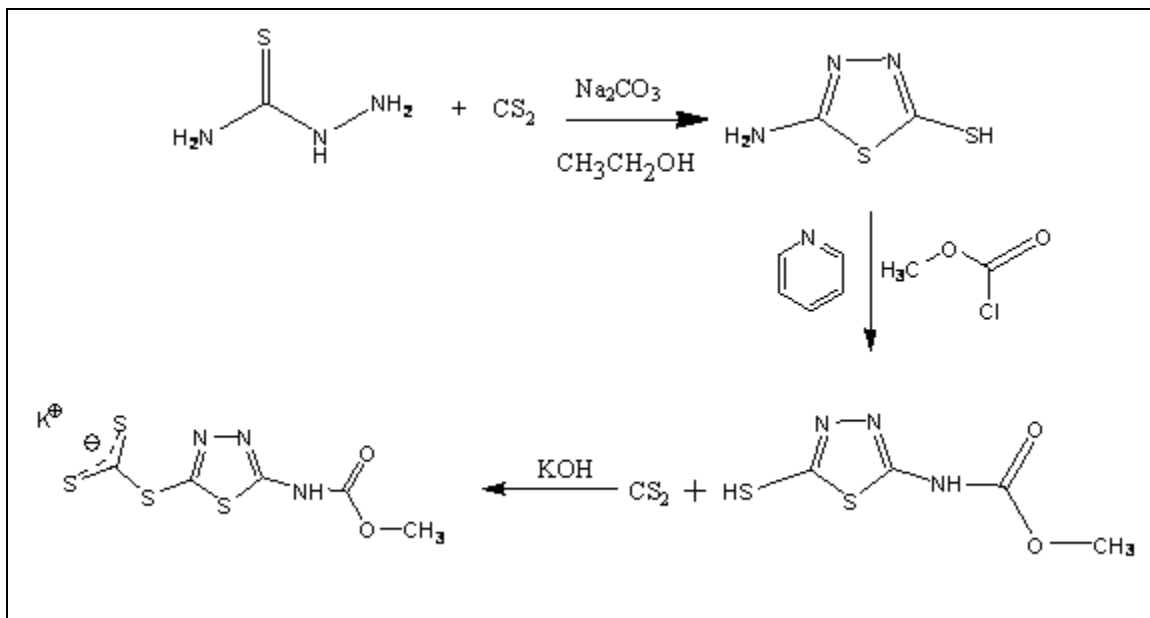
Results and discussion

The presence of $-SCS_2$ moiety and isomethane group in thiazole compound may contribute greatly to the chemistry of organic and inorganic sulfur compounds which may have structural as well as biological and industrial importance. This may come in general from unique properties of sulfur, being an ideal soft atom in the mobilization of electrons in thiocarbonate complexes, which is an important property in the biological system, and indeed a number of biological models were synthesized containing isomethane and thiocarbonate group in specific structure requirement to match the required biological behavior.

For all that have been mentioned it became of interest to synthesize a series of transition metal complexes with thiadiazole, thiocarbonate especially with first transition row. For this purpose potassium salts of 2-carbomethoxy amino-5-mercapto 1,3,4-thiadiazole and 2-N(4-N,N dimethylamino benzyl) 5-mercapto 1,3,4-thiadiazole were prepared a yellow and orange powder were isolated respectively, and utilized to prepare a series of complexes with Mn, Fe, Ni, Co, Cu, and Cd metal ions which were studied by different available analysis. In addition to that, which is known to possess their biological activity and to investigate the coordination behavior of the new ligands toward some transition metal ions and compare the biological activity of the ligands with their prepared complexes.

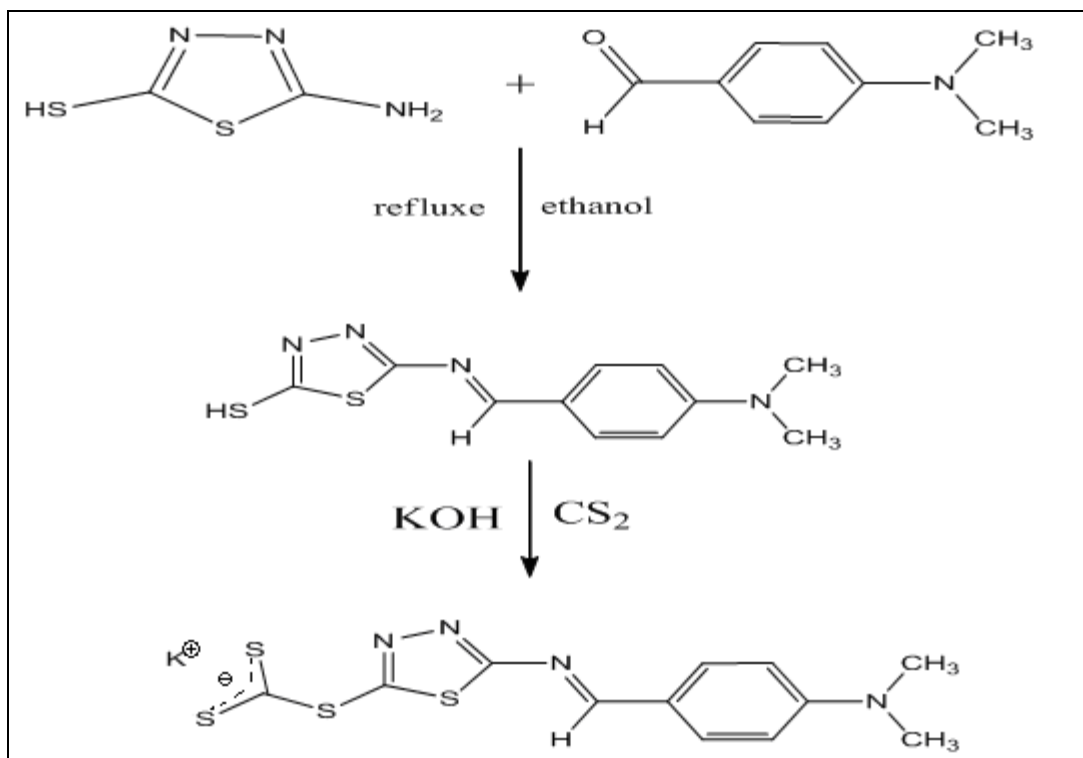
3-1 preparation of ligands.

Ligand(LI) was prepared from the reaction of 2-carbomethoxy amino-5-mercapto 1,3,4-thiadiazole with CS_2 in presence of KOH in ethanolic solution. The following scheme illustrates the structure of LI :-



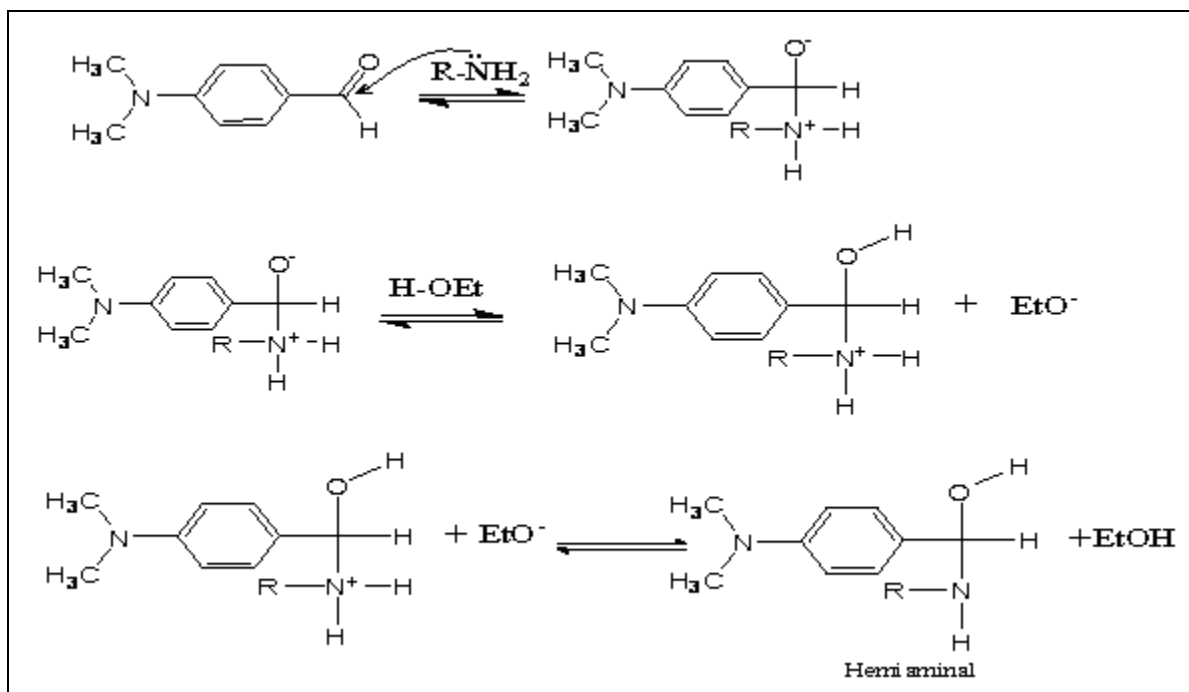
Scheme :-(3-1) Preparation of potassium 2-carbomethoxy amino-5-trithiocarbonate 1,3,4-thiadiazole (LI)

Ligand (LII) prepared from the reaction of 2-N(4-N,N dimethylamino benzyl)edine -5-mercapto 1,3,4-thiadiazole with CS_2 in presence of KOH in ethanolic solution the following scheme illustrates the structure of the LII

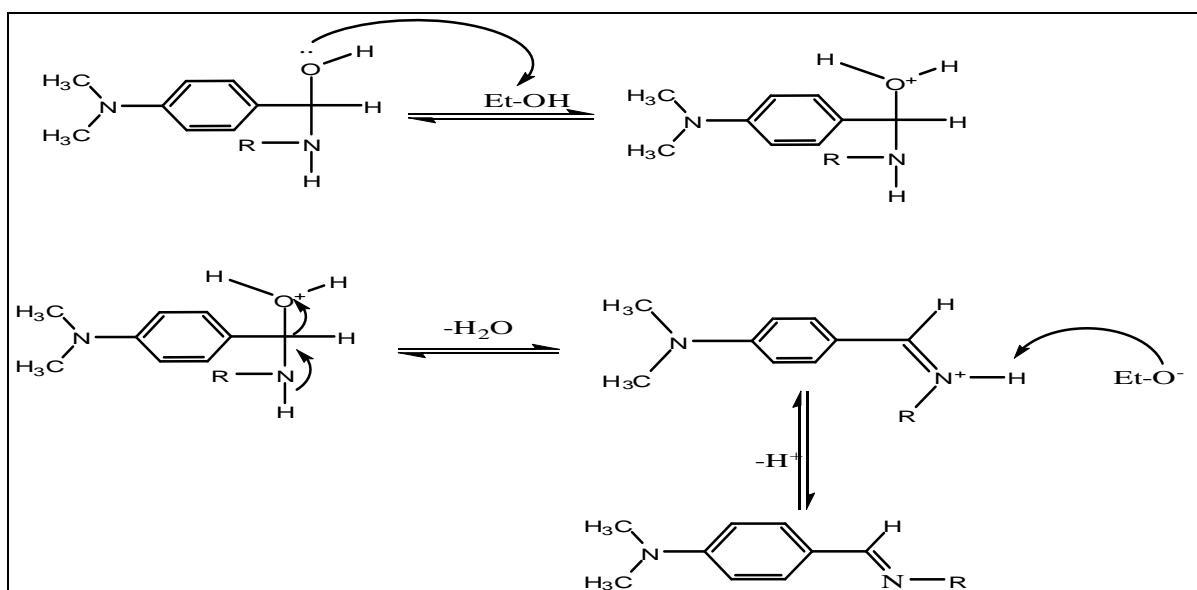


Scheme:-(3-2) Preparation of potassium 2-N(4-N,N-dimethylamino benzyl)edine-4-trithiocarbonate 1,3,4-thiadiazole (LII)

And the suggested mechanisms of isomethain derivative as follows:-



The addition step can be obtained by two reactions Acid-Base by using ethanol as solvent. ⁽⁶⁶⁾



The prepared trithiocarbonate chelating derivatives were characterized by FT-IR, Uv-Vis spectra and melting point. The yellow and orange crystalline products were found to be high soluble in DMSO and they were found to be stable toward air and moisture.

3-2 - Reaction of new ligands with some transition metals

The interaction of trithiol chelating ligands derivatives with the appropriate metal salt under study in ethanol solvent .Crystalline products with different colors depending on metal ions were obtained. The physical and analytical data of all these complexes are given in table (3-1) and (3-2) . The results obtained from metal analysis are a satisfactory agreement with the theoretical are calculated. The suggested molecular formula were also supported by spectra (FT-IR , Uv-Vis spectrophotometer) as well as magnetic susceptibility and conductivity measurements which are described in table (3-3)

Complex	Color	m.p (⁰ C)	Yield (%)	Metal content (%)	
				Cal.	Found
A	Pale yellow	230-233	72	-	-
B	Light yellow	180	68	-	-
LI	Yellow	210	62	-	-
Cd LI	white	240 d	54	13.02	13.05
Cu LI	Green	235 d	60	13.3	12.8
Ni LI	Green	260 d	48	6.30	6.40
Co LI	Dark green	230 d	64	10.83	10.79
Fe LI	Brown	120 d	55	10.01	10.03
Mn LI	Brown	190	41	6.22	6.30

d: decomposed

Table (3-2): Physical properties for the ligand LII and its metal complexes

Complex	Color	m.p (⁰ C)	Yield (%)	Metal content (%)	
				Cal.	Found
C	Orange	200	69	-	-
LII	Dark orange	150	70.0	-	-
Cd LII	Light orange	270 d	65.5	13.56	13.60
Cu LII	Brown	240 d	54.1	12.69	12.8
Ni LII	Light brown	290 d	55.5	7.14	7.20
Co LII	Dark brown	250 d	52.3	11.15	11.00
Fe LII	Dark brown	260 d	68.8	7.20	7.22
Mn LII	Brown	235 d	70	6.14	6.00

Table (3-3):-Chemical formula and the name of LI and LII and their metal complexes

Symbol	Molecular formula	Name
LI	$C_5H_4O_2S_4K$	Potassium 2-carbomethoxyamino-5-trithiocarbonate 1,3,4-thiadiazole
Cd LI	$[Cd(LI)_2] \cdot 3C_2H_5OH$	Bis(2-carbomethoxyamino-5-trithiocarbonate 1,3,4-thiadiazole) cadmium(II) .3 ethanol
Cu LI	$[Cu_2(LI)_2Cl_2(H_2O)_2] \cdot 3C_2H_5OH$	di- μ -chloro-bis(2-carbomethoxyamino-5-trithiocarbonate 1,3,4-thiadiazole) copper(II).3ethanol
Ni LI	$[Ni(LI)_2Cl_2] \cdot 2H_2O$	diChlorobis(2-carbomethoxyamino-5-trithiocarbonate 1,3,4-thiadiazole) nickel(II). 2hydrate
Co LI	$[Co(LI)(H_2O)Cl] \cdot 3H_2O$	Chloroqua(2-carbomethoxyamino-5-trithiocarbonate 1,3,4-thiadiazole) cobalt .3hydrate
Fe LI	$[Fe_2(LI)_2(OH)_2 \cdot Cl_4] \cdot 4H_2O$	di- μ -hydroxo-tetrachloro bis (2-carbomethoxyamino-5-trithiocarbonate 1,3,4-thiadiazole) iron(III),4hydrate
Mn LI	$[Mn(LI)_2(H_2O)_2](OAc)_2 \cdot 2H_2O$	diaquabis(2-carbomethoxyamino-5-trithiocarbonate 1,3,4-thiadiazole) manganese(II). Actate 2hydrate
LII	$C_{12}H_{11}N_4S_4K$	Potassium 2-N(4-N,N-dimethylaminobenzyl)edine-4-trithiocarbonate 1,3,4-thiadiazole
Cd LII	$[Cd(LII)_2] \cdot 4C_2H_5OH$	bis(2-N(4-N,N-dimethylaminobenzyl)edine-4-trithiocarbonate 1,3,4-thiadiazole) cadmium(II).4ethanol
Cu LII	$[Cu_2(LII)_2(H_2O)_4Cl_2] \cdot 2H_2O$	Bis- μ -(2-N(4-N,N-dimethylaminobenzyl)edine-4-trithiocarbonate 1,3,4-thiadiazole)dichlorotetraqua copper(II). 2 hydrate
Ni LII	$[Ni(LII)_2(H_2O)_2 \cdot Cl_2] \cdot C_2H_5OH$	diChloro-bis(2-N(4-N,N-dimethylaminobenzyl)edine-4-trithiocarbonate 1,3,4-thiadiazole)diaqua nickel(II) ethanol
Co LII	$[Co_2(LII)_2(H_2O)_4Cl_2] \cdot 2.5C_2H_5OH$	Bis- μ -(2-N(4-N,N-dimethylaminobenzyl)edine-4-trithiocarbonate 1,3,4-thiadiazole)dichlorotetraqua cobalt(II). 2,5 ethanol
Fe LII	$[Fe_2(LII)_4(OH)_2] \cdot 5H_2O$	di- μ -hydroxotetakis(2-N(4-N,N-dimethylaminobenzyl)edine-4-trithiocarbonate 1,3,4-thiadiazole) Iron(III). 5hydrate
Mn LII	$[Mn(LII)_2(H_2O)_2(OAc)] \cdot 3H_2O$	Acetate-bis(2-N(4-N,N-dimethylaminobenzyl)edine-4-trithiocarbonate 1,3,4-thiadiazole)diaqua manganese(II).3hydrate .

single ν C-S and shifted to higher frequency by $(16) \text{ cm}^{-1}$, these indicating the participation of disulfur atoms coordination^(70,71), therefore the ligand may be considered to behave as bidentate(s,s). There is no appreciable change took place in the absorption of the stretching C=N, NCS of thiadiazole ring and ν_{COC} mode and carbonyl group in these complexes, this excluded the possibility of nitrogen and oxygen atoms participation in coordination.

The IR spectra of iron, nickel and manganese complexes shows that the stretching frequency of $\nu_{(\text{C}=\text{N})}$ and $\nu_{(\text{NCS})}$ bands undergo shifting to the higher frequency with low intensity by $(23) \text{ cm}^{-1}$, and the absorption bands of ν_{COC} mode and carbonyl group shifted to lower frequency by $(13) \text{ cm}^{-1}$, this indicating the participation of nitrogen of the ring and oxygen of the acetate coordination^(70,71). This was further indicated by appearance $\nu_{\text{M-N}}$ and $\nu_{\text{M-O}}$ bands absorption^(70,71). This ligand may be considered to behave as bidentate(N,O). There is no appreciable change happened in SCS₂ group in these complexes, this excluded the possibility of thial group participation in coordination.

A broad band was observed around to $(3450-3363) \text{ cm}^{-1}$ in the spectra of the complexes, assigned to a $\nu_{\text{O-H}}$ and suggested the presence of water or ethanol molecule in the crystal lattice of the complex⁽⁷²⁾.

FT-IR spectra of LII and its metal complexes

The spectra of iron and cadmium complexes Fig (3-16) and (3-12), shows that the partial band ν C---S undergo splitting into three weak bands with lowering frequency (940, 937, 930), and the vibrational band of double bond $\nu\text{C}=\text{S}$ underwent to higher frequency by $(18) \text{ cm}^{-1}$, while the single ν C-S band was shifted to higher frequency by $(9) \text{ cm}^{-1}$, these indicating the participation of disulfur atoms coordination and which is further indicated by appearance of M-S vibration band^(70,71), table (3-5). NO appreciable change in the absorption bands of imine azomethine, amine of $\nu(\text{Ar-N})$ and $(\nu_{(\text{C}=\text{N})}, \nu_{(\text{NCS})})$ of the ring took place, this excluded the coordination of the nitrogen of these modes to the central ions.

In cobalt and copper complexes spectra, Fig (3-15) and (3-13), the azomethine stretching frequency shifts from 1591 to 1581 cm⁻¹, this shifting to the lower frequency indicates complexation via nitrogen azomethine moiety^(70,71). The stretching frequencies of partial ν C---S band, undergo splitting into three weak bands and the vibration frequency of the double band, and singlet band of the thiol underwent to higher frequency by (18) cm⁻¹ and higher frequency for singlet by (6) respectively. Moreover, new bands have been observed in (550), (516) and (430), (408) which can be attributed to the ν_{M-N} and ν_{M-S} respectively, therefore the ligand may be considered to behave as a tridentate (N,S,S) as a bridge.

NO appreciable change in the vibration bands of the $\nu_{(C=N)}$ and $\nu_{(NCS)}$ of the ring and ν Ar-N happened, this excluded the coordination of the nitrogen of these modes to central ions.

In the spectra of manganese and nickel complexes Fig (3-17) and (3-14), two bands were observed in the azomethine $\nu_{(C=N)}$ region, one correspond to unshifted $\nu_{(C=N)}$ cm⁻¹, the other shifted at lower frequency with higher intensity at (1581) cm⁻¹. This behavior refer to different coordination modes of the ligand, i.e. one ligand coordinate through nitrogen of $\nu_{(C=N)}$ group, the other through the dithiol atoms only the last of Coordination was confirmed by the splitting band of ν C---S into three weak bands with lowering frequencies, and stretching vibration band of ν C=S and ν C-S underwent to the higher frequency by (14) cm⁻¹ and higher frequency for by C-S (8) cm⁻¹ respectively^(70,71), table (3-5). Furthermore, new bands have been observed in (540), (550) and (430) cm⁻¹ for Mn(II), which can be attributed to the ν_{M-N} and ν_{M-S} respectively. NO appreciable change in the absorption ν Ar-N and $\nu_{(C=N)}$, $\nu_{(NCS)}$ of the ring took place, this excluded the coordination of the nitrogen of amine and nitrogen of the ring to the metal ions.

A broad band was observed around (3371- 3300 cm⁻¹) in the spectra of the complexes, assigned to a ν_{O-H} and suggested the presence of water or ethanol molecule in the crystal lattice of the complex⁽⁷²⁾.

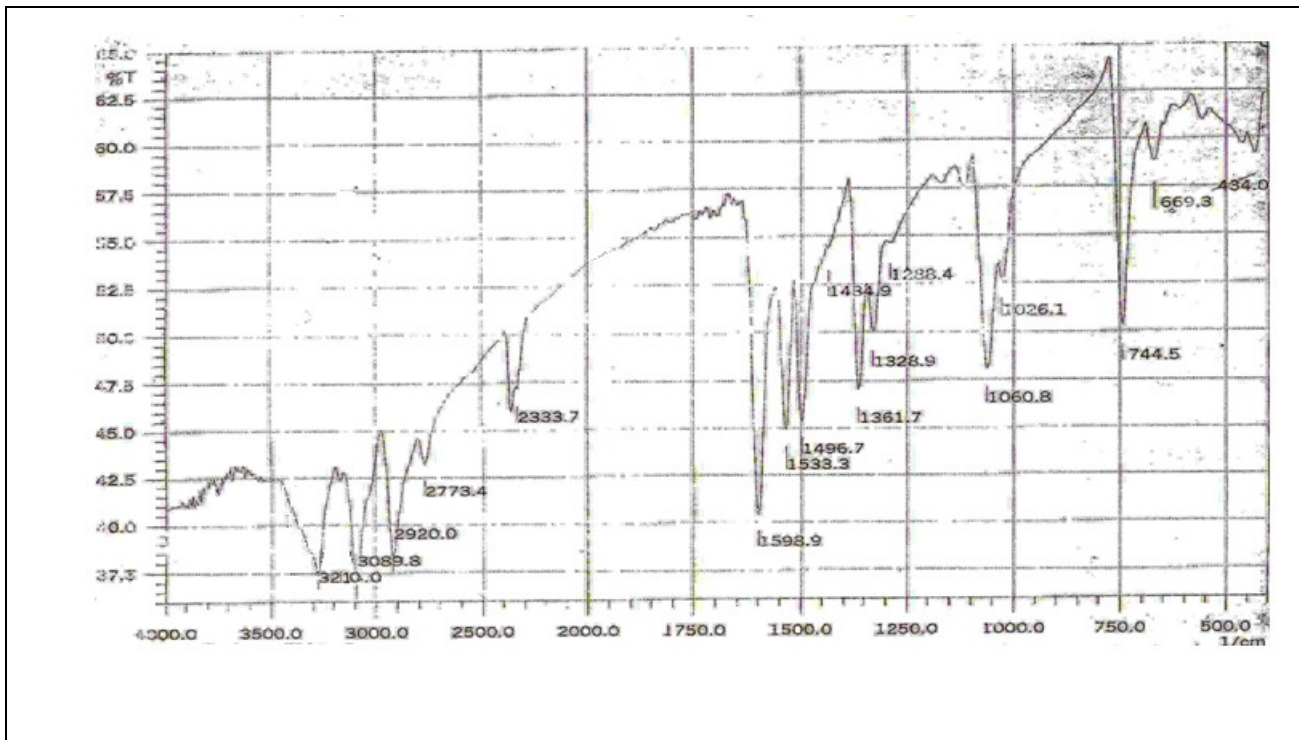


Fig (3-1): FT-IR spectra of 2-amino-5-mercapto -1,3,4-thiadiazole (A)

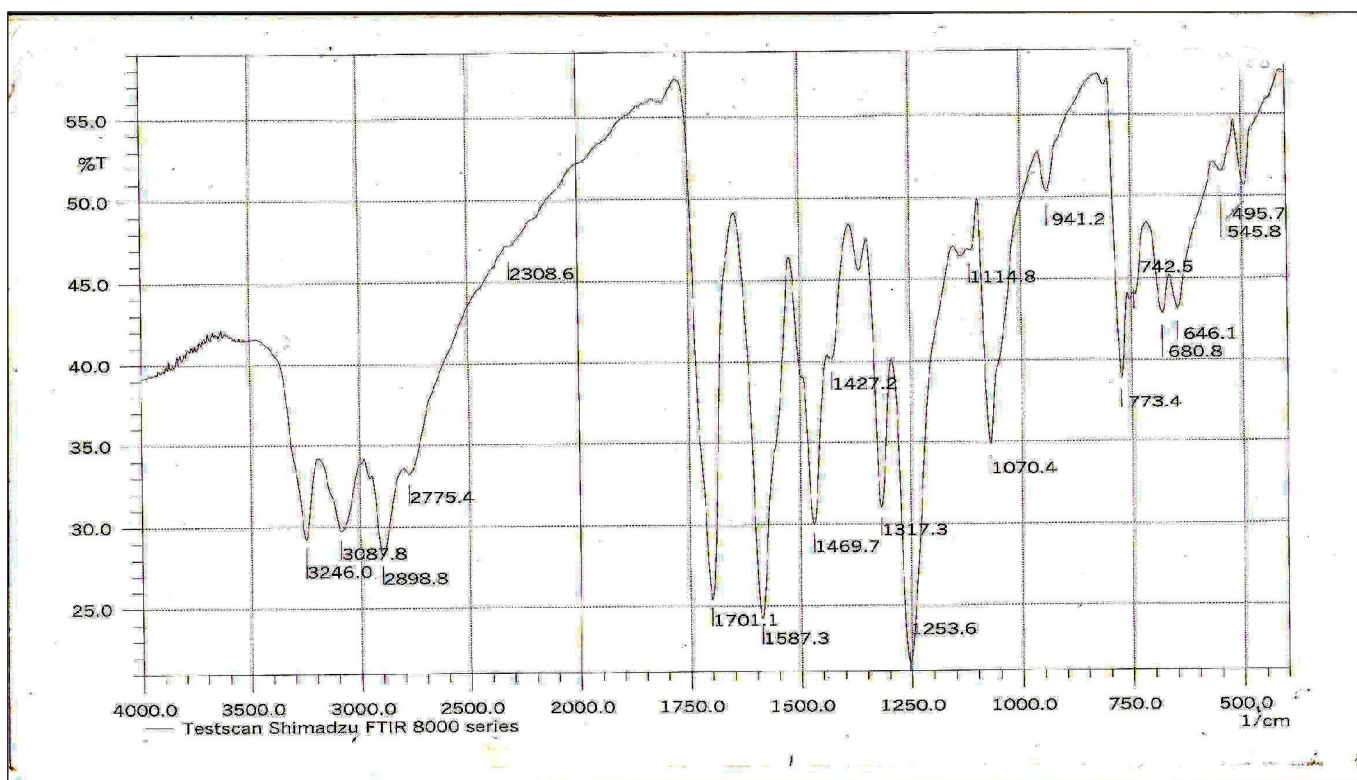


Fig (3-2): FT-IR spectra of 2-carbomethoxy amino-5-mercapto1,3,4 thiadiazole(B)

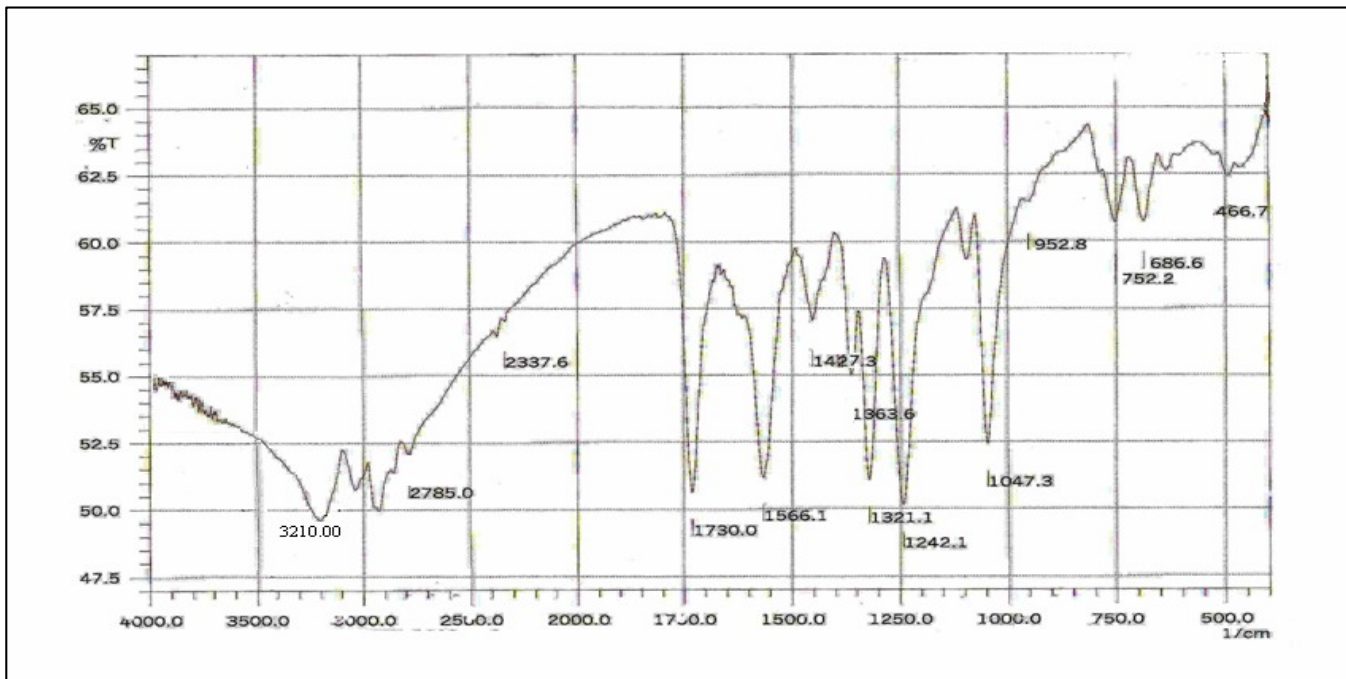


Fig (3-3): FT-IR spectra of (LI)

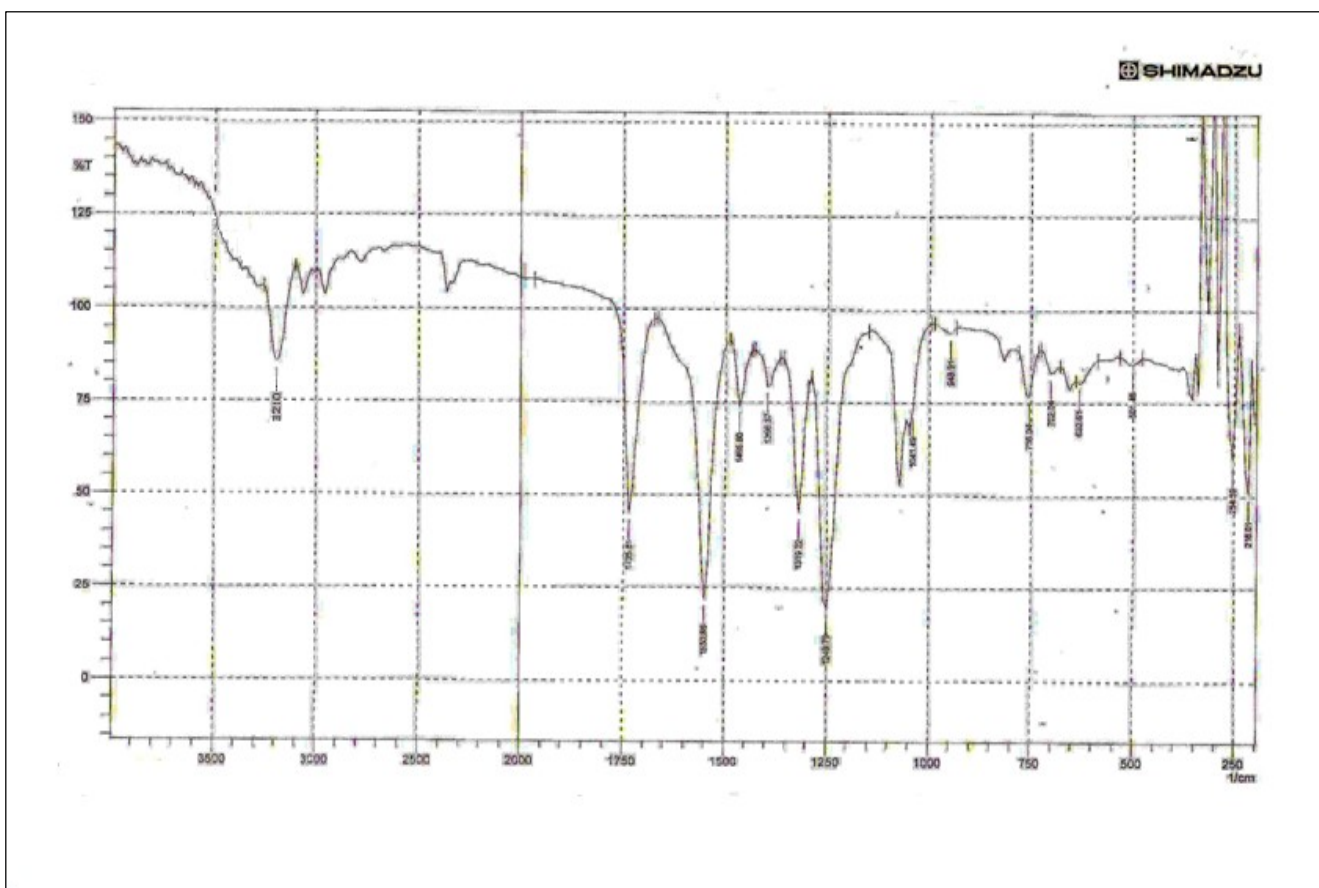


Fig (3-4): FT-IR spectra of (Cd LI)

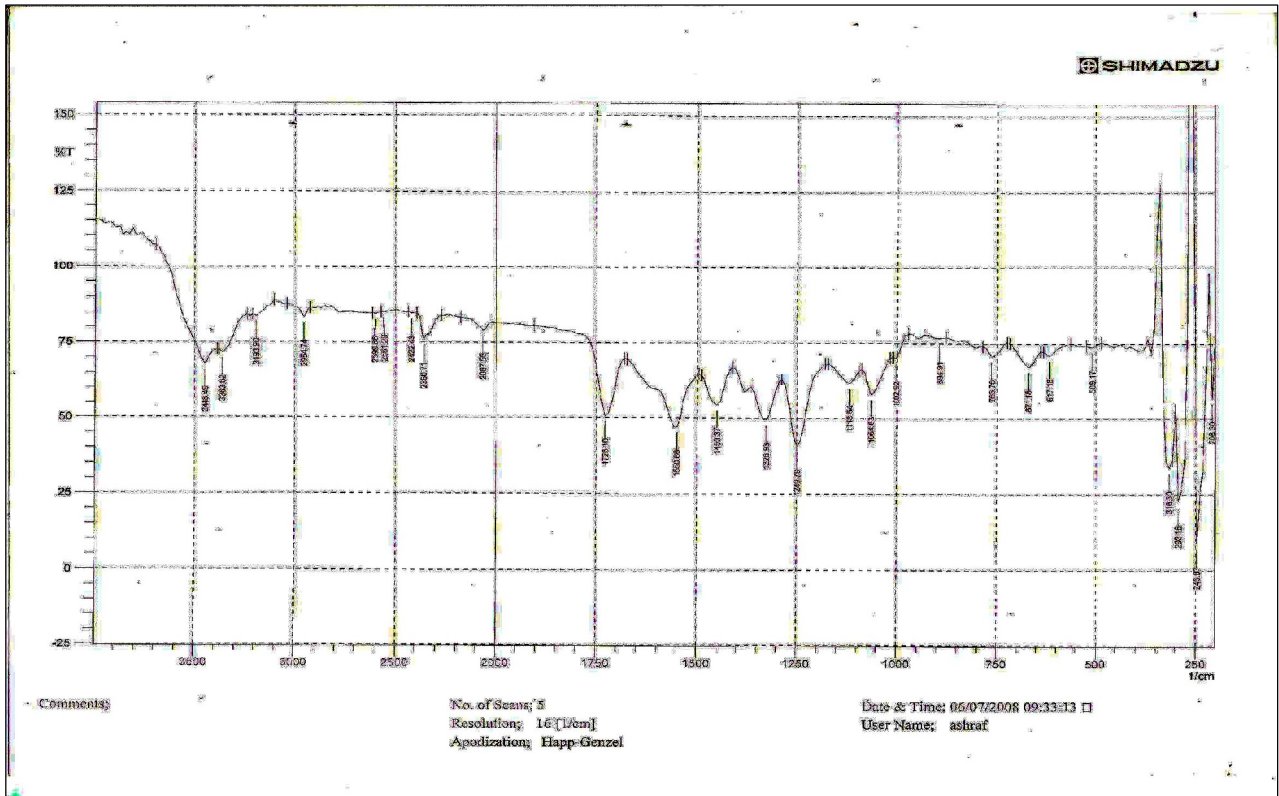


Fig (3-5): FT-IR spectra of (Cu LI)

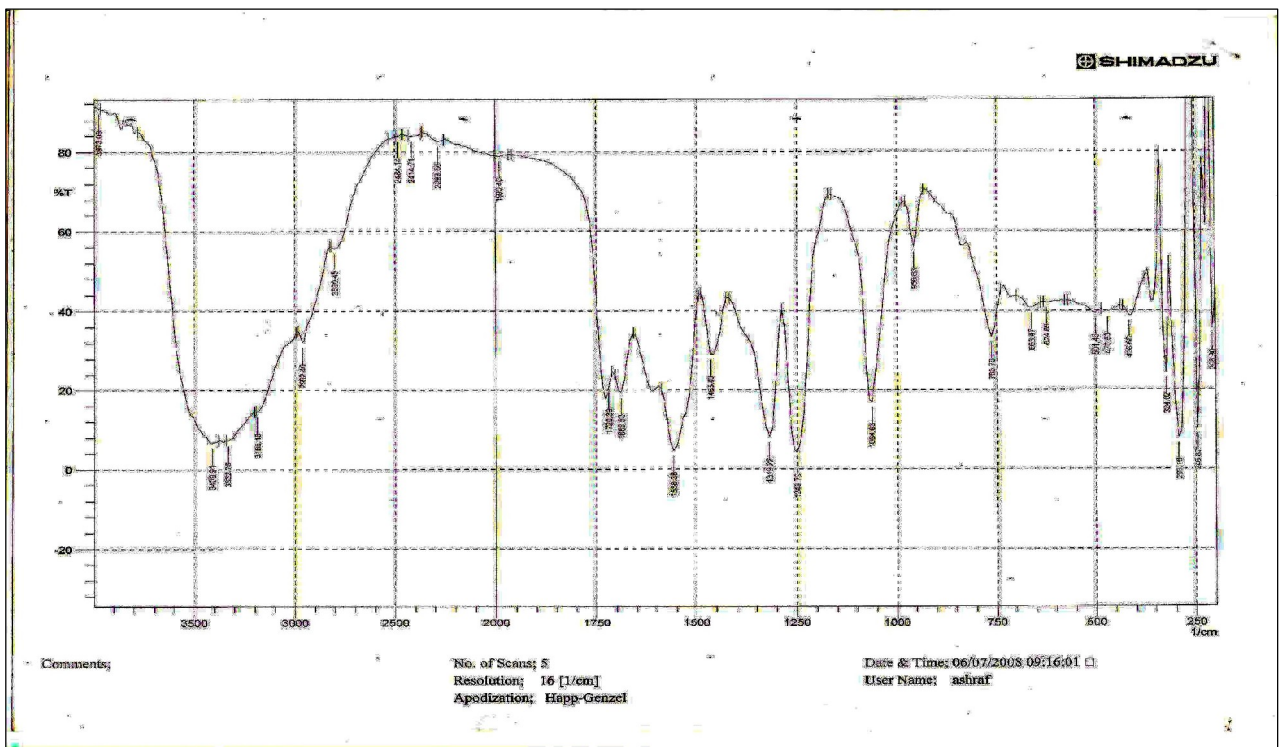


Fig (3-6): FT-IR spectra of(NiLI)

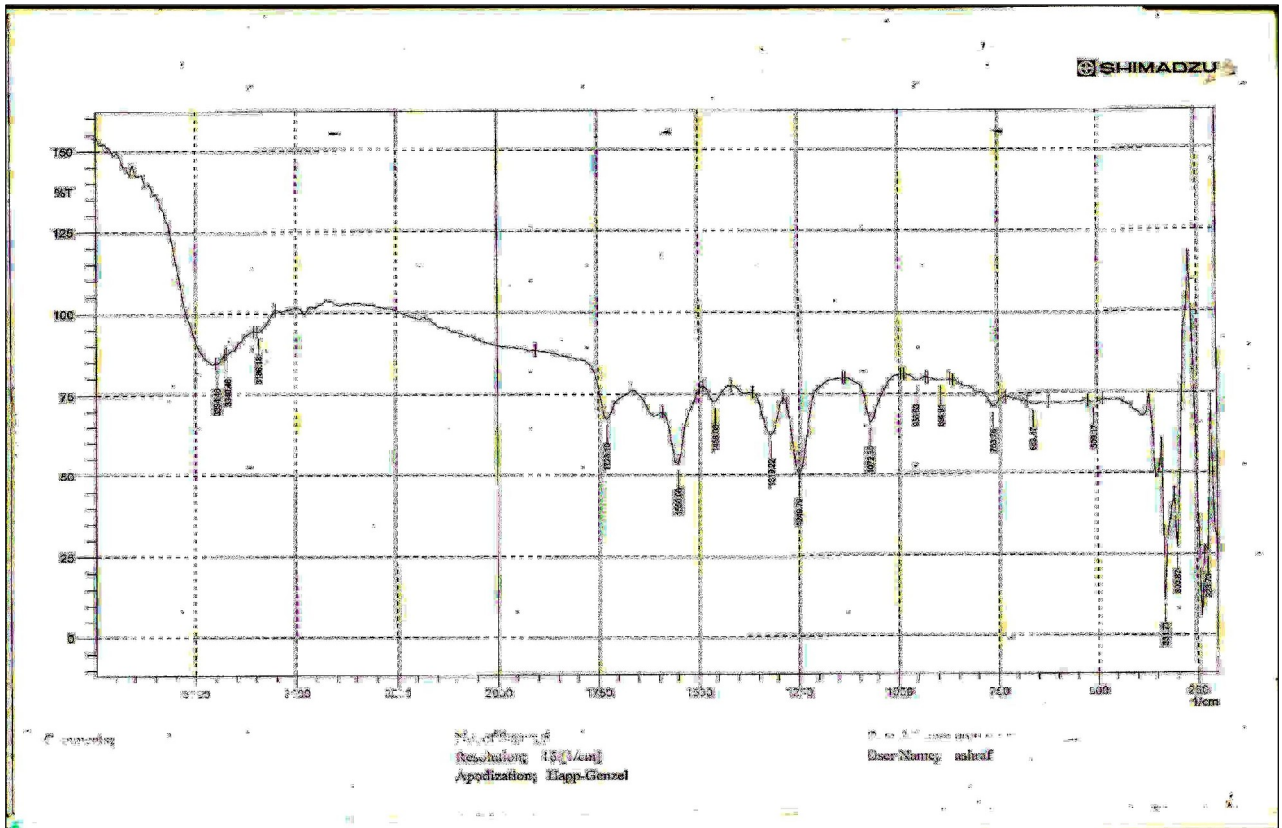


Fig (3-7): FT-IR spectra of (Co LI)

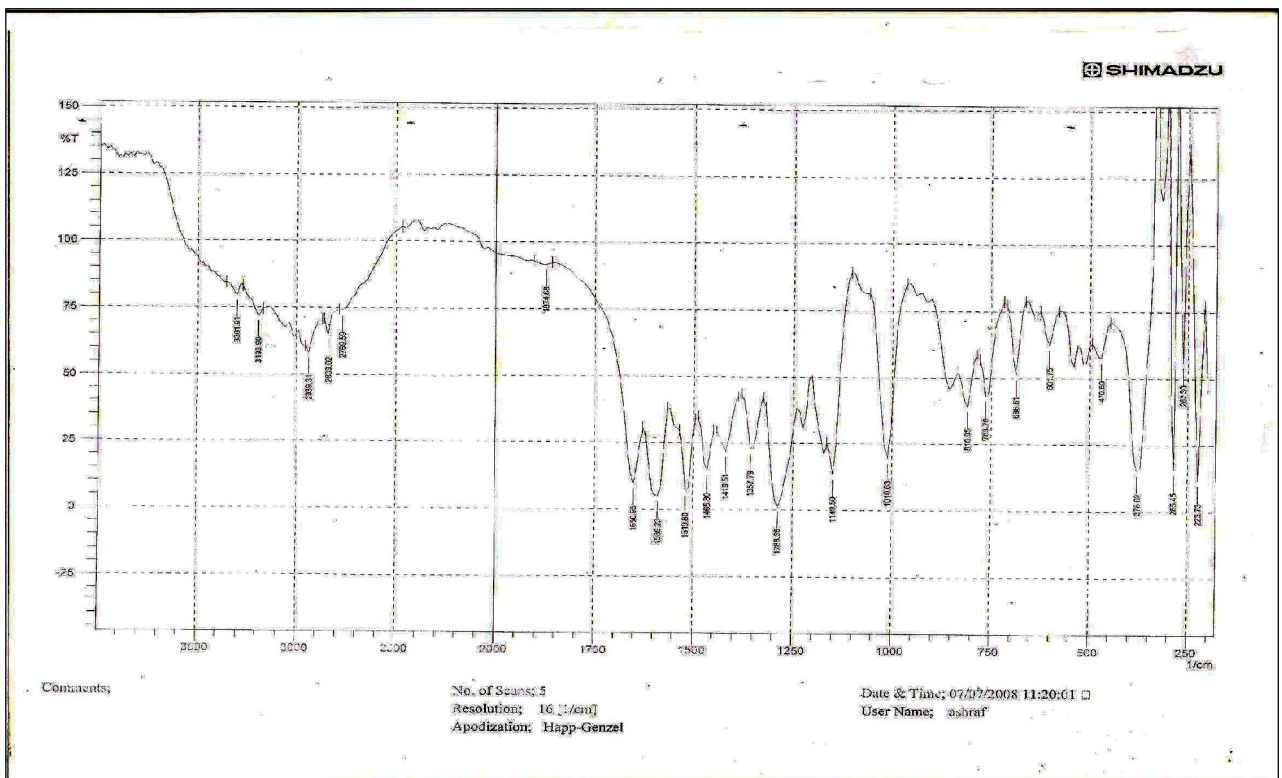


Fig (3-8): FT-IR spectra of (Fe LI)

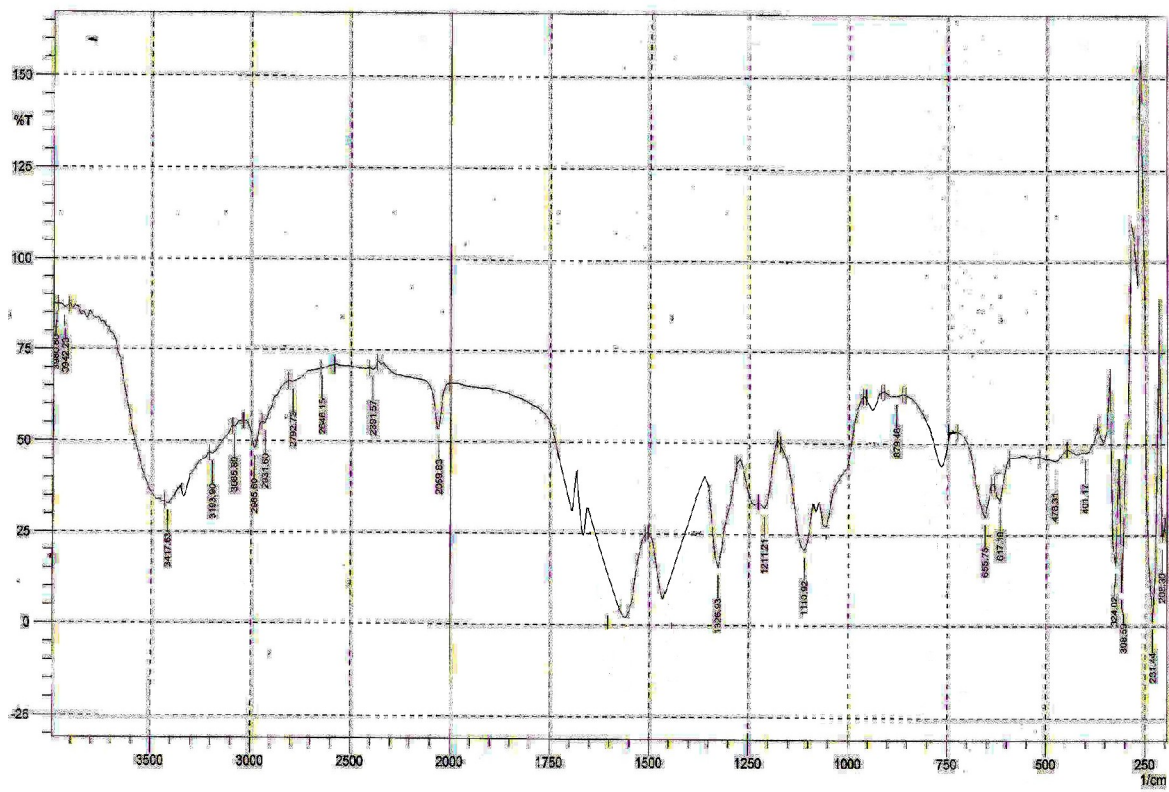


Fig (3-9): FT-IR spectra of (Mn LI)

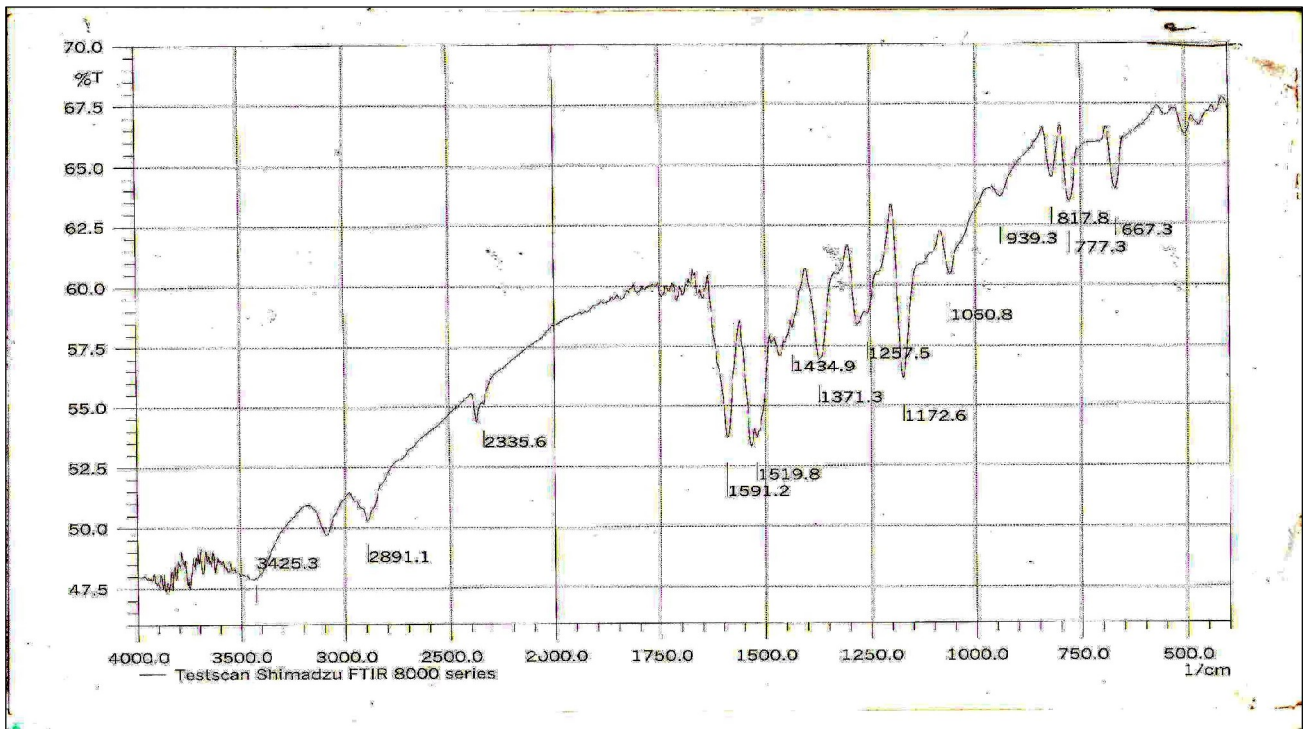


Fig (3-10): FT-IR spectra of 2-N(4,4-dimethylamino benzyliden)-5-mercapto 1,3,4-thiadiazole (C)

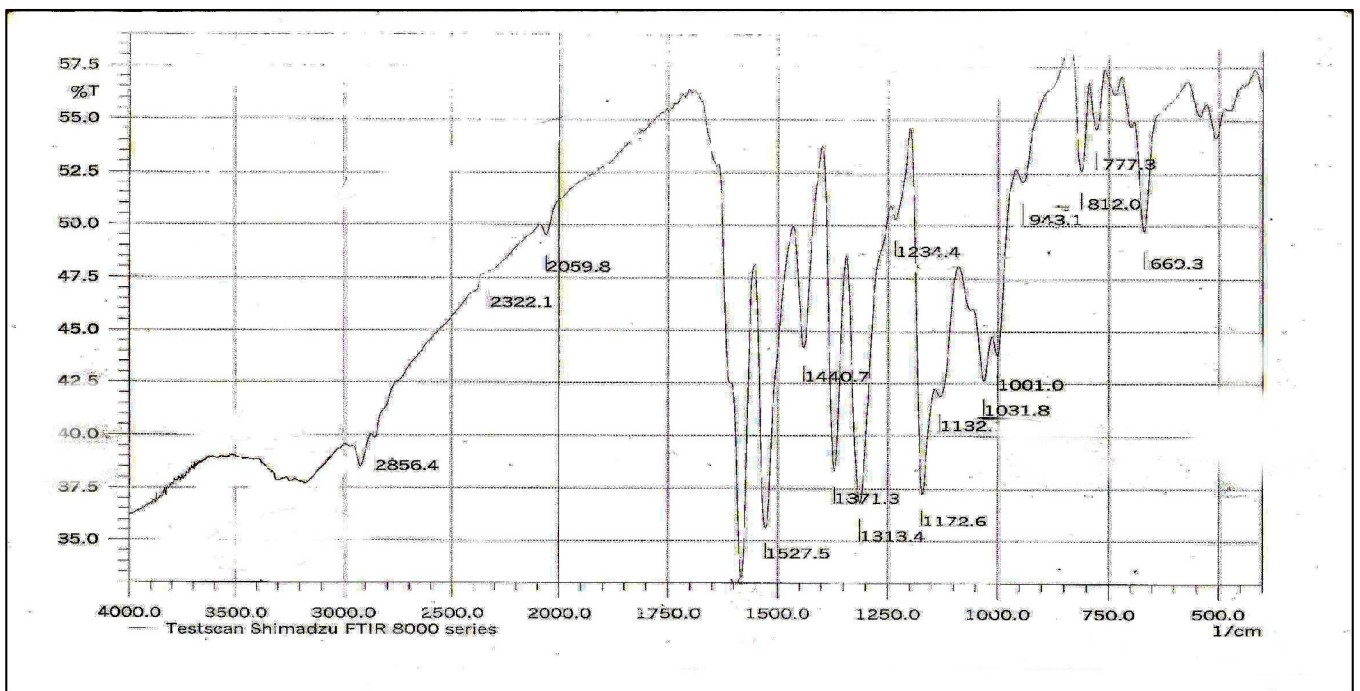


Fig (3-11): FT-IR spectra of potassium 2-N(4-N,N-dimethylamino benzyliden)-4-trithiocarbonate 1,3,4-thiadiazole (LII).

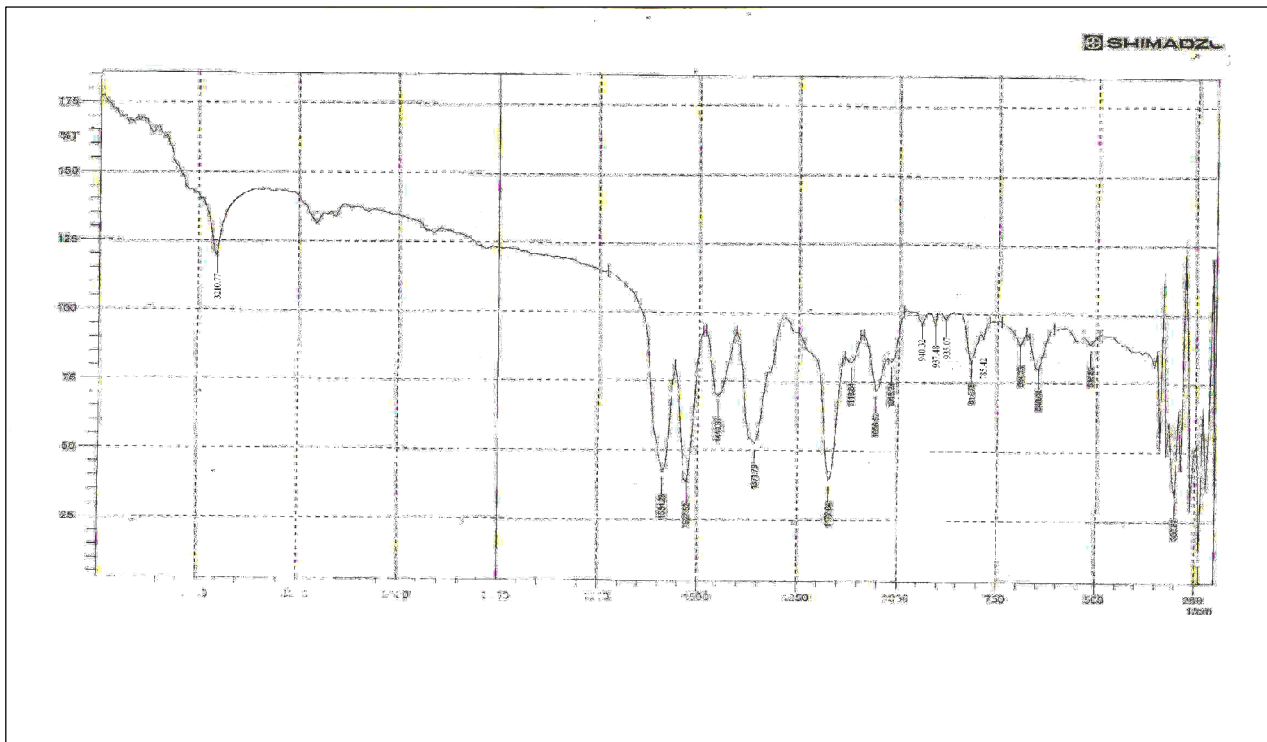


Fig :(3-12) FT-IR spectra of (Cd LII)

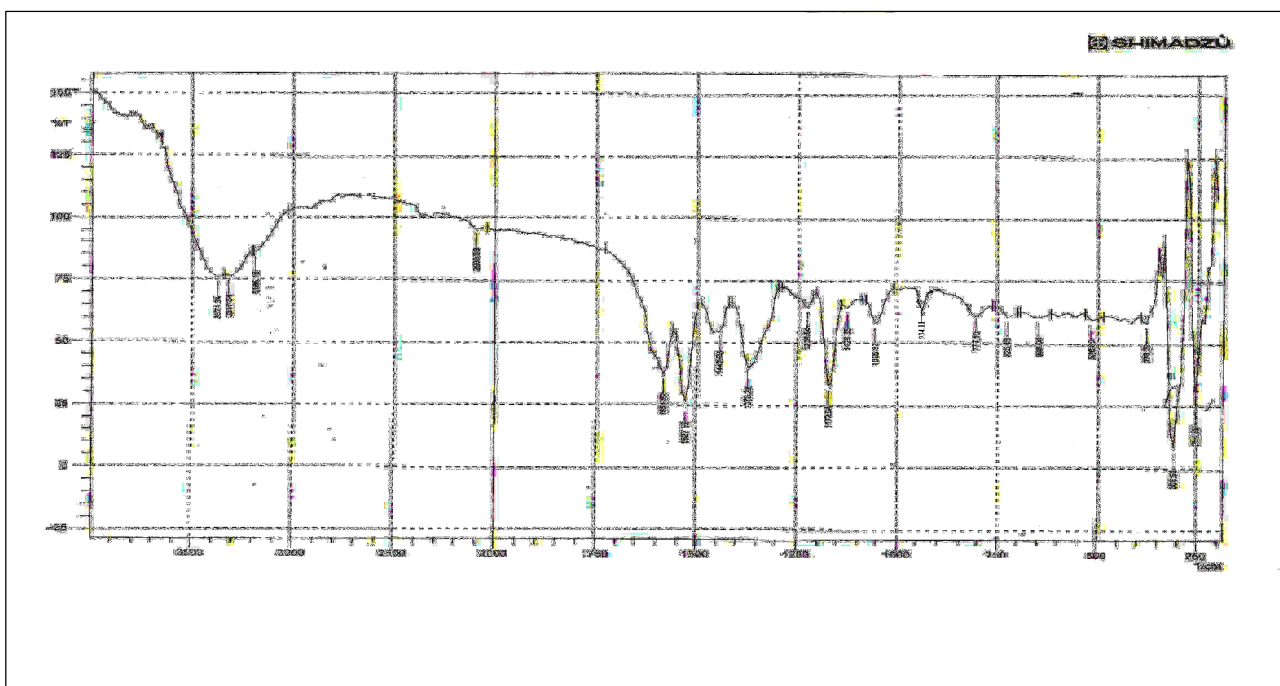


Fig (3-13): FT-IR spectra of (Cu LII)

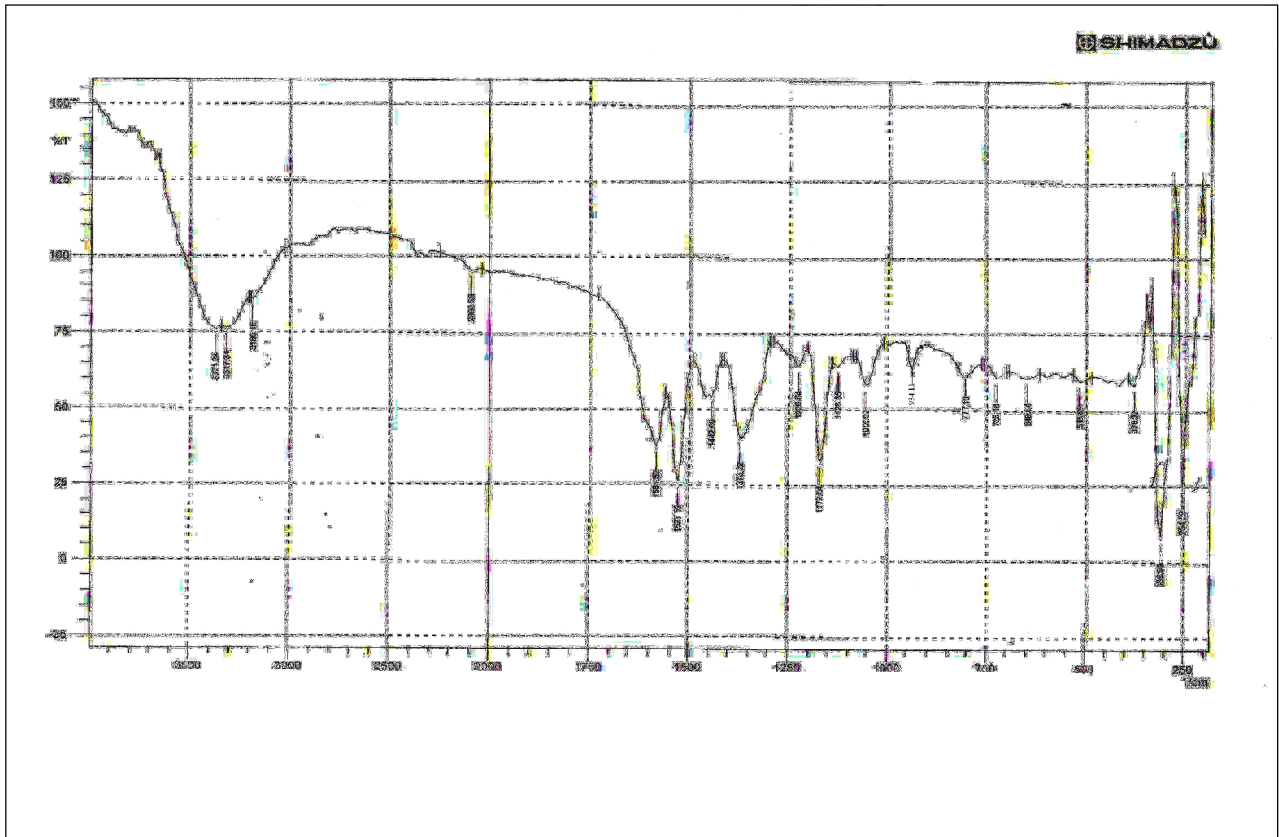


Fig (3-14): FT-IR spectra of (Ni LII)

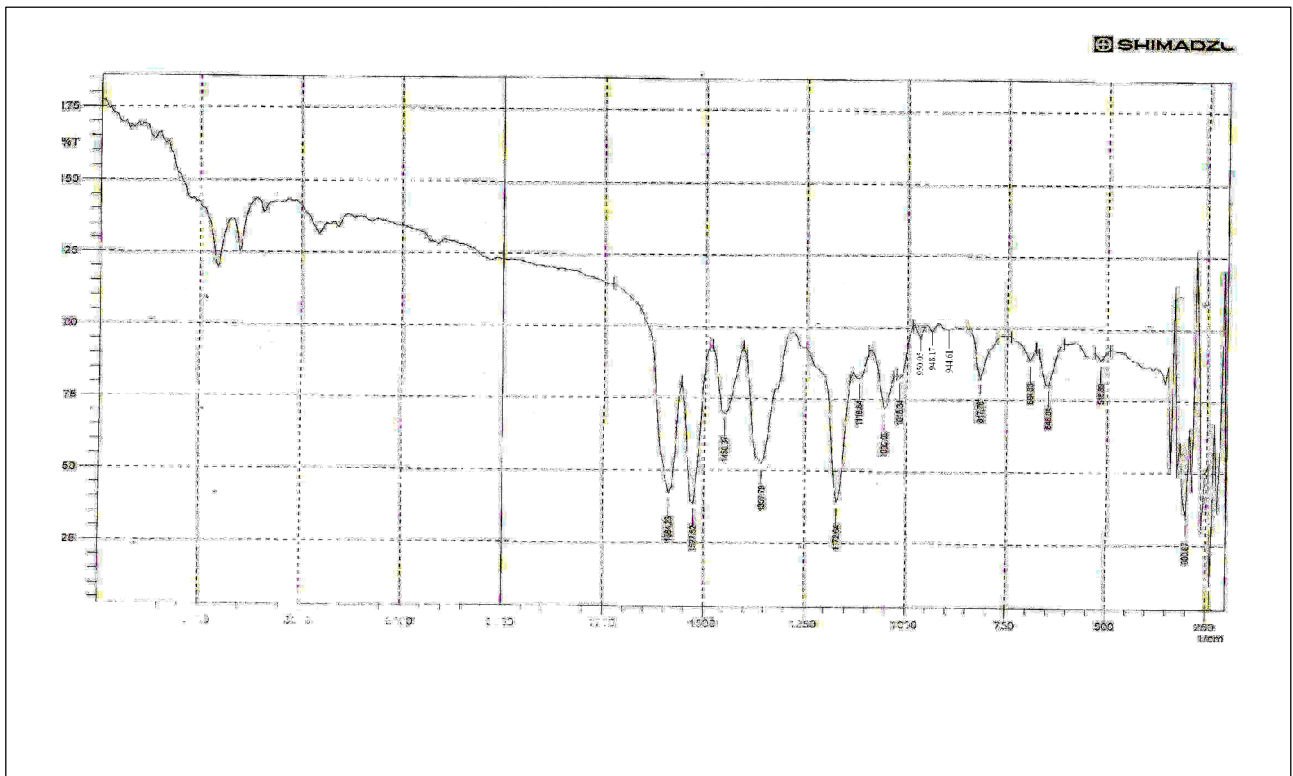


Fig (3-15) :FT-IR spectra of (Co LII)

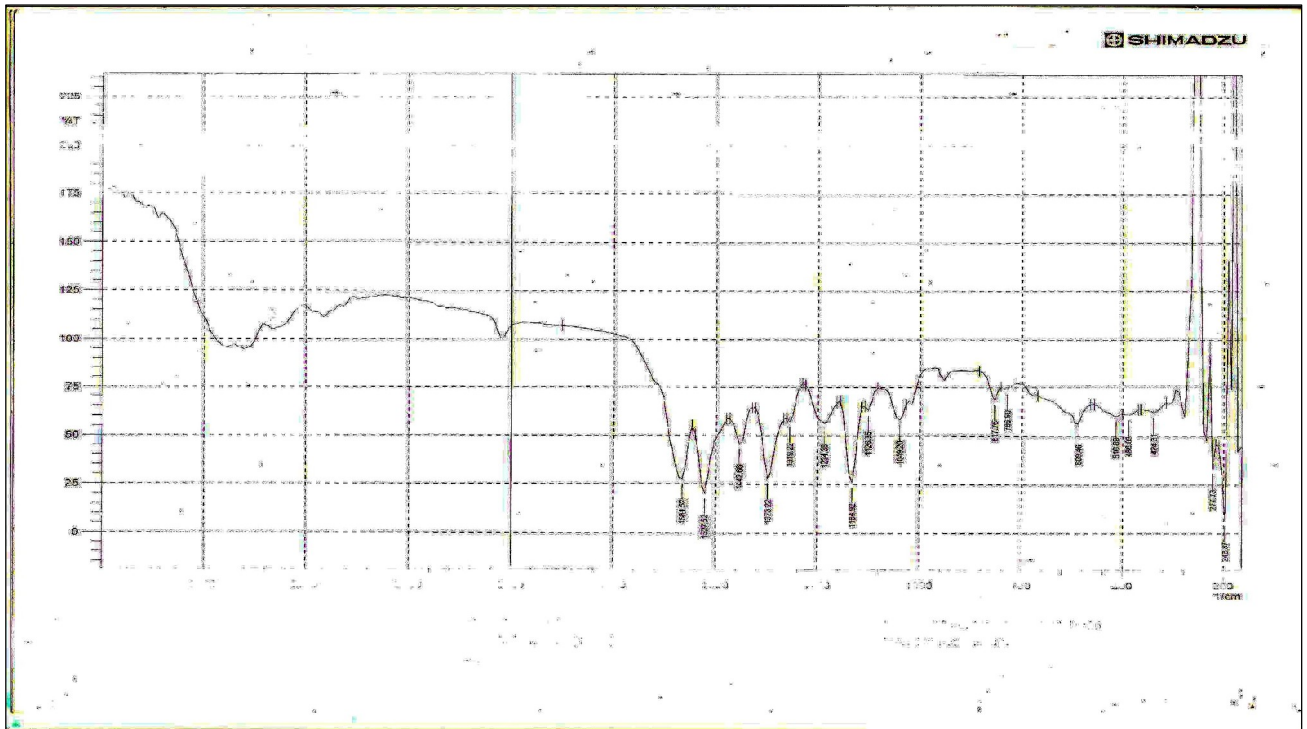
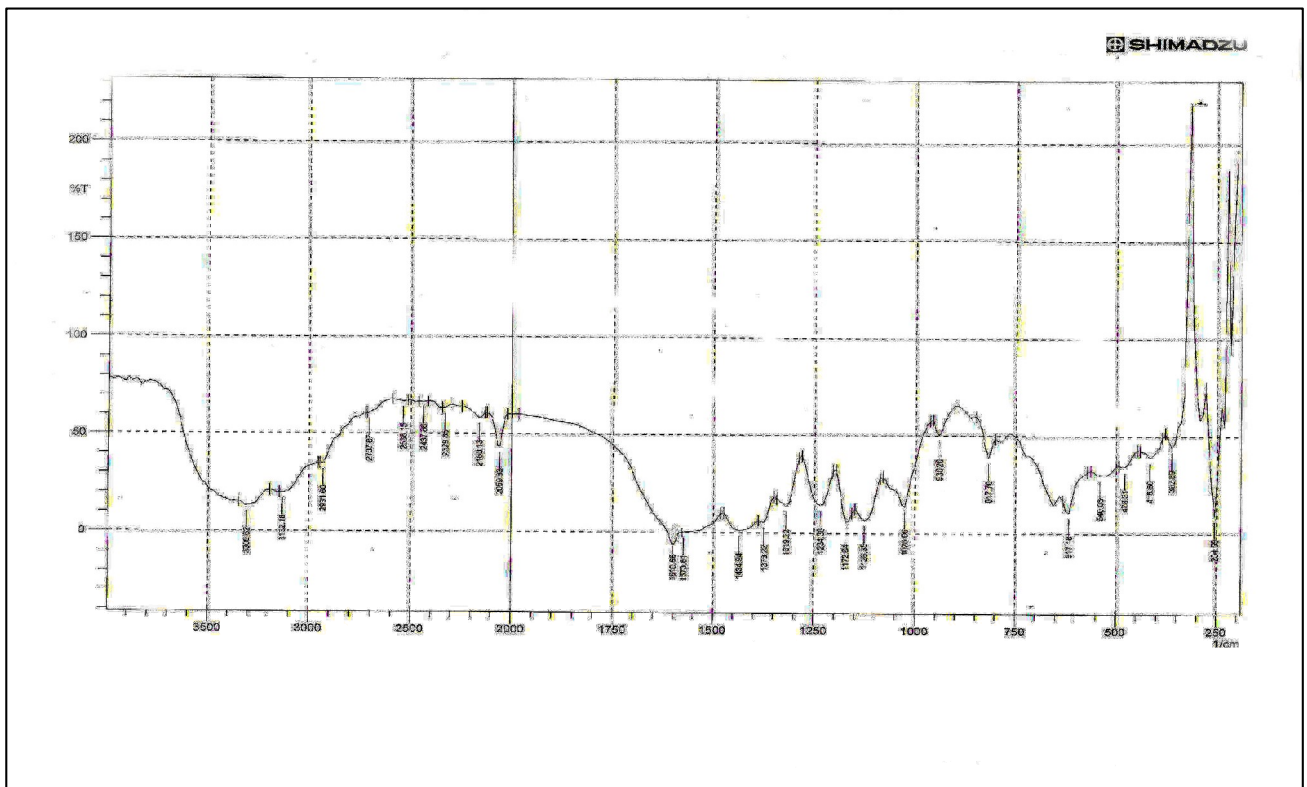


Fig (3-16): FT-IR spectra of (Fe LII)



Fig(3-17):FT-IR spectra of (Mn LII)

Table (3-4):- Selected bands of thiadiazole trithiocarbonate complexes (cm⁻¹)

			<i>Characteristic of SCS₂ fragment</i>							
Compound	ν O-H	ν C=N	ν NCS	ν C=S	ν C-S	ν C---S	ν C-O-C	ν M-N	ν M-S	ν M-X
I L		-1517 1566	1427	-952 900	752	1049-1130	1083	-	-	-
Cd LI	4300	1550- 1600 sh	1465	950- 894	756	1041-1142	1082	495	445	-
Cu LI	3448- 3363	1550- 1603sh	1450	942- 870	763	1002-1118- 1149	1080	905	455	Cu-O 470 CuCl 370
Ni LI	3409	1558- 1590sh	1485	940- 892	763	1080-1150	1086	501	470	-
Co LI	3394- 3340	1550- 1580sh	1458	945- 870	763	1020-1138	1082	470	430	M-Cl 350
Fe LI	3301	1519- 1589	1465	950- 894	763	1010-1149	1085	535	470	378
Mn LI	3417	1558- 1604	1442	941- 879	786	1010-1110- 1139	1079	478	401	-

Table (3-5):- Number of the most diagnostic bands of the prepared ligand and its complexes in cm^{-1}

Comp.	ν O-H	ν C=N Isomethaine	ν C=N ring	ν C=S	ν C-S	ν NCS	ν C--S	ν Ar-N	ν M-N	ν M-S	ν M-O	ν M-X
LII	-	1591	1527	943	777	1440	1001-1031-1132	1371	-	-	-	-
Cd LII	3400	1589	1537	933	792	1450	1016-1031-1116- 1117	1373	538	420	-	385
Cu LII	3450	1581	1527	935	788	1442	1018-1041-1118- 1164	1373	516	408	455455	392
Ni LII	3371	1561-1590sh	1527	937	794	1442	1056-1126-1172	1373	516	432	447	390
Co LII	3355	1581	1527	932	790	1442	1058-1122-1172	1371	550	430	509	390
Fe LII	3400- 3300	1581-1592sh	1527	930	786	1442	1020-1049-1128- 1146	1373	535	424	488	392
Mn LI	3400- 3309	1560-1604sh	1573	935	789	1434	1026-1056-1126- 1172	1373	540	416	478	-

3-3-2 -Electronic spectra magnetic properties and molar conductivity:-

The UV-Vis absorption spectra of the newly prepared complexes is of crucial importance besides the magnetic and conductivity measurement 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- orbital of the transition metal and the molecular orbital formed between the metal and the ligands there are four types of electronic spectra .^(76,77)

- a- Ligand spectra: these types of spectra are associated principally with the ligand only.
- b- Charge transfer spectra: these types involve electronic transition between the metal and the ligand.
- c- d-d and f-f spectra: these type of spectra are associated principally with the metal due to the effect of the ligand .
- d- Counter –ion spectra: these type of spectra involves spectra of ion and its associated with the complex .

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

Measuring magnetic susceptibility contributes to the determination of the 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⁽⁷⁸⁾

$$\mu_{s.o} = 2 (S(S+1))^{1/2}$$

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 (3-6) and (3-7).

These values were corrected for diamagnetic effect using the following relationship^(78,79)

$$\mu_{\text{eff}} = 2.828 (X_A \cdot T)^{1/2}$$

$$X_A = X_M - D \quad X_M = X_g \cdot \text{M.wt}$$

Where

T = temperature (298 K)

X_A = Atomic susceptibility

X_M = Molar susceptibility

X_g = Gram susceptibility

D = Correction factor

The molar conductance value 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^(80,81)

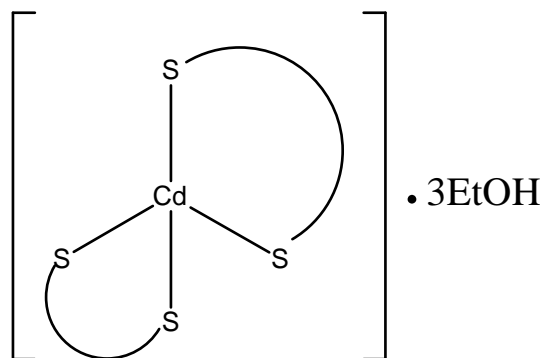
According to the results obtained from the electronic spectra, magnetic measurements, conductivity measurements, in addition to the metal analysis the stereochemistry around the metal ion were been suggested

3-3-2-1 Electronic spectra of the LI complexes , with Cd(II) ,Cu(II) ,Ni(II) ,Co(II) , Fe(III) , and Mn(II).

Cadmium (II) complex (Cd LI)

Generally , Zinc ,cadmium , and mercury ions behave similarly with respect to their coordination number , which may be 2 ,4, 5 and 6 and the most probable is the 4 and 6 coordination number ^(3,41) . The prepared complex is colorless and diamagnetic which is expected for d^{10} ions , since the Uv-Vis spectra of this complex gave a lot of information, so some shifting and change in the shape of the bonds were compared with those of the free ligand , therefore, the possible geometry around this ion can be suggested Fig(3-19)by considering the metal analysis , FT-IR , spectra and taking in account the available structures in the literature ^(2,3) . These observation let us to suppose tetrahedral geometry for (Cd LI) complex .

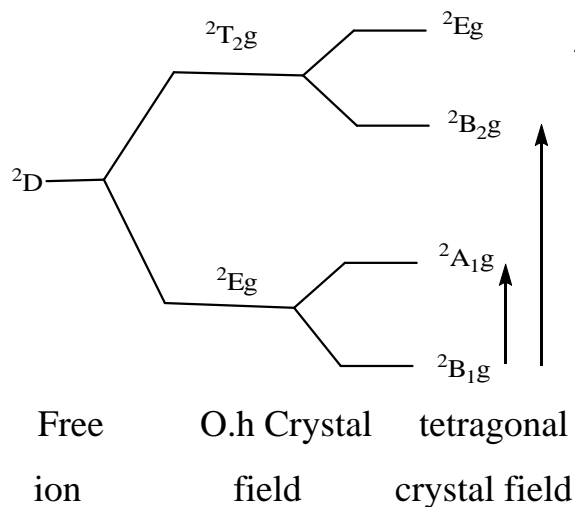
The conductivity measurements showed that the (Cd LI) complex was (non conducting).



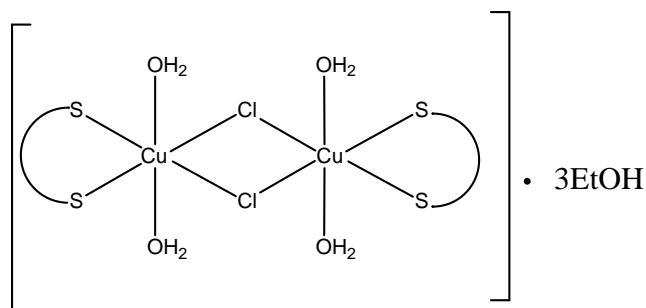
Copper (II) complex (Cu LI)

According to the HSAB rule , copper (II) is soft atom and its high affinity for sulfur donor is expected to contribute to strong M-S bond ⁽⁴¹⁾ . Cu (II):-compounds are blue or green because of single broad absorption band in the region (11000-16000 cm^{-1}) ⁽⁸²⁾ . The d^9 ion is characterized by large distortion for octahedral symmetry and the band is unsymmetrical, being the results of a number of transition which are by no means easy to assign unambiguously. The free ion

ground 2D term is expected to split in a crystal field in the same way as the 5D term of the d^4 ion and similar interpretation of the spectra is like wise expected , and according to the following ^(41,77) diagram.

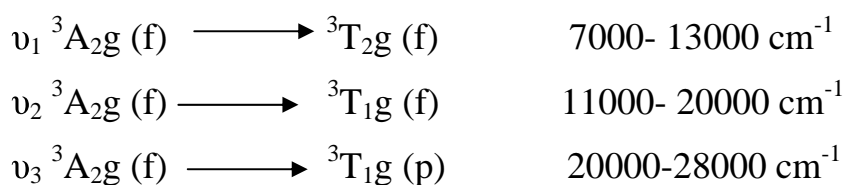


unfortunately , this is more difficult of the greater overlapping of bands, which occur in the case of Cu (II), In present work , the green complex show a board band at (12901 cm^{-1}) can assigned to $^2B_{1g}$ $^2B_{2g} \rightarrow ^2B_{1g} \rightarrow ^2E_g$, transition Fig. (3-20). The magnetic effect have been measure for the complex (1.02 B.M.) , this value in the range of dimeric octahedral geometry ^(83,84) . The conductivity measurement showed that the complex was non ionic , Table (3-6). From above results, in addition to IR spectra, flame atomic absorption analysis, gave a good support to suggest the following structure



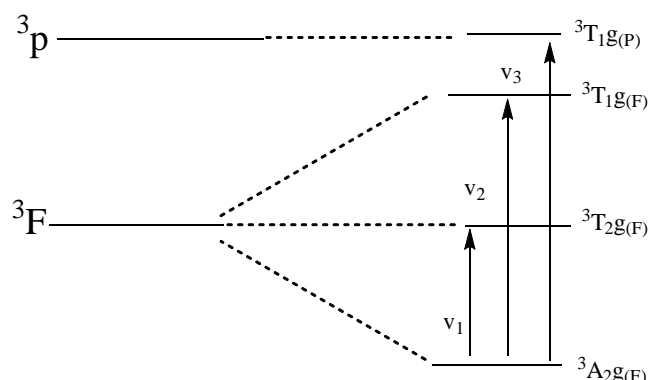
Nickel (II) Complexes (Ni II)

Nickel (II) forms a large numbers of complexes encompassing coordination numbers 4, 5, and 6 in structural types of ligands⁽³⁾. The coordination number of Ni (II) rarely exceeds 6 and its principles stereochemistries are octahedral and square planner, tetrahedral with rather fewer examples of trigonal bipyramidal or square pyramidal^(3,41). In octahedral field three spin allowed transitions are expected to appear because of the splitting of the free ion, ground term 3F and presence of 3P , these bands can be assigned as



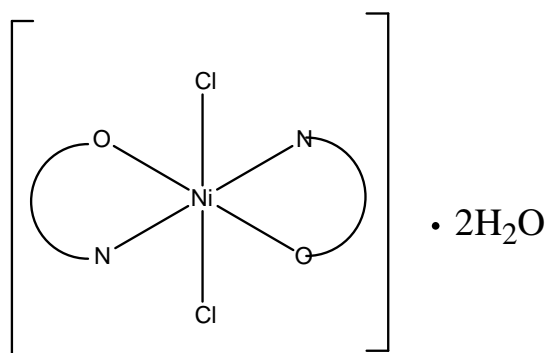
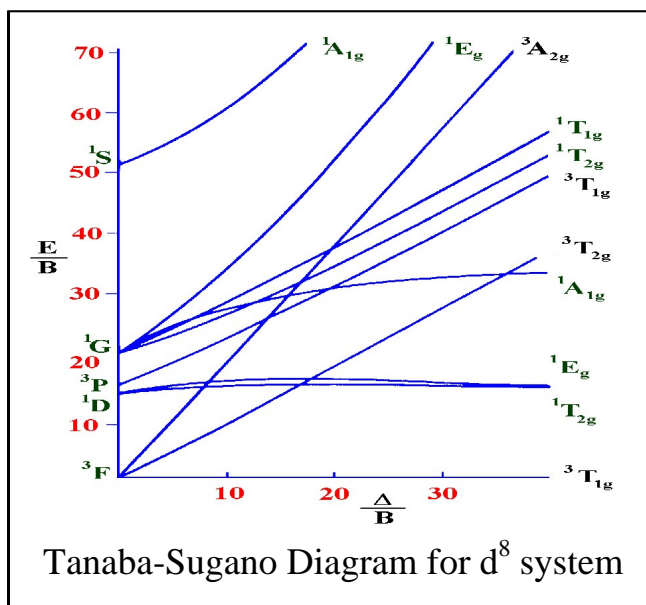
It is also evidence of weak spin-forbidden transition spin triplet to singlet was appear in the region (12000-13900 cm^{-1}) $^3A_{2g} \longrightarrow ^1E_g$ ⁽⁸⁵⁾.

The term symbol for the ground state of Ni(II) ion 3F can split on octahedral crystal as follow



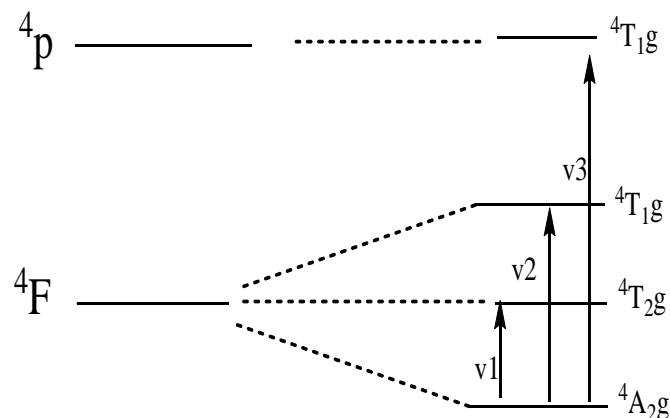
The Uv-Vis spectra of the present green Ni(II) complex, Fig. (3-21), showed two bands at (14,750 cm^{-1}) and (24,096 cm^{-1}) can be assigned ν_2 and ν_3 respectively^(41,86) and weak band at (10,080) cm^{-1} can be assigned

to (ν_1) transition ^(41,77). The Racah parameters B' , β and the value of $10Dq$ (ν_1) also calculated by reference to Tanabe-Sugano diagram for d^8 configuration. The value of the calculated μ_{eff} was (2.7 BM). This value is in the range of octahedral geometry ⁽⁴¹⁾. The conductivity measurement showed that the complex to be non ionic. From spectroscopic study and metal analysis, the following structure can be postulated.



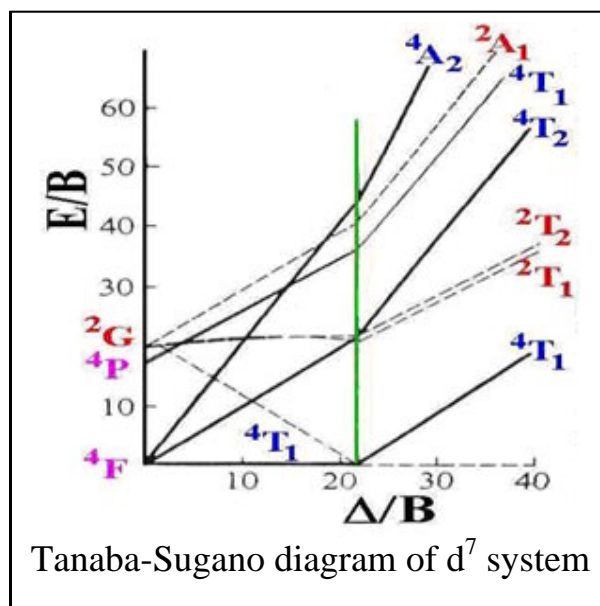
Cobalt (II) complexe (Co LI)

The electronic spectra of present work exhibit the following features (a) the intensities of the band are high (because of d-p mixing), and there are a little difference in intensity between ligand field and charge transfer bands (b) the presence of a group of band in the range $14,000-17,500\text{cm}^{-1}$ (indeed a triply splitting band). These features along with the dark green color of the complexes suggests a tetrahedral geometry around spin-free Co(II) ion ^(87,88). The spin-allowed transitions are as follow:



Inspection of the spectral data of a number of tetrahedral Co (II) complexes revealed that the two bands 16,393 and 14,771 cm⁻¹ of present complexes can be assigned to v₃ split, while v₂ expected in the range 5000 - 6000 cm⁻¹ can't be measured. v₁ is expected to be in the range 3000 - 5000 cm⁻¹, for that most of workers assigned only v₃ band and make neither further assignment to v₂ or v₁ nor calculated the ligand field parameters B'; β or 10Dq, In present work we looked for v₁ in the infrared spectrum of this assignment it was possible to calculate v₂, B', β and 10Dq by fitting the ratio of v₁/v₃ to Tanaba-Sogano diagram d⁷ configuration

, taking v₃ as the average value two splits, the results are shown in table (3-6) which are compatible to those of known tetrahedral Co (II) complexes. The fit of the upper band to tanaba-sugano d⁷ diagram predicts that the ⁴T_{1g} (p) term should lie at (15,058) cm⁻¹ above the ground term, in place of the averaged experimental value of



15,582 cm⁻¹. The internal consistency of the interpretation is particularly good and gives an acceptable account of the spectrum; On the other hand the value of β suggested a considerable covalent bonding between metal and L-atom.

The magnetic measurement showed that the complex paramagnetic (4,73BM), which in accordance with high spin tetrahedral^(89,90), The value of spin orbit coupling constant (λ) has been calculated and compared with the value free ion (-178) cm^{-1} , this constant was calculated using the following equation

$$\mu_{\text{obs}} = \mu_{\text{S.O}} - 15.49 \lambda / 10Dq$$

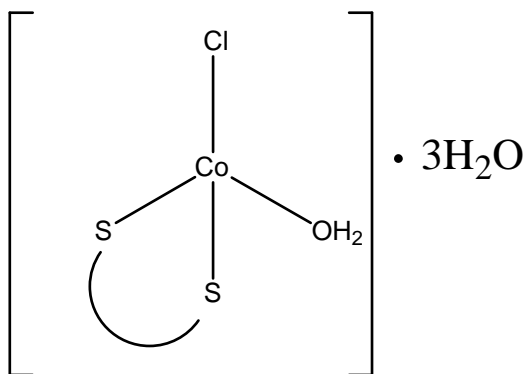
$$4.73 = 3.873 - 15.49 \lambda / 3467$$

Where

μ_{obs} = the observed effective magnetic moment

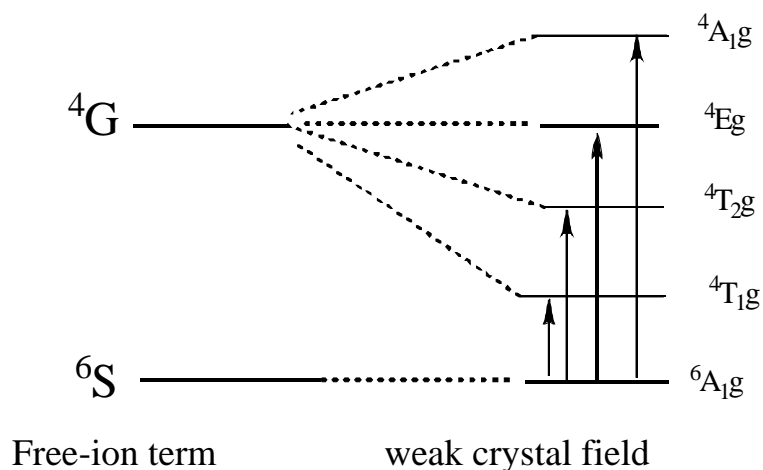
$\mu_{\text{S.O}}$ = the electronic spin only magnetic moment

The observed value of λ for the complex was (-192,3) cm^{-1} and it was less than the value of the free ion and doesn't fit in the range of the regular geometry, rather it fit with in value for distorted tetrahedral^(87,88). The molar conductivity measurements in DMSO showed that the complex was non electrolyte. According to these results and previous data the following structure can be proposed



Iron (III) complex (Fe LI)

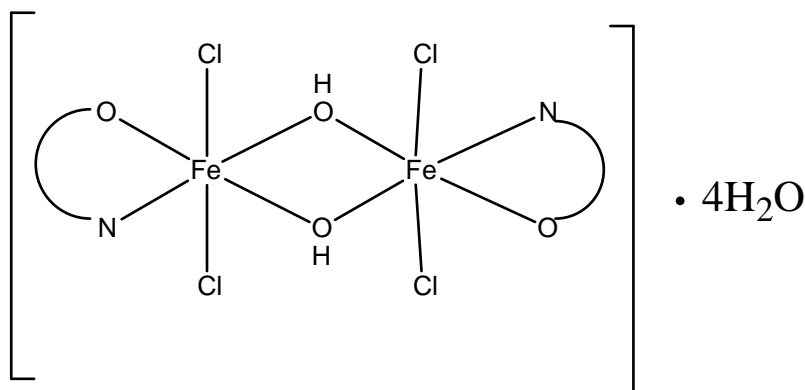
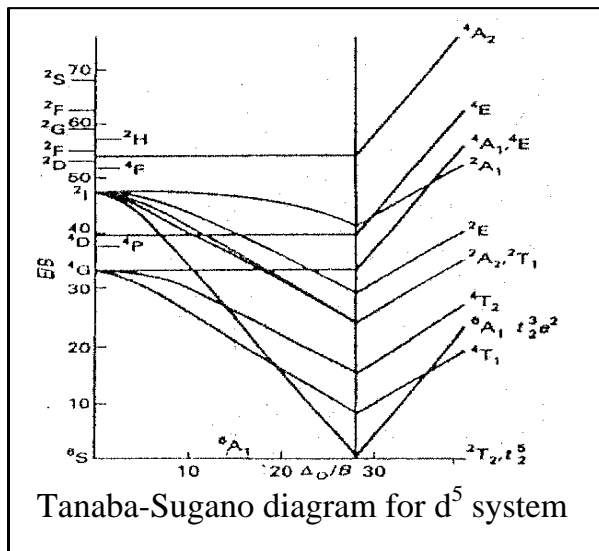
The majority of iron complexes are octahedral, but tetrahedral and square pyramidal ones are also important⁽⁴¹⁾. Iron (III) is isoelectronic with manganese (II), but much less is known of the details of Fe(III) spectra because of the much greater tendency of the trivalent ion to have charge transfer bands in near ultraviolet region with strong low energy in the visible that obscure the very weak, spin-forbidden d-d band^(2,41). The Fe(III) complexes of dithiocarbamates are well known^(91,92) and it can be concluded that (a) iron is in the (+3) oxidation state in weak field environment (i.e. high spin d^5 configuration), the ground term of the high spin Fe(III) ion is the sextet the only sextet term of the d^5 configuration in octahedral stereochemistry is the ${}^6A_{1g}$. Consequently, there can be no spin-allowed transitions are correlated by the following diagram⁽⁷⁷⁾.



Table(3-6) assign these transitions to their respective value. The proposed assignment are compatible with those assumed by other workers^(91,93), (b) by comparison to the spectral data discussed by couvanis et,al.⁽⁹³⁾ about the intensity and position of the bands in regard to structural formula of monomeric and dimeric iron(III) thiol ligands and can be deduced that iron complex is a dimer rather than monomer.

The value of crystal field strength ($10Dq$), inter electronic repulsion parameter B^{λ} and nephelauxetic parameter β were calculated by filling the ratio ν_1/ν_2 to the tanaba – sugano diagram for d^5 configuration

The magnitude of $10 Dq$ reflected the relative strength of dithio ligand to be in the weak side of the spectrochemical series ^(79,80) and is comparable to the values found for such complexes. The B' and the low β value suggests a considerable orbital overlap and covalent nature of the metal donor link. This is expected, since the ligand do belong to the thio type, i.e. dithiocarbamates, sulfides, dithiophosphate, ---- etc. which are local in the end of the nephelauxetic series and have the strongest effect and is in accordance with the high polarizability and high reducing power of S-atom ^(79,80). The value of the magnetic moment of this compound was (5.16BM), this value is the range of octahedral geometry ⁽⁸⁰⁾. The conductivity measurement showed the complex to be non-ionic, therefore the following structure can be postulated



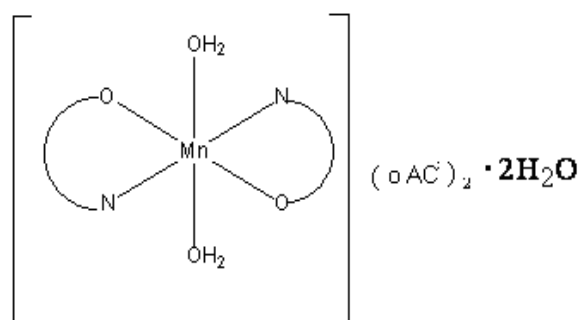
Manganese (II) complex (Mn LI)

The electronic spectra of Mn(II) complex was recorded in the DMSO solution ,spectra assignment were obtained by filling the observed spectra of the Tanaba-Sugsno diagram for d^5 configuration values of B' , β and $10Dq$ computed there from ⁽⁷⁷⁾ .

Two observations have to be pointed out : (I) a series of very weak , some were narrow bands , were observed in manganese spectra, this is expected because the only sextet term of the d^5 configuration in octahedral stereochemistry in the ${}^6A_{1g}$,consequently there can be no spin –allowed transition ⁽⁷⁷⁾ .

Furthermore the energies of the 4E_g (G) and ${}^4A_{1g}$ (G) terms don't change much relative to the ${}^6A_{1g}$ ground term as $10Dq$ change , as seen from the Tanaba-Sugano diagram , therefore the bands corresponding to transition between the ground term and these two term are not appreciably broadened by vibronic coupling ^(77,94) . The values of nephelauxetic ratio , β , evaluated as the ratio of the term separation in the complex , B' to that in the free ion are high Table (3-6).

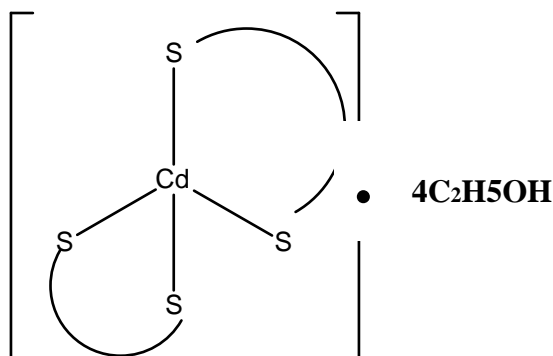
This is in keeping with the general opinion that manganese (II) complex was highly ionic ^(88,94).The electronic spectra coupled with magnetic (4.88 BM) and conductivity measurement showed that the complex was ionic indicating octahedral geometric around Mn(II) ion.



3-3-2-2 Electronic spectra of The complexes ,LII with Cd(II) Cu(II),Ni(II) ,Co(II) , Fe(III) , and Mn(II).

Cadmium (II) complex (Cd LII)

The Uv-Vis spectra of Cd(II) ion have some transition found in the region (200-445nm) , can be assigned as intraligand transition , and this transition of d^{10} gave a lot of information . The prepared complex was diagrammatic and conductivity measurement showed that the complex was non conductive , So from these information and atomic absorption analysis in addition to IR study , the tetrahedral geometry structure can be suggested .

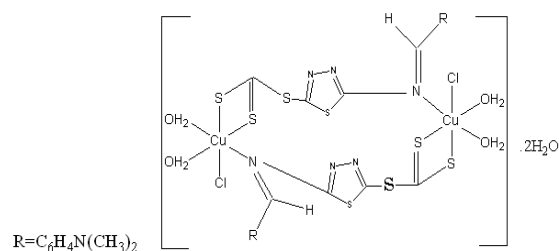


Copper (II) complex (Cu LII)

Electronic spectrum of the brown complex is shown in Fig (3-27) , table (3-7) .The brown color was attributed to the single broad absorption band in the region (16000-140000 cm^{-1})⁽⁸⁰⁾ . The d^9 ion configuration characterized by large distortion from octahedral geometry . Oh , complex for Cu(II) usually have three bands but unfortunately these bands can not be clearly assigned ,This difficulty is due to the greater overlapping of the bands , which usually occurs in the case of Cu(II) complexes .

The center of the broad band has been assigned at (14814 cm^{-1}) , this band refers to distortion octahedral geometry (Jahn-Teller distortion)^(95,96) and can be assigned as $^2E_g \longrightarrow ^2T_{2g}$ and other band founds in the region

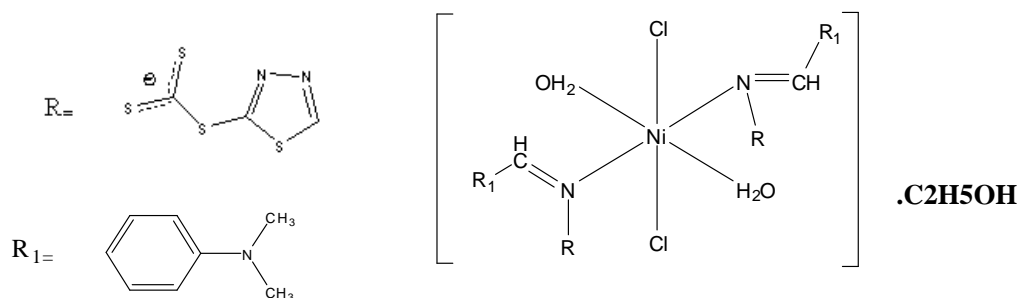
($37037,23955 \text{ cm}^{-1}$) can be assigned as intraligand . The magnetic susceptibility of Cu(II) complex was (1.2 BM) , and conductivity measurement showed that the complex was non ionic ,so from previous data and analysis the following structure can be suggested.



Nickel (II) Complex (Ni LII)

Electronic spectra of (Ni LII) , Fig(3-28) have shown four bands ,one at $(13,947) \text{ cm}^{-1}$ refer to the spin forbidden transition ${}^3\text{A}_2\text{g} \longrightarrow {}^1\text{E}_\text{g}$ and the other three bands ($11,135$, $15,748$ and $23,255 \text{ cm}^{-1}$) which refer to transition ${}^3\text{A}_2\text{g} \longrightarrow {}^3\text{T}_2\text{g} (\text{f})$, ${}^3\text{A}_2\text{g} \longrightarrow {}^3\text{T}_1\text{g} (\text{f})$ and ${}^3\text{A}_2\text{g} \longrightarrow {}^3\text{T}_1\text{g} (\text{p})$ respectively . The values ligand field , β and B' were calculated using Tanaba-Sugano diagram for d^8 system, Table (3-7).

The magnetic moment of the brown complex was (2.0 BM)and conductivity measurement showed that the present complex was non ionic , from previous data octahedral geometry was assumed for Nickel (II) complex



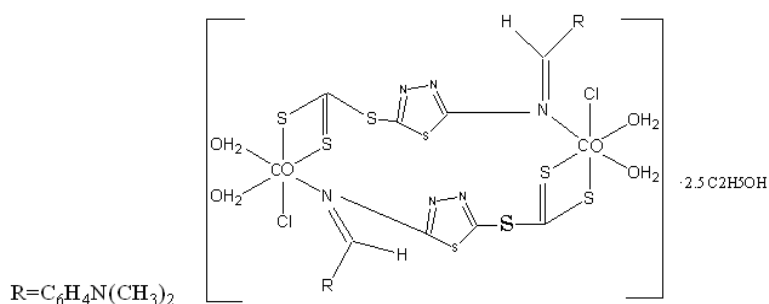
Cobalt (II) complex (Co LII)

The spectra of this complex, have show three bands at (10,040,15,070 and 19,980 cm^{-1}), which were assigned to the transition ${}^4T_{1g} \longrightarrow {}^4T_{2g}$ ${}^4T_{1g} \longrightarrow {}^4A_{2g}$ and ${}^4T_{1g} \longrightarrow T_{1g}(p)$ respectively.

The ligand field and ν_2 , β , B' was calculated using Tanaba-Sugano diagram d^7 system table (3-7).

The magnetic moment of this complex was (4.90 BM) proved that the complex was paramagnetic and have three unpaired electrons indicating a high spin octahedral configuration. The conductivity measurement has shown the complex was non-ionic .

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

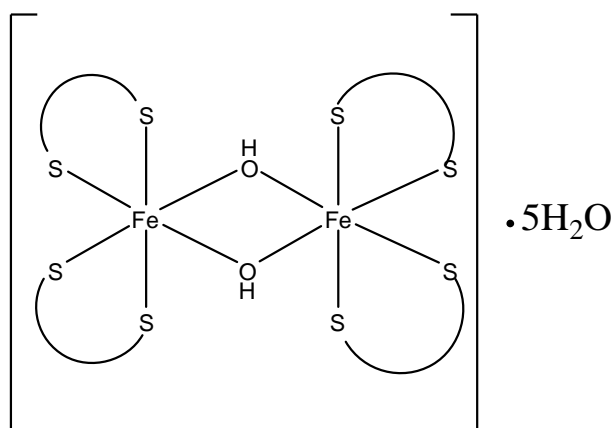


Fe (III) complex (Fe LII)

The spectrum behavior of this brown complex Fig (3-30) was similar to that of the complex Fe LI , was also showed three bands at (11.695, 18.518 and 26.315 cm^{-1}) that refer to ${}^6A_{1g} \longrightarrow {}^4T_{1g}(G)$, ${}^6A_{1g} \longrightarrow {}^4T_{2g}(G)$ and ${}^6A_{1g} \longrightarrow {}^4A_{1g} + {}^4E_g(G)$ respectively .

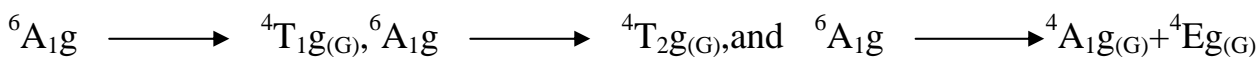
The ligand field, β , B' and characteristic bond was calculated with the references to T.S diagram, d^5 configuration, Table (3-7). The magnetic moment of this complex was (4.91 BM).Conductivity measurement

showed that the complex was non ionic and from previously data and IR , atomic absorption analysis the following structure can be suggested .



Mn (II) complex (Mn LII)

The spectral behavior of this brown complex is similar with that shown in complex Mn LI. Table (3-7) was showed three bands (12,658- 18,834 and 26,505 cm^{-1}) which was assigned to the transitions



respectively . The values of racha parameter , naphelanxetic and 10 Dq were calculated references to Tanaba-Sugano diagram d^5 configuration table (3-7). The magnetic measurement of the complex was (4.9BM) showed the complex to be paramagnetic and five unpaired electrons indicating a high spin octahedral configuration . The conductivity measurement showed that the complex was non ionic . From these results an octahedral geometry proposed in following structure.

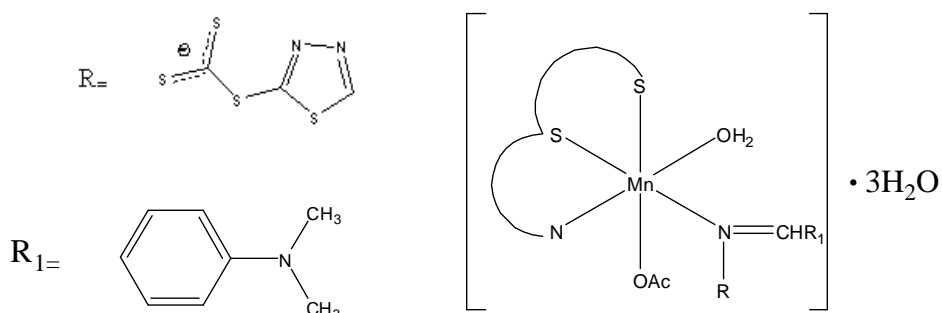


Table (3-6) Electronic spectral data, magnetic moment, conductivity and suggested structure for LI and complexes

Comp.	Bands cm^{-1}	Assignment	B	B'	Dq/B'	β	10Dq	15B'	μ_{eff}	$\mu_{\text{s}} \text{cm}^{-1}$	Suggested structure
Cd LI	$\nu_1=23.786$ $\nu_2=23.051$ $\nu_3=28.571$	I L C T							0.00	26	Th
Cu LI	$\nu_1=12.901$	${}^2\text{B}_{1\text{g}} \longrightarrow {}^2\text{B}_{2\text{g}}$ ${}^2\text{E}_{\text{g}} \longrightarrow {}^2\text{B}_{2\text{g}}$							1.02	21	O.h
Ni LI	$\nu_1=10.080$ - 10,098cal $\nu_2=14.750$ $\nu_3=24.096$	${}^3\text{T}_{2\text{g}(\text{F})} \longrightarrow {}^3\text{A}_{1\text{g}}$ ${}^3\text{T}_{1\text{g}(\text{F})} \longrightarrow {}^3\text{A}_{1\text{g}}$ ${}^3\text{T}_{1\text{g}(\text{P})} \longrightarrow {}^3\text{A}_{1\text{g}}$	1035	570	1.8	0.55	10.262	10.098	2.70	23	O.h
Co LI	$\nu_1=3394$ $\nu_2=4993$ cal $\nu_3=15.582$	${}^4\text{T}_{2(\text{F})} \longrightarrow {}^4\text{A}_2$ ${}^4\text{T}_{1(\text{F})} \longrightarrow {}^4\text{A}_2$ ${}^4\text{T}_{2(\text{P})} \longrightarrow {}^4\text{A}_2$	1120	693	0.5	0.61	3467	4995	4.73	20	T.h
Fe LI	$\nu_1=11.312$ (10.327) cal $\nu_2=17.857$ $\nu_3=24.691$	${}^4\text{T}_{1\text{g}(\text{G})} \longrightarrow {}^6\text{A}_{1\text{g}}$ ${}^4\text{T}_{2\text{g}(\text{G})} \longrightarrow {}^6\text{A}_{1\text{g}}$ ${}^4\text{A}_{1\text{g}} + {}^4\text{E}_{\text{g}} \longrightarrow {}^6\text{A}_{1\text{g}}$	1300	771	1.3	0.59	10.030	10.327	5.16	15	O.h
Mn LI	$\nu_1=10.183$ (11.742) cal $\nu_2=24.096$ $\nu_3=26.881$	${}^4\text{T}_{1\text{g}(\text{G})} \longrightarrow {}^6\text{A}_{1\text{g}}$ ${}^4\text{T}_{2\text{g}(\text{G})} \longrightarrow {}^6\text{A}_{1\text{g}}$ ${}^4\text{A}_{1\text{g}} + {}^4\text{E}_{\text{g}(\text{G})} \longrightarrow {}^6\text{A}_{1\text{g}}$	860	850	1.1	0.98	9350	11.742	4.88	18	O.h

I L C T: Internal ligand charge transfer

Table (3-7) Electronic spectral data, magnetic moment, conductivity and suggested structure for LII and complexes

Compo.	Bands cm^{-1}	Assignment	B	B'	Dq/B'	β	10Dq	15B'	μ_{eff}	$\mu_{\text{s}} \text{Cm}^{-1}$	Suggested structure
Cd LII	$\nu 1 = 22,347$ $\nu 2 = 27.027$ $\nu 3 = 32.894$	I L C T →							0	18	Th
Cu LII	$\nu 1 = 14.84$	${}^2\text{Eg} \longrightarrow {}^2\text{T}_{2g}$							1.2	28	Oh
Ni LII	$\nu 1 = 11.135,$ $\nu 2 = 15.748$ $\nu 3 = 23.255$	${}^3\text{A}_{2g} \longrightarrow {}^3\text{T}_{2g}$ ${}^3\text{A}_{2g} \longrightarrow {}^3\text{T}_{1g}$ ${}^3\text{A}_{2g} \longrightarrow {}^3\text{T}_{1g(p)}$	1035	559.3	1.9	0.54	10.627	10.267	2.0	22	Oh
Co LII	$\nu 1 = 10.040$ $\nu 2 = 15.070-$ 20.055 cal $\nu 3 = 19.980$	${}^4\text{T}_{1g} \longrightarrow {}^4\text{T}_{2g}$ ${}^4\text{T}_{1g} \longrightarrow {}^4\text{A}_{2g}$ → ${}^4\text{T}_{1g} \longrightarrow {}^4\text{T}_{1g(p)}$	1120	661	1.8	0.59	11.896	20.055	4.90	29	Oh
Fe LII	$\nu 1 = 11.695$ $\nu 2 = 18.518$ $\nu 3 = 26.315$	${}^6\text{A}_{1g} \longrightarrow {}^4\text{T}_{1g(G)}$ ${}^6\text{A}_{1g} \longrightarrow {}^4\text{T}_{2g(G)}$ ${}^6\text{A}_{1g} \longrightarrow {}^4\text{A}_{1g} + {}^4\text{Eg(G)}$	1300	829.2	1.35	0.63	11.194	10.797	4.91	27	Oh
Mn LII	$\nu 1 = (12.658-$ 11,688) cal $\nu 2 = 18.348$ $\nu 3 = 26.505$	${}^6\text{A}_{1g} \longrightarrow {}^4\text{T}_{1g(G)}$ → ${}^6\text{A}_{1g} \longrightarrow {}^4\text{T}_{2g(G)}$ ${}^6\text{A}_{1g} \longrightarrow {}^4\text{A}_{1g} + {}^4\text{Eg(G)}$	860	852.5	1.5	0.99	12.787	11.685	4.9	26	Oh

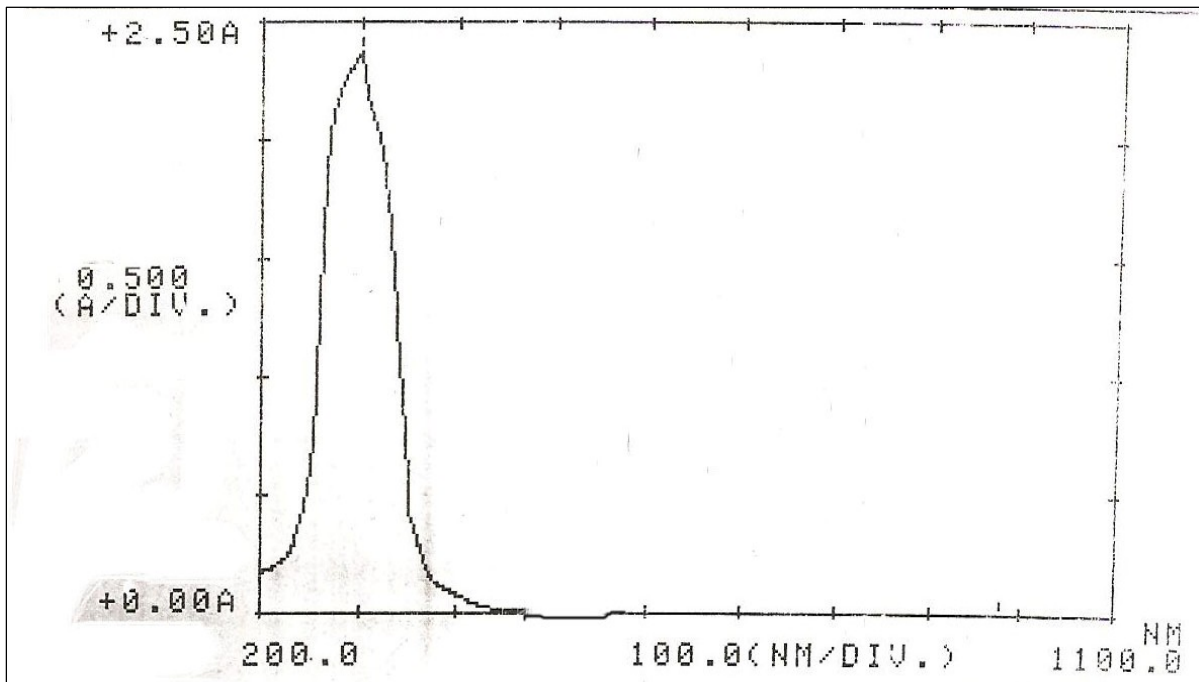


Fig (3-18):- Uv-Vis spectra of complex LI

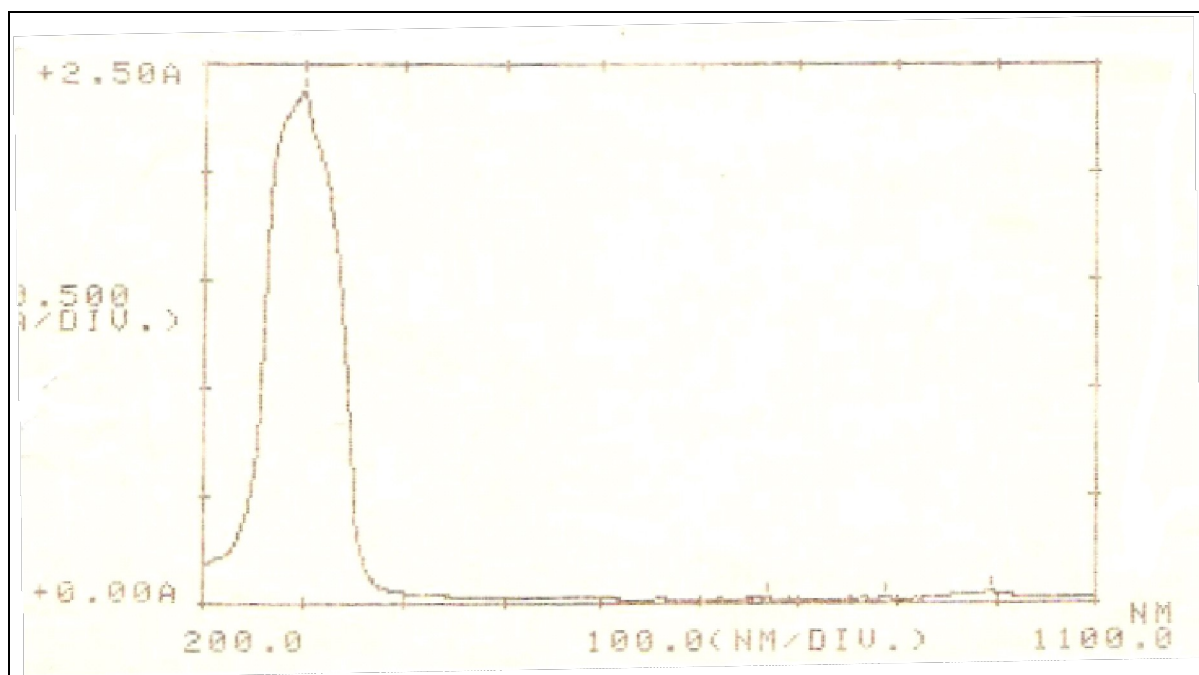


Fig (3-19):- Uv-Vis spectra of complex Cd LI

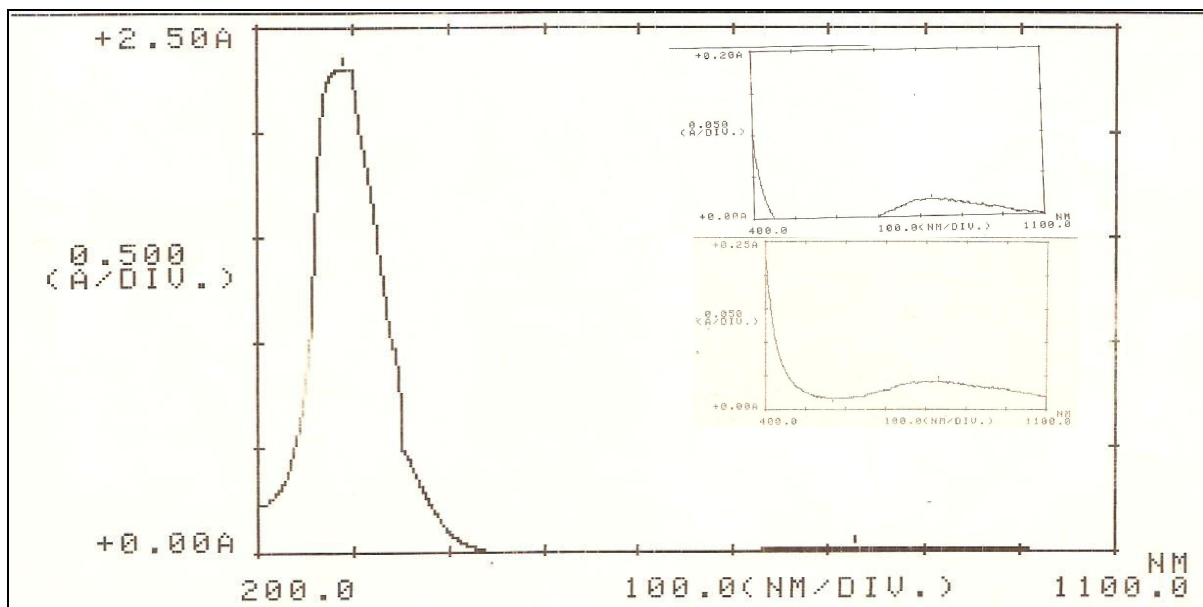


Fig (3-20):- Uv-Vis spectra of complex Cu LI

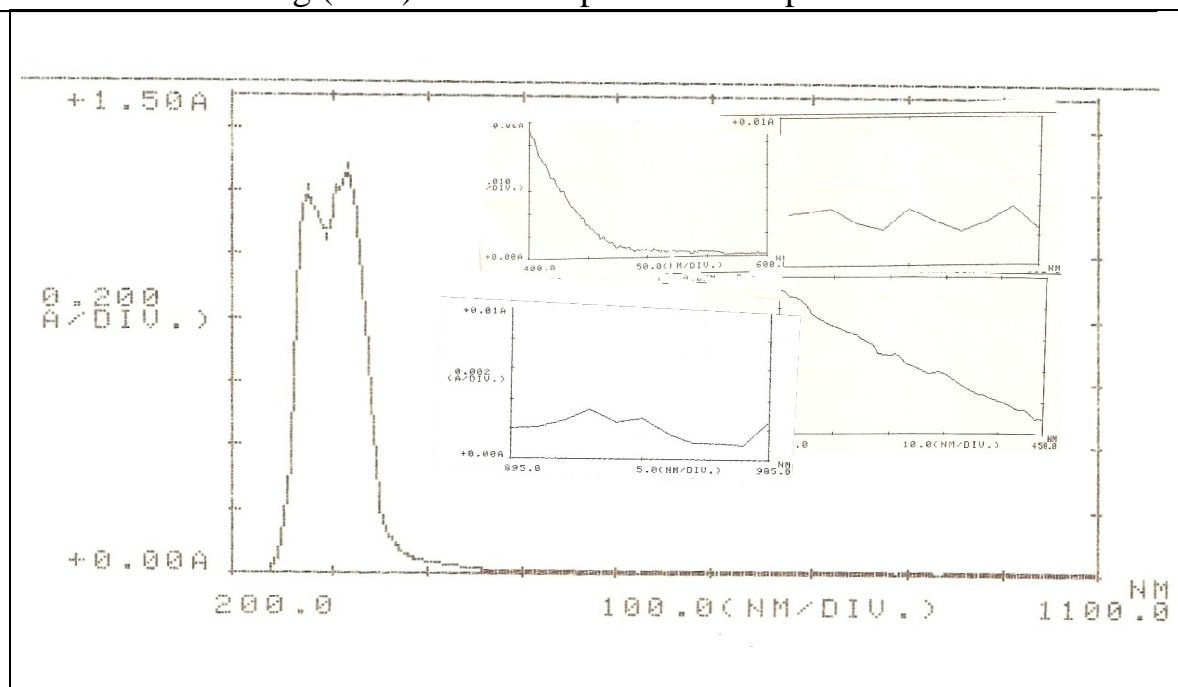


Fig (3- 21) :- Uv-Vis spectra of complex Ni LI

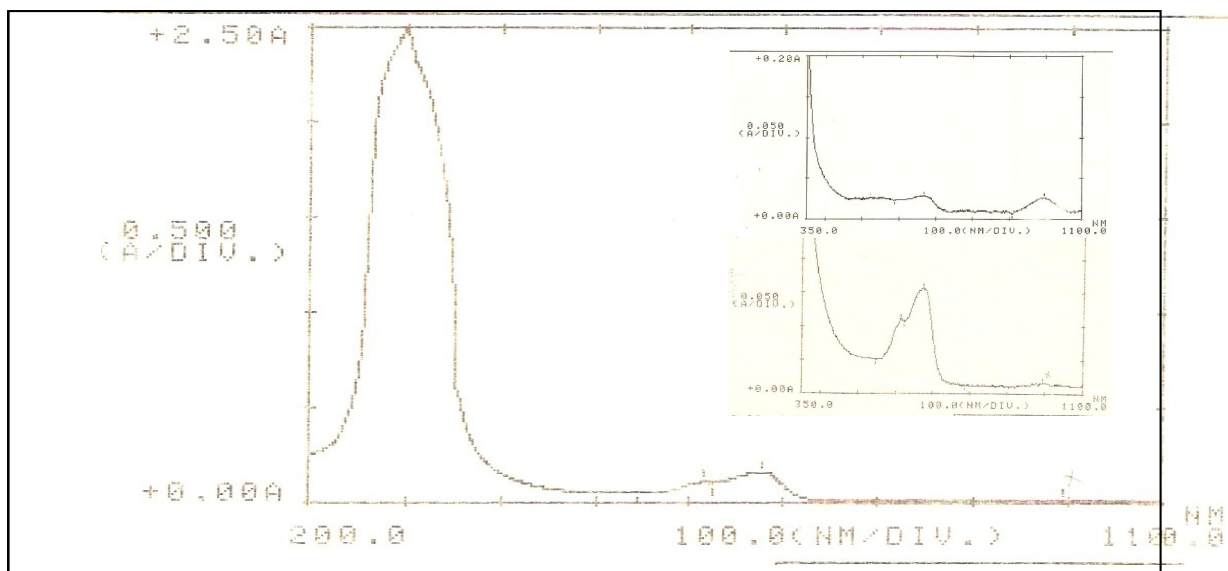


Fig (3-22):- Uv-Vis spectra of complex Co LI

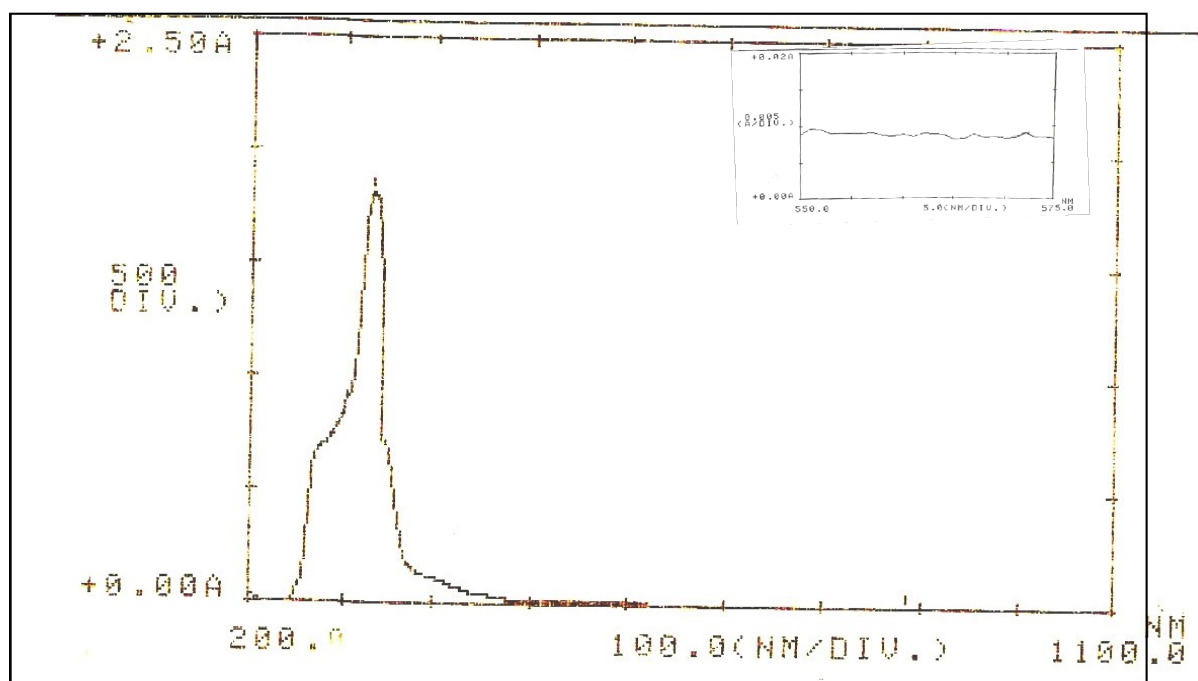


Fig (3-23):- Uv-Vis spectra of complex Fe LI

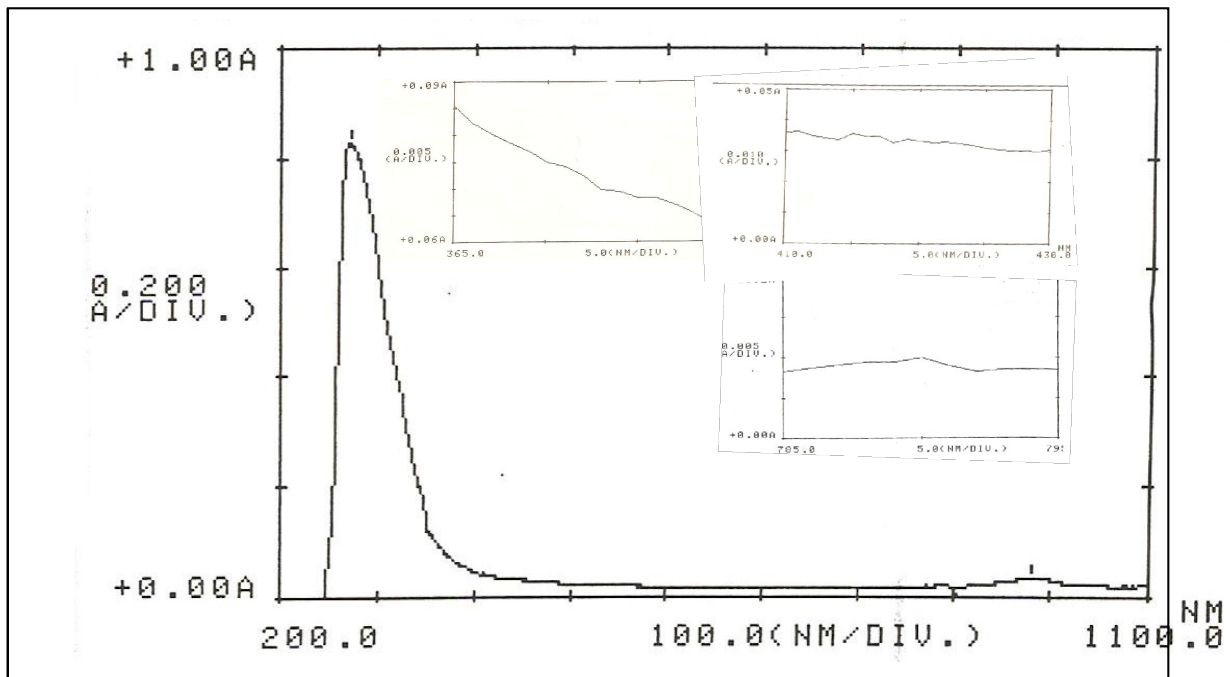


Fig (3-24):- Uv-Vis spectra of complex Mn LI

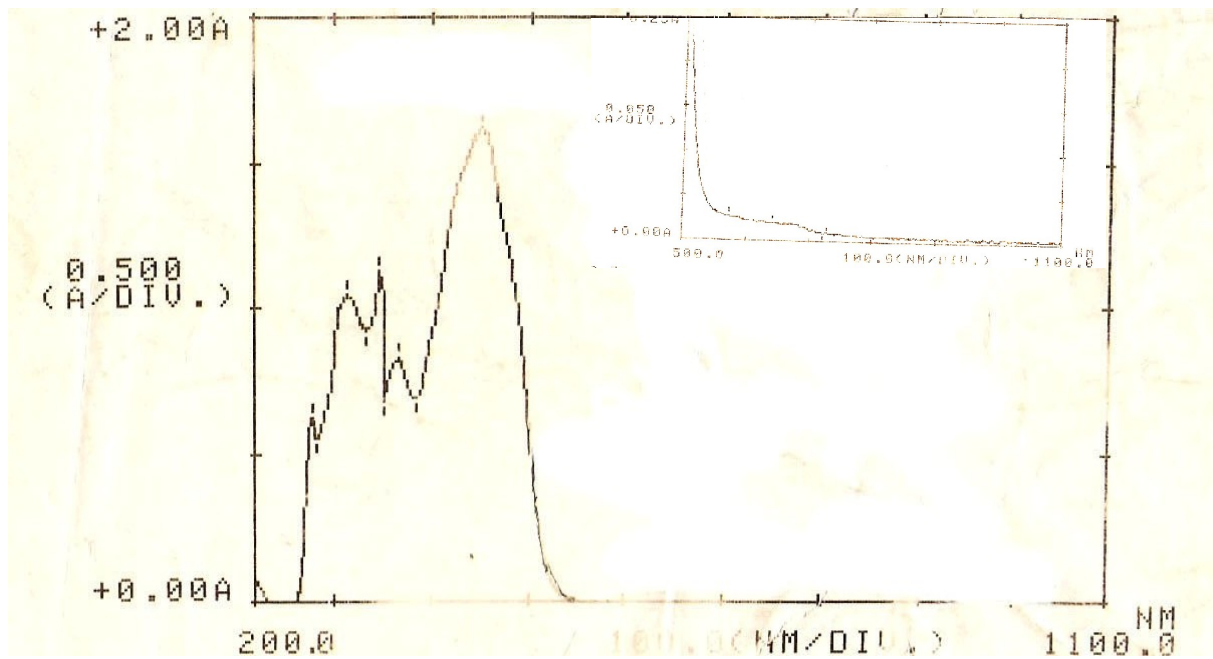


Fig (3-25):- Uv-Vis spectra of complex LII

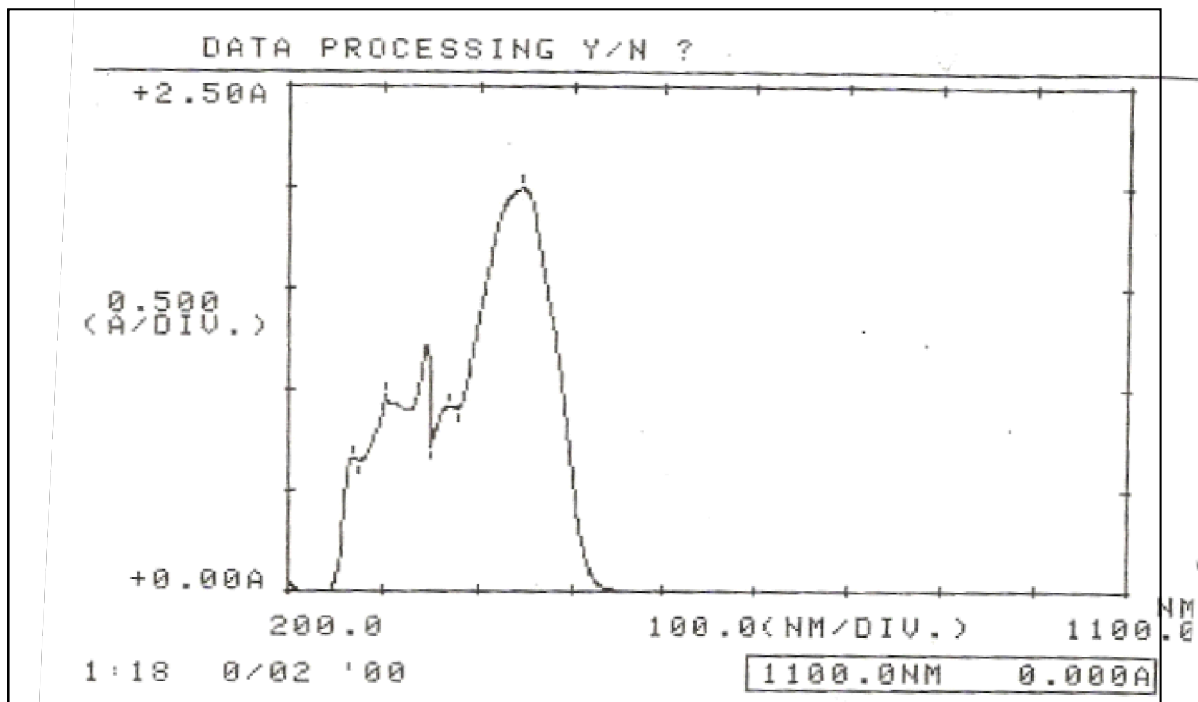


Fig (3-26):- Uv-Vis spectra of complex Cd LII

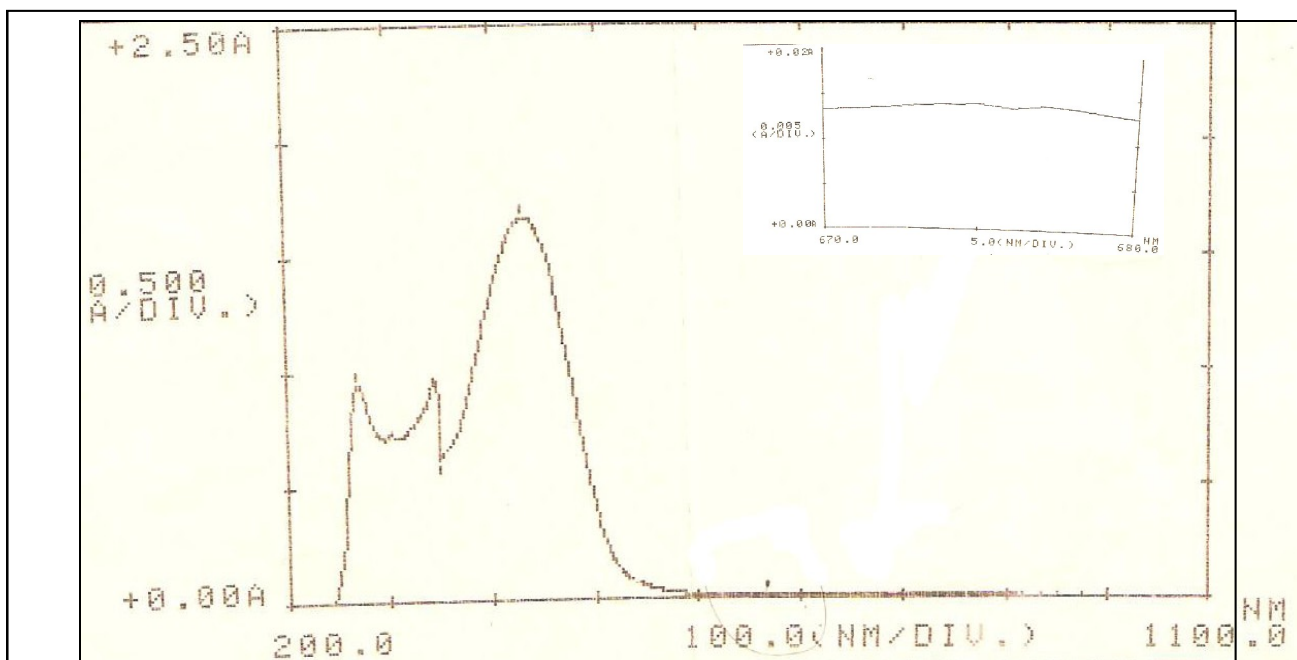


Fig (3-27):-Uv-Vis spectra of complex Cu LII

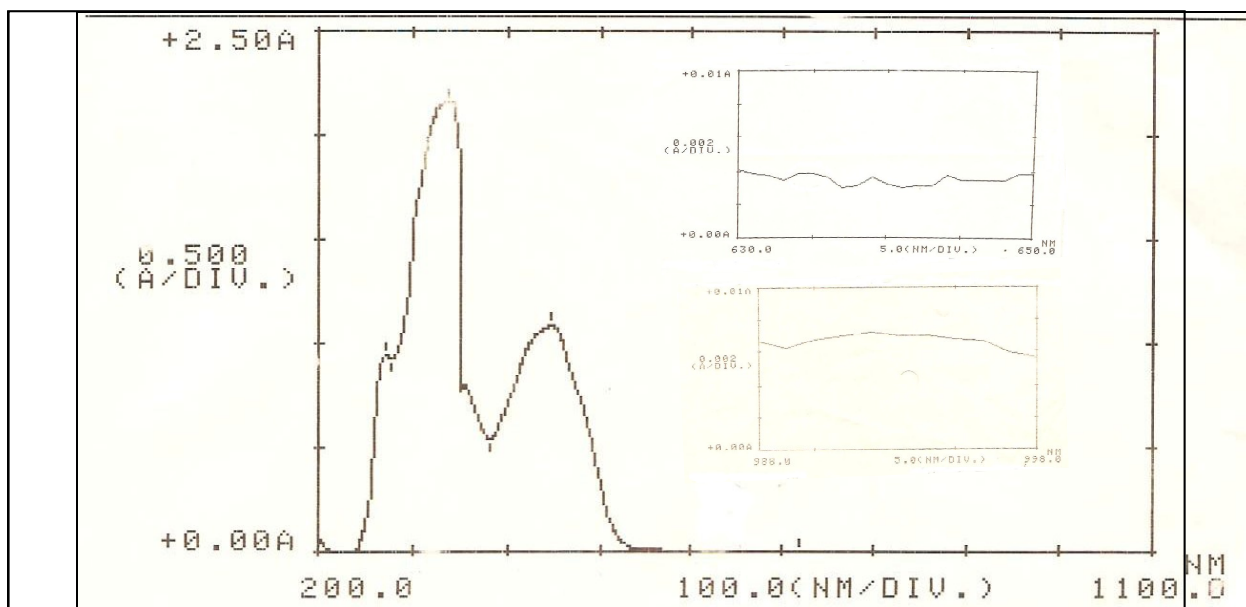


Fig (3-28):- Uv-Vis spectra of complex Ni LII

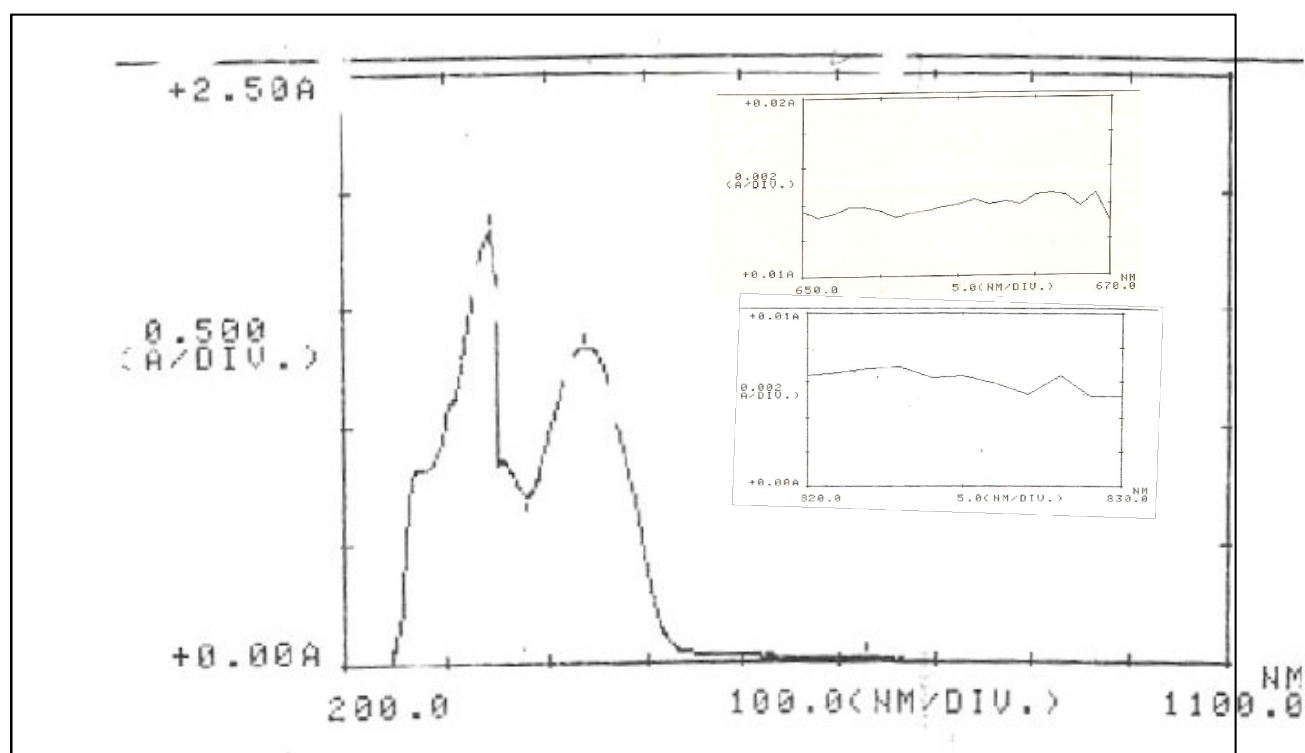
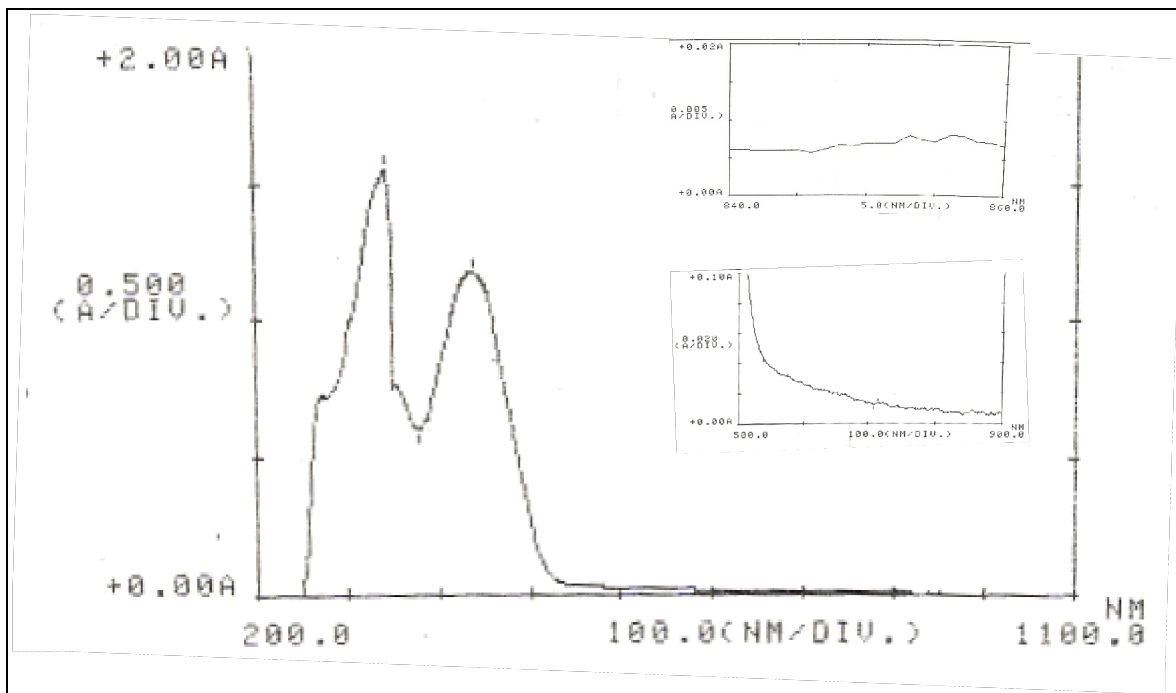


Fig (3-29):-Uv-Vis spectra of complex Co LII



Fig

(3-30):- Uv-Vis spectra of complex Fe LII

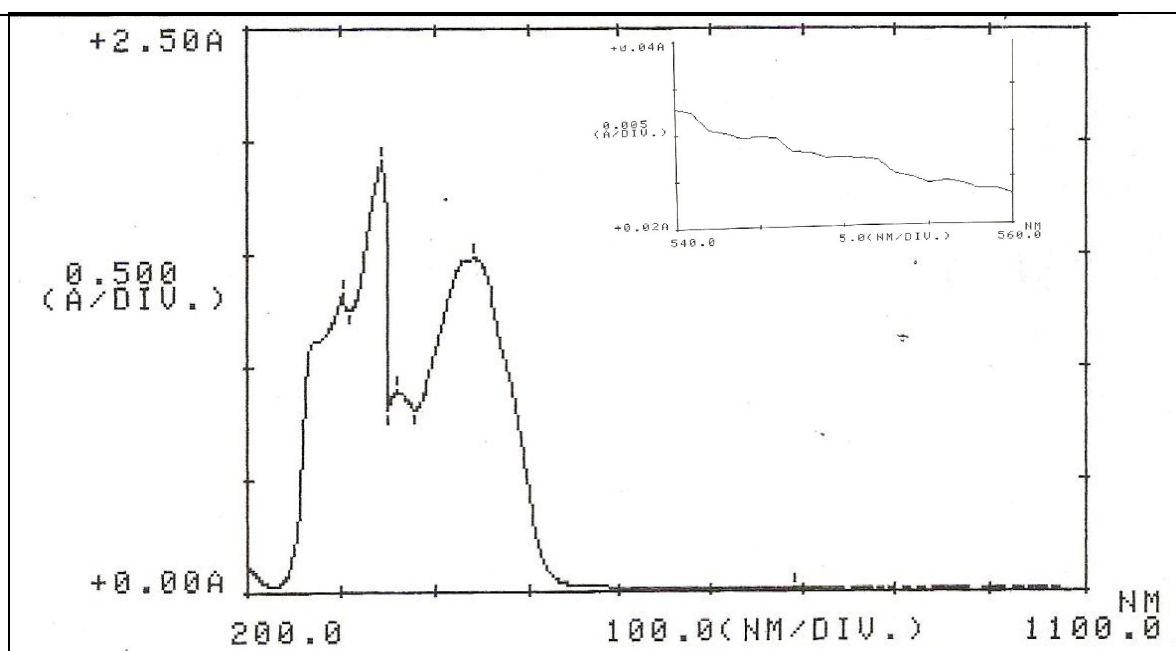


Fig (3-31):- Uv-Vis spectra of complex Mn LII

Chapter four

Biological activity

Chapter four

Introduction

Microorganisms causes different kinds of diseases to human and animals. Discovery of chemotherapeutic agents played a very important role in controlling and preventing such diseases.

Chemotherapeutic agents are isolated either from living organisms known as antibiotics like penicillin and tetracycline etc ,or they are chemical compounds prepared by chemists such as the sulfa drugs ,etc.⁽⁹⁷⁾ Microorganisms have the ability to develop resistance to these chemotherapeutic agents and such strains which are resistant cause major problems in the treatment of microbial infections .

For this reason , searching for new antimicrobial is a continues process and great efforts have been employed to find new antibiotics or new chemical compounds with good antimicrobial activity which might be suitable to be used as chemotherapeutic agents .

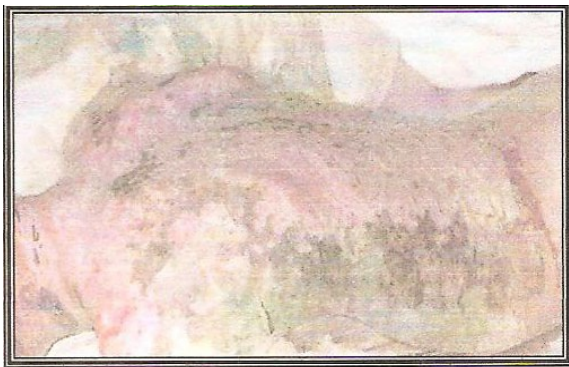
4-1 *pseudomonas areuginosa*

Pseudomonas areuginosa is motiled by means of a single polar flagellum fig (4-1)and(4-2) .The organisms grow readily and rapidly , some strains can grow in a variety of aqueous solutions ever in distilled water ⁽⁹⁷⁾ .The bacterium generally utilizes oxygen as the final electron acceptor in breakdown of nutrients. Under certain circumstances, however, it can also grow anaerobically , as when nitrate is available . Nitrate substitutes for oxygen as a final electron acceptor , an example of anaerobic respiration . Strain of *p. aeruginsoe* often produce one or more water soluble pigments , which can be red, yellow , or dark brown . Commonly they produce a fluorescent yellowish pigment called pyoverdin , which combines with a blue pigment , pyocyanin to produce the striking green color characteristically seen in infected wounds and in growth media ⁽⁹⁷⁾ .

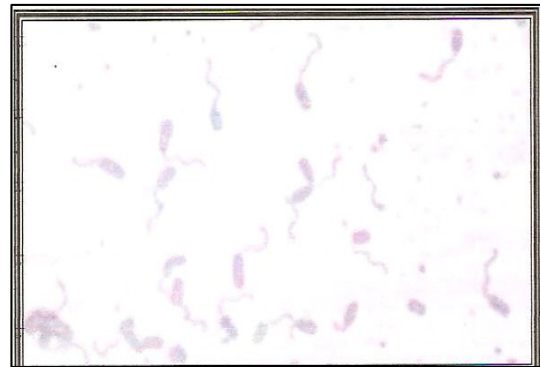
In hospital , the bacterium in the leading cause of noscomial lung infections and a common cause of wound infections , especially of thermal burns . Burns have a large exposed area of dead tissue free of any body defenses

and ,therefore, are ideal sites for infection by bacteria from the environment or normal flora . Almost any opportunistic pathogen can infect burns ,but *Pseudomonas aeruginosa* is among common and havedest to treat⁽⁹⁷⁾.

In burns and other wounds, *Pseudomonas aeruginosa* can often color the tissue green from pigments released from the bacteria fig (4-1) . It is especially dreaded because it often invades the blood stream and causes chills, fever ,skin lesion and shock. (4-2).



Fig(4-1):Extensive burn infected with *P. aeruginosa*



Fig(4-2)*P. aeruginosa* has a single polar flagellum

4-2 *staphylococcus aureus* bacteria

Staphylococcus aureus are gram-positive cocc. That arrange themselves in cluster fig(4-3).They grow readily acrobically or anacrobically and are salt tolerant , probably because they evolved on the skin where evaporation concentrates the salt in sweat . The most important species are *S. epidermidis* and *S. aureus* . Both species survive well in the environment , making it easy for them to transfer from one person to another.⁽⁹⁷⁾

Staphylococci lead the causes of wounded infections , both surgical fig(4-4) and accidental *staphylococci* are commonly present in the nostrils or the skin of 30 or more recognized species of *Staphylococci* , only two account for most human wounded infections⁽⁹⁷⁾ .

Staphylococcus are pyogenic , meaning that they characteristically cause the production of purulent discharge , otherwise , known as pus.

They usually cause an inflammatory raction , with swelling , redness, and pain . If the infected area is extensive or if the infection has spread to the general circulation , fever is prominent symptom . wound infection by some strains produce the toxic shock syndrome , with high fever , muscle aches ,and life-threatening shock , sometimes accompanied by a rash and diarrhea .



Fig (4-3) *staphylococcus aureus* in pus the dark-colored dots are *Staphylococci* the red object , leukocytes



Fig (4-4) surgical wound infected due to *staphylococcus aureus* the stitches pull through the infected tissue coursing the wound to open

4-3 Experimental

4-3-1 microbiology tests:-

In this work , the antibacterial test was performed according to disc diffusion method ⁽⁹⁷⁾. Compounds were assayed for their antimicrobial activity in vitro against one strain of Gram - negative bacteria (*Pseudomonas areuginosa*) and one strain of Gram-positive bacteria (*Staphylococcus aureus*) .

4-3-2 Isolation and Diagnosis :-

Pseudomonas areuginosa and *Staphylococcus aureus* were obtained from the biological activity was performed by biotechnology .

4-3-3 Activation

The previous bacteria were activated in a Nutrient Growth medium at 37 °C for 24 hour.

4-3-4 Sensitivity test:-

The prepared agar and petri dishes were sterilized by autoclaving for 15 min at 121°C .The agar was surface inoculated uniformly from the broth culture of the testing microorganisms.

All the compounds were prepared freshly by dissolving them in DMSO to obtain a final concentration at 10mM and 5mM, these plates were incubated at 37 °C for 24 hour

4-4 Bactericidal activity

The observation of table (4-1) and fig (4-7 and 4-8)shows the following as being concluded:-

- 1-The results of antibacterial activity study for the trithiocarbonate derivates LI and LII showed that the new compounds inactive against the studied bacteria at low and high concentration.

2- Generally , the result of the prepared complexes exhibited antibacterial activity toward *Pseudomonas areuginosa* bacteria was more than the complexes inhibition on *Staphylococcus aureus* bacteria , especially at high concentration .

3-The results of the antibacterial activities of LII complexes showed more than the LI complexes toward G^+ ve bacteria when we use high concentration .

4- The results reflected to the copper and iron complexes for both ligands , there is on or less effect on G^+ ve and G^- ve bacteria when we use low concentration .

5-The study of the antibacterial activities revealed that the cobalt and cadmium complexes for LI and LII toward G^- ve and G^+ ve bacteria show highly activity in both concentration , in addition to that the nickel complex toward G^- ve bacteria show highly activity in low concentration as can be shown in fig (4-5, 4-6).

6-Biological evaluation 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 both the heterocyclic ligand and the metal present in these complexes .

Table(4-1):-Antibacterial activity for LI and LII and their metal complexes

Symbol.	<i>Pseudomonas areuginosa</i>		<i>Staphylococcus aureus</i>	
	5mM	10mM	5mM	10mM
LI	-	-	-	-
Cu LI	++	++	-	-
Mn LI	++	++	-	+
Cd LI	++	++	+	++
Ni LI	-	++	+	-
Co LI	+	++	+	++
Fe LI	-	-	-	-
LII	-	-	-	-
Cd LII	++	++	+	+++
Fe LII	-	+	+	+
Ni LII	+++	+	+	-
Co LII	-	-	+	++
Mn LII	-	-	-	-
Cu LII	-	-	-	-

(-) : No Inhibition

(+):Slow Inhibition

(++):Moderate Inhibition

(+++): Highly Inhibitio

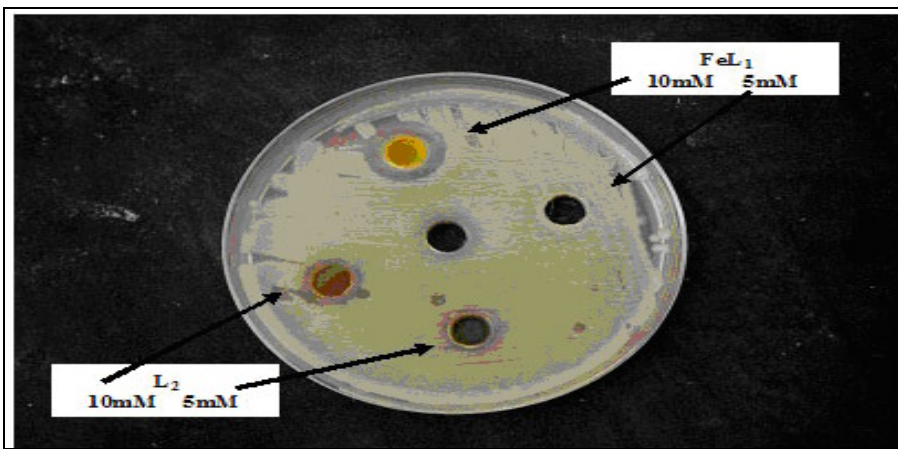
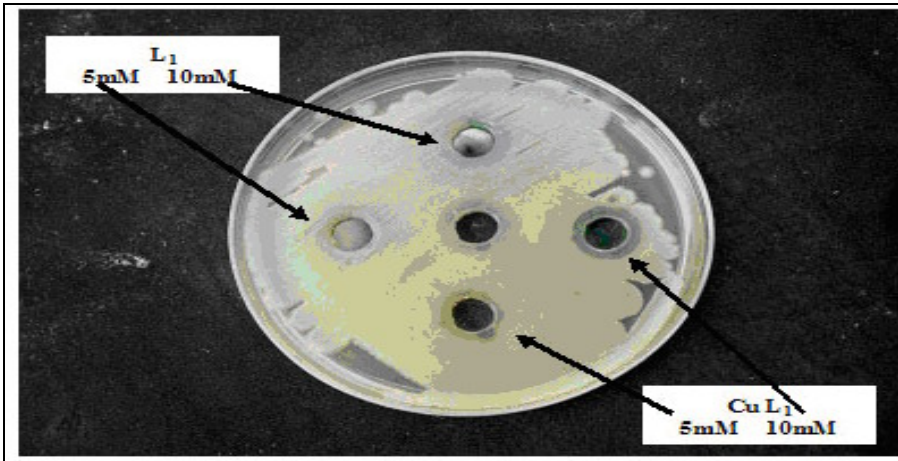
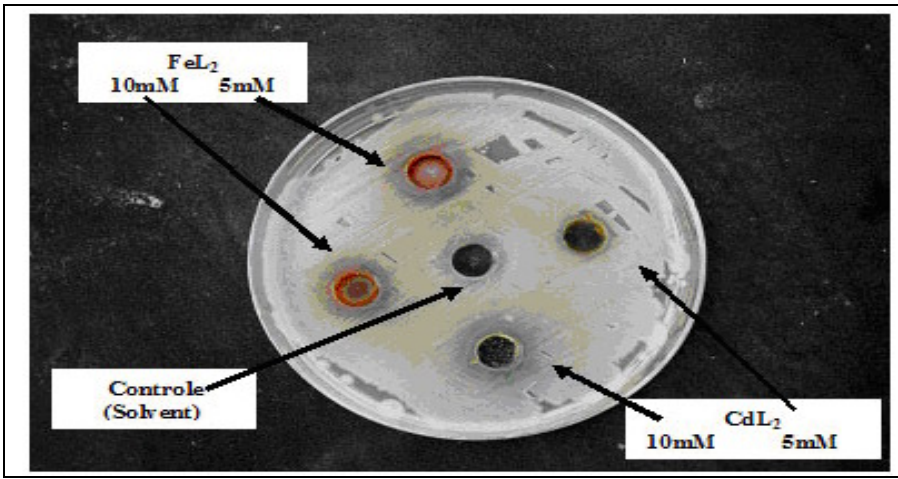
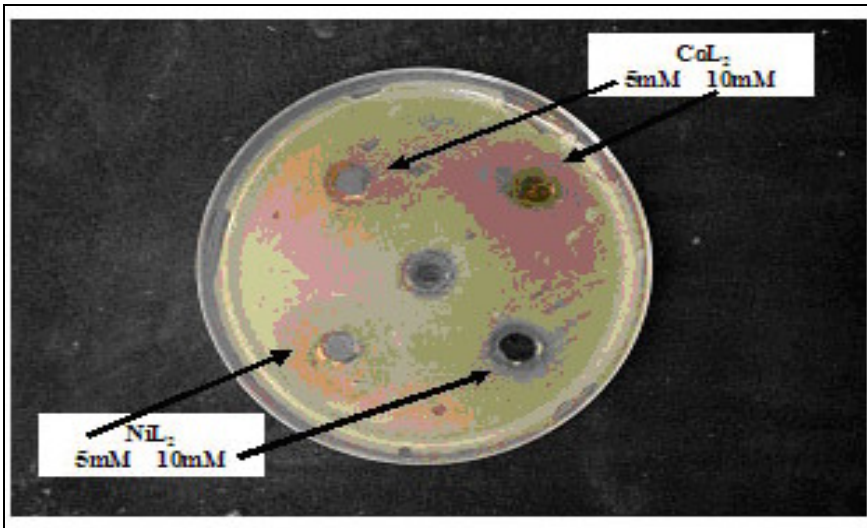
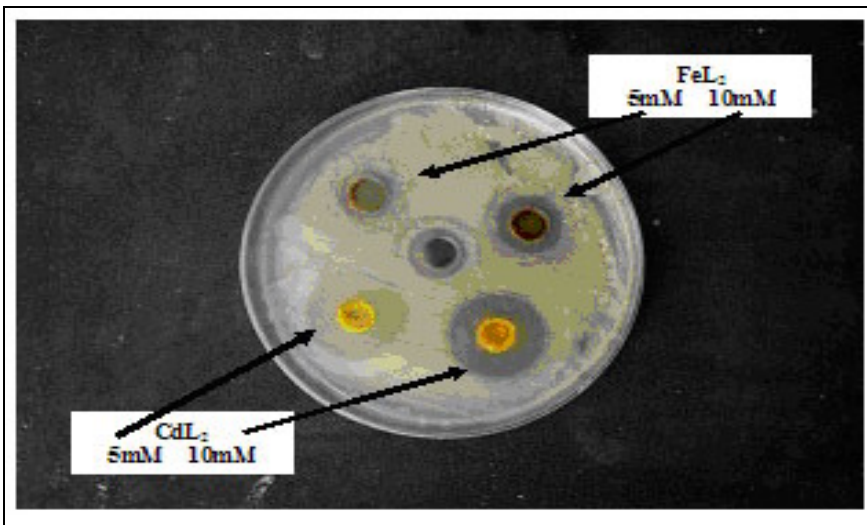
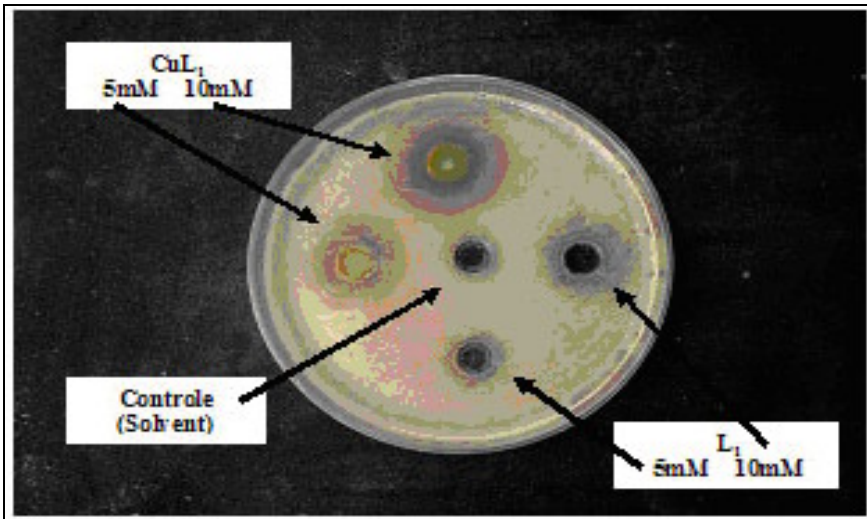


Fig (4-5) : Antibacterial activity for prepared complexes toward *Staphylococcus aureus*



Fig(4-6): Antibacterial activity for prepared complexes toward *Pseudomonas aeruginosa*

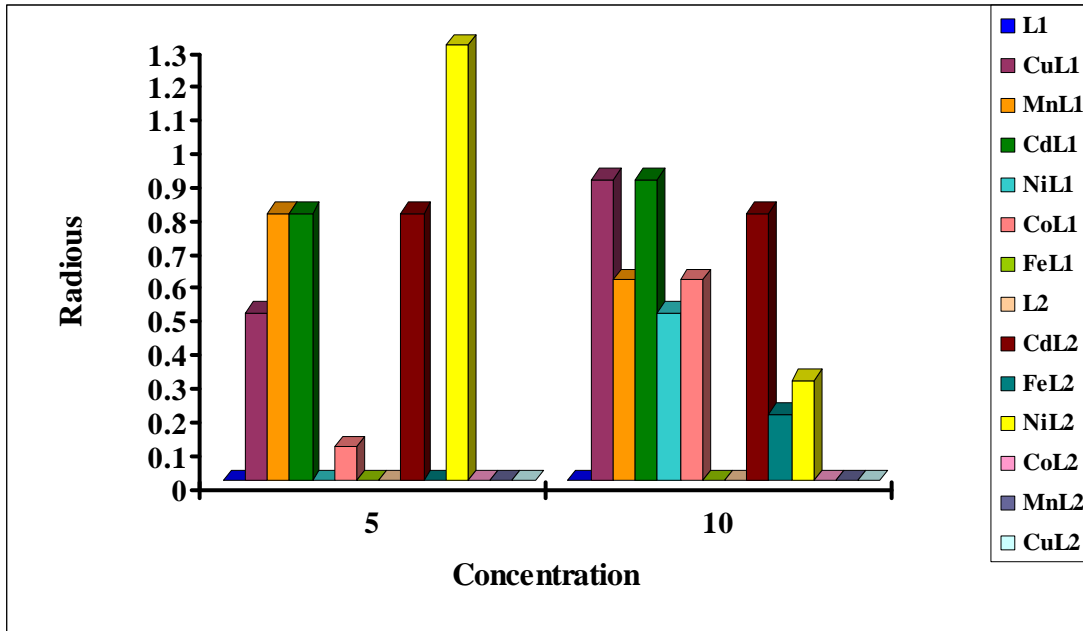


Fig (4-7): Show the effect of *Pseudomonas aeruginosa* bacteria toward LI and LII complexes

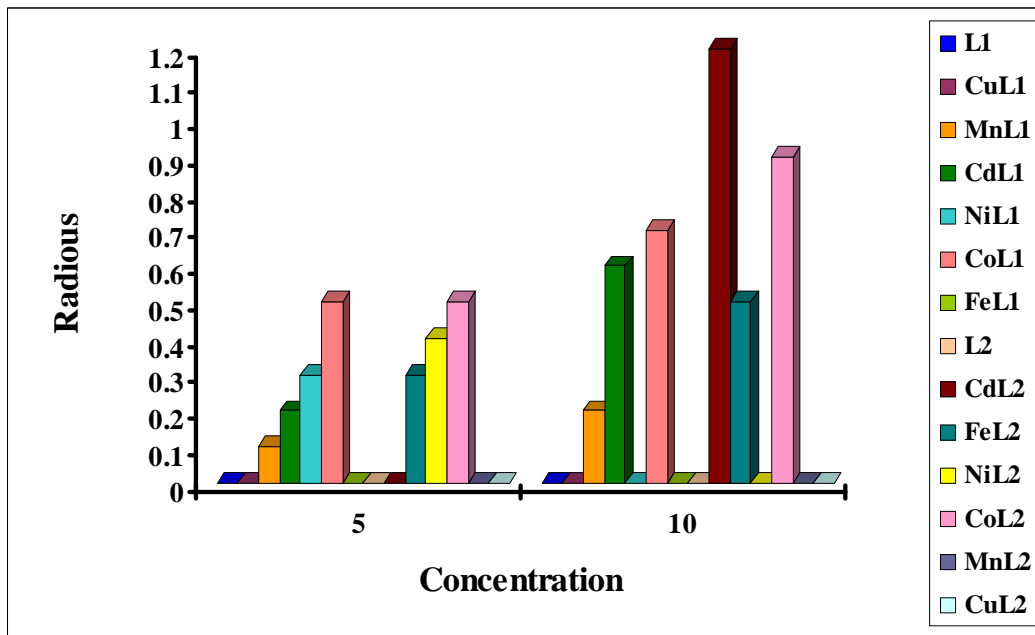


Fig (4-8): Show the effect of *Staphylococcus aureus* bacteria toward LI and LII complexes

Suggestion of the future work:-

- 1- Using CHN , NMR technique to completely identify the structure of trithiocarbonate derivatives .
- 2- Synthesis of new sets of complexes for all the prepared ligands using other set of metal ions (heavy metals or representative metals) .
- 3- Synthesis and Isolation of new organic compounds by using different aldehydes to study the effect of this substitute on trithiocarbonate with their metal complexes and compare their chemical and biological activities with new compounds .
- 4- More details investigation and required to reveal the biological activity of new compounds against other microorganisms.
- 5- Further , theoretical studied on the new compounds such as the evaluating of electronic spectral and vibrational spectra.
- 6- Performing kinetic and thermodynamic studies for the new ligands and their metal complexes .

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الخلاصة

تم في هذا البحث تحضير ليكاندين جديدين الليكاند الاول (بوتاسيوم (2-كاربوميثوكسي امينو -5- تراثايو كاربونيت 1,3,4 ثايديازول (LI) من مفاعلة (2-كاربوميثوكسي امينو 5-مركبتو 1,3,4 ثايديازول بوجود كاربون سلفايد و هيدروكسيد البوتاسيوم .

بينما الليكاند الثاني تم تحضيره من مفاعلة (4) N,N -ثنائي مثيل امينو بنزالديهيد -5- مركبتو 1,3,4 ثايديازول بوجود كاربون ثاني سلفايد و هيدروكسيد البوتاسيوم للحصول على (2) N,N -4) N -ثنائي مثيل امينو (5- تراثايو كاربونيت 1,3,4 ثايديازول (LII) تم تشخيص الليكاندين بالطرائق الفيزيائية المناسبة و هي طيف الاشعة تحت الحمراء و الانتقالات الالكترونية إضافة إلى درجة الانصهار .

استعملت اليكاندات الجديدة لتحضير عدد من المعقدات الجديدة مع ايونات بعض العناصر الانتقالية [Cd(II), Cu(II), Ni(II), Co(II), Fe(III), and Mn(II)] اذ تم تشخيص و دراسة تراكيب المعقدات الجديدة في الحالة الصلبة باستخدام اطياف الاشعة تحت الحمراء و فوق البنفسجية المرئية و قياسات التوصيلية النوعية فضلا عن الحساسية المغناطيسية و تقنية التحليل الكمي للعناصر و ذلك باستخدام تقنية الامتصاص الذري اللهبى .

اعطى تفاعل (LI) مع ايونات [Cd(II), Cu(II), Ni(II), Co(II), Fe(III), and Mn(II)] اعطت معقدات النحاس (II) و الحديد (III) و المنغنيز (II) و النيكل (II) الصيغ الجزيئية التالية
 $[Cu_2(LI)_2Cl_2(H_2O)_2] \cdot 3C_2H_5OH$, $[Fe_2L_2(OH)_2 Cl_4] 4H_2O$,
 $[Ni L_2 Cl_2] \cdot 2H_2O$, $[Mn L_2 (H_2O)_2](OAC)_2 \cdot 2H_2O$ ذات اشكال ثمانية السطوح .
كما اعطى معقد الكوبلت و الكادميوم الصيغ الجزيئية التالية $[Co LI(H_2O) Cl] \cdot 3H_2O$
 $[Cd (LI)_2] \cdot 3C_2H_5 OH$ ذات اشكال رباعية السطوح.

بينما اشكال معقدات النحاس (II) و الحديد (III) و المنغنيز (II) و النيكل (II) مع الليكاند (LII) الصيغ الجزيئية التالية:
 $[Cu_2(LII)_2 (H_2O)_4 Cl_2] \cdot 2H_2O$
 $[Ni(LII)_2 (H_2O)_2 \cdot Cl_2] \cdot C_2H_5OH$ ، $[Mn(LII)_2(H_2O)_2 (oAc)] \cdot 3H_2O$
 $[Fe_2(LII)_4 (OH)_2] \cdot 5H_2O$ ، $[Co_2(LII)_2 (H_2O)_4 Cl_2] \cdot 2.5H_2O$ الاشكال ثمانية السطوح.
بينما اعطى معقد الكادميوم (II) الصيغ الجزيئية ذات شكل رباعي السطوح $[Cd(LII)_2] 4C_2H_5OH$ و بهذا اتضحت عدد من الخصائص التركيبية و السلوكية المختلفة من خلال دراسة الكيمياء التناسقية لمعقدات اليكاندات الجديدة .

فسرت طبيعة التاصر بين الفلز و الذرات المانحة في الليكاند و قدرة كذلك درجة التشوه كما تم حساب معامل راکاح و المجال الليکاندي باستخدام مخططات تانايا-سوکانو المناسبة.

تم تقييم الفعالية البايولوجية لجميع المركبات المحضرة ضد نوعان من البكتريا *Pseudomonas aureuginosa* و *Staphylococcus aureus* باستخدام تركيزين عالي (10 ملي مول) و واطئ (5 ملي مول) في وسط زرع متعادل و قد اظهرت النتائج زيادة كبيرة في فعالية بعض المعقدات بالمقارنة مع الليکاندين المحضرة منها و تم تفسير الفعالية المضادة للبكتريا الى حصول التأثير المتداوب للفعالية بين الفلز و الليکاند فضلا عن الاختلاف في تركيب المركبات المحضرة .

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

وَقُلْ رَبِّ ادْخُلْنِي مَدْخَلَ صِدْقٍ

وَأَخْرِجْنِي مَخْرَجَ صِدْقٍ وَاجْعَلْ لِي مِنْ

لَدُنْكَ سُلْطَانًا نَصِيرًا

صدق الله العظيم

سورة الإسراء آية (80)



جمهورية العراق
وزارة التعليم العالي و البحث العلمي
جامعة النهرين
كلية العلوم / قسم الكيمياء

تحضير و الدراسة التركيبية و الفعالية البايولوجية لمعقدات بعض العناصر الانتقالية لبعض مشتقات ثلاثي الثايوكاربانيت الجديدة

رسالة

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

من قبل
هدى قاسم جبر

بكالوريوس علوم كيمياء جامعة النهرين...2006
باشراف

الاستاذ الدكتور اباد حمزة جاسم

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