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Ministry of Higher Education and Scientific Research
University of Baghdad
College of Education for Pure Science (Ibn-Al-Haitham)
Department of Chemistry

Synthesis and characterization of some new amino acid derivatives with some of metal ions and study of their biological activity

A thesis Submitted

To the Council of College of Education for Pure Science (Ibn Al-Haitham) /University of Baghdad in Partial Fulfillment of the Requirements for the Degree of master in Inorganic Chemistry

By

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2019 Ac **1441 Ah**

سَنُرِيهِمْ آيَاتِنَا فِي الْآفَاقِ وَفِي أَنْفُسِهِمْ
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بِرَبِّكَ أَنَّهُ عَلَىٰ كُلِّ شَيْءٍ شَهِيدٌ

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I certify that this thesis was prepared under my supervision at the Department of Chemistry, College of Education for pure science (Ibn Al-Haitham) at Baghdad University in partial requirements for the Degree of master in Inorganic Chemistry and this work has never been puplished anywherelse.

Signature:

Supervisor:

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In the view of the available recommendation, I forward this thesis for debate by the examining committee.

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Examination Committee

We chairman and members of the examination committee, certify that we have studied this thesis presented by the student **Abbas Mohammed Abbas** and examined her in its contents and that, we have found its worthy to be accepted for the Degree of Masster of Philosophy in Chemistry with (Excellent)

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Date: 07/11/2019

DEDICATION

To everything that I have:

My Mother and my Father's souls

To my wife and my son and daughtar

To my brothers and sisters

For all my freinds whom that stood with me

For all one taugth me

For my Supervisor prof. Dr. B.M.Sarhan

I dedicate this work…

Abbas

Acknowledgment

Praise be to God, and God's blessing and peace be on our prophet Mohammed and his, who rescued mankind from darkness to light

I praise God almighty very much for granting me success to complete this study. Then I present my deepest gratitude and greatest appreciation to the virtuous lecturer (Prof. Dr. Basima Mohsin Sarhan) whom obliged me by suggesting the subject of the research and bore the responsibilities of supervision. Therefore, I wish to her everlasting health, happiness, success and long life.

In addition, I extend my deep gratitude for the deanery of the College of Education for pure science Ibn-Al-Haitham and the head of chemistry department (Prof.Dr. Mhamad J. Al-jeboori) and to all my virtuous professors in the department of chemistry, College of Education for pure science (Ibn-Al-Haitham).

Abbas

Abstract

In this research, two new ligands were prepared from serine derivatives with their metal complexes, the first ligand (L_1), (2-(3-acetylthioureido) -3-hydroxypropanoic acid) (ATP) was performed by reaction of acetyl chloride with ammonium thiocyanate with serine in the acetone as a solvent, the ligand (L_2) [3-hydroxy-2-(3-(4-nitrobenzoyl)thiouriedo) propanoic acid] (NTP), was prepared by reaction of 4-nitro benzoyl chloride and ammonium thiocyanat with serine in the acetone as a solvent and stirred for 6 hurs.

The ligands (ATP) and (NTP) were characterized by FTIR , -NMR, (^{1}H, ^{13}C-NMR), micro elemental analysis (C.H.N.S) and UV-Vis spectra, the molecular formula of the two ligands were concluded :-

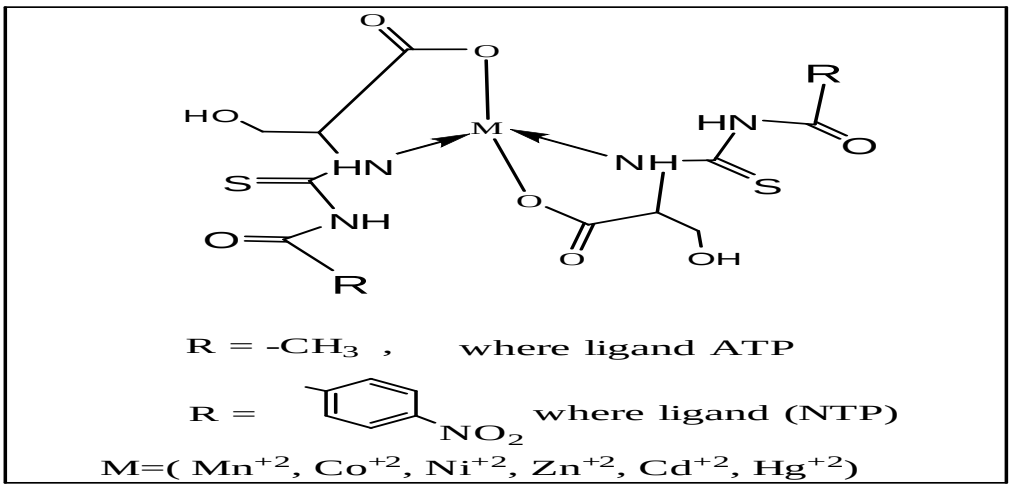
(ATP) $L_1 = C_6H_{10}N_2O_4S$

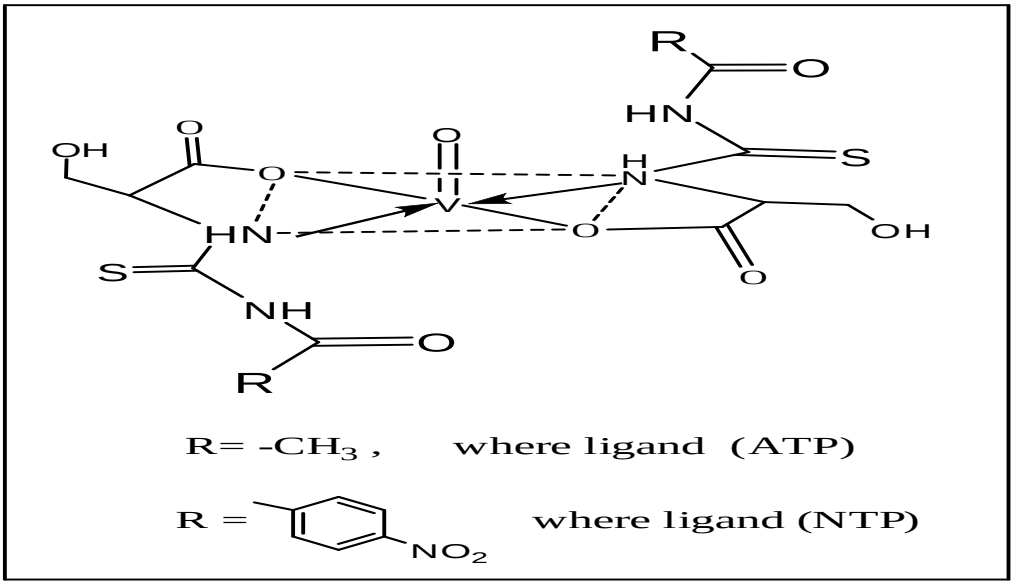
(NTP) $L_2 = C_{11}H_{11}N_3O_6S$

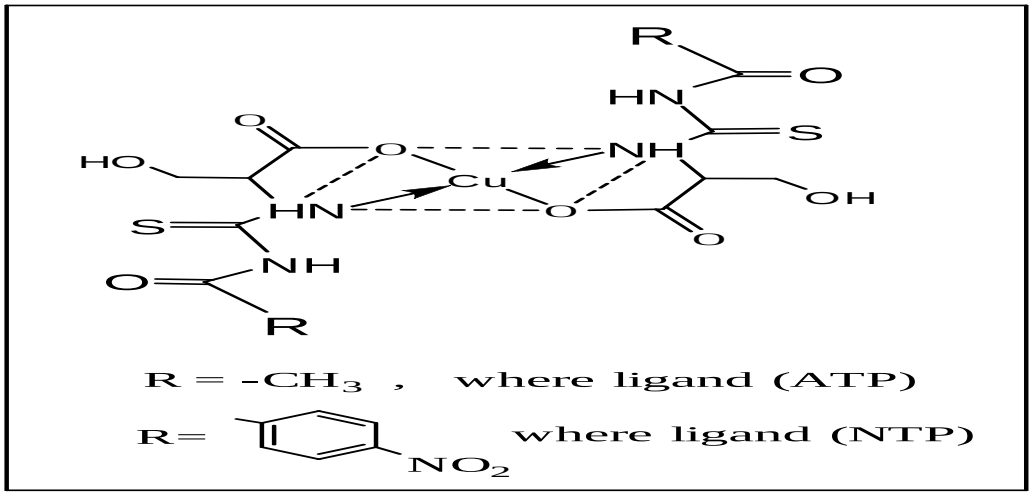
The two ligands L_1(ATP) and L_2 (NTP) were react with some of metal ions like (VO^{+2}, Mn^{+2}, Co^{+2}, Ni^{+2}, Cu^{+2}, Zn^{+2}, Cd^{+2} and Hg^{+2}) to prepare the complexes that characterized by the solubility in some solvents, melting point , FT-IR, electronic spectra (UV-Vis), molar conductivity, magnetic susceptibility measurement, elemental micro analysis(C.H.N.S) and atomic absorption for some complexes.

The results given at these measurements, concluding the complexes of (Mn^{+2}, Co^{+2}, Ni^{+2}, Zn^{+2}, Cd^{+2} and Hg^{+2}) have the tetrahedral geometry, while square planer geometry with complexes of (Cu^{+2}) and the square pyramid for complexes with (VO^{+2}).

The two ligands and their metal complexes against the two types of bacteria (***Staphylococcus aurea and Escherichia coli)*** and one type of fungi(***Candida albicance***) were showed deferent biological activity that inhibit the growth of microorganisms.







Scheme: Chemical structure of complexes

List of contents

List of tables

List of Figures

List of Schemes

List of Abbreviation

sympol	*name*
ATP	(2-(3-acetylthioureido)-3-hydroxypropanoic acid)
NTP	3-hydroxy-2-(3-(4-nitrobenzoyl) thiouriedo) propanoic acid
DMSO	Dimethyl silfoxide
FT-IR	Fourier Transform Infrared.
^{1}H-NMR	Proton Nuclear Magnetic Resonance.
^{13}C-NMR	Carbon^{13} Nuclear Magnetic Resonance.
UV-Vis	Ultraviolet and Visible
B.M	Bohr magnetons
M.p	Melting point
Dec.	Decomposition
ε_{max}	Molar absorptivity
υ	Stretching
λ	Wave length
C.N	Coordination number
Fig.	figure
Es.	Essential
No.Es	Non-essential
D	Magnetic corrected factor
IMI	Imidazole
DMI	Di imidazole
G^{+}	Gram positive
G^{-}	Gram negative

Chapter One

Introducation

1-Amino Acids

Chemical compounds are characterized by containing two active groups the Carboxylic group (COOH) and the amine group (-NH_2). Amino acids are the basic units for the formation of proteins and peptides by union with each other by peptide bonds [1] .

The amine group link in the carbon chain determines the type of amino acid[1,2], as shown in Fig(1-1).

Alpha-amino acids, where the amino group is linked to the carbon atom No. 2 after carbon atom carboxylic group and is numbered in alpha Cα.

Beta-amino acids, if the amino group linked to carbon No. 3 after the carbon acid group Cβ.

Gamma-amino acid, the amino acid is bound by the carbon No.4 after the carboxyl carbon group Cγ.

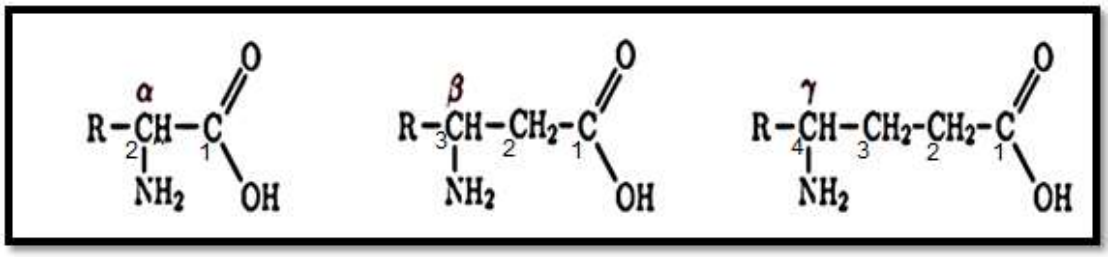


Fig (1-1) Types of amino acids

The human body contains 20 different amino acids in the side group (R), all of them alpha type, where the group (R) were linked to the carbon atom (α) [3], as shown in Fig. (1-2).

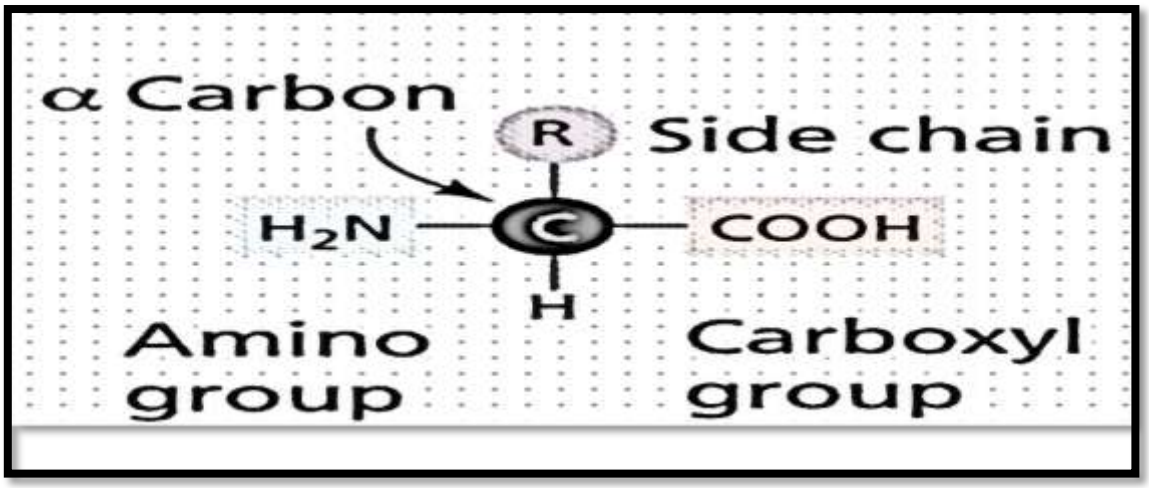


Fig. (1-2) The general structure for α-amino acid

Amino acids play an important role in cell building, tissue repair and synthesis of antibodies that resist various types of bacteria and viruses and interfere in the manufacture of many compounds such as hormones, enzymes and pigments, also it represents the intermediate state of cellular metabolism[4]. α-Amino acids (αAA) are one of the most important and versatile building blocks for both biological and chemical synthesis[5] .

Amino acids differ in the difference of the side group (R). The size of this group (R) differs from the hydrogen only as in the glycine, through the medium group as in the alanine to the larger group, the heterogeneous ring in the tryptophan [6].

All the amino acids present in the human body are L-amino acid, in which the (α-c) carbon atom contains four different groups, except the glycine amino acid, where the non- kerali alpha-carbon atom is because it contains two hydrogen atoms [7,8] .

(1-1)Classification of amino acids:

There are several classifications of amino acids depending on their importance to humans or the nature and type of the side group (R) and these categories:

The first classification: In terms of importance to the human and divided into two types [3,9] .

1-Essential amino acids: Include acids that cannot be synthesized within the body so it needs to be addressed with food.

2-Non-essential amino acids: Include the acids produced by the body in sufficient quantities ,Table(1-1) describes the types mentioned earlier:

Table (1-1) Essential and non-essential amino acids

Essential	Non essential
Iso leucine	Alanine
Leucine	Asparagine
Lysine	Aspartate
Methionine	Cysteine
Phenylalanine	Glutamate
Thronine	Glutamine
Tryptophan	Glycine
Valine	Proline
Arginine	Serine
Histidine	Tyrosine

The second classification: In terms of polarity or not polarity the side group (R) includes [10], as shown in Table (1-2).

1- Non-polar amino acids.

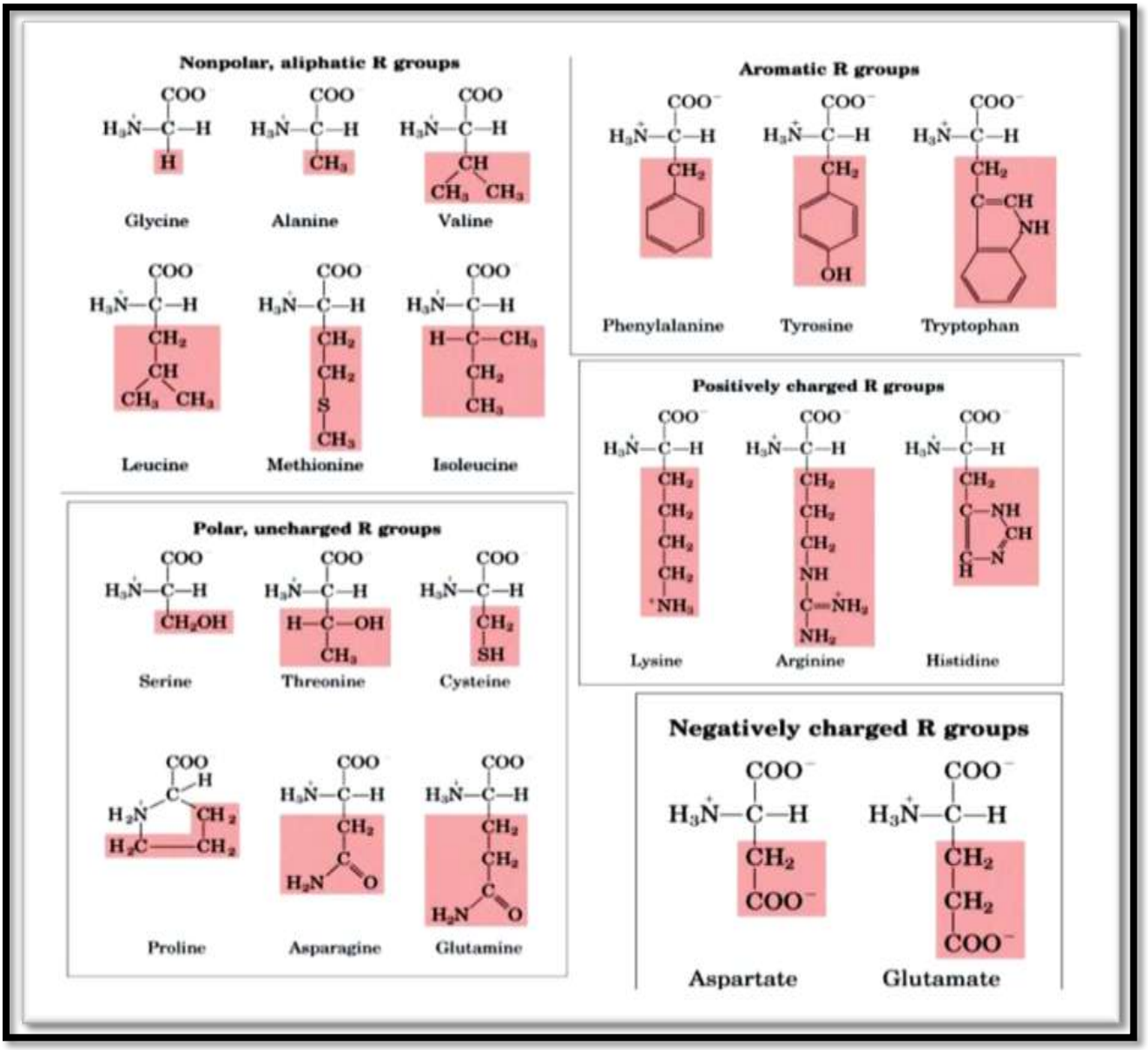
2- Polar amino acid, and in turn be on three types:-

a- Polar uncharged amino acid.

b- Polar positively charged amino acid.

c- Polar negatively charged amino acid.

Table (1-2) Amino acid classes in terms of polarity



The third classification: In terms of acidity and alkalinity and include three types [11,12].

1-Neutral amino acids: The acid contains one amino group and one carboxylic group such as alanine and cysteine.

2-Acidic amino acids: It contains one amino group against the presence of two groups of carboxylic acid (Aspartic acid).

3-Basic amino acids: There are two groups of amine versus one Carboxylic group (Arginine and Histidine).Table(1-3) describes acidic and alkaline nature as well as the polar nature and nutritional significance of amino acids.

Table (1-3) Types and some properties of amino acid

Amino acid	Symb.3	Symb.1	M.W g/mol	Polar (R)	Acid/base (R)	Es.-non es
Alanine	**Ala**	**A**	89.1	Non polar	Neutral	Non.es
Arginine	**Arg**	**R**	174.20	Polar	Basic	Es.
Asparagin	**Asn**	**N**	132.12	Polar	Neutral	Non.es.
Aspartic acid	**Asp**	**D**	133.10	Polar	Acidic	Non es.
Cysteine	**Cys**	**C**	121.16	Polar	Neutral	Non es.
Glutamin	**Gln**	**Q**	146.15	Polar	Neutral	Non es.
Glutamic acid	**Glu**	**E**	147.13	Polar	Acidic	Non es.
Glycine	**Gly**	**G**	75.07	Non polar	Neutral	Non es.
Histidine	**His**	**H**	155.16	Polar	Basic	Es.
Isoleucine	**Ile**	**I**	131.17	Non polar	Neutral	Es.
Leucine	**Leu**	**L**	131.17	Non polar	Neutral	Es.

Lysine	**Lys**	**K**	146.19	Polar	Basic	Es.
Methionine	**Met**	**M**	149.21	Non polar	Neutral	Es.
Phenylalanine	**Phe**	**F**	165.19	Non polar	Neutral	Es.
Proline	**Pro**	**P**	115.13	Non polar	Neutral	Non es.
Serine	**Ser**	**S**	105.09	Polar	Neutral	Non es.
Threonine	**Thr**	**T**	119.12	Polar	Neutral	Es.
Tryptophan	**Trp**	**W**	204.23	Polar	Neutral	Es.
Tyrosin	**Tyr**	**Y**	181.19	Polar	Neutral	Non es.
Valine	**Val**	**V**	117.15	Non polar	Neutral	Es.

A modern classification of amino acids is called phine classification as shown in Fig. (1-3)

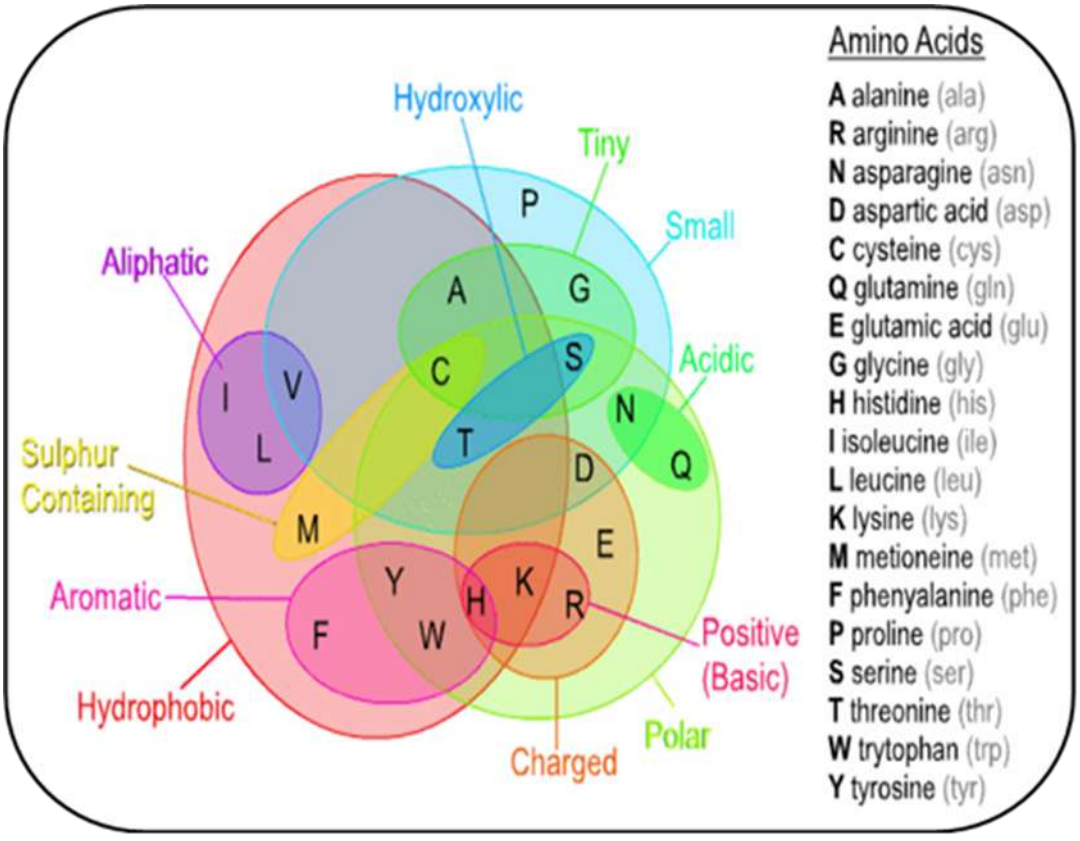


Fig (1-3) Phine types of amino acids

1-2 Serine

Serine (ser) is a class of neutral or uncharged polar amino acids fig (1-4). The lateral group (R) of the hydroxyl group is composed of the methylated group CH_2, a non-essential amino acid that is synthesized within the body and is a source to store glucose in the liver and muscles and works to strengthen the immune system by filling the need for antibodies and works to create the outer envelope of lipid acid located around the nerve fibers [13,14].

It can be considered as the most distinguished member of the amino acids and its interaction with different nanostructures is important because of the three functional groups that render better control and flexibility in comparison to the rest of the amino acids [15].

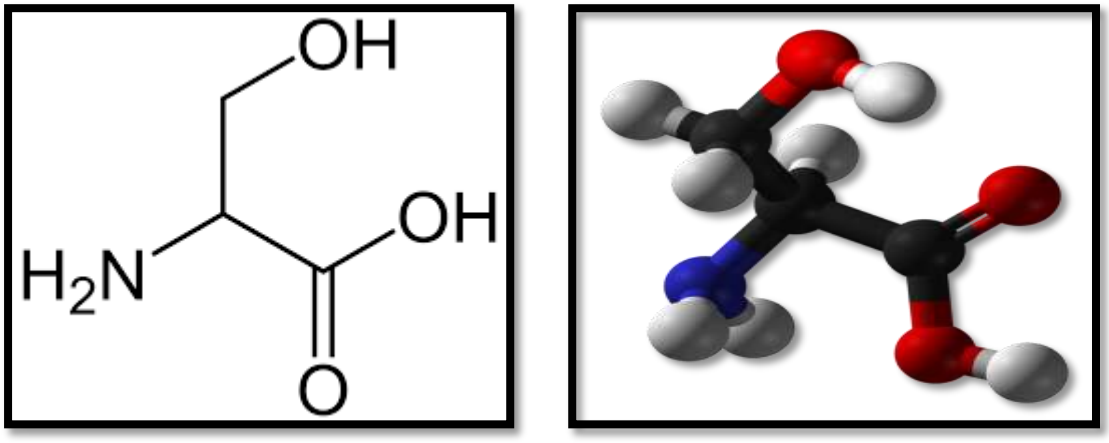


Fig.(1-4)Serine structure and its spatial dimensions

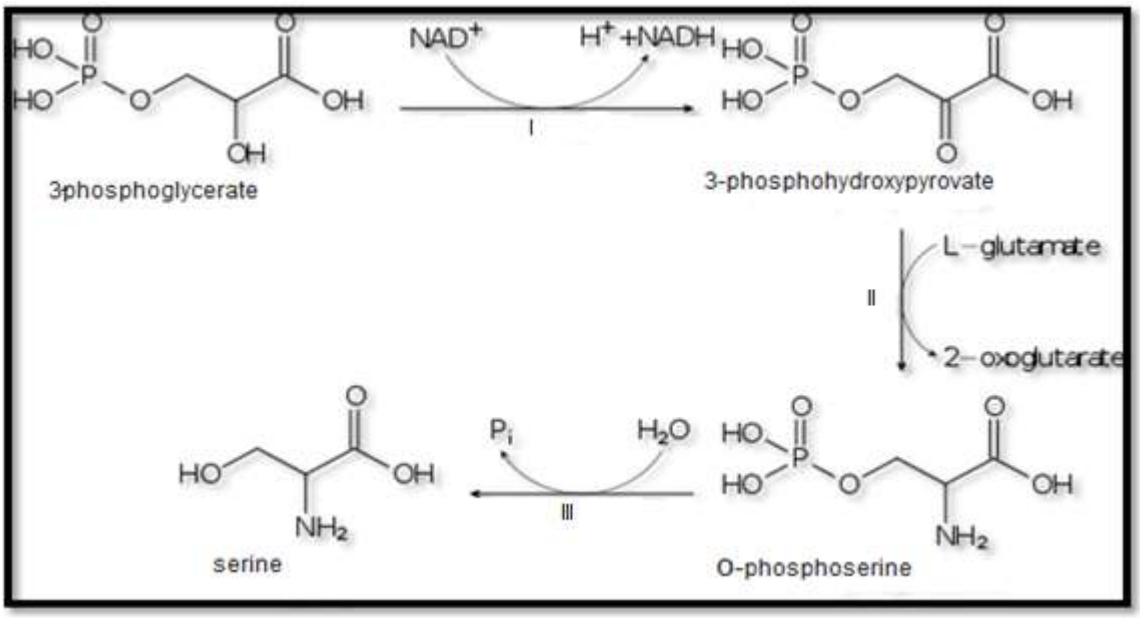
The chemical formula $C_3H_7NO_3$, a solid white color, the degree of melting point 228℃ and its molecular weight 105.09 gm / mol. Table (1-4) illustrates some of the properties of serine.

Table (1-4) Some physical properties of serine

Properties	
The Chemical formula	$C_3H_7NO_3$
Molar mass	105.09 g·mol^{-1}
Appearance	white crystals
Density	1.603 g/cm^3 (at 22 °C)
Melting point	246 °C
Solubility in water	Soluble
Acidity (pK_a)	2.21 (carboxyl), 9.15 (amino)

1.2.1 Biosynthesis of serine:

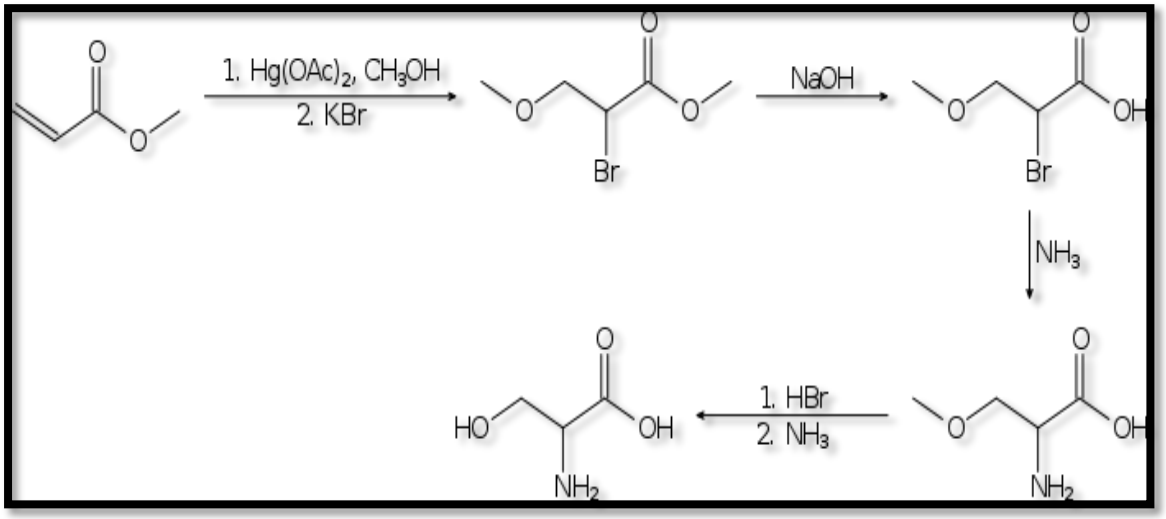
Serine synthesis from glycolytic intermediate, 3-phosphoglyserate. The latter is converted to serine through the successive action oh 3-phosphoglycerate dehydrogenase(I), phosphoserine aminotransferase dehydrogenase(II) and 3-phosphoserine phosphatase(III).This pathway is present in several tissues including brine, kidney, testes and liver [16, 17], Scheme(1-1).



Scheme (1-1) Biosynthesis of Serine

1.2.2 Industrial synthesis of serine:-

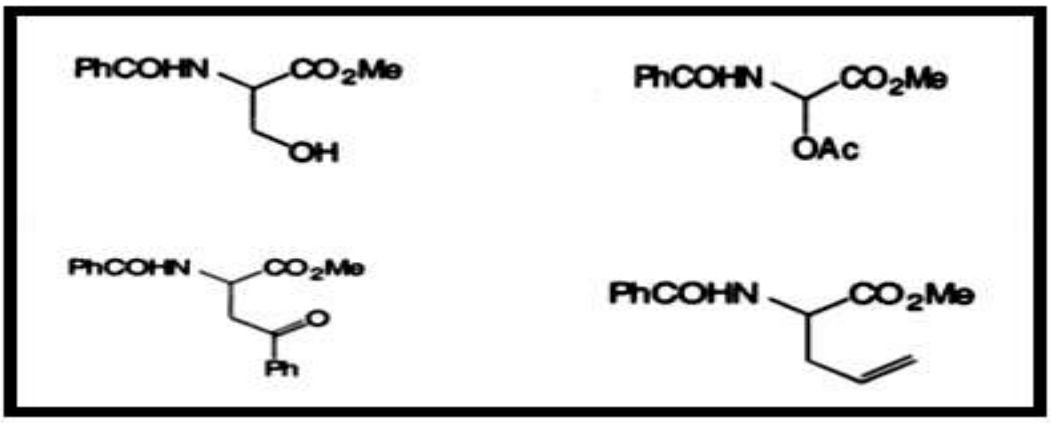
Serine can produced by fermentation, with an predictable 100-1000 tones at year produced [18], in the laboratory, racemic serine can be prepare from the methyl acrylate by several steps [19], scheme (1-2) illustrate these steps.



Scheme (1-2) Industrial synthesis of serine

1.3 Serine derivatives

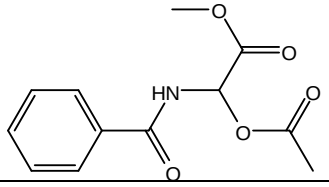
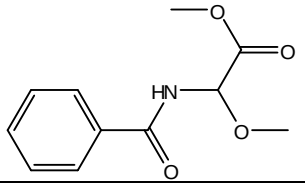
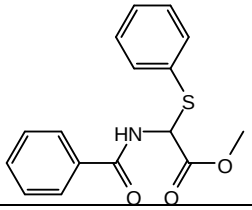
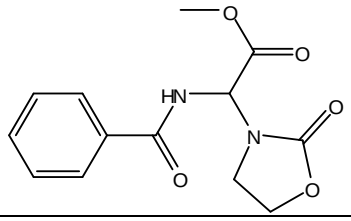
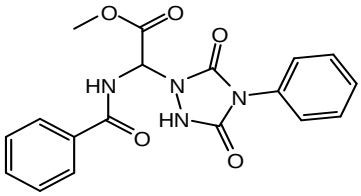
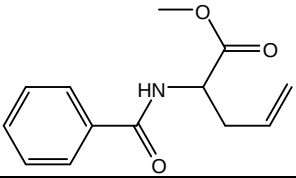
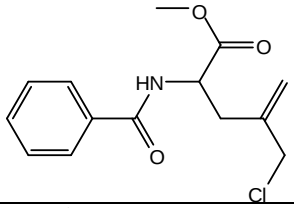
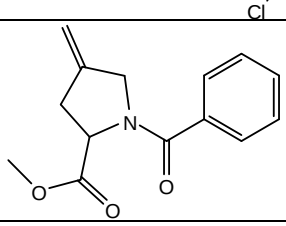
Many compounds were synthesized from serine at last years and it have an imported in medicine and industrial at 2002 Alicia Boto and co-worker prepare some of compound from serine derivatives by reaction the serine and (diacetoxyiodo) benzene (DIB) and iodine at room temperature and under sunlight irradiation for 2 h, these compounds were characterized by ^{1}H,^{13}C-NMR, Ms-HRMS and (C.H.N.S)[20]. Fig(1-5)



Fig(1-5) Some of serine derivatives

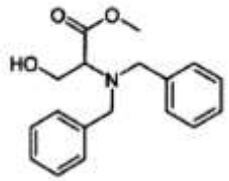
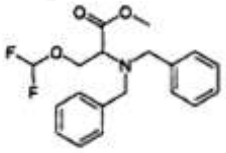
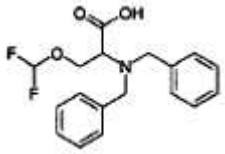
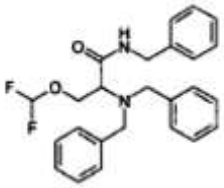
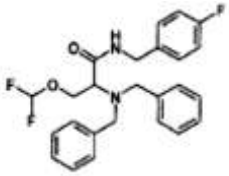
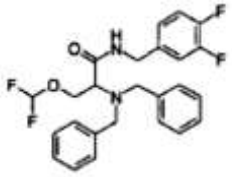
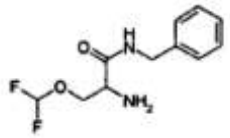
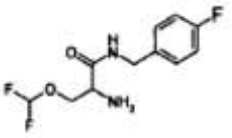
In 2007 Alicia Boto and co-worker prepare serious of serine derivatives by β-fragmentation of primary O-radicals derivative from serine, like Methyl (Acetyloxy) (benzoylamino) acetate, Methyl 2-Benzamido-2(2-oxooxazolidin-3-yl) acetate and Methyl-2-Benzamido-2(3,5-dioxo-4-phenyl-1,2,4-triazolidin-1-yl)acetate, These compounds were characterized by 1H,13C-NMR,(C.H.N.) and IR, Table(1-5)shown some of these derivatives with their structure [21].

Table (1-5)Some of serine derivatives

Name of serine derivatives	Structure
Methyl(Acetyloxy)(benzoylamino)acetate	
Methyl 2-Benzamido-2-methoxyacetate	
Methyl 2-Benzamido-2(phenylthio)acetate	
Methyl-2-Benzamido-2(2-oxooxazolidin-3-yl)acetate	
Methyl-2-Benzamido-2(3,5-dioxo-4-phenyl-1,2,4-triazolidin-1-yl)acetate	
Methyl-2-Benzoylamino-4-pentenoate	
Methyl-2-Benzoylamino-4(chloromethyl)-4-pentenoate	
Methyl-N-Benzoyl-4-methylenepyrrolidine-2-carboxylate	

In 2013 many of serine derivatives were indicate with their treatment of anxiety disorders by international application published under the patent cooperation treaty (PCT), all these compound were characterized by ^{1}H-NMR specra, Table (1-6) show some of these derivatives [22].

Table (1-6) Some of serine derivatives

Name	Structure of serine derivatives
Methyl2-(dibenzylamino)-3-hydroxypropanoate	
Methyl2-dibenzylamino-3-difluoromethoxy-propionate	
2-(Dibenzylamino)-3-(difluoromethoxy) propanoic acid	
2-(Dibenzylamino)-3(difluoromethoxy)-N-benzylpropanamide	
2-Dibenzylamino-3-difluoromethoxy-N-(4-fluorobenzyl) propionamide	
2-Dibenzylamino-N- (3,4-difluoro-benzyl)-3-difluoromethoxy propion-Amide	
2-Amino-N-benzyl-3-(difluoromethoxy)propanamide	
2-Amino-3-difluoromethoxy-N-(4-fluorobenzyl) propionamide	

In 2015 Ana M. Cardoso and co-worker, isolated new serine derivatives from Gemini surfactants using column chromatography, these compound were characterized by surface charge, hydro dynamic diameter and stability. Fig (1-6) show this derivatives [23].

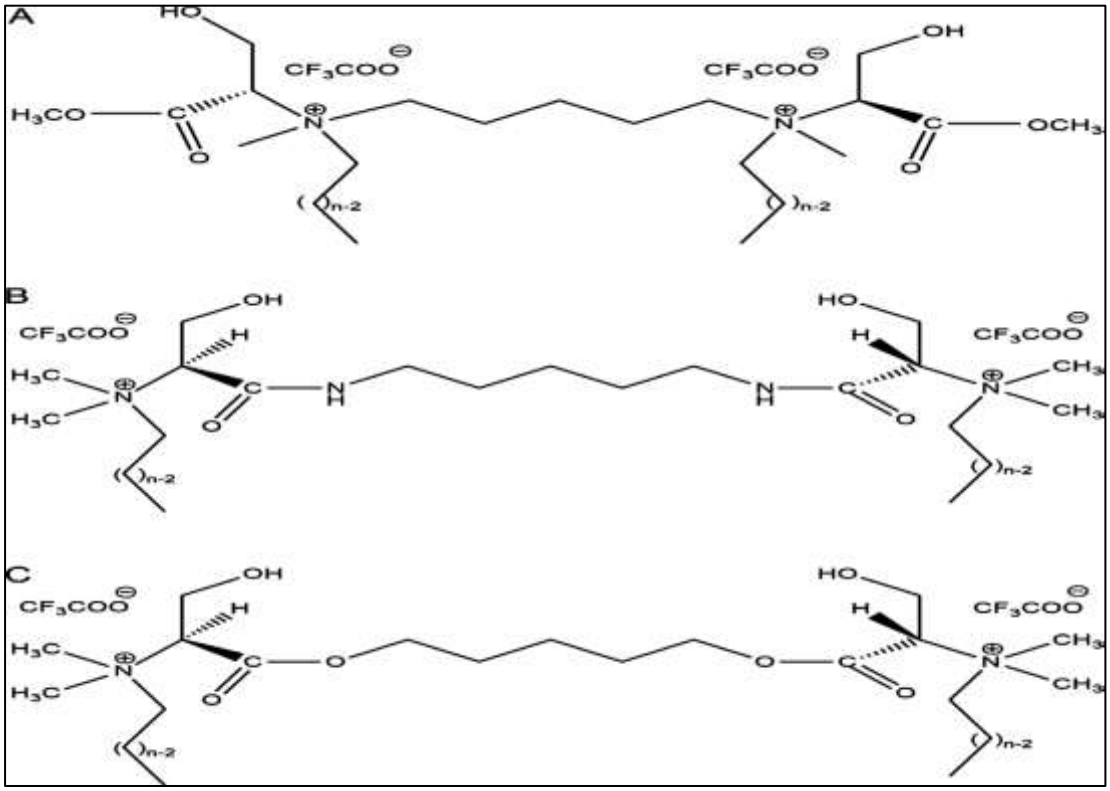


Fig (1-6) Some of serine derivatives

In 2015 Ebrahim M. pour and co-worker prepared a new serine derivatives (4-toluenesulfonyl-L-serine) by reaction serine with 4-toluenesulfonyl chloride in sodium hydroxide solution, compounds were characterized by IR, ^{1}H-NMR,UV-Vis and XRD [24], Fig (1-7) .

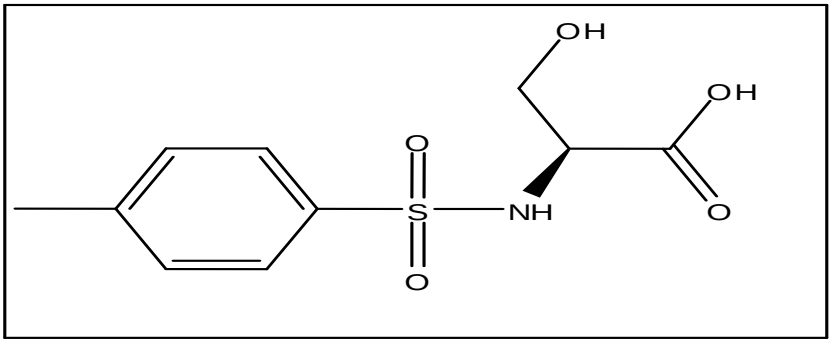
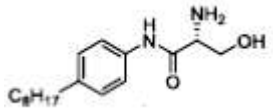
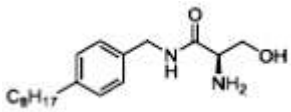
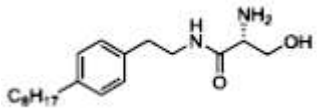
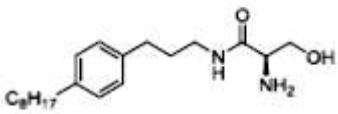


Fig (1-7) 4-toluenesulfonyl-L-serine

In 2018 Yoon sin oh and co-worker synthesized some of serine derivatives from the reaction the 2-amino-2-[2-(4-octylphenyl)ethyl] propane-1,3-diol (Fingolimod) or its derivatives with serine, these compounds were characterized by ^{1}H,^{13}C-NMR, High resolution mass spectra . Table (1-7) shows some of these compounds [25].

Table (1-7) Some of compounds derived from serine

	compound	stracture
1	(R)-2-Amino-3-Hydroxy-N-(4-Octylphenyl)Propanamide	
2	(R)-2-Amino-3-Hydroxy-N-(4-Octylbenzyl)Propanamide	
3	(R)-2-Amino-3-Hydroxy-N-(4-Octylphenethyl)Propanamide	
4	(R)-2-Amino-3-Hydroxy-N-(3-(4-Octylphenyl)Propyl) Propanamide	

1.4-amino acid and their derivatives complexes:

At resent years, many of complexes were prepare by deferent methods and with deferent ligands, which synthesized from amino acid or its derivatives.

In 2012 ,Mohammad Hakimi and co-worker recorded many of complexes of copper only with the common alpha amino acid or its derivatives, they are recorded (46)complexes with glycine, (23)complexes of alanine, (12)complexes of arginine, (9) complexes of tryptophan, (5) complexes of histidine, (3) complexes of lysine, (3)complexes of Lucien, (2) complexes of aspartate, (4) complexes of phenylalanine, (12) complexes of valine, (2) complexes of tyrosine, (3) complexes of glutamine, (1)complex of methionine, (2) complexes of isoleucine, (5) complexes of threonine, (3) complexes of serine, and (1) complex of proline [26].Table (1-7) shows one complex for each amino acid.

Table (1-8) some complexes of amino acid

Amino acid	compound	Cord. No.	Ref.
Glycine	cis-Aqua-bis(glycinato-O,N)copper(II)	5	[27]
Alanine	trans-bis(D,L-a-Alaninato-O,N)copper(II) monohydrate	4	[28]
Arginine	(L-Arginine-O,N)chloro-(1,10-phenanthroline)copper(II) chloride hydrate	5	[29]
Trptophane	(di(2-pyridyl)amine) (tryptophanato)copper(II) perchlorate dihydrate	4	[30]
Histidine	bis(L-Histidine)copper(II)nitrate dihydrate	6	[31]
Lysine	(d-Lysinato)(l-lysinato)copper(II) dichloride dihydrate	4	[32]
Leucine	bis(L-Leucinato)copper(II)	4	[33]
Aspartate	Aqua(L-Aspartate-imidazole copper(II)) dihydrate	5	[34]
Phenylalanine	Aqua(1,10-phenanthroline-N,N)(L-phenylalanine-O,N)copper(II) nitratemonohydrate	5	[35]

Valine	cis-aqua-bis((S)-valinato)copper(II)	5	[36]
Tyrosine	Aqua-(1,10-phenanthroline-N,N')-L-tyrosine-copper(II) perchloratesesquihydrate	5	[37]
Glutamine	trans-bis(L-glutamine-O,N)copper(ii)	4	[38]
Methionine	Aqua-(2,2'-bipyridyl)-(L-methionine)copper(II) perchlorate hydrate	5	[39]
Isoleucine	trans-bis(D,L-Isoleucine-O,N)-copper(II)	4	[40]
Threonine	Aqua-(1,10-phenanthroline)-(L-threonine)copper(II) perchlorate	5	[41]
Serine	D-Serine-L-serine-copper(II)	4	[42]
Proline	Aqua-(L-proline-L-alanine)copper(II) sesquihydrate	4	[43]

In the 2017 fatih sevgi and co-worker were prepare a new ligands derived from glycine and phenylalanine by react them with 2-hydroxy naphthaldehyde these ligands react with [M=Zn,Cu,Ni(1:1 Td), Co,Fe(1:2 Oh)] the complexes were characterized by ^{1}H,^{13}C-NMR, elemental analyses, melting point, FT-IR, magnetic susceptibility and thermal analyses(TGA), Fig(1-8) shown these complexes [44].

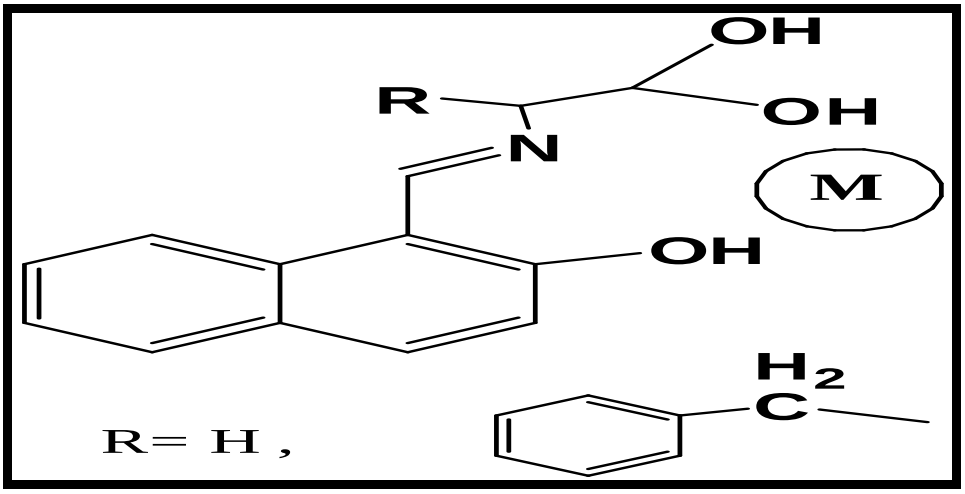


Fig (1-8) General structure of the complexes with glycine or phenylalanine and 2-hydroxy naphthaldehyde

At the same year Violet Dhayabaran and co-worker synthesis new metallic complex of (Co^{+2}) and (Zn^{+2}) with amino acid-nucleobase by simple chemical reaction of metal salt with amino acid L-histidine and nucleobase adenine as ligands. The synthesized complexes were identified by elemental analysis, conductmetric measurements, FT-IR, UV-visible, ^{1}H &^{13}C NMR, mass spectroscopy and magnetic measurements[45], fig(1-9) shown the general structure of these complexes.

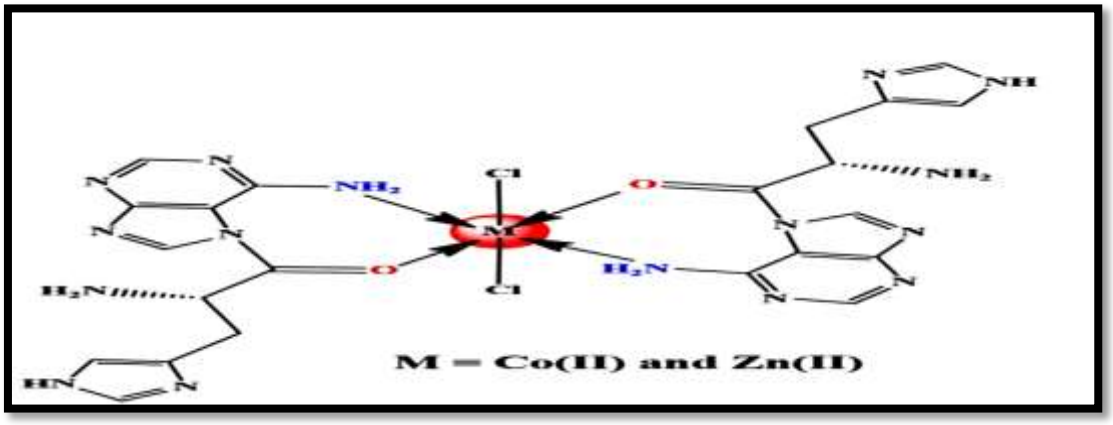
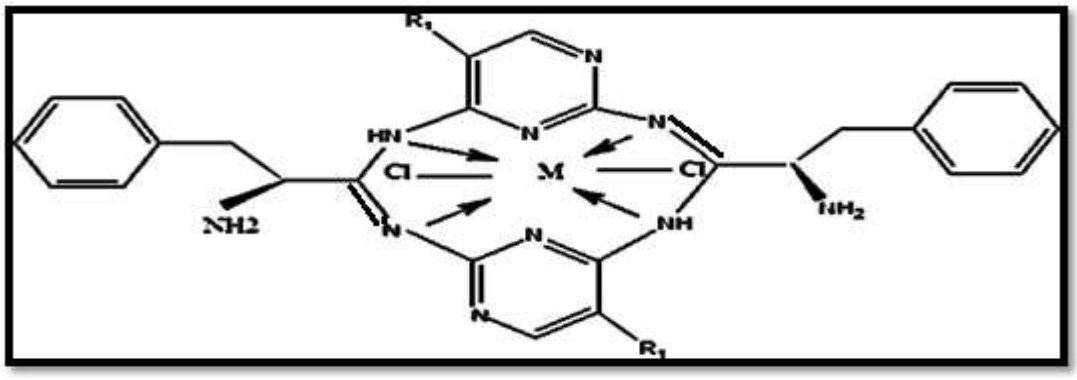


Fig (1-9) Chemical structure of the complexes with the ligand L-Histidine derivatives

B.Mary Juliet and co-worker synthesized micro membered macro cyclic complexes with Mn(II),Co(II) and Cu(II), the ligand prepare by react the trimethoprim with hot solution of the L- phenylalanine, these complexes were characterized by IR, UV-Vis, (C.H.N) and magnetic susceptibility[46] as shown in Fig(1-10).



Fig(1-10) General structure the complexes with the ligand phenyl alanine derivatives

H. Wang and co-worker obtained anew Ni(II)complex by reaction of $Ni(NO_3)_2$ with N-(pyridyl-3-sulfonyl)-L-threonine in $MeOH/H_2O$ under different pH values, the complex characterized by IR, (C.H.N), XRD [47] , Fig(1-11).

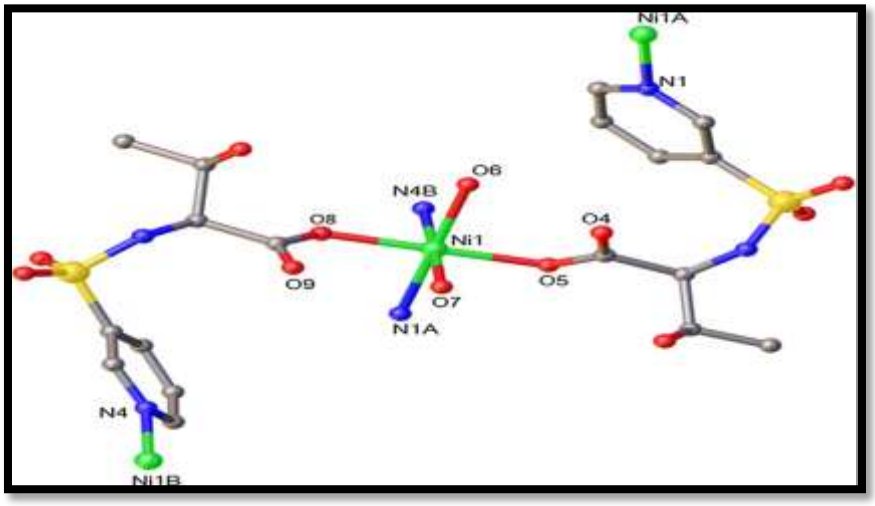


Fig (1-11) Structure the complex of Ni(II)with N-(pyridyl-3-sulfonyl)-L-threonine

Thiago a.D. Rodrigues and co-worker, study the toxity complex of copper with L-glutamate, The complex were characterized by IR, UV-Vis, elemental analysis and potential titration [48], the complex shown in fig(1-12).

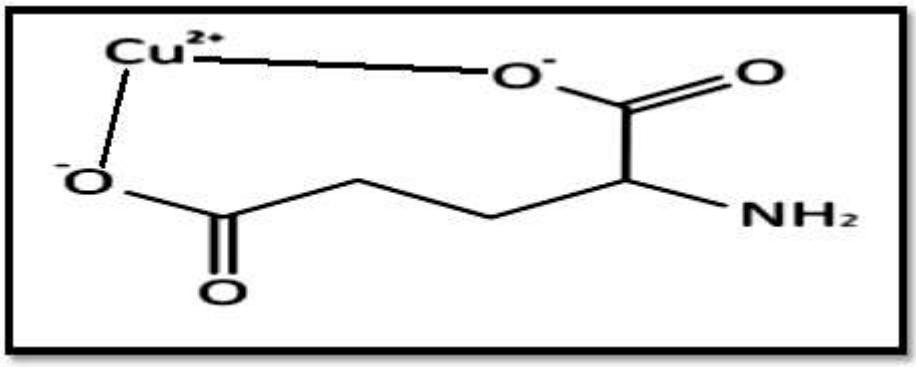


Fig (1-12) Structure the complex of Cu(II) with L-glutamate

Abdel-Rahman L.H and co-worker were synthesized new complexes with glutamine, glutaric , glutamic acid and imidazole derivatives, the complexes have been deduced from elemental analysis, infrared and electronic spectra, conductivity measurements, and thermo gravimetric analysis[49]. The structure of $[Fe(glu)(IMI)_2]. 4H_2O$ and $[Co(glu)(IMI)_2(CH_3COO)]. 2H_2O$ and other complexes were shown in Fig(1-13..to 1-15).

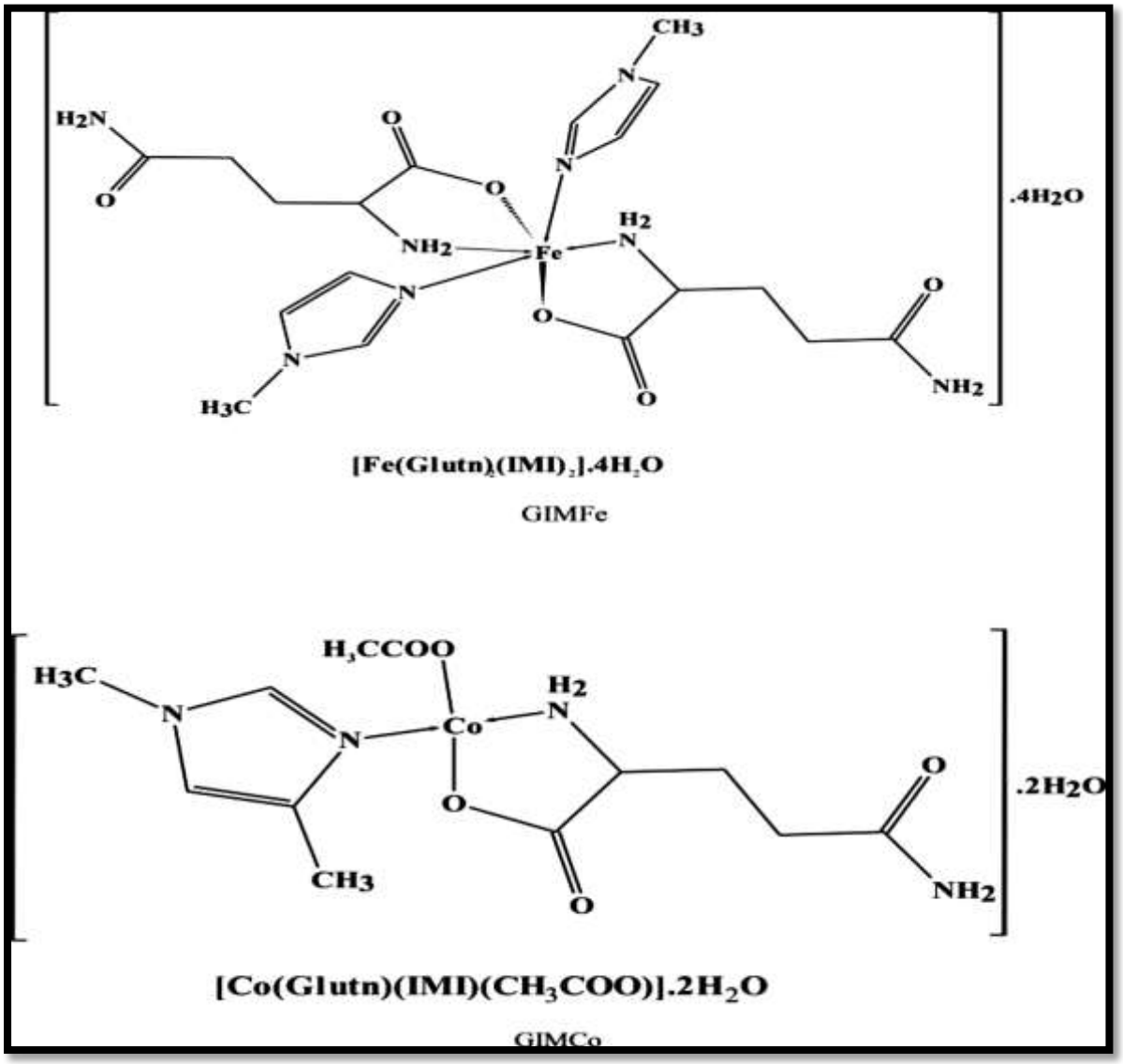


Fig (1-13) Chemical structure Complexes of Fe and Co with glutamine

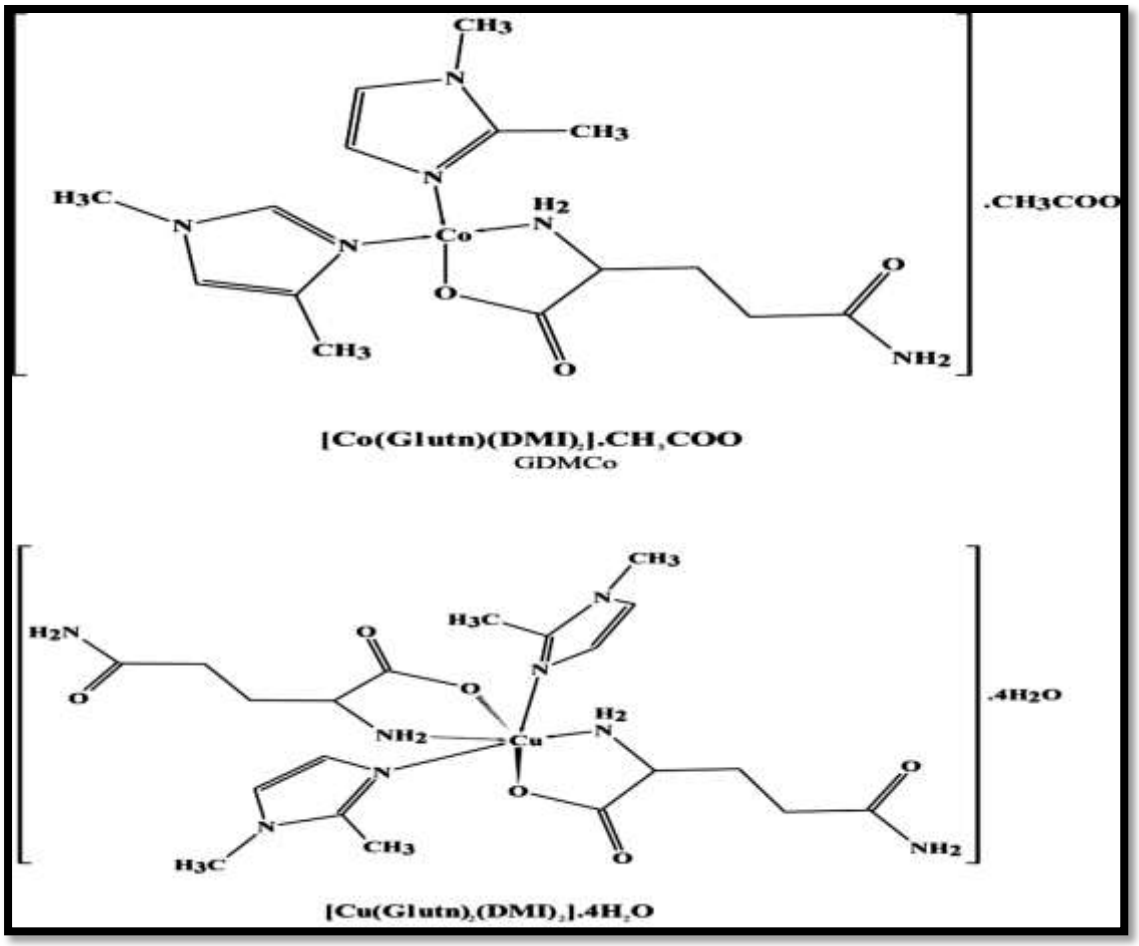


Fig (1-14) Complexes of Co and Cu with glutamine

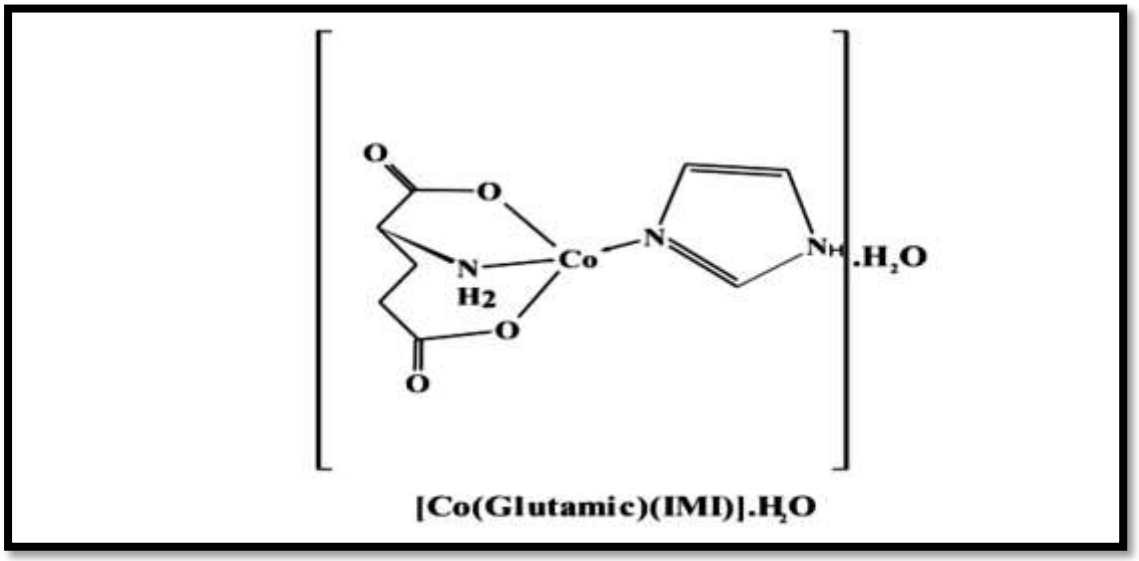


Fig (1-15) The complex of Co with glutamic acid

Edjane R. dos Santos and co-worker ,were synthesized new complexes of Ru(II)with phenanthroline,1,4-bis(diphenylphosphino) butane containing amino acids (Glycine, L-Alanine, L-Valine, L-Tyrosine, L-Methionine or L-Tryptophan) the complexes was synthesized and characterized by IR, ^{13}C and ^{1}H NMR spectroscopies [50] . fig(1-16) show some of these complexes.

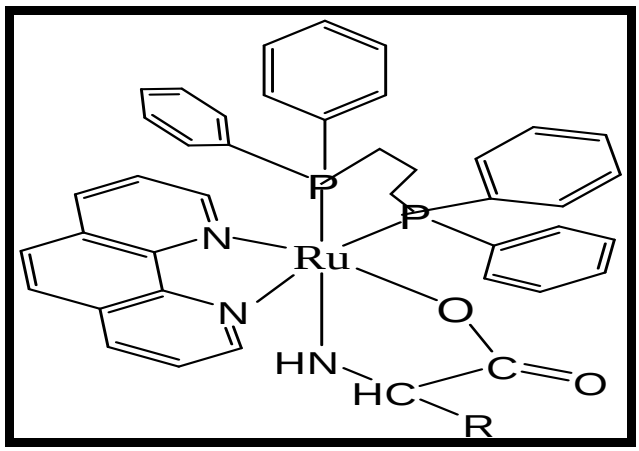


Fig. (1-16) Complexes of Ru(II)with deferent amino acid

Maria L. Perrone and co-worker ,were synthesized a new di nuclear complex with copper(II) the ligand were derived from L-histidene, the complex were characterized by UV-Vis,^{1}H-NMR, magnetic susceptibility [51], the complex shown in the Fig(1-17).

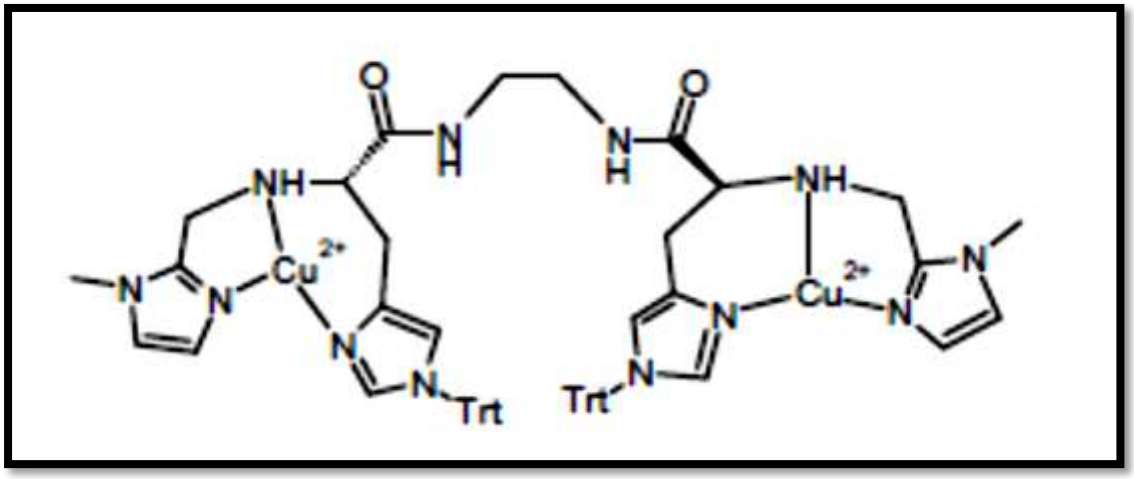


Fig. (1-17) Di nuclear complex of Cu(II) with histidine derivatives

Nan Zhang, and co-worker, were synthesized and study the proteasome-inhibitory activity in human breast cancer three novel L-tryptophan-containing cadmium complexes which given the formats $Cd(C_{17}H_{15}N_4O_2)_2.2CH_3OH$, $Cd(C_{17}H_{15}N_2O_3)_2.2CH_3OH$, $Cd(C_{16}H_{12}N_2O_2SBr)_2.2CH_3OH$, these complexes were characterized by 1H-NMR, IR, elemental analysis [52], Fig(1-18) shown the structure of these complexes.

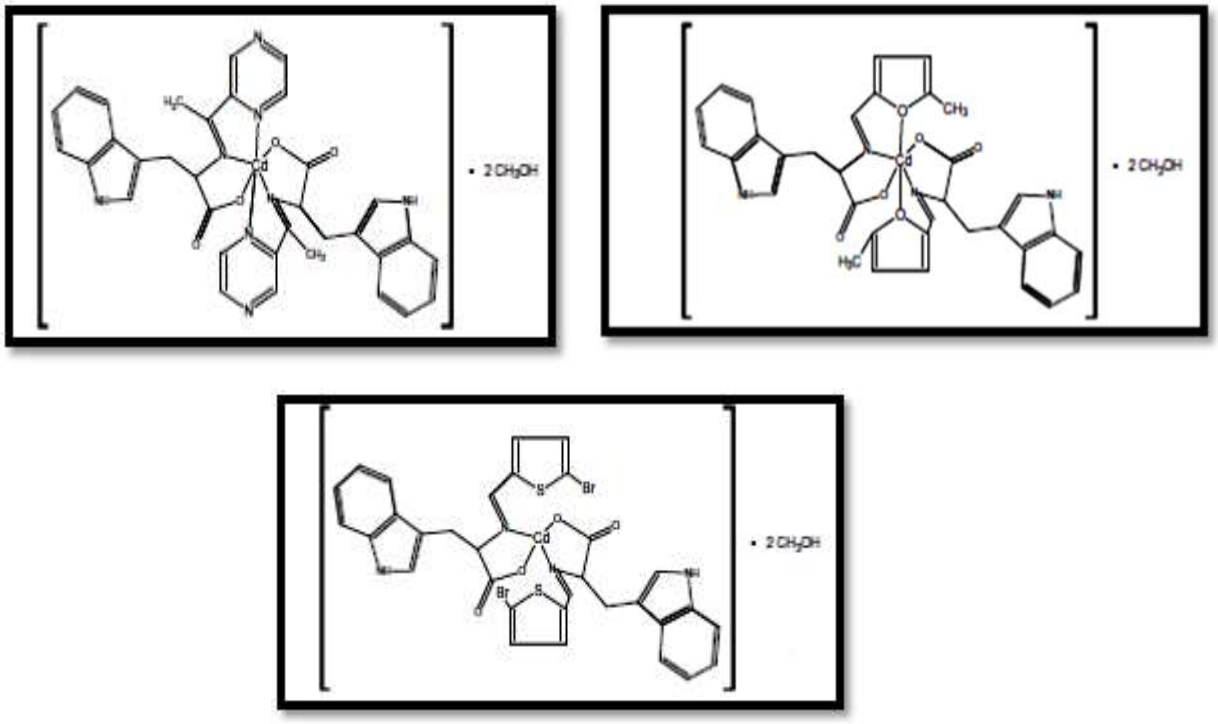


Fig. (1-18) Complexes of Cd(II) with tryptophan and other compounds

S. Dhakshanamoorthy, and co-worker where synthesized two types of complexes of copper(II) with serine and (phen or bpy), it characterized by elemental analyses, ultraviolet-visible, infrared, and electron paramagnetic resonance (EPR) spectral studies[53], as shown in Fig(1-19).

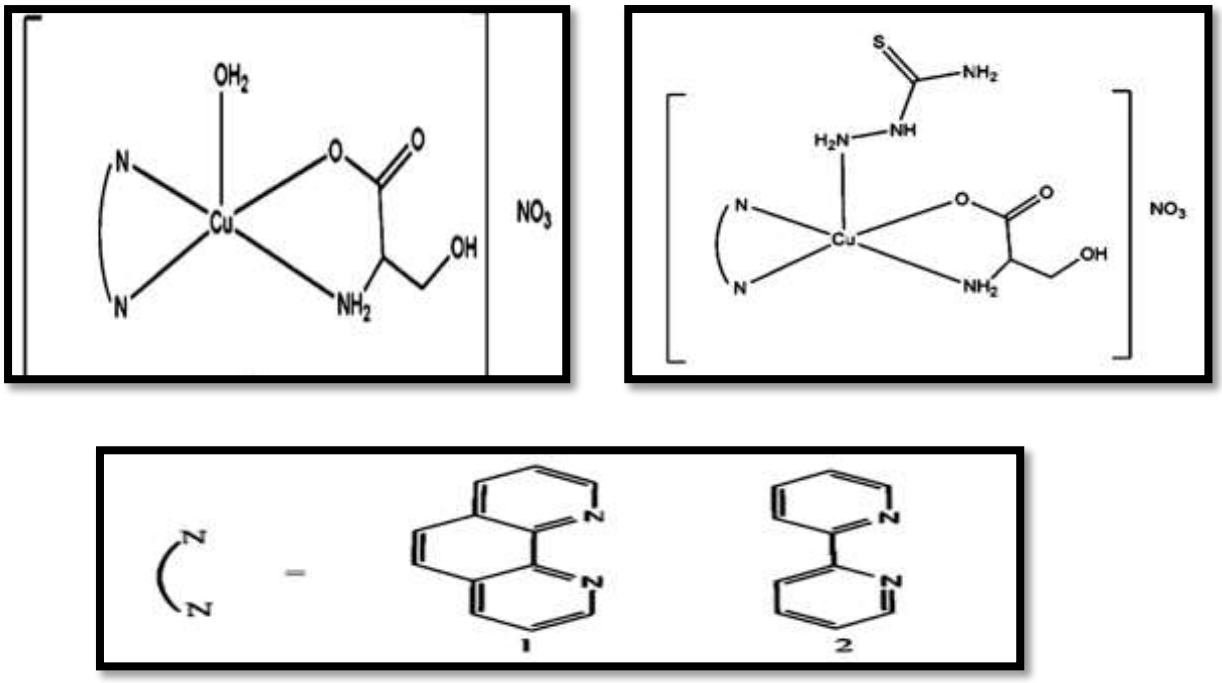


Fig.(1-19) Complexes of Cu(II)with serine and(phen or bpy)

Darko Vusak and co-worker, prepared new complexes with serine by Reactions of copper(II) sulfate with 1,10-phenanthroline , L-serine.The complexes given the formula , $[Cu(L\text{-}ser)\ (H_2O)\ (phen)]_2SO_4.\ xH_2O$, $[Cu(Lser)(CH_3OH)(phen)]_2SO_4.\ xCH_3OH$, these complexes were characterization by X-ray [54], Fig(1-20) shown these complexes.

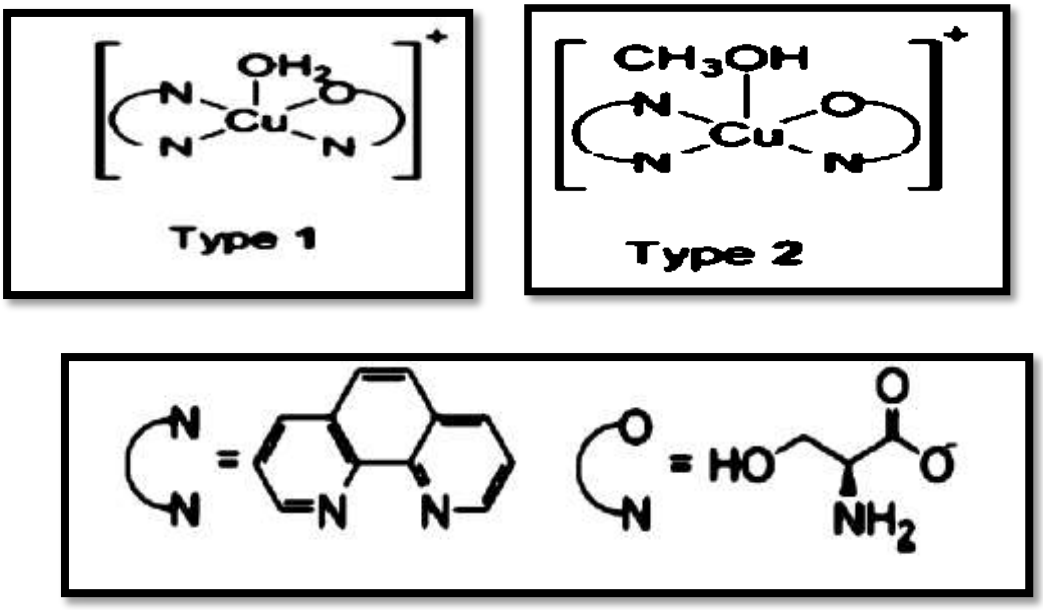


Fig.(1-20) Complexes of Cu(II) ion withe serine and other compound

B.Z.Naema and co-workers were synthesis and characterized new metal complexes with tyrosine derivative ,the complexes were characterized by FT-IR,UV-Vis, Atomic absorption, C.H.N.S, and other methods[55] . Fig. (1-21) show the general formula for these complexes.

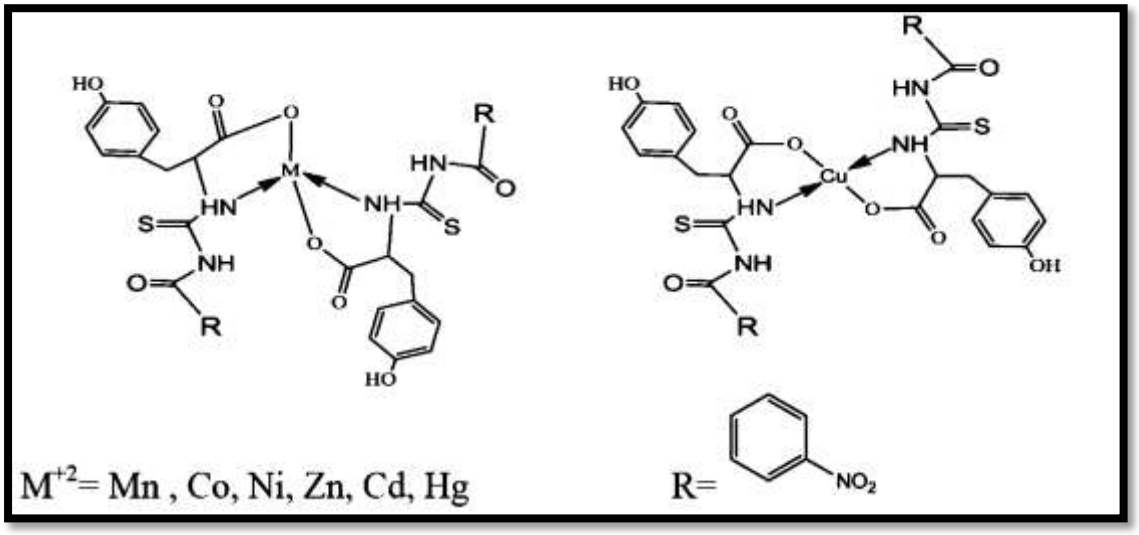


Fig.(1-21) General chemical structure of the complexes with the tyrosine derivative

In 2018 A.Z.Kalaf and co-workers were synthesis and identification some complexes with ligand derivate from tryptophan the complexes were characterized by C.H.N.S, FT-IR, UV-Vis, atomic absorption, magnetic susceptibility[56] . Fig. (3-22)show the general formula of these complexes.

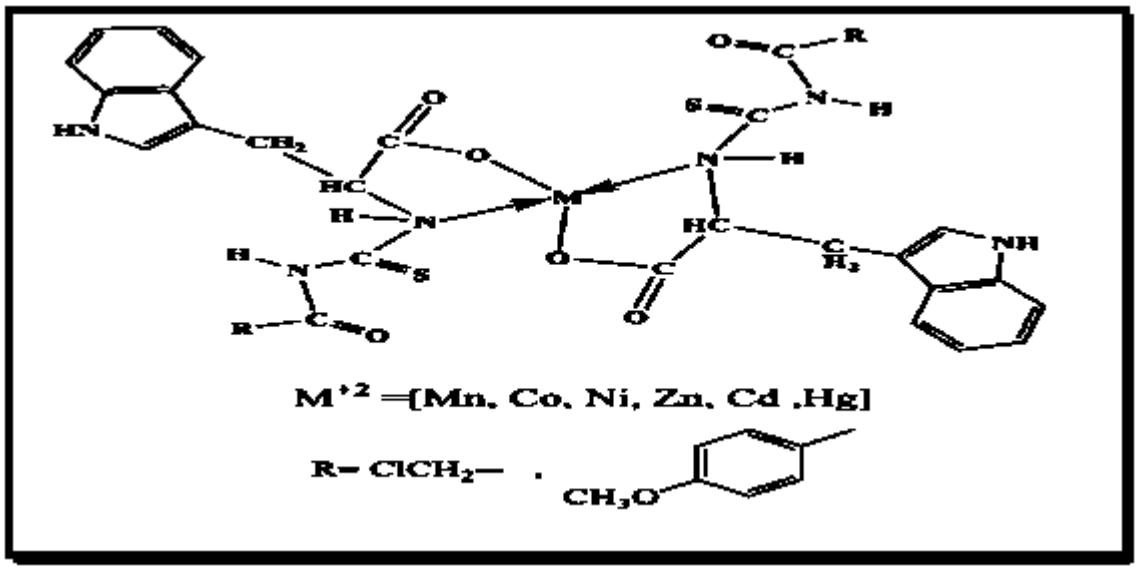


Fig. (1-22) General chemical structure of the complexes with the tryptophan derivative

(1-5) Aim of the work

1. Synthesis of two ligands (ATP) and (NTP) by the reaction of the (Acetyl chloride) or (4-nitrobenzoyl chloride) and ammonium thiocyanat with serine.

2. Synthesis of the metal complexes by the reaction of the prepared ligands with metal ions (M^{+2} =VO, Mn, Co, Ni, Cu, Zn, Cd and Hg).

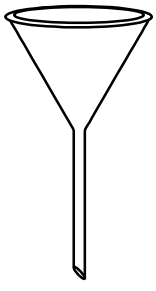
3. Characterization of the two prepared ligands by different techniques like (FT-IR, UV-Vis, ^{1}H,^{13}CNMR spectra, and micro elemental analysis(C.H.N.S).

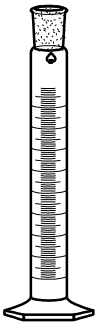
4. Characterization of all the prepared complexes using (FT-IR and U.V-Vis, molar conductance, flame atomic absorption, magnetic susceptibility measurements and micro elemental analysis (C.H.N.S)for some metal complexes,and proposed the suitable geometrical structure depending on that data.

5. Studying biological activity of the two ligands and their complexes with two groups of bacteria (*Staphylococcus aureu*) and (*Escherichia coli*), also with one group of fungi(*Candida albicance*).

Chapter Two

Experimental Part





(2-1) instrumentals

2.1.1 Infrared Spectra

The infrared spectra of ligands and their metal complexes were recorded using the Shimadzu, FT-IR-8300, Infrared Spectrophotometer ,at ministry of Industry, Ibn sina company and University of Baghdad College of Education for Pure Science, Ibn al-Haytham, Department of Chemistry, by using KBr tablets in the range (4000-400) cm^{-1}.

2.1.2 Electronic spectra

The ultraviolet - visible spectra of ligands and their complexes were recorded using a device (Shimadzu UV-160 A-Visible Recording Spectrophotometer) at ministry of Industry, Ibn Sina company and Ibn al-Haytham, College of Pure Sciences / Laboratory using $DMSO_{d6}$ solvent with a concentration of 10^{-3} molar.

2.1.3 NMR spectra(^{1}H,^{13}C-NMR)

The NMR spectra of the prepared ligands from the serine derivative (ATP) and (NTP) Ultra Shield 300 M Hz Switzerland at Al al-Bayt University / Jordan and using $DMSO_{d6}$ and TMS as aggregates to determine the zero point.

2.1.4 Magnetic Measurements

The magnetic sensitivity of the prepared complexes at room temperature were determined at the University of Nahrain and using a Model MSB-MKT Balance Magnetic Susceptibility and the magnetic correction factor (D) was calculated using Pascal constants for the constituent atoms of the prepared complexes.

2.1.5 Molar Conductivity measurement

The molar conductivity of the complexes were measured by using a conductivity meter (jenway conductivity meter 4070) with a concentration of 10^{-3} M in the $DMSO_{d6}$ solvent and at room temperature 35C.

2.1.6 Melting Point measurement

The melting points of both ligands and their complexes were measured using a device (Stuart Melting Point Apparatus).

2.1.7 Flam Atomic Absorption analysis

The ratio of the metal in complex was determined using the atomic absorption flam technique by using Shimadzu AA680 GBC 933 Plus at Ibn Sina Accurate analysis of elements.

2.1.8-Micro elemental analysis(C.H.N.S)

The elemental analysis(C.H.N.S) were determination for the prepared ligands and some of their complexes at Al al-Bayt University / Jordan using the Euro Vector EA 3000A device.

2.1.9 Study of the Biological Activity

At this study two groups of bacteria was testing ,and one type of fungi.

1- Gram-positive bacteria *Staphylococcus aurous*.
2- Gram-negative bacteria *Escherichia coli*.
3- *Candida albicance* (group of fungi).

These bacteria and fungi are choseing because they are very important in the medical and it can caused some diseases.

Four dishes were chosen from each grope of bacteria and fungi to test the compounds activity by using method inhibition zone and measured it by millimeter unit after 24 hours.

(2.2)-Chemicals

Table (2-1) The chemicals used with the name of origin.

No.	Chemical martials	Formula	Purity %	Company
1-	Acetone	C3 H6 O	99.9	Romel
2-	Ethanol	$CH_3 CH_2 OH$	99.9	
3-	Dimethyl sulphoxide	$(CH_3)_2 SO$	99.9	
4-	Dimethylformamide	$(CH_3)_2 NHCO$	99	B.D.H
5-	L-serine	$C_3H_7NO_3$	99	
6-	Diethyl ether	$(C_2 H_5)_2 O$	99	
7-	4-nitro benzoyl chloride	$C_7H_4NO_3Cl$	98	
8-	Ammonium thiocyant	NH_4SCN	98	
9-	acetyl chloride	CH_3COCl	98	
10-	Potassium hydroxide	KOH	99	
11-	Vanadyl (II) Sulphate -1-hydrate	$VOSO_4. H_2O$	99	
12-	Manganese(II)Chloride-4-hydrate	$MnCl_2. 4H_2O$	99	
13-	Zinc (II) Chloride	$ZnCl_2$	99	Merck
14-	Cobalt (II) Chloride -6-hydrate	$CoCl_2. 6H_2 O$	99	
15-	Nickel (II) Chloride -6-hydrate	$NiCl_2. 6H_2O$	99	
16-	Copper (II) Chloride -2-hydrate	$CuCl_2. 2H_2 O$	99	
17-	Mercury(II) Chloride	$HgCl_2$	98	
18-	Methanol	$CH_3 OH$	99.9	Seeizer-Hannover
19-	Cadmium(II) Chloride -1-hydrate	$CdCl_2. H_2O$	99.5	Riedel-Dehaena

2.3. Synthesis of the ligands

2.3.1 Synthesis of the ligand (ATP)

The ligand (ATP) were prepare by two steps [57] :-

A- Solution from (2g, 26 mmol)of ammonium thiocyanate in(25 mL) of acetone, then added (1.86mL, 26 mmol) of acetyl chloride to the former solution and stirred about 3 hours.

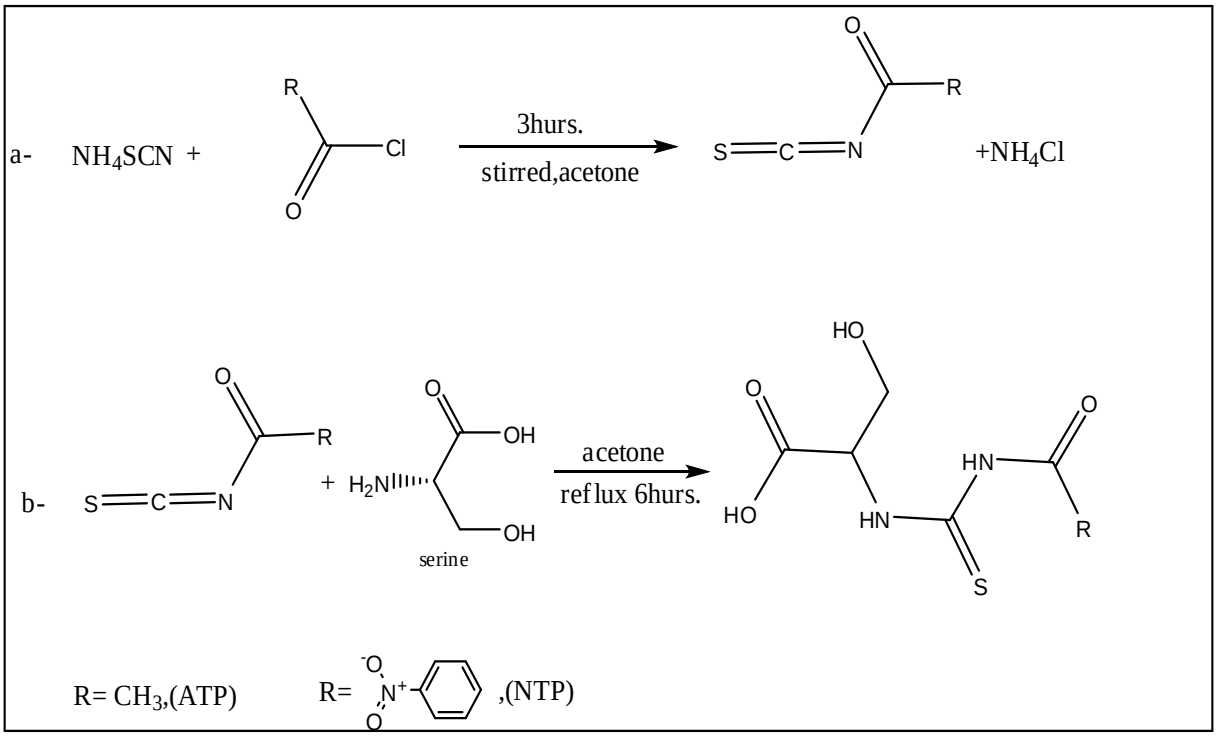
B-Solution of (2.77g, 26 mmol) of the serine amino acid in (15 mL) acetone then filtered the former solution above serine solution, refluxed the mixture for 6 hours and leave it to dry. The product is deep-yellow solid.

2.3.2 Synthesis of the ligand (NTP)

The ligand (NTP) were prepare by two steps [57] :-

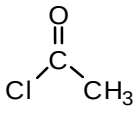
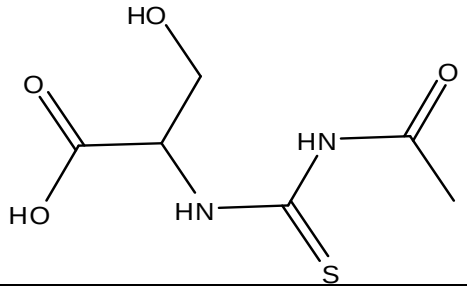
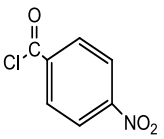
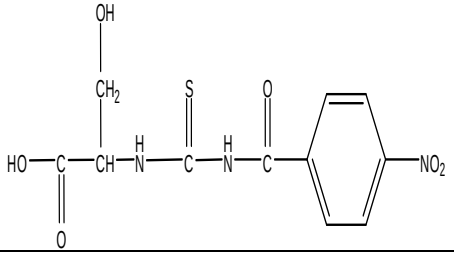
A-Solution of (2g, 26mmol) of ammonium thiocyanate in(25 mL) of acetone, then dissolved (4.82g, 26mmol) of 4-nitro benzoyl chloride ,mixed the two solution and stirred about 3 hours.

B-Solution of (2.77g, 26mmol) of the serine amino acid in (15 mL) acetone then filtered the former solution above serine solution, the mixture was refluxed for 6 hours and leave it to dray. The product is orange powder. Scheme (2-1) shows the general equation to prepare these ligands.



Scheme (2-1) The general equation to prepare the ligands

Table (2-2) Type and amount of acid chloride (RCOCl) and the structure of the ligands

Type of acid chloride	amounts	Structure of acid chloride	Structure of ligand	Ligand`s symbols
Acetyl chloride	**1.86 ml**			**ATP**
4-nitro benzoyl chloride	**4.82 g**			**NTP**

2.3 Synthesis of complexes

2.3.1 Synthesis of metal complexes with (ATP)ligand

A solution of (0.112g , 2mmol) of KOH in 10 ml ethanol was added to (0.412g, 2mmol) of (ATP) ligand, and setting the pH between(7-8), then adding metallic salt solution(1mmol in 10 ml ethanol), mixed them and stirred to3 hours, then filtering the product solution and washing it by distilled water and ethanol, at last leave the filtered to dry. Table (2-3) show the amounts of metallic salts that used to prepare the complexes with (ATP).

Table (2-3) Weights of metallic used to prepare metal complexes with (ATP)

metal salt	**$HgCl_2$**	**$CdCl_2.H_2O$**	**$ZnCl_2$**	**$CuCl_2.2H_2O$**	**$NiCl_2.6H_2O$**	**$CoCl_2.6H_2O$**	**$MnCl_2.4H_2O$**	**$VOSO_4.H_2O$**
W. (g)	0.272	0.201	0.136	0.170	0.237	0.237	0.200	0.180
complex	**$[Hg(ATP)_2]$**	**$[Cd(ATP)_2]$**	**$[Zn(ATP)_2]$**	**$[Cu(ATP)_2]$**	**$[Ni(ATP)_2]$**	**$[Co(ATP)_2]$**	**$[Mn(ATP)_2]$**	**$[VO(ATP)_2]$**

2.3.2-Synthesis of metal complexes with ligand (NTP)

A solution of (0.112g, 2mmol) of KOH in 10 ml ethano ladded to(0.626g, 2mmol) of (ATP) ligand to and setting the pH between(7-8),then adding metallic salt solution(1mmol in 10ml ethanol), mixed this mixture and stirred to 3 then filtering the product solution and washing it by distilled water and ethanol, at last leave the filtered to dry. The table (2-2) show the amounts of metal salts that used to prepare the complexes with (NTP).

Table (2-4) Weights of metal salts used to prepare metal complexes with (NTP)

metal salt	**$HgCl_2$**	**$CdCl_2.H_2O$**	**$ZnCl_2$**	**$CuCl_2.2H_2O$**	**$NiCl_2.6H_2O$**	**$CoCl_2.6H_2O$**	**$MnCl_2.4H_2O$**	**$VOSO_4.H_2O$**
W. (g)	0.272	0.201	0.136	0.170	0.237	0.237	0.200	0.180
complex	**$[Hg(NTP)_2]$**	**$[Cd(NTP)_2]$**	**$[Zn(NTP)_2]$**	**$[Cu(NTP)_2]$**	**$[Ni(NTP)_2]$**	**$[Co(NTP)_2]$**	**$[Mn(NTP)_2]$**	**$[VO(NTP)_2]$**

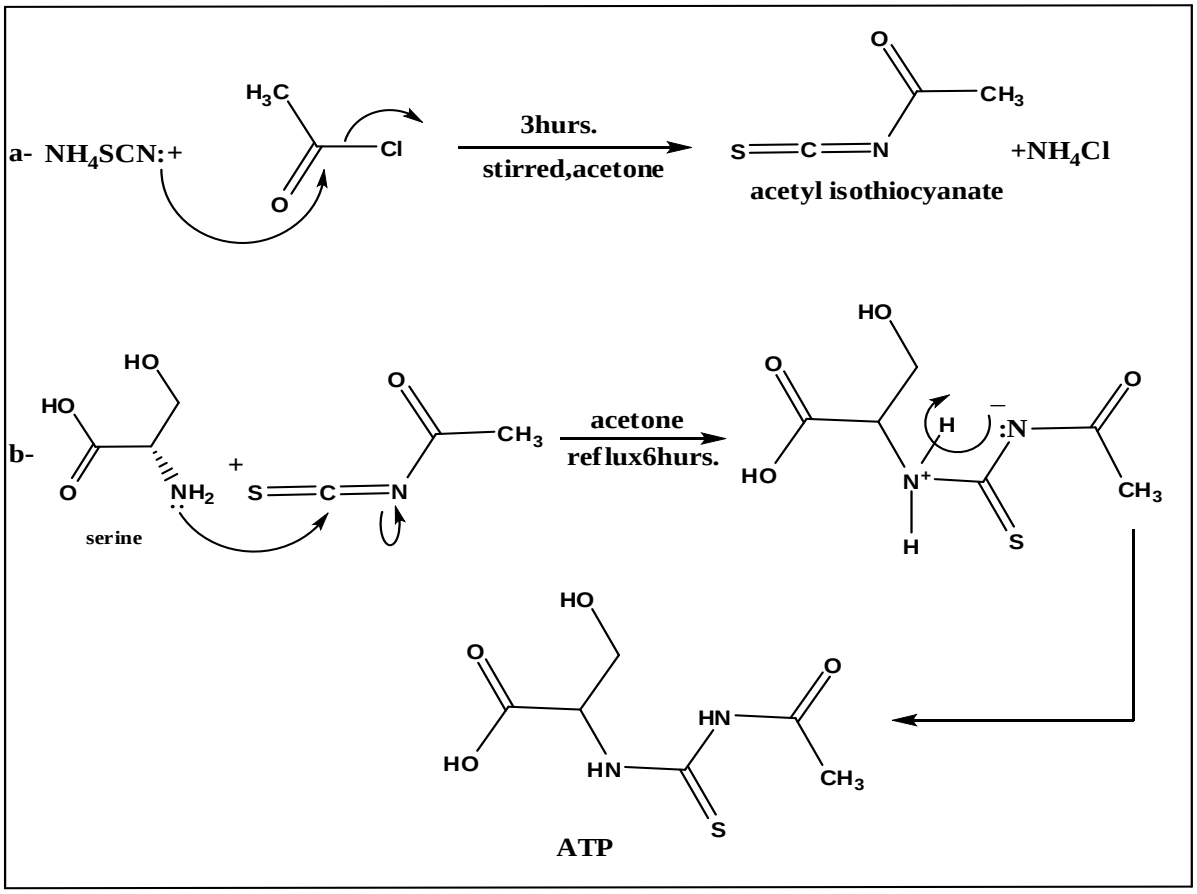
Chapter Three

Results & Discussion

3.1 Synthesis of ligand(ATP)

3.1.1 The suggested mechanism for synthesis the ligand (ATP).

The ligand (ATP) is a serine derivative and it prepare at two steps the first step was by reaction of ammonium thiocyanate with of acetyl chloride, the second step was addition the former filtered to from serine by using acetone as solvent. The product was yellow (ATP), as shown in scheme (3-1).



Scheme (3-1) The suggested mechanism for synthesis the ligand (ATP)

3.1.2 The micro elemental analysis of (ATP)

From the micro elemental analysis (C.H.N.S) for the ligand (ATP) the molecular formula ($C_6H_{10}O_4N_2S$) was given to it, some of its physical properties are show in the table (3-1).

Table(3-1) Micro elemental analysis for the ligand(ATP)

Formula	Color	M.W g/mol	M.P	Yield (%)	calc.(%) and (Found)(%)			
					C	H	N	S
$C_6H_{10}O_4N_2S$	Yellow	206	120-122	76	34.95	4.85	13.59	15.53
					(34.97)	(4.34)	(14.00)	(15.48)

3.1.3. FT-IR spectrum of ligand (ATP)

The FT-IR spectrum for serine, fig (3-1) show abroad band at (3440)cm^{-1} which due to the amino group (NH_2)and other abroad band at(3070cm^{-1}) due to (OH) group ,two bands appear at(1597cm^{-1}) and(1459cm^{-1}) which due to (COO_{asy})and(COO_{sy}) respectively [58].

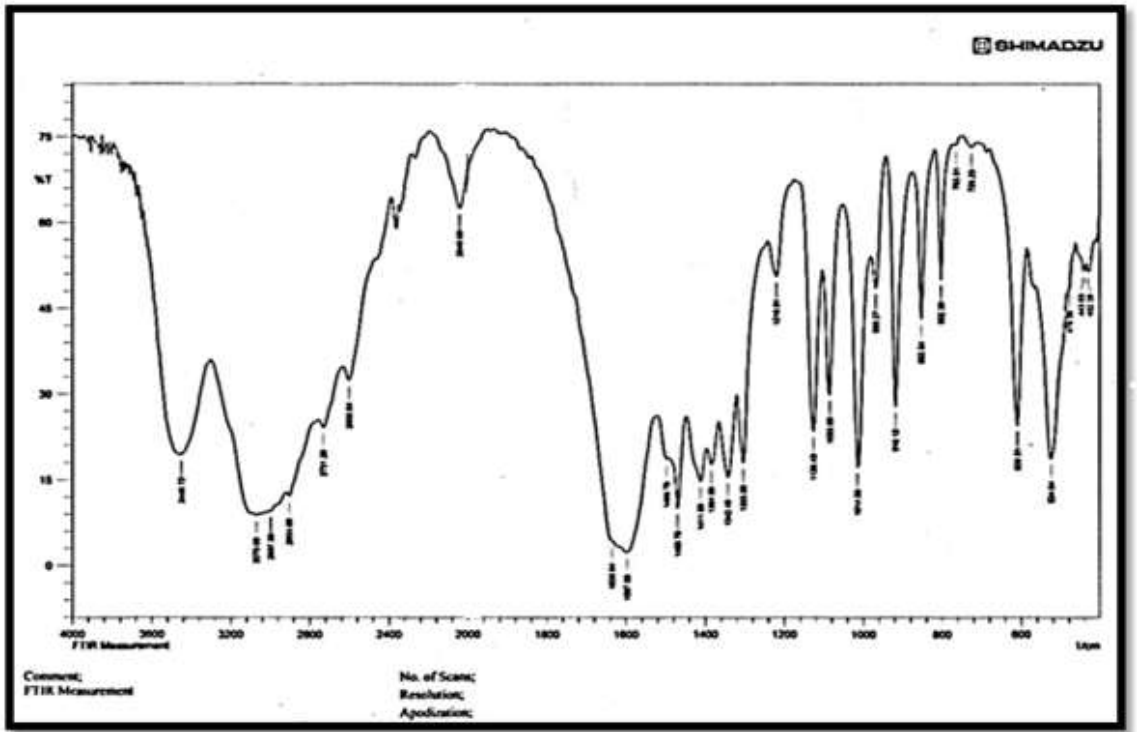


Fig.(3-1): FT-IR spectrum of serine

While the FT-IR spectrum of the ligand (ATP), Fig.(3-2)shown bands below:-

A band at(3213cm^{-1}) for (NH) and other band at (3018cm^{-1}) which due to (OH)group ,strong band at(1654cm^{-1}) for (C=O), strong band too at(1234cm^{-1}) due to(C=S) and another two bands at(1701cm^{-1}) (1373cm^{-1}) for(COOasym)and(COOsym) respectively [59,60], Table(3-2) illustrate these bands.

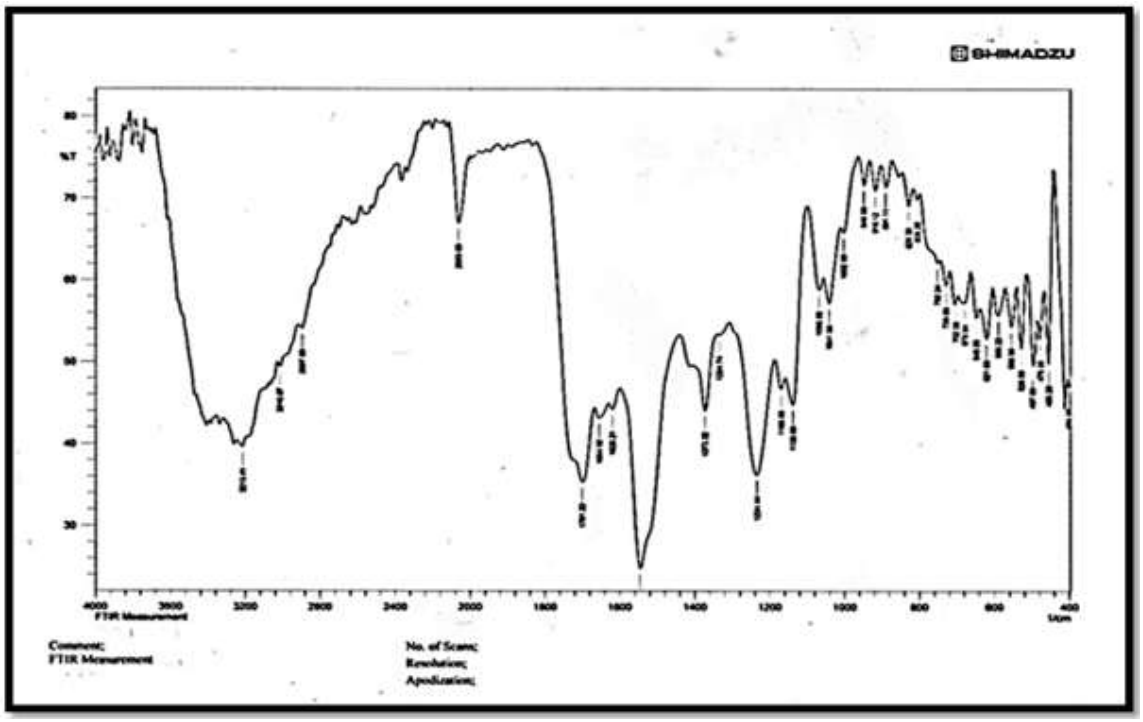


Fig.(3-2) FT-IR of ligand (ATP)

Table(3-2) FT-IR spectral data of(ATP) by cm^{-1}

group	U(COO) Asym cm^{-1}	U(COO) Sym Cm^{-1}	U(NH_2) / U(NH) cm^{-1}	U(OH) cm^{-1}	U(C=S) cm^{-1}	U(C=O) cm^{-1}
serine	1597(s)	1459(s)	3440(m) / -----	3070(m)	---	---
ATP	1701(s)	1373(s)	----- / 3213(m)	3018(m)	1234(s)	1654(m)

3.1.4 NMR spectra of the ligand(ATP)

a- ^{1}H-NMR spectrum

The (^{1}H-NMR) spectrum of the ligand (ATP) shown in Figure (3-4) showed the following signals:

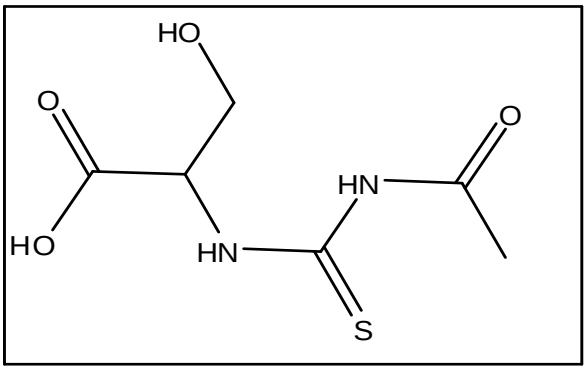


Fig. (3-3)The structure of the ligand(ATP)

Singlet peak at δ (1.996ppm) to (3H,CH_3) and the spectrum showed a signal at δ (2.505ppm) for solvent protons dimethyl sulfoxid ($DMSO_{d6}$), the spectrum showed doublet signal at δ(2.005ppm) for (2H,CH_2) and triplet signal at δ(3.578ppm) to (1H.CH), singlet signal at δ(4.854ppm) for (1H,OH alcohol), so singlet at δ(7.997ppm) due to $(1H,NH)_{amine}$, singlet peak at δ(11.126ppm) for $(1H,NH)_{amide}$, also single peak at δ(11.270)ppm due to (1H,COOH) the high chemical shift for carboxyl proton as a result to the resonance at this group.[61] . Table (3-3) shown the signals chemical shift by ppm for ligand (ATP).

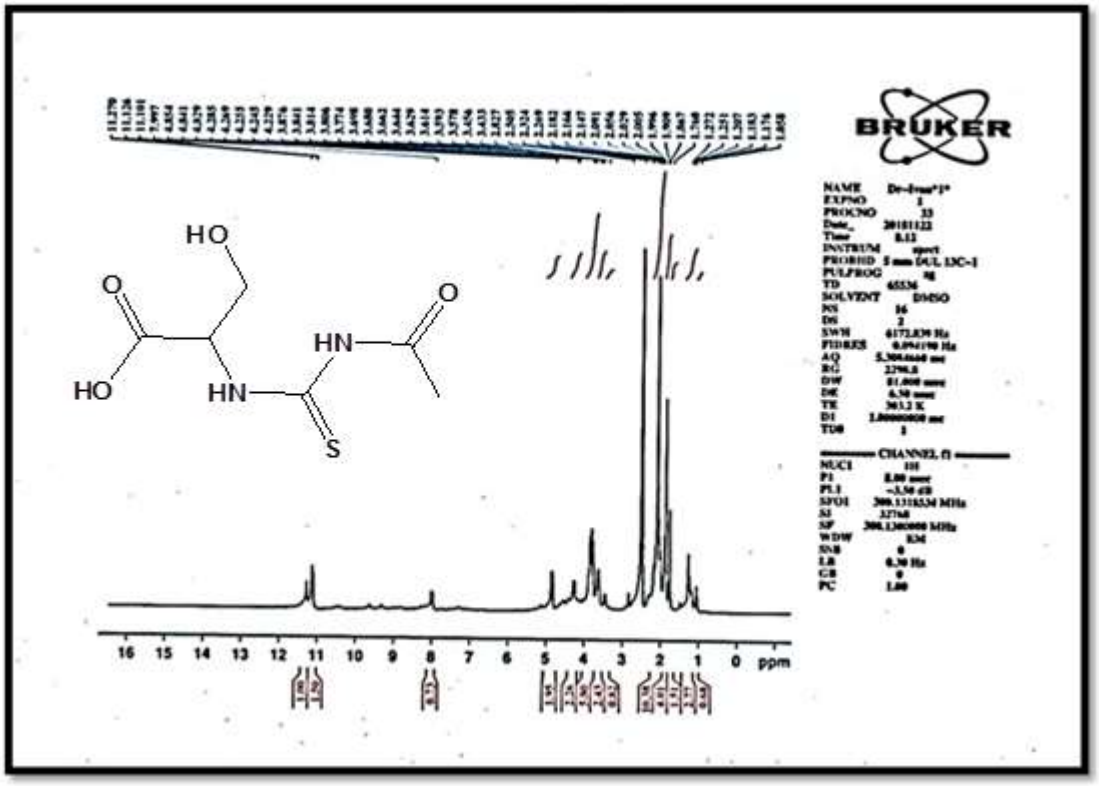


Fig.(3-4) ^{1}H-NMR spectrum of the ligand(ATP)

Table (3-3) ^{1}H-NMR Spectral data for ligand (ATP)

Compound	Functional groups	(ppm) δ
ATP	s (3H,CH_3CO)	1.996
	d (2H,CH_2)	2.005
	t (1H,CH)	3.578
	s (1H,OH)	4.854
	s (1H,NH_{amine})	7.997
	s (1H,$NH_{sec\ amide}$)	11.126
	s (1H,COOH)	11.270

b- The(^{13}C-NMR) spectrum of (ATP).

The (^{13}C, NMR) spectrum for the ligand (ATP) Figure (3-5) showed the following signals

The signal at δ (22.383ppm)which are assigned to (CH_3) and the spectrum showed signals between δ (38.680-39.789ppm) for solvent dimethyl suffixed ($DMSO_{d6}$), the spectrum showed a singlet signal at δ(54.6008ppm) for (CH_2) and other signal at δ(61.366ppm) to (CH) and a signal at δ(170.650ppm) for (COOH), singlet peak at δ(172.182ppm) due to (C=Osec amide) and singlet peak at δ(179.959ppm) for(C=S)[62], Table (3-4).

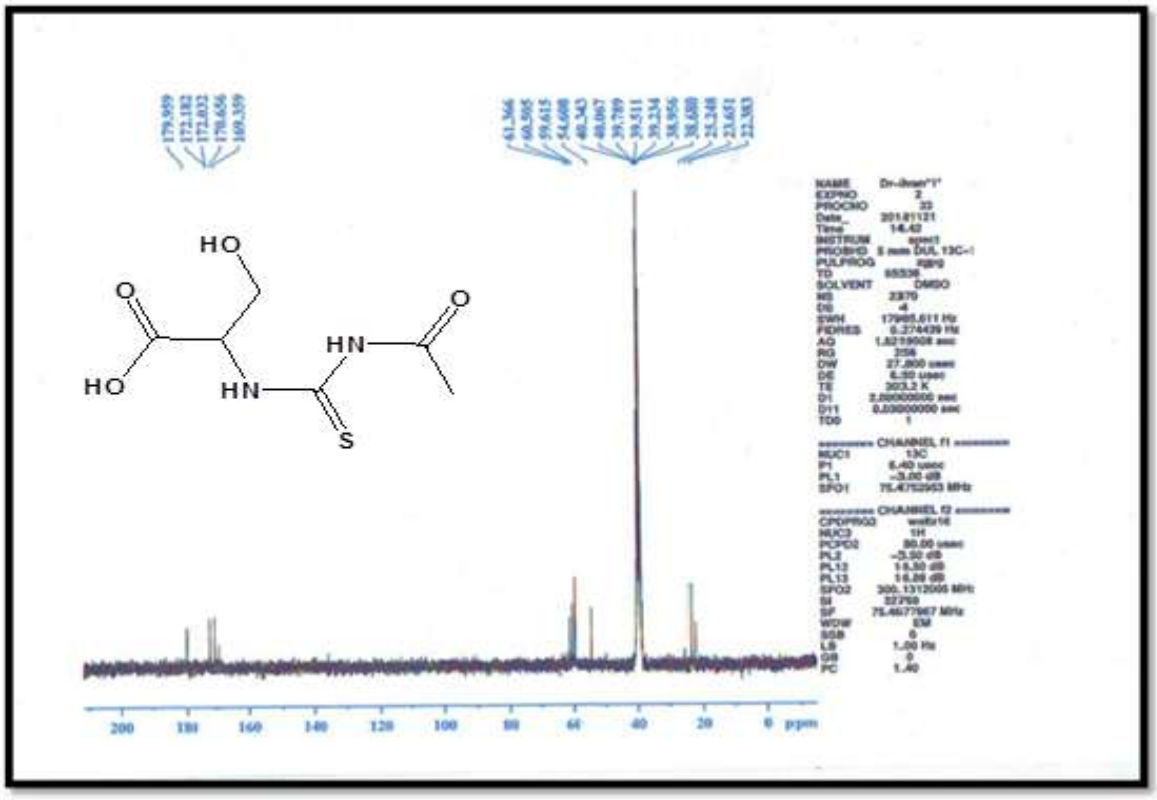


Fig.(3-5) ^{13}C-NMR spectrum of (ATP)

Table(3-4) Show the ^{13}C-NMR spectral data of (ATP) in $DMSO_{d6}$ solvent

Compound	Functional grop	ppm δ
ATP	(CH_3)	(22.380-25.245)
	(CH_2)	60.505
	(CH)	61.366
	(COOH)	170.656
	(C=O sec amine)	172.032
	(C=S)	179.959

(3.1.5) UV-Vis Spectrum of(ATP)

The UV-Vis spectrum of the free ligand(ATP), fig(3-6) and displays a strong peak at (36363)cm^{-1} due to $\pi \rightarrow \pi^*$ and (28985)cm^{-1} which refers to $n \rightarrow \pi^*$ [63,64], Table (3-5).

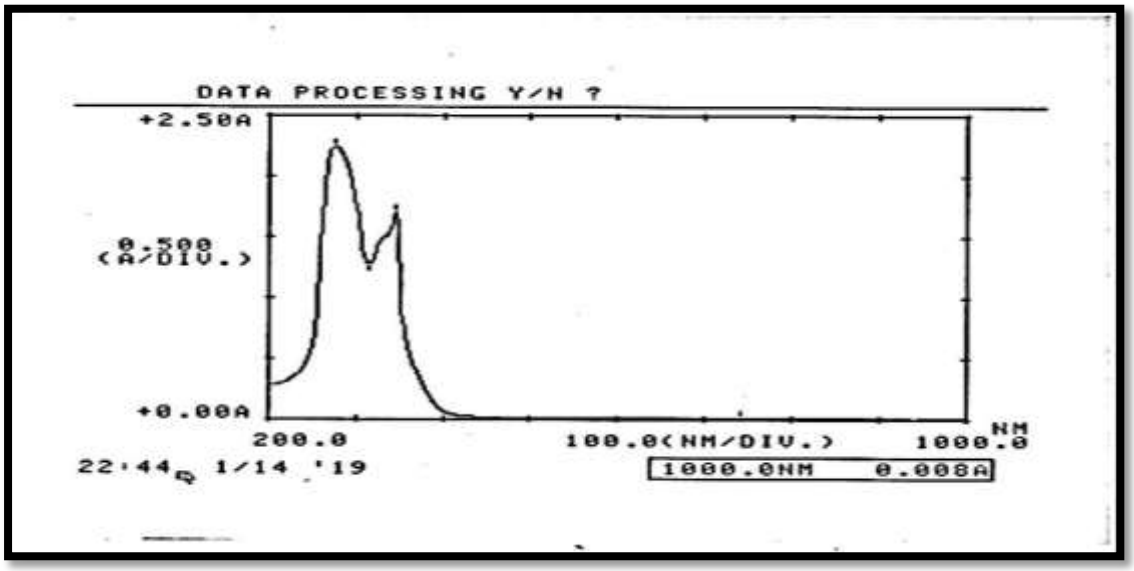


Fig.(3-6) UV- Vis spectrum of ligand (ATP)

Table (3-5) Electronic spectra data of the ligand(ATP)

Compound	λ(nm)	υ(cm^{-1})	A	ε_{max} ($molar^{-1}cm^{-1}$)	Transitions
(ATP)	275 345	36363 28985	2.245 1.701	2245 1701	π ⟶ π* n ⟶ π*

3.1.6 The solubility of ligand (ATP).

The ligand ATP show different ability to solubility in some solvent, Table (3-6) illustrate this data.

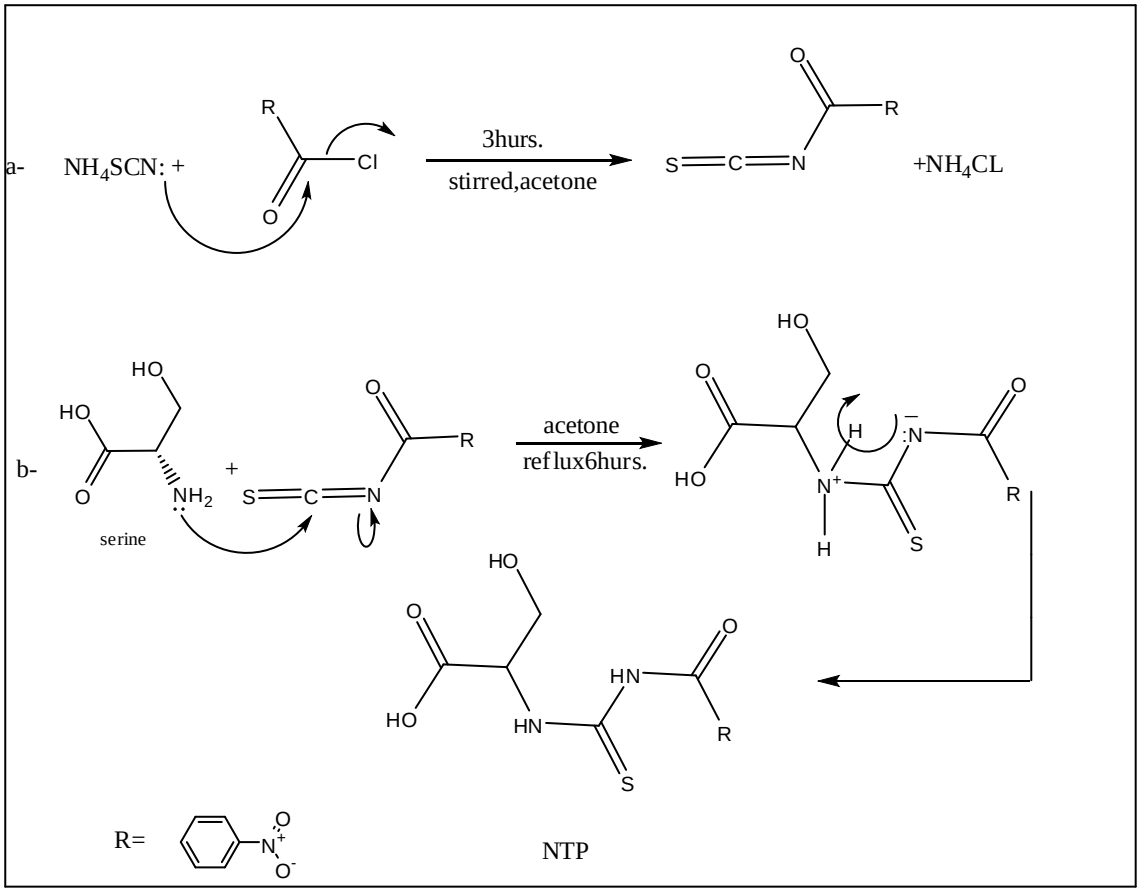
Table (3-6) Solubility of ligand(ATP)

	H_2O	DMF	MeOH	EtOH	$(Me)_2CO$	DMSO	Hexan	$CHCl_3$	$(Eh)_2O$
ATP	-	+	+	÷	+	+	-	-	-

3.2 Synthesis of ligand (NTP).

3.2.1 The suggested mechanism for the synthesis of the ligand (NTP)

The ligand (NTP) is a serine derivative and it was prepared at two steps, the first steep was by reaction of ammonium thiocyanate with of 4-nitro benzoyl chloride, second step was addition the former filtered to serine by using acetone as a solvent ,the product was dark yellow (NTP), as shown in scheme(3-2).



Scheme (3-2) The mechanism suggested for synthesis of ligand (NTP)

3.2.2 The micro elemental analysis of the ligand (NTP)

From the micro elemental analysis (C.H.N.S) for the ligand (NTP) the molecular formula ($C_{11}H_{11}O_6N_3S$) was given to it. Some of its physical properties shown in Table(3-7).

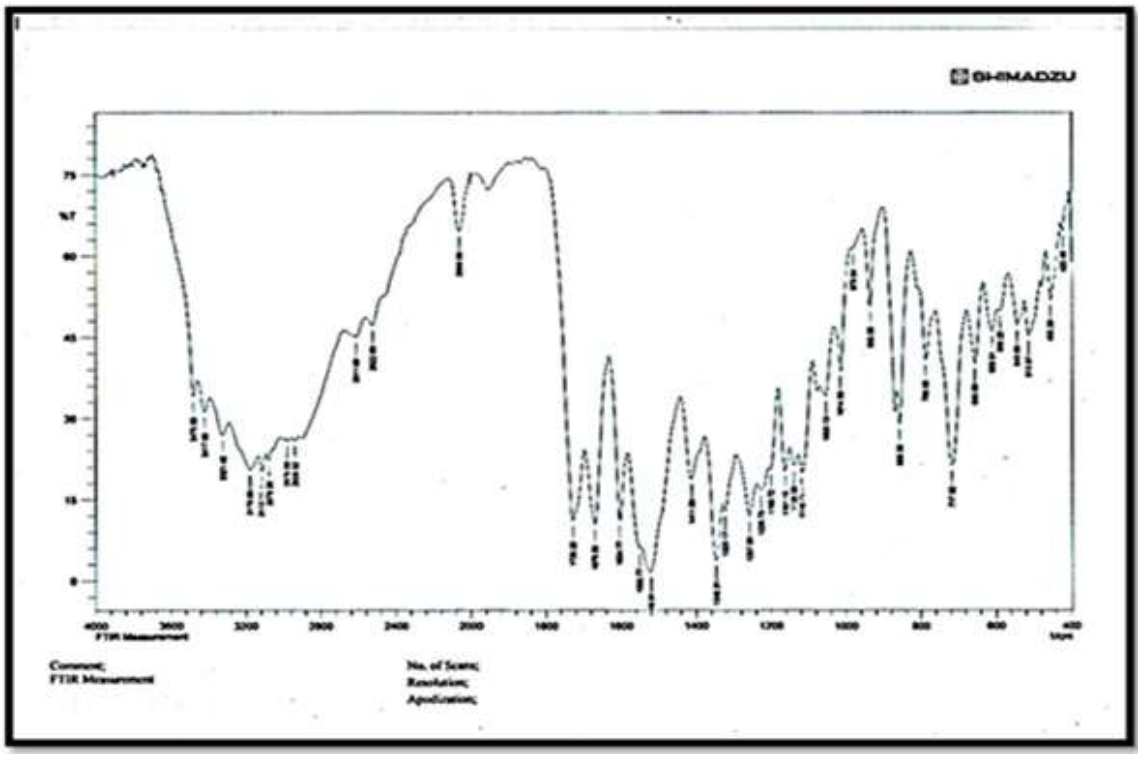
Table(3-7) Micro elemental analysis and some physical properties of the ligand(NTP)

Formula	color	M.W g/mol	M.P	Yield (%)	calc.(%) and (Found)(%)			
					C	H	N	S
$C_{11}H_{11}O_6N_3S$	Dark yellow	313	148-150	83	42.17	3.51	13.41	10.22
					(42.47)	(3.14)	(13.77)	(10.18)

3.2.3.FT-IR spectrum of ligand (NTP)

The spectrum for ligand (NTP) shown the bands below Fig.(3-7):-

A band at(3417cm^{-1}) can be attributed for (NH) and other band at (3178 cm^{-1}) which due to (OH) group, strong band at(1676cm^{-1}) for(C=O), medal band too at(1257cm^{-1}) due to(C=S) and two bands at(1728cm^{-1}) (1346cm^{-1}) for (COOasym) and(COOsym) respectively [65,66], Table(3-8)shown this data.



Fig(3-7) FT-IR Spectrum of the ligand (NTP)

Table (3-8) FT-IR spectral data of the ligand (NTP)

	U(COO) asym	U(COO) Sym	U(NH) cm-1	U(OH) cm^{-1}	U(C=S) cm^{-1}	U(C=O) cm^{-1}
NTP	1728(s)	1346(s)	3417(m)	3178(m)	1257(m)	1676(s)

3.2.4. NMR spectra of ligand (NTP).

a-^{1}H-NMR spectrum

The NMR spectrum (^{1}H-NMR) of the ligand (NTP). Fig (3-8) showed the following signals:

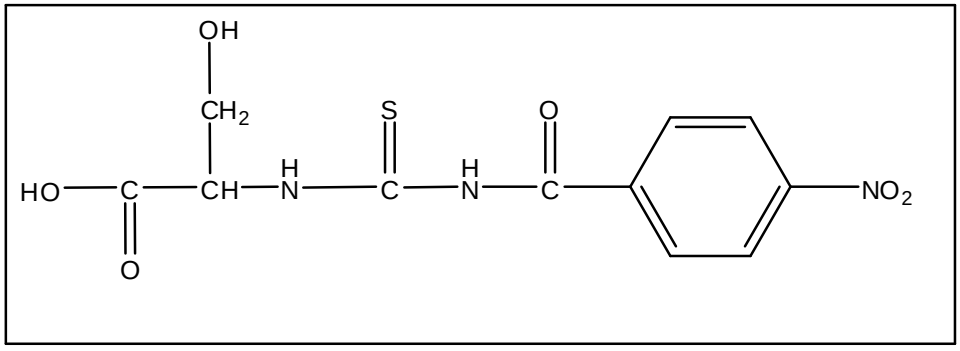


Fig.(3-8) Structure of the ligand (NTP)

Multiple signals due to $DMSO_{d6}$ solvent between δ(2.098-2.509ppm), spectrum showed triplet signal at δ(1.549ppm) which assigned to (1H,CH) and doublet signal at δ(3.430ppm) to (2H.CH_2), singlet signal at δ(4.912ppm) for (1H,OH), so singlet at δ(7.680ppm) due to (1H,NH_{amide}), a duplet at δ(8.111-8.364 ppm) due to(4H, $_{aromatic}$), also a single peak at δ(8.082ppm) for (1H,$NH_{sec\ amide}$) and singlet signal at (11.287ppm) due to(1H,COOH) [66] . Table(3-9) shown the signals chemicals shift by ppm for (NTP).

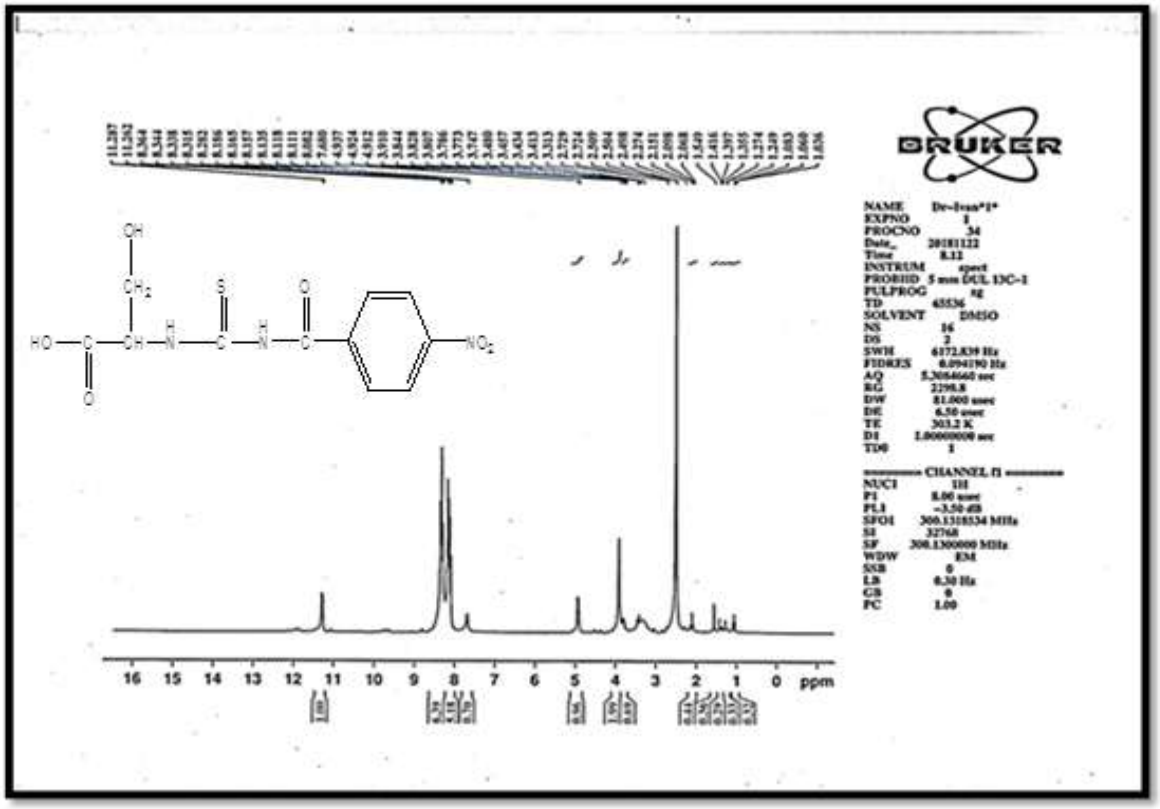


Fig.(3-9) ^{1}H-NMR spectrum of ligand(NTP)

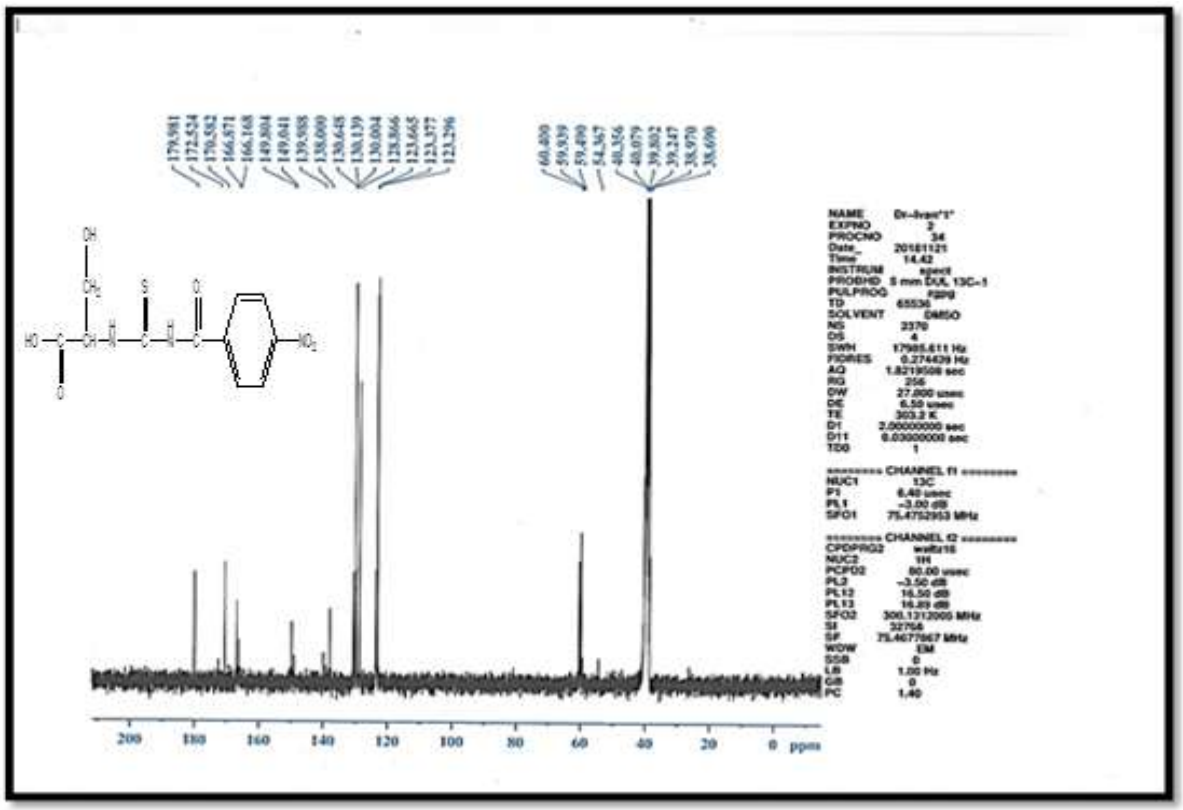
Table (3-9) ^{1}H-NMR spectral data of ligand (NTP)

Compound	Functional groups	δ (ppm)
NTP	t(1H,CH)	1.549
	d(2H,CH_2)	3.480
	s(1H,OH)	4.912
	s (1H,NH amine)	7.680
	s(1H,NH sec amide)	8.082
	(d-d)(4H,aromatic proton)	(8.111-8.364)
	s(1H,COOH)	11.287

b-The ^{13}C-NMR spectrum of the ligand (NTP)

The (^{13}C-NMR) spectrum for ligand (NTP) shown in Fig. (3-10) showed the signals below:-

Signals between δ(38.690-40.356ppm) for solvent dimethyl sulfoxid ($DMSO_{d6}$) and a singlet signal at δ(59.490ppm) for (CH_2) and other signal at δ(60.400ppm) to (CH),and multiple signals between δ(123.296-149.804ppm) for(4C $_{aromatic}$), singlet peak at δ(166.168ppm) due to (C=O $_{sec\ amide}$) and singlet peak at δ(170.582ppm) for (COOH), single peak at δ(179.981ppm) for (C=S) [62]. Table (3-10) shown the signals chemical shift by ppm for (NTP).



Fig(3-10) ^{13}C-NMR spectrum of the ligand(NTP)

Table(3-10) ^{13}C-NMR spectral data of (NTP)

Compound	Functional groups	δ (ppm)
NTP	(C,CH_2)	59.490
	(C,CH)	60.400
	(C, aromatic)	(123.296-149.804)
	(C=O sec amine)	166.168
	(COOH)	170.582
	(C=S)	179.981

3.2.5- UV-Vis.Spectrum of the ligand (NTP).

The electronic transition spectrum of (NTP) in $DMSO_{d6}$ solvent, Fig.(3-11) show a sharp absorption in (36363cm^{-1}) due to $\pi \longrightarrow \pi^*$ and other absorption at (26455cm^{-1}), which refers to $n \longrightarrow \pi^*$ [67,68] ,as shown in Table (3-11).

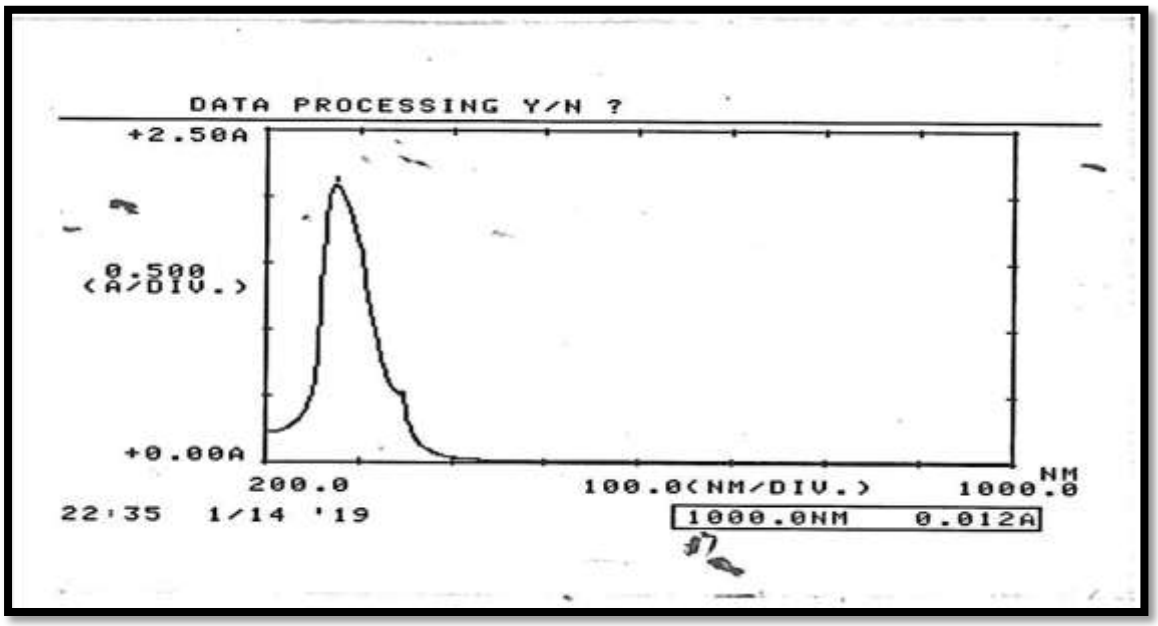


Fig.(3-11) UV-Vis. Spectrum of the ligand(NTP)

Table (3-11) Electronic spectral Data of the ligand(NTP)

Compound	λ(nm)	υ(cm^{-1})	A	ε_{max} ($molar^{-1}cm^{-1}$)	Transition
(NTP)	275 378	36363 26455	2.082 0.500	2082 500	π ⟶ π* n ⟶ π*

3.2.6 The solubility of the ligand (NTP) in some solvents.

The ligand (NTP) shown a deferent ability to soluble in the solvents and in the R.T, Table (3-12) illustrate this ability.

Table (3-12) Solubility of the ligand (NTP)

	H_2O	DMF	MeOH	EtOH	Acetone	DMSO	Hexan	$CHCl_3$	$(Eh)_2O$
NTP	÷	+	÷	÷	+	+	÷	-	÷

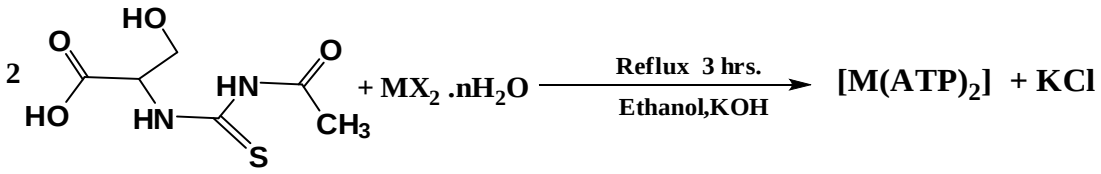
(+)= soluble , (÷) = sparingly, (-) = in soluble.

(3.3) Synthesis and characterization of the prepared Complexes

(3.3.1) Synthesis of the metal Complexes with the ligand (ATP)

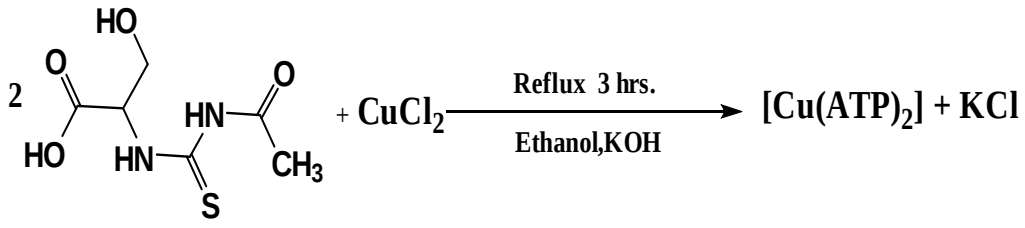
All the complexes were prepare in the similar way, as pointed in experimental part , eight metal complexes prepare from the metallic ions (Hg^{+2},Cd^{+2} ,Cu^{+2}, Zn^{+2} ,Ni^{+2}, Mn^{+2} , Co^{+2} and VO^{+2}) at base line (pH=7-8) and molar ratio(2:1)(ligand: metal).

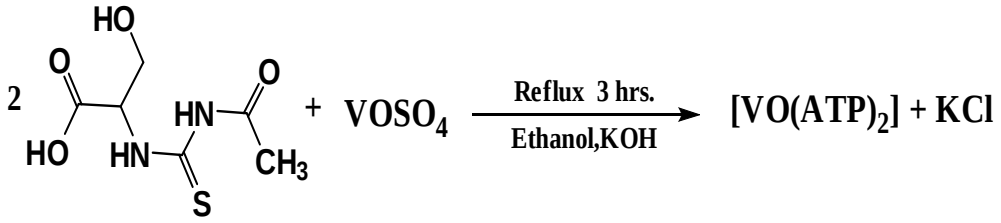
The prepared metal complexes were isolated by filtered the product copounds and washed by water and pure ethanol then leave it to dried at R.T, the product where soiled crystal different by colors and melting point. Scheme (3-3) illustrates this preparation.



M=(Mn^{+2},Co^{+2},Ni^{+2},Zn^{+2},Cd^{+2} and Hg^{+2})

X= Cl^{-}





Scheme (3-3) Synthetic route for the preparation of metal complexes with the ligand (ATP)

3.3.2 Characterization of metal Complexes with ligand (ATP)

3.3.2.1 The Solubility

The solubility was tested at library temperature with deferent solvent, Table (3-13) shown the solubility of the ligand (ATP) and its complexes.

Table (3-13) Solubility of (ATP) and its complexes

Compuond / Solvent	ATP	$[Hg(ATP)_2]$	$[Cd(ATP)_2]$	$[Zn(ATP)_2]$	$[Cu(ATP)_2]$	$[Ni(ATP)_2]$	$[Co(ATP)_2]$	$[Mn(ATP)_2]$	$[VO(ATP)_2]$
H_2O	-	-	÷	-	-	+	+	+	÷
DMF	+	+	+	+	+	+	+	+	+
CH_3OH	+	-	-	-	-	+	÷	÷	÷
CH_3CH_2OH	÷	-	-	-	-	-	-	-	-
$(CH3)_2CO$	+	-	-	-	-	-	-	-	-
DMSO	+	+	+	+	+	+	+	+	+
n-Hexan	-	-	-	-	-	-	-	-	-
$CHCl_3$	-	-	-	-	-	-	-	-	-
$(CH_3CH_2)O$	-	-	-	-	-	-	-	-	-

(+)= soluble , (÷) = sparingly, (-) = insoluble

3.3.2.2 The micro elemental analysis (C.H.N.S)

The calculate values of the elemental analysis had a good agreement with the found values for the some complexes with the ligand (ATP), Table (3-14) showed this values and some other properties of the ligand (ATP) and its complexes.

Table (3-14) Micro elemental analysis and some of physical properties of the ligand (ATP) and its metal complexes

Compounds	M.w g.mol^{-1}	Color	M.P°C	Yield (%)	Micro elemental analysis(%)calc. (found)				
					C	H	N	S	M
Lignd(ATP) $C_6H_{10}N_2O_4S$	206	yellow	120-122	76	34.95 (34.97)	4.85 (4.34)	13.59 (14.00)	15.53 (15.48)	ـــ
[VO(ATP)$_2$]	476.9	dark green	310(dec)	70	30.19	3.77	11.74	13.42	10.67
[Mn(ATP)$_2$]	464.9	orang	226	66	30.97	3.87	12.04	13.76	11.80 (11.11)
[Co(ATP)$_2$]	468.9	dark brown	184	68	30.71 (29.82)	3.83 (3.98)	11.94 (11.21)	13.64 (13.65)	12.56 (11.89)
[Ni(ATP)$_2$]	468.7	Deep green	202	78	30.72	3.84	11.94	13.65	12.52 (12.52)
[Cu(ATP)$_2$]	473.5	Brown yellow	242	75	30.41 (29.77)	3.80 3.05	11.82 (11.38)	13.51 (13.10)	13.41 (13.88)
[Zn(ATP)$_2$]	475.4	yellow	231	61	30.29	3.78	11.78	13.46	13.75 (13.87)
[Cd(ATP)$_2$]	522.4	yellow	222(dec)	79	27.56 (27.85)	3.44 (3.73)	10.71 (10.44)	12.25 (12.52)	21.51 (20.96)
[Hg(ATP)$_2$]	610.6	brown	326(dec)	77	23.58	2.94	9.17	10.84	32.85

3.3.2.3 Magnetic Measurements of the prepared complexes with ligand (ATP)

These measurements used for characterize the number of unpaired electrons at the complexes were leads to the nature of the ligands [69].

The magnetic moment calculate from the magnetic susceptibility:

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

where:

X_A= Atomic susceptibility were corrected from diamagnetic, ($X_A = X_M$-D)

T = temperature in Kelvin (K).

Molar susceptibility is calculate from the gram susceptibility by the following principle [70,71] :

$X_M = X_g$. M.wt

Where: X_M =molar susceptibility

X_g =gram susceptibility

M.wt =molecular weight for complex.

The (μ_{eff}) of $[VO(ATP)_2]$ complex were 1.75 B.M, $[Mn(ATP)_2]$ were 6.04 B.M, $[Co(ATP)_2]$ were 4.96 B.M, $Ni(ATP)_2]$ were 3.63 B.M, $[Cu(ATP)_2]$ were 1.72 B.M, $[Zn(ATP)_2]$, $[Cd(ATP)_2]$and$[Hg(ATP)_2]$ were 0.00 B.M. these values were accepted with the high spin field and as result that the ligand were weak[72]. Table (3-15) show all the values of Magnetic susceptibilities data of ligand (ATP) complexes.

Table(3-15)Magnetic susceptibility of metal complexes with(ATP)at 25°C

Complexes	Weight susceptibility $X_g.10^{-6}$	molar susceptibility $X_M.10^{-6}$	atomic susceptibility $X_A.10^{-6}$	μ_{eff}(B.M)	No. of unpaired electrons	Proposed geometry
$[Vo(ATP)_2]$	2.52	1201.78	1298.72	1.75	1	Square pyramidal
$[Mn(ATP)_2]$	32.75	15225.47	15322.41	6.04	5	Tetrahedral
$[Co(ATP)_2]$	21.81	10226.71	10323.65	4.96	3	Tetrahedral
$[Ni(ATP)_2]$	11.63	5450.98	5547.92	3.63	2	Tetrahedral
$[Cu(ATP)_2]$	2.42	1145.87	1242.81	1.72	1	Square planer
$[Zn(ATP)_2]$	0.00	0.00	0.00	0.00	0	Tetrahedral
$[Cd(ATP)_2]$	0.00	0.00	0.00	0.00	0	Tetrahedral
$[Hg(ATP)_2]$	0.00	0.00	0.00	0.00	0	Tetrahedral

D(ATP)= -96.94×10^{-6}

3.3.2.4 Molar Conductivity Measurements of complexes with the ligand (ATP)

The molar conductivity can used to identify the ionic compound formula in solution [73]. The molar conductivity values of the prepared in $DMSO_{d6}$ solvent were appeared in the range (1.76-9.44)$S.cm^2.mole^{-1}$ indicating their non-electrolyte nature. Table (3-16) shows the data.

Table (3-16) Molar conductivity data of the ligand (ATP) and its complexes

Compound	Molar conductivity ($sec.cm^2.mol^{-1}$)
[Vo(ATP)2]	1.76
[Mn(ATP)2]	7.63
[Co(ATP)2]	7.36
[Ni(ATP)2]	9.44
[Cu(ATP)2]	4.15
[Zn(ATP)2]	6.57
[Cd(ATP)2]	5.87
[Hg(ATP)2]	7.75

3.3.2.5 FT-IR Spectral data of metal Complexes with the ligand(ATP).

The characteristic vibrations of ligand (ATP)and their complexes as KBr disc are described in table(3-17). The spectrum of free ligand(ATP) Fig(3-2) shows medium band at(3213cm^{-1}) this could be attributed to υ(N-H). While the other medium band at(3018cm^{-1}) due to (OH). Other band at(1701cm^{-1}), which belong to $\upsilon(COO)_{asym}$ and (137cm^{-1})for $\nu(COO)_{sym}$, a strong band at ν(1654cm^{-1}) due to ν(C=O)group, υ(C=S)were found at(1234cm^{-1}) [74,75] .

The FT-IR spectra of the prepared complexes fig(3-12to3-19)exhibited υ(N-H)in the range of (3408-3390cm^{-1}) which shows a shifted to the higher frequencies in compared with free ligand suggested. The possibility of coordination of the ligand with metal through the nitrogen atom at the amine group[76,77]. Absorption assigned for $\upsilon(COO)_{sym}$ was noted at the range (1396-1419cm^{-1}) were shifted to higher frequencies by(23-46cm^{-1}). While the band caused by $\upsilon(COO)_{asym}$ appeared at the rang(1616-1654cm^{-1}) were Shifted to lower frequencies by(85-47cm^{-1}) which refer to the attach carboxylic group with the central metal ion [78,79] .

The stretching vibration bands υ(C=S) and υ(C=O)carbonyl group also shows not change or very slight in their frequencies were that refer to not coordinate the ligand with the metal ion, so that a band at (975cm^{-1}) shown at vanadel complex which due to (V=O)bound [80].

Metal-oxygen and metal-nitrogen bands where confirmed by the presence of the stretching vibration of υ(M-O) and υ(M-N) in the range (478-493cm^{-1}) and (428-474cm^{-1}), respectively.

Table (3-17) FT-IR Spectral data of ligand (ATP)and its metal complexes.

Compound	υ(Coo) Asym cm^{-1}	υ(Coo) Sym cm^{-1}	Δυ	υ(NH) υ(OH) cm^{-1}	υ(C=S) cm^{-1}	υ(C=O) cm^{-1}	υ(MN) cm^{-1}	υ(MO) cm^{-1}	υ (VO) cm^{-1}
ATP	1701(s)	1373(s)	------	3213(m) 3018(m)	1234(s)	1654(m)	---	---	---
$[VO(ATP)_2]$	1639(s)	1415(s)	224	3408(b)	1230(m)	1661(S)	432(m)	482(m)	975 (s)
$[Mn(ATP)_2]$	1618(s)	1415(s)	203	3390(b)	1230(m)	1658(m)	455(m)	478(m)	---
$[Co(ATP)_2]$	1620(M)	1415(m)	205	3394(b)	1242(m)	1653(m)	462(m)	486(m)	---
$[Ni(ATP)_2]$	1620(M)	1419(s)	201	3402(b)	1228(m)	1635(m)	455(m)	492(m)	---
$[Cu(ATP)_2]$	1654(M)	1411(m)	243	3390(b)	1234(m)	1654(m)	459(m)	492(m)	---
$[Zn(ATP)_2]$	1627(m)	1411(m)	216	3394(b)	1234(m)	1658(m)	428(m)	482(m)	---
$[Cd(ATP)_2]$	1616(m)	1419(m)	197	3408(b)	1230(m)	1650(m)	466(b)	493(m)	---
$[Hg(ATP)_2]$	1624(m)	1396(m)	228	3406(b)	1219(m)	1647(m)	474(m)	489(m)	---

s= strong m=medium w= weak b= broad

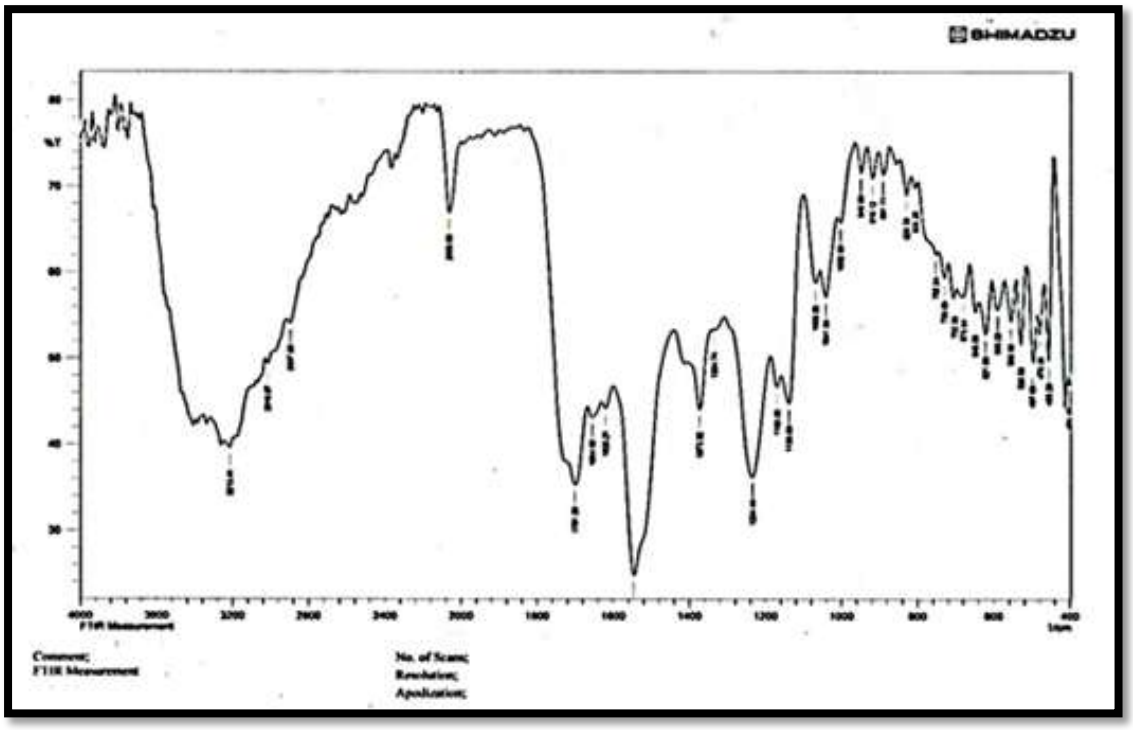


Fig.(3-2)FT-IR spectrum of the ligand (ATP)

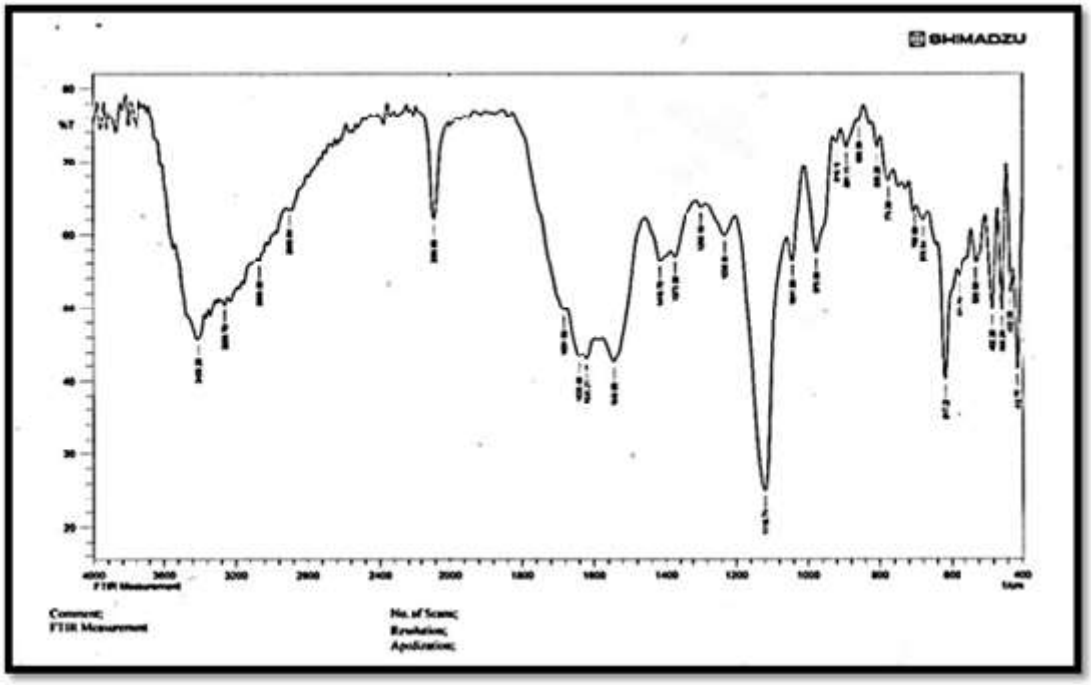


Fig.(3-12)FT-IR spectrum of [VO(ATP)$_2$]complex

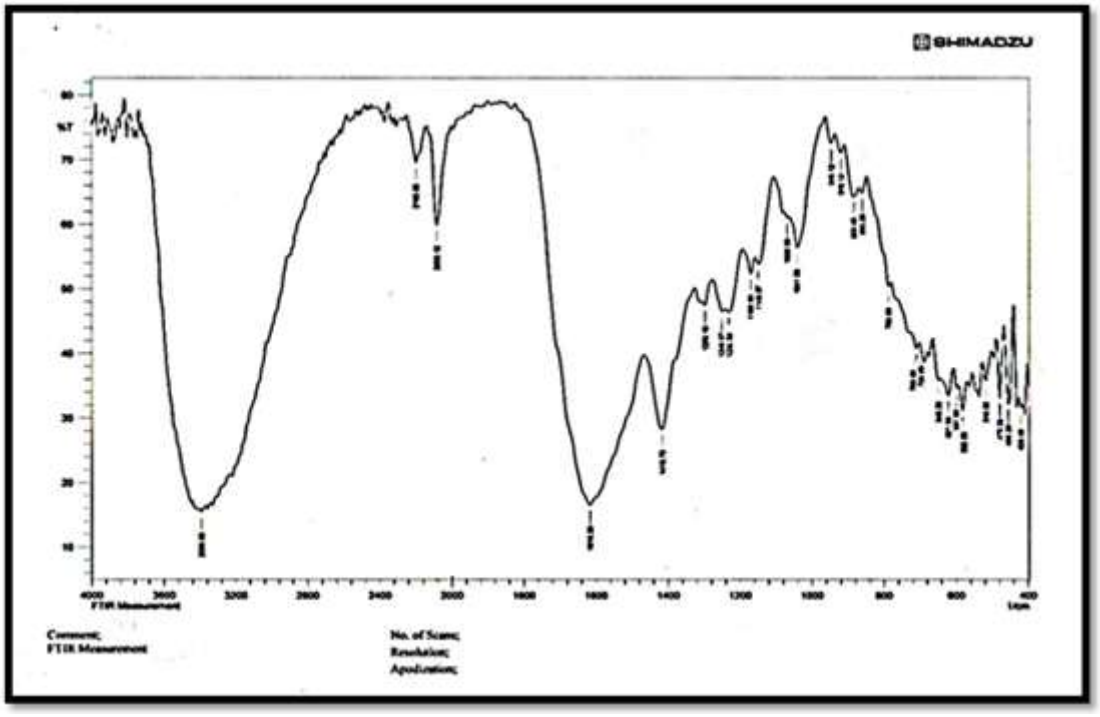


Fig.(3-13)FT-IR spectrum of [Mn(ATP)$_2$]

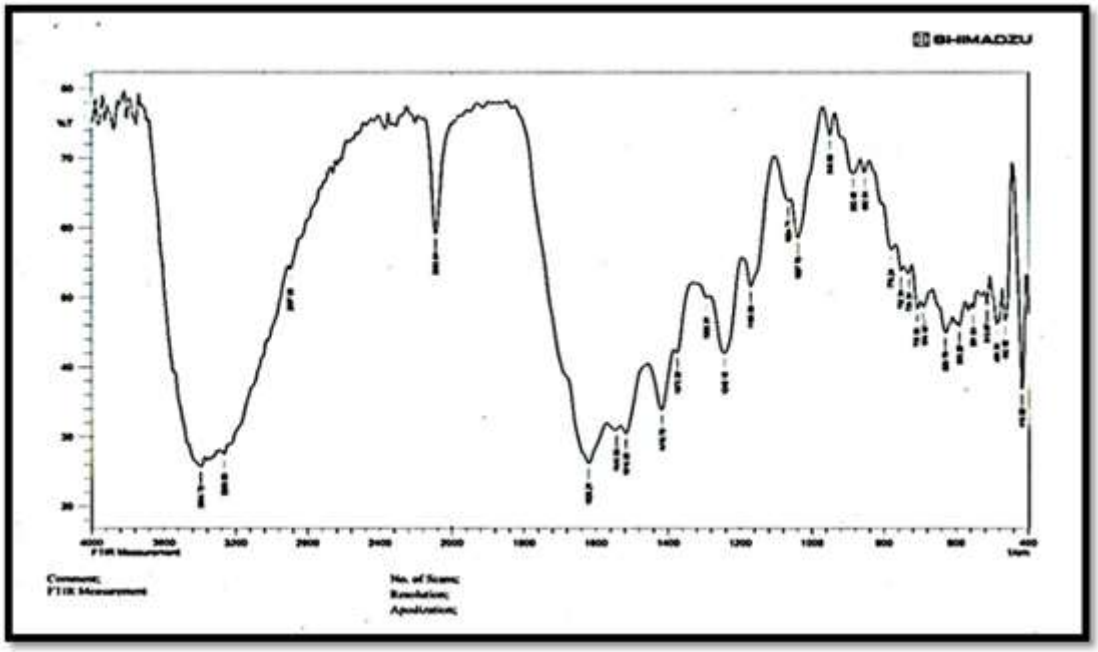


Fig.(3-14) FT-IR spectrum of [Co(ATP)$_2$]

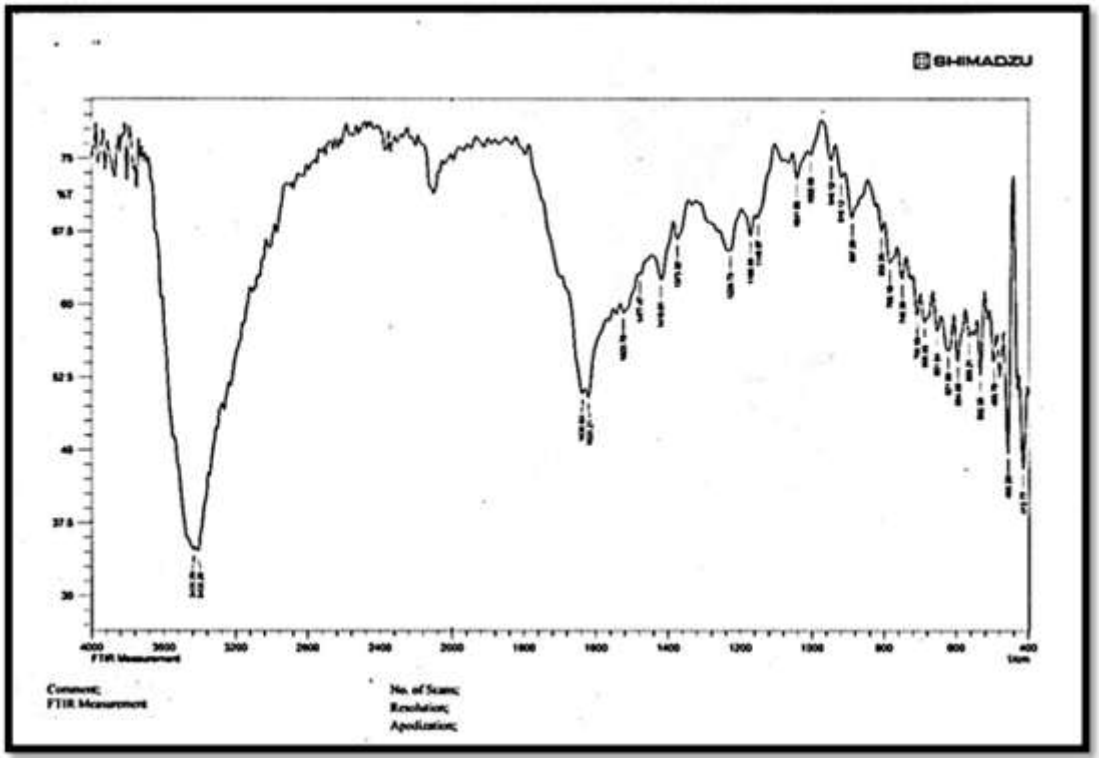


Fig.(3-15) FT-IR spectrum of $[Ni(ATP)_2]$

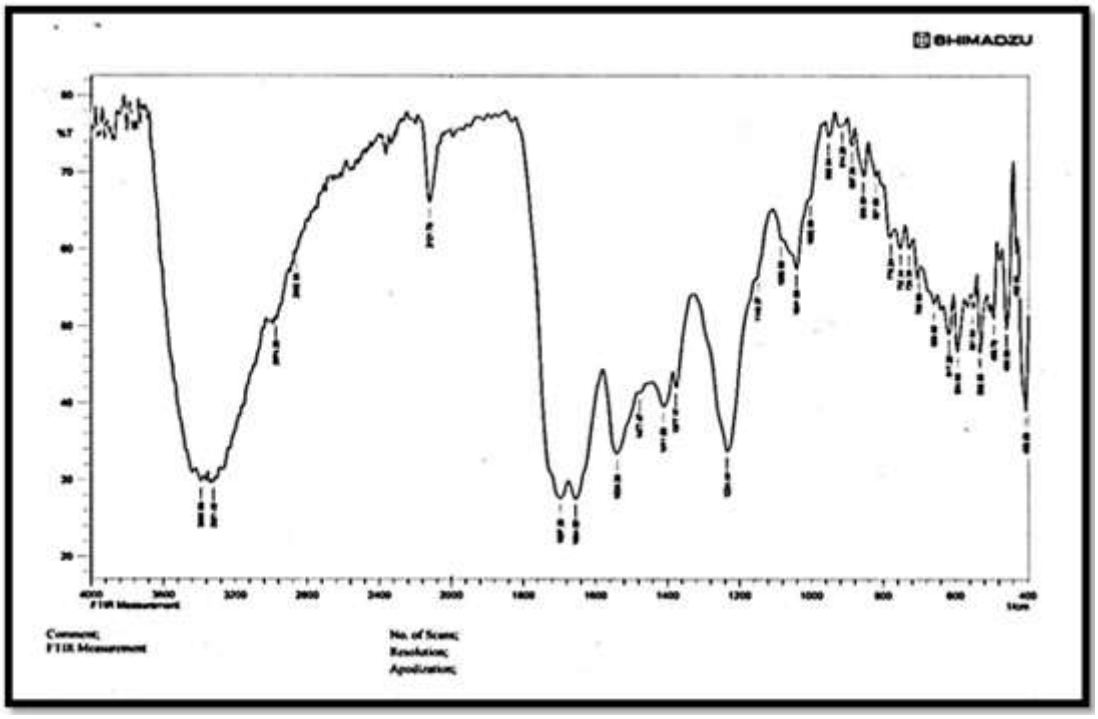


Fig.(3-16) FT-IR spectrum of $[Cu(ATP)_2]$

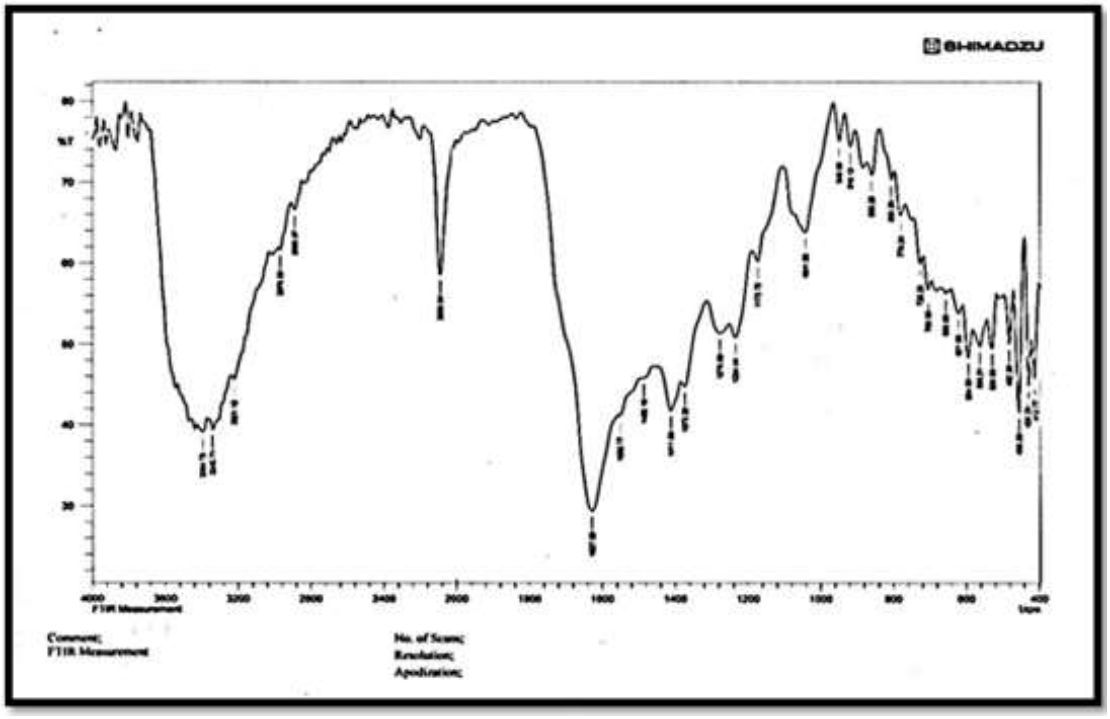


Fig.(3-17) FT-IR spectrum of [Zn(ATP)$_2$]

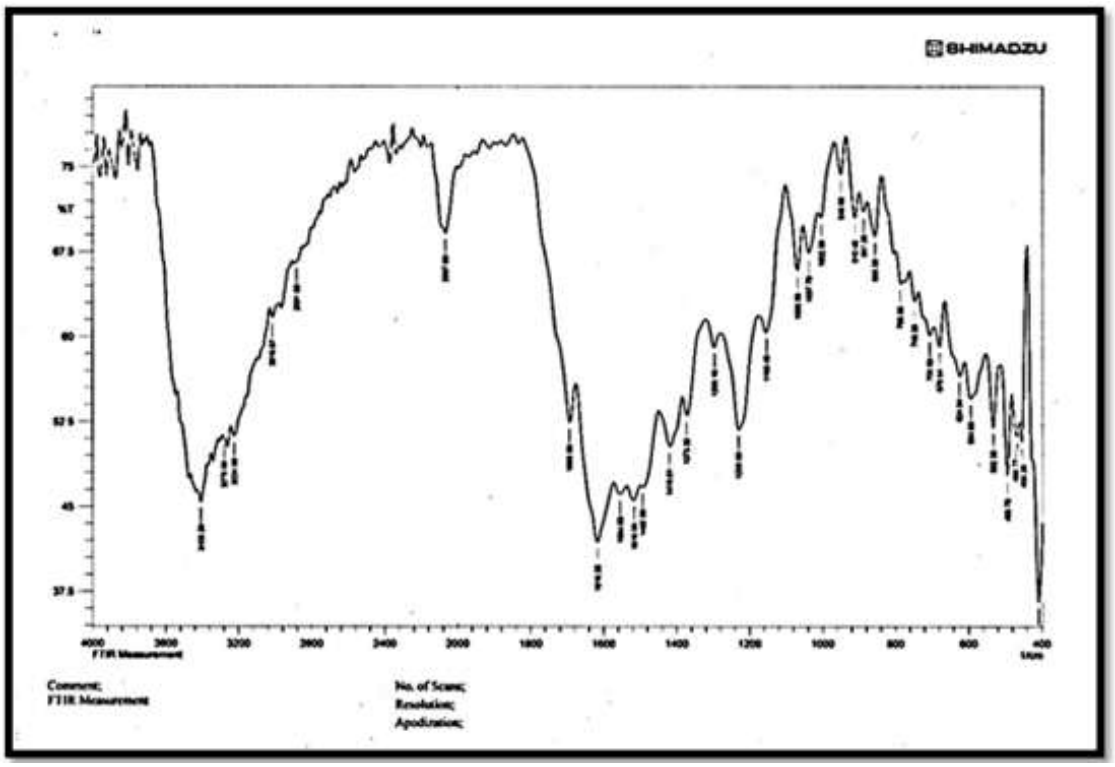


Fig.(3-18) FT-IR spectrum of [Cd(ATP)$_2$]

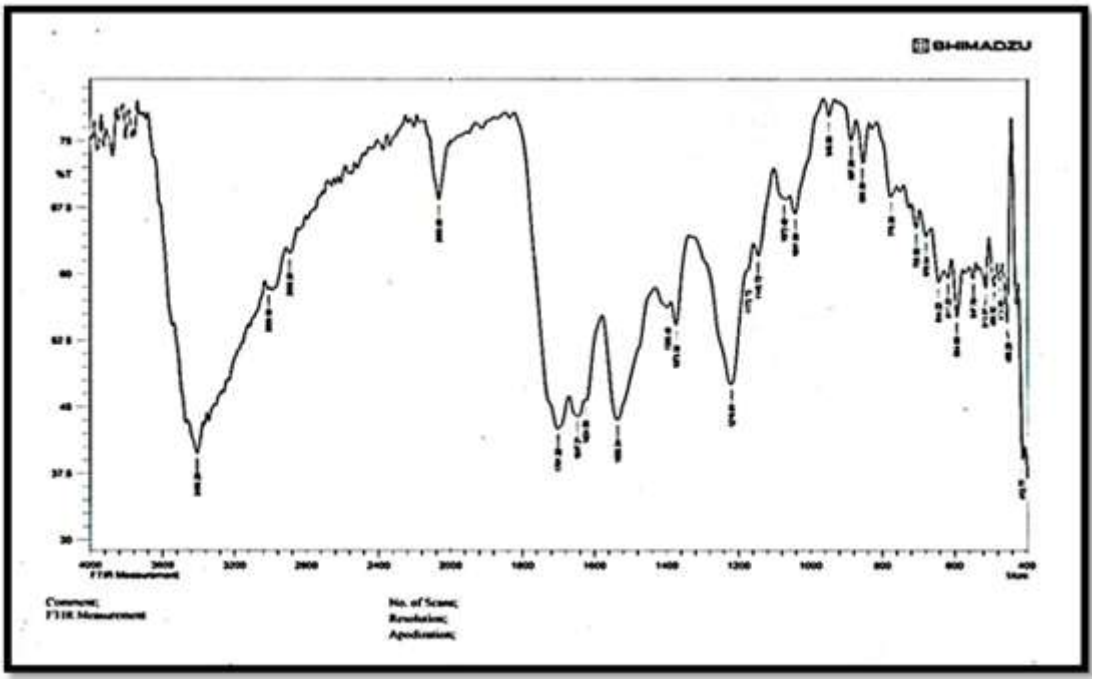


Fig.(3-19) FT-IR spectrum of $[Hg(ATP)_2]$

3.3.2.6 UV-Vis Spectra of ligand (ATP) and its metal complexes.

The ligand (ATP)

The spectrum of ligand (ATP) fig(3-6) show two bands at (36369 cm^{-1}) and (28985cm^{-1}) which are due to to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ respectively [81].

$[VO(ATP)_2]$ complex

The dark green complex displays three bands ,the first at (36101cm^{-1}) due to ligand-filed, the second was at(28735cm^{-1}) which belongs to charge transfer, and last band at(16393cm^{-1}) which due to $^2B_2 \longrightarrow {}^2E$ transition[81].

$[Mn(ATP)_2]$ complex

The orang complex of Mn^{+2} shows band at (36101cm^{-1}), which belongs to ligand-field also other band at (28735cm^{-1}) which is due to charge transfer, band at(13227cm^{-1}) caused by the electronic transition $^6A_1 \rightarrow {}^4T_{2(G)}$,the last band at(12070$cm^{-1}$) which du to $^6A_1 \longrightarrow {}^4T_{1\,(G)}$ [82].

$[Co(ATP)_2]$ complex

The Dark brown complex of Co^{+2} shows five bands, at ($36496cm^{-1}$), ($30303cm^{-1}$),($27932cm^{-1}$) ,($15432cm^{-1}$)and ($11627cm^{-1}$) which due to ligand-field, (C.T) , $^4A_{2(f)} \xrightarrow{v_3} {}^4T_{1(p)}$, $^4A_{2(F)} \xrightarrow{v_2} {}^4T_{1(F)}$ and $^4A_2 \rightarrow {}^4T_{2(F)}$ transition respectively.

The inter electronic repulsion parameter B^- was establish to be ($565.5cm^{-1}$) from the relation ($\beta = B^- / B_O$), were β was found to be equal (0.582).These parameters are accepted to Co^{+2} tetrahedral complex [83] .

$[Ni(ATP)_2]$ complex

The electronic spectrum of deep green complex of Ni^{+2} has shown five bands at ($36231cm^{-1}$), ($30581cm^-1$) , ($27932cm^{-1}$) ,($13888)cm^{-1}$)and ($10989)cm^{-1}$) revealed the following electronic transition; ligand-field, (C.T) ,$^3T_{1(F)} \rightarrow {}^3T_{1(P)}$, $^3T_{1(F)} \rightarrow {}^3A_{2(F)}$, $^3T_{1(F)} \rightarrow {}^3T_{2(F)}$ respectively.

The B^- value establish to be (590.2) cm^{-1}) while β was found (0.567), These are the characteristics for tetrahedral complexes of Ni^{+2} [84].

$[Cu(ATP)_2]$ complex

The spectrum of brown-yellow complex of Cu^{+2} shows four bands at ($35971cm^{-1}$),($31055cm^{-1}$) ,($27777cm^{-1}$) and($16000cm^{-1}$) which due to the ligand-field,(C.T), $^2B_1g \longrightarrow {}^2A_1g$, and $^2B_1g \longrightarrow {}^2B_2g$ respectively[84].

$[Zn(ATP)_2]$ complex

The yellow complex of Zn^{+2} shows two bands at($36231cm^{-1}$) and($28901cm^{-1}$) are due to electronic transition the ligand-field and charge transfer respectively.

$[Cd(ATP)_2]$ complex

The spectrum of yellow complex of Cd^{+2} showed one absorptions band at($35587cm^{-1}$) due to ligand field.

$[Hg(ATP)_2]$ complex

The brown complex showed one absorptions band at(35842cm^{-1}) due to ligand-field[84] .Table (3-18)illustrate this electronic transition and figures(3-20 to 3-27) shows this spectrum.

Table (3-18)The data of Electronic spectral for metal complexes with the ligand (ATP)in DMSO solvent

Compound	λ(nm)	ῡ(cm^{-1})	A	ε_{max} $molar^{-1}$ cm^{-1}	Transitions
ATP	**275** **345**	**36363** **28985**	**2.245** **1.701**	**2245** **1701**	**π** ⟶ **π*** **n** ⟶ **π***
$[VO(ATP)_2]$	277 348 610	36101 28735 16393	1.679 0.732 0.88	1679 732 88	L.F C.T $^2B_2 \longrightarrow {}^2E$
$[Mn(ATP)_2]$	277 348 756 828	36101 28735 13227 12070	2.146 1.476 0.016 0.014	2146 1476 16 14	L.F C.T $^6A_1 \longrightarrow {}^4T_{2\,(G)}$ $^6A_1 \longrightarrow {}^4T_{1\,(G)}$
$[Co\ (ATP)_2]$	274 330 358 648 860	36496 30303 27932 15432 11627	2.048 1.040 0.768 0.026 0.018	2048 1040 768 26 18	L.F C.T $^4A_{2\,(F)} \longrightarrow {}^4T_{1\,(P)}$ mix C.T $^4A_{2\,(F)} \longrightarrow {}^4T_{1(F)}$ $^4A_{2\,(F)} \longrightarrow {}^4T_{2\,(F)}$
$[Ni(ATP)_2]$	276 327 358 720 910	36231 30581 27932 13888 10989	1.812 0.953 0.650 0.020 0.018	1812 953 650 20 18	L.F C.T $^3T_1 \longrightarrow {}^3T_{1\,(P)}$ mix C.T $^3T_1 \longrightarrow {}^3A_{2\,(F)}$ $^3T_1 \longrightarrow {}^3T_{2\,(F)}$
$[Cu(ATP)_2]$	278 322 360 625	35971 31055 27777 16000	2.227 1.982 1.189 0.120	2227 1982 1189 120	L.F C.T $^2B_1g \longrightarrow {}^2A_1g$ mix C.T $^2B_1g \longrightarrow {}^2B_2g$
$[Zn\ (ATP)_2]$	276 346	36231 28901	1.892 0.911	1892 911	L.F C.T
$[Cd(ATP)_2]$	281	35587	2.425	2425	L.F
$[Hg(ATP)_2]$	279	35842	2.216	2216	L.F

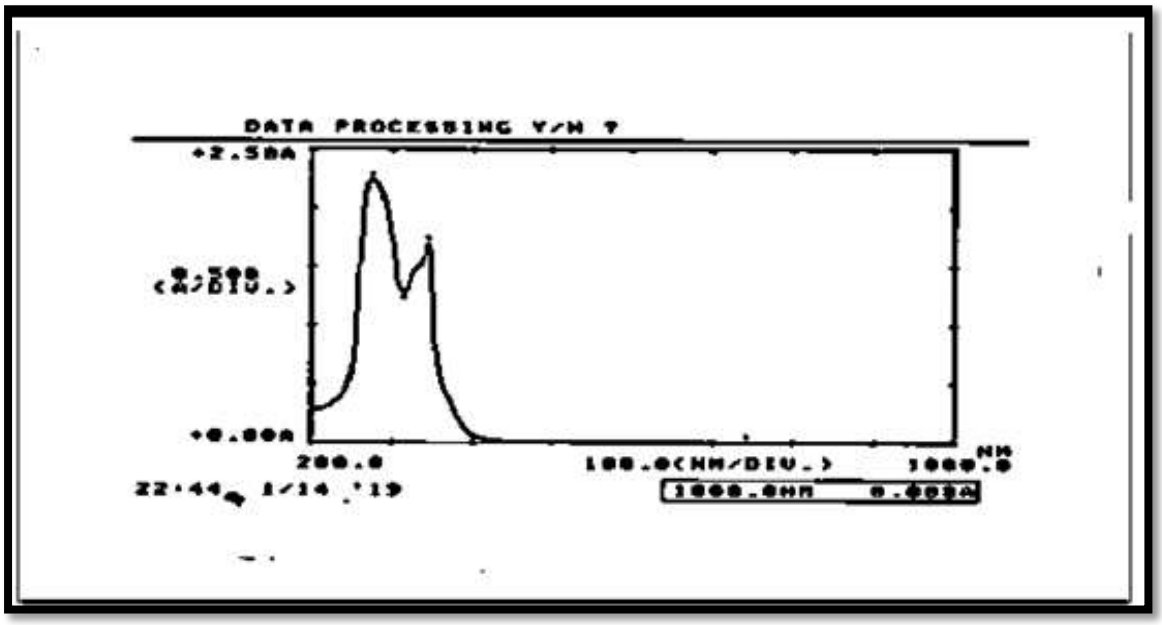


Fig.(3-6) UV-Vis. Spectrum of ligand(ATP)

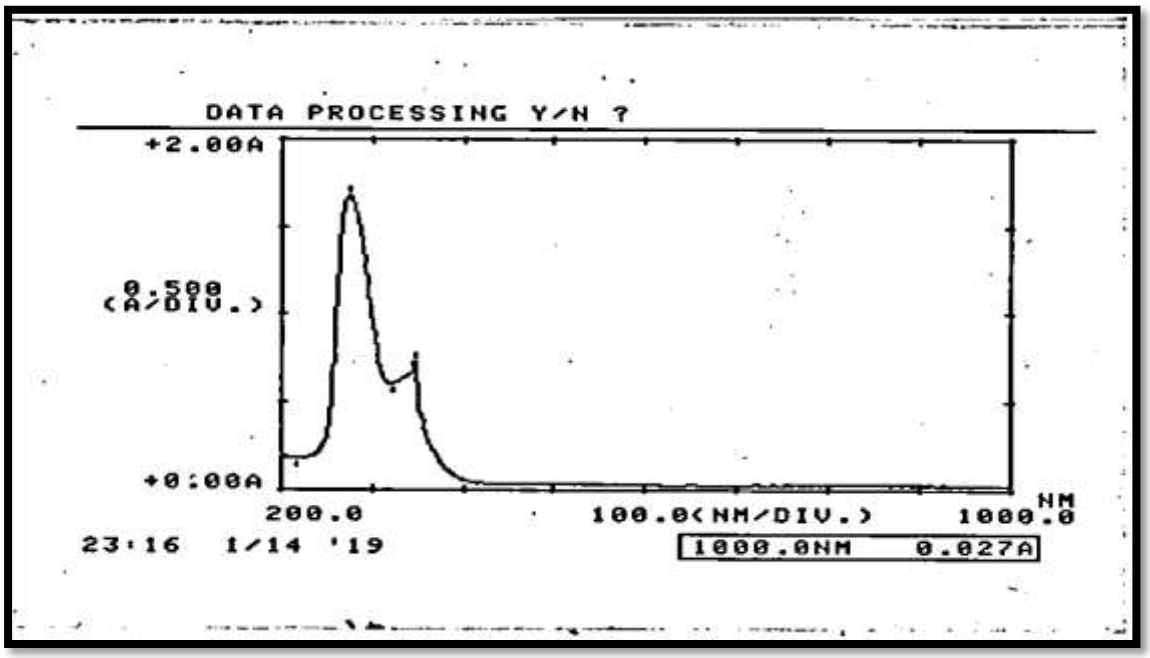


Fig.(3-20)UV-Visible spectrum of[$VO(ATP)_2$]

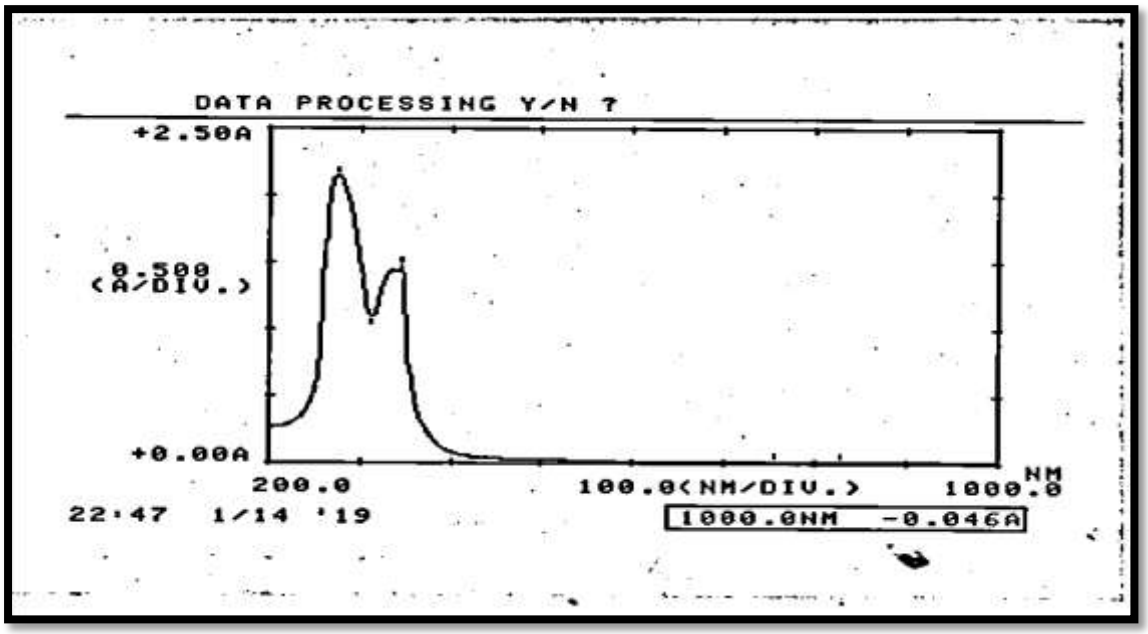


Fig.(3-21)UV-Visible spectrum of[$Mn(ATP)_2$]

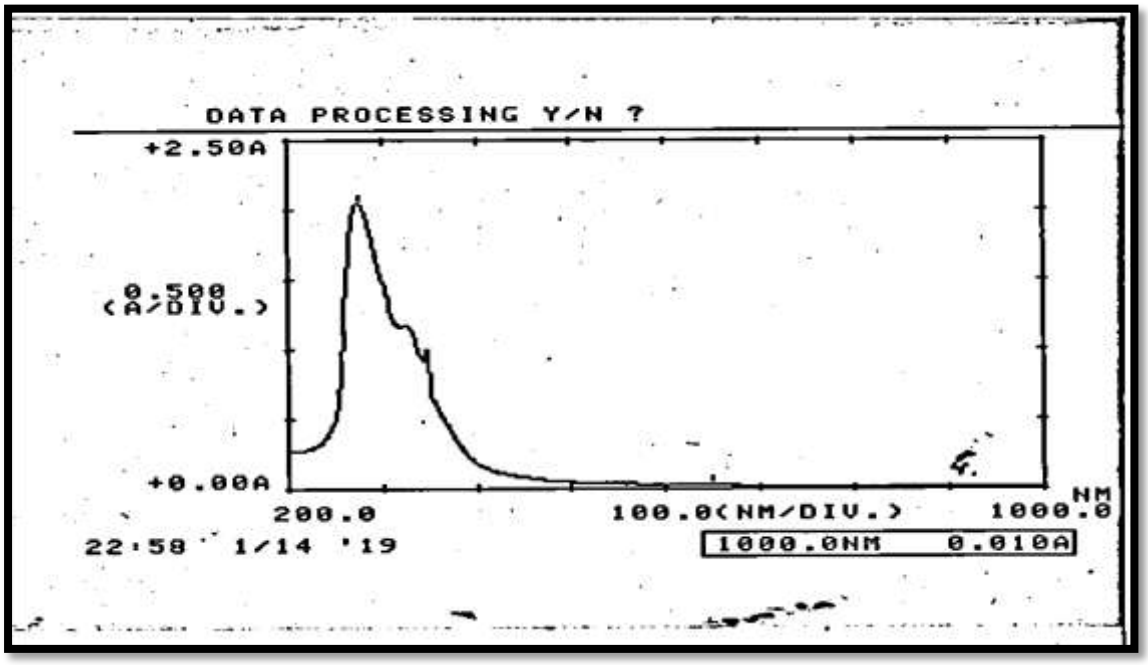


Fig.(3-22)UV-Visible spectrum of[$Co(ATP)_2$]

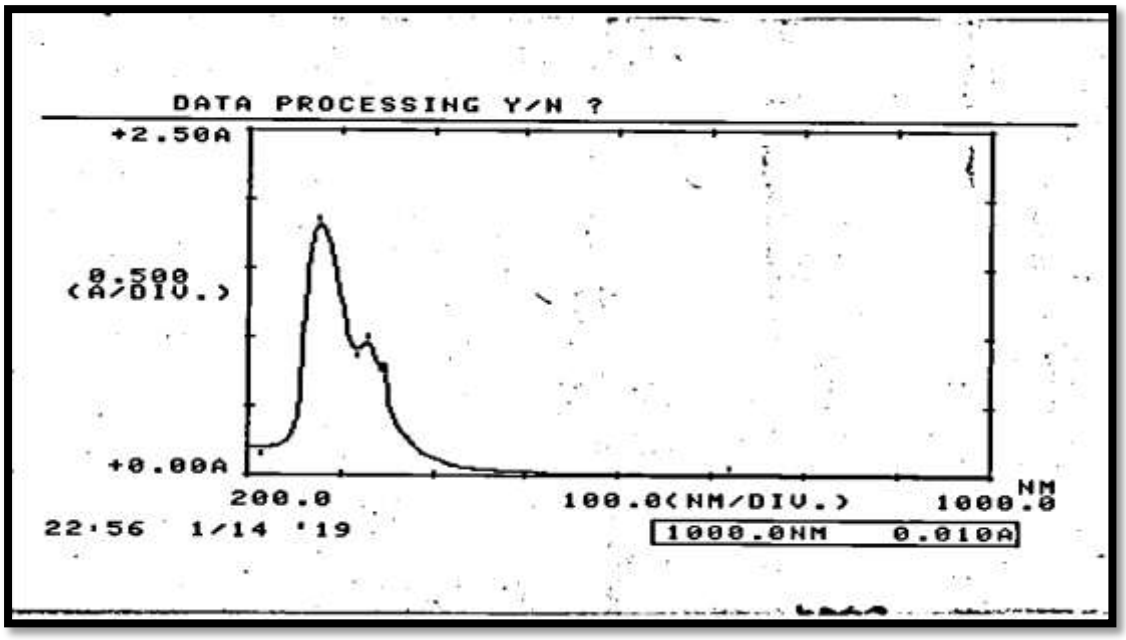


Fig.(3-23)UV-Visible spectrum of[$Ni(ATP)_2$]

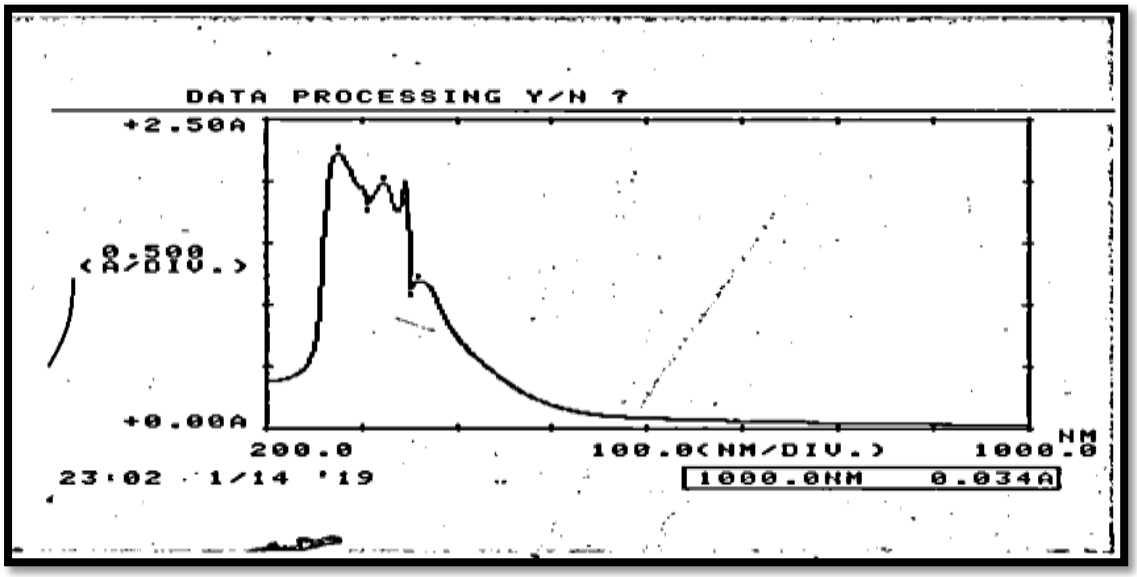


Fig.(3-24)UV-Visible spectrum of[$Cu(ATP)_2$]

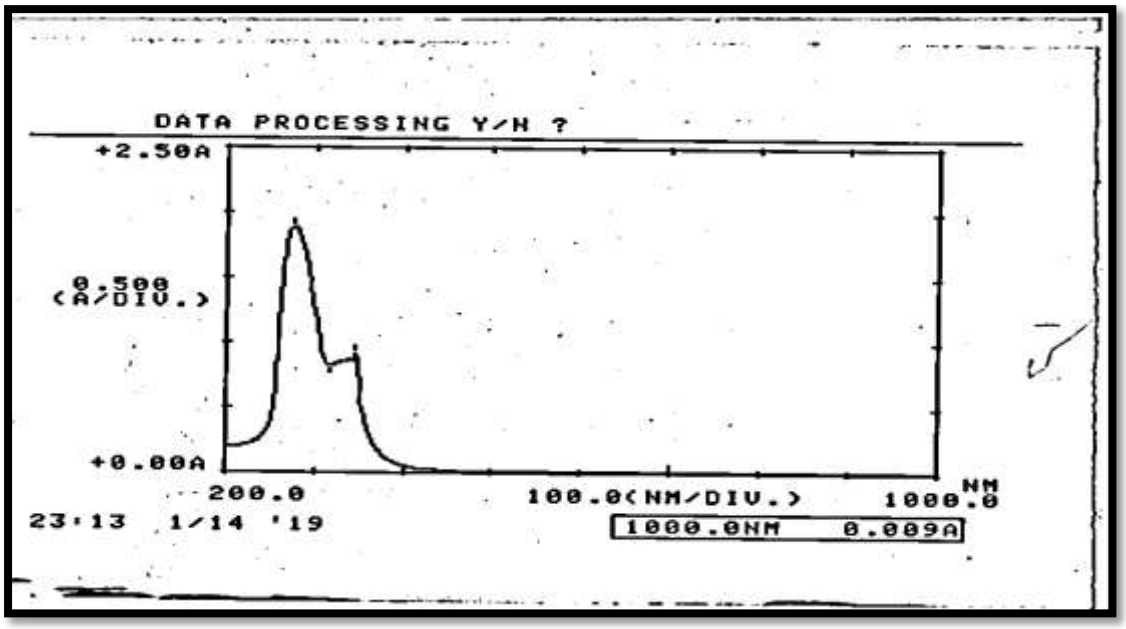


Fig.(3-25)UV-Visible spectrum of[$Zn(ATP)_2$]

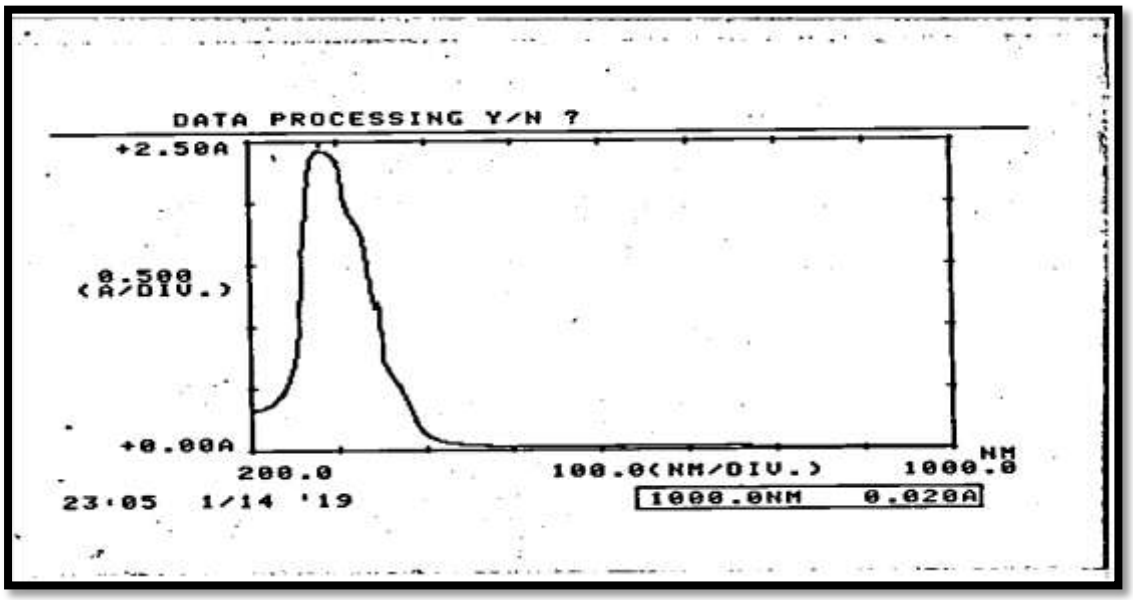


Fig.(3-26)UV-Visible spectrum of[$Cd(ATP)_2$]

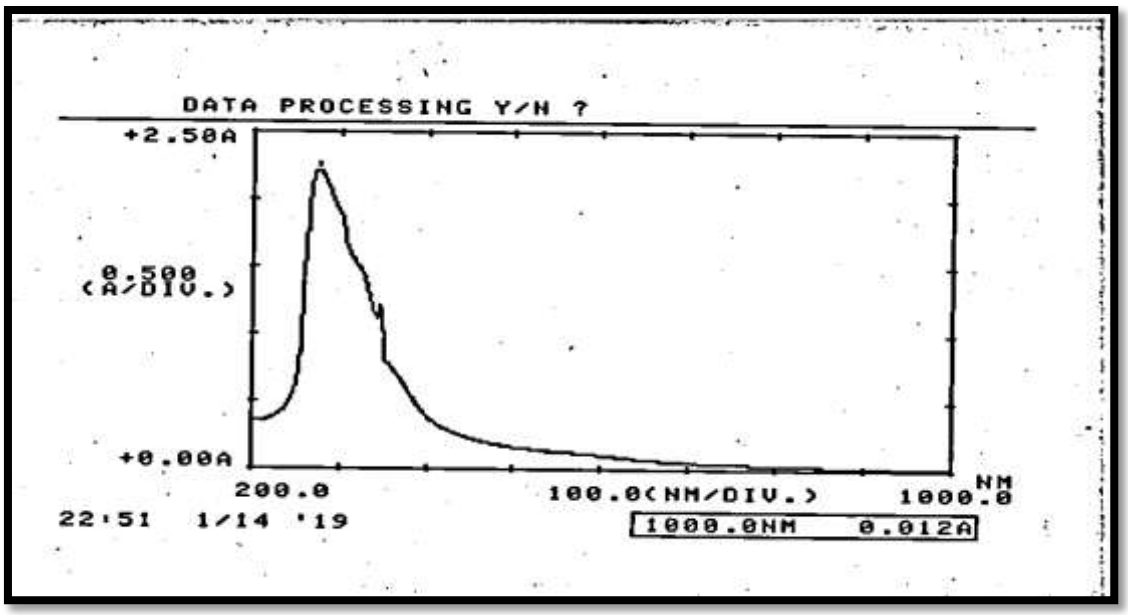
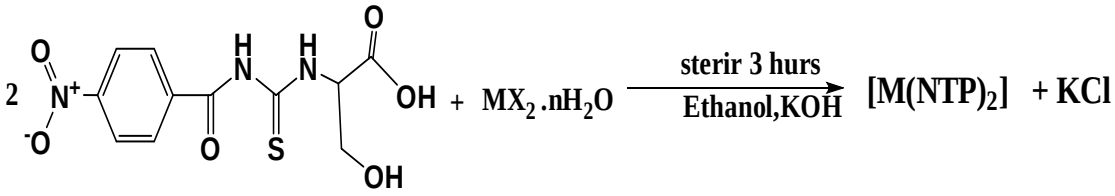


Fig.(3-27)UV-Visible spectrum of[$Hg(ATP)_2$]

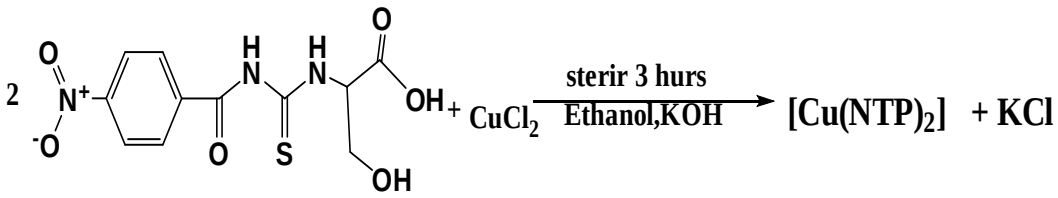
(3.3.3) Synthesis of metal complexes with the ligand (NTP).

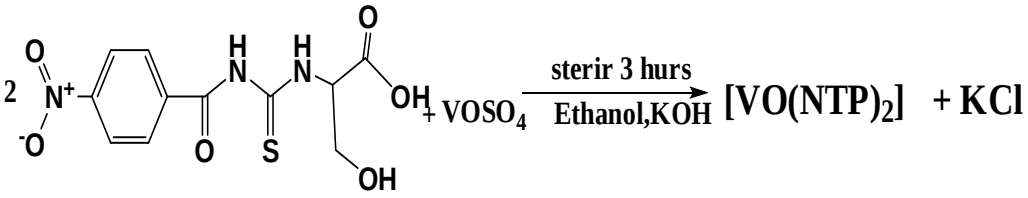
All the complexes were prepared in the similar way, as optioned in chapter two, eight metal complexes prepared from the metal ions (Hg^{+2},Cd^{+2}, Cu^{+2}, Ni^{+2}, Co^{+2}, Mn^{+2} and VO^{+2}) at base line (pH=7-8) and molar ratio(2:1)(ligand:metal). The metallic complexes product where soiled crystal and the following scheme illustrate this way and the assumed geometry shape.



M=(Mn^{+2},Co^{+2},Ni^{+2},Zn^{+2},Cd^{+2},Hg^{+2})

x= Cl^-





Scheme (3-4) Synthetic route for the preparation of metal complexes with the ligand (NTP)

3.3.4 Characterization of the prepared Complexes with Ligand (NTP)

3.3.4.1 The Solubility

The solubility of the ligand (NTP) and its complexes was tested in library temperature with deferent solvents, Table (3-19).

Table (3-19) Solubility of ligand (NTP) and its complexes

Compound / Solv.	NTP	$[Hg(NTP)_2]$	$[Cd(NTP)_2]$	$[Zn(NTP)_2]$	$[Cu(NTP)_2]$	$[Ni(NTP)_2]$	$[Co(NTP)_2]$	$[Mn(NTP)_2]$	$[VO(NTP)_2]$
H2O	÷	-	÷	-	÷	÷	-	-	-
DMF	+	+	÷	+	+	+	+	+	+
CH_3OH	÷	-	-	-	-	+	÷	+	÷
CH_3CH_2OH	÷	-	-	-	-	÷	÷	÷	-
$(CH3)_2CO$	+	-	-	+	-	+	+	+	-
DMSO	+	+	+	+	+	+	+	+	+
n-Hexan	÷	-	-	-	-	-	-	-	-
$CHCl_3$	-	-	÷	÷	-	-	-	-	-
$(CH_3CH_2)O$	÷	-	-	-	-	-	-	-	÷

(+)=soluble, (÷) = sparingly, (-) = in soluble

3.3.4.2 The micro elemental analysis (C.H.N.S)

The calculated values of the elemental analysis have a good agreement with the found values for the some complexes with the ligand (NTP),Table(3-20) showed this values and some other properties of the ligand(NTP) and its complexes.

Table (3-20)Micro elemental analysis and some of physical properties of the ligand(NTP) and their metal complexes.

Compound	M.w g.mol^{-1}	Color	M.P°C	Yield (%)	Elemental micro analysis(%)calc. (found)				
					C	H	N	S	M
Lignd(NTP) $C_{11}H_{11}N_3O_6S$	313	Dark yellow	148-150	83	42.17 (42.47)	3.51 (3.14)	13.41 (13.77)	10.22 (10.18)	ـــ
[VO(NTP)$_2$]	690.9	deep green	172	64	38.21	2.89	12.15	9.26	7.36
[Mn(NTP)$_2$]	678.9	yellow	194	62	38.88 (38.63)	2.94 (2.77)	12.37 (12.27)	9.42 (9.87)	8.08 (8.45)
[Co(NTP)$_2$]	682.9	black green	307(d)	69	38.59	2.92	12.30	9.37	8.62 (8.73)
[Ni(NTP)$_2$]	682.7	Green yellow	177	64	38.66 (38.75)	2.92 (2.93)	12.30 (12.37)	9.37 (9.92)	8.59 (8.39)
[Cu(NTP)$_2$]	687.5	green yellow	192	70	38.40	2.90	12.21	9.30	9.23 (9.21)
[Zn(NTP)$_2$]	689.4	orang	183	61	38.29 (38.62)	2.90 (2.70)	12.18 (12.67)	9.28 (9.09)	9.48 (9.65)
[Cd(NTP)$_2$]	736.4	Deep yellow	210	77	35.85	2.71	11.40	8.69	15.26 (15.26)
[Hg(NTP)$_2$]	824.6	yellow	318(d)	78	32.01	2.42	10.18	7.76	24.32

3.3.4.3 Magnetic Measurements for the complexes with (NTP).

The (μ_{eff}) of [VO(NTP)$_2$] complex were 1.70 B.M , [Mn(NTP)$_2$] were 5.88 B.M, [Co(NTP)$_2$] were 4.53 B.M, Ni(NTP)$_2$] were 3.11 B.M, [Cu(NTP)$_2$] were 1.71 B.M, [Zn(NTP)$_2$], [Cd(NTP)$_2$], Hg(NTP)$_2$] were 0.00 B.M. These values were accepted with the high spin field and as result that the ligand were weak [72], Table (3-21) show all the values of Magnetic susceptibilities data of ligand (NTP) complexes.

Table (3-21) Magnetic susceptibility data of metal complexes with the ligand (NTP) at 25 ° C

Complexes	wight sensitivity Xg.10-6	Molar sensitivity. $X_M.10^{-6}$	atomic sensitivity. $X_A.10^{-6}$	μ_{eff}(B.M)	No.of unpaired electrons	Proposed geometry
$[VO(NTP)_2]$	1.58	1091.622	1213.212	1.70	1	Square pyramidal
$[Mn(NTP)_2]$	21.23	14413.04	14534.64	5.88	5	Tetrahedral
$[Co(NTP)_2]$	12.45	8502.10	8623.69	4.53	3	Tetrahedral
$[Ni(NTP)_2]$	5.78	3946.01	4067.6	3.11	2	Tetrahedral
$[Cu(NTP)_2]$	1.61	1109.934	1231.524	1.71	1	Square planer
$[Zn(NTP)_2]$	0.00	0.00	0.00	0.00	0	Tetrahedral
$[Cd(NTP)_2]$	0.00	0.00	0.00	0.00	0	Tetrahedral
$[Hg(NTP)_2]$	0.00	0.00	0.00	0.00	0	Tetrahedral

$D(NTP)= -121.59\times10^{-6}$

3.3.4.4 Molar Conductivity Measurements of the ligand (NTP) and its complexes.

The molar conductivity can used to recognize the ionic compound formula in solution [73] ,it's measured in $DMSO_{d6}$ solvent and it appeared at the range(1.15-6.42)$S.cm^2.mole^{-1}$. Table(3-22).

Table (3-22) Molar conductivity data of the ligand (NTP) and their complexes

Compound	Molar conductivity ($sec.cm^2.mol^{-1}$)
$[VO(NTP)_2]$	1.15
$[Mn(NTP)_2]$	6.42
$[Co(NTP)_2]$	5.00
$[Ni(NTP)_2]$	4.53
$[Cu(NTP)_2]$	4.56
$[Zn(NTP)_2]$	6.06
$[Cd(NTP)_2]$	5.10
$[Hg(NTP)_2]$	5.40

3.3.4.5- FT-IR Spectra of metal Complexes with the ligand (NTP)

The characteristic vibrations of ligand (NTP) and their complexes as KBr disc were described in table(3-23). The spectrum of free ligand (NTP) fig(3-7) exhibited medium band at(3417cm^{-1}) this could be attributed to υ(N-H), While the other medium band at (3178cm^{-1}) due to (OH). Other band at(1728cm^{-1}), which belong to $\upsilon(COO)_{asym}$ and (1346cm^{-1}) for $\nu(COO)_{sym}$, strong band at ν(1676cm^{-1}) due to ν(C=O)group, υ(C=S)were found at(1257cm^{-1}) [74,75] .

The FT-IR spectra of the prepared complexes, Fig (3-28 to 3-35) exhibited υ(N-H)in the range of (3462-3425cm^{-1}) which shown a shifted to the higher frequencies in compared with free ligand suggested.

The possibility of the coordination of ligand with the metal ion through the nitrogen atom in the amine group [76,77]. Absorption assigned for $\upsilon(COO)_{sym}$ was noted at range (1400-1419cm^{-1}) shifted to higher frequencies by(54-73cm^{-1}). While the band affected by $\upsilon(COO)_{asym}$ appeared between (1624-1604cm^{-1}) Shifted to the lower frequencies abut(104-124cm^{-1}) were indicates the attach carboxylic group to the metal ion [78,79].

The stretching vibration bands υ(C=S) and υ(C=O) carbonyl group either show no change or very little in their frequencies therefore indicating do not coordinate to the metal ion ,a band at (975cm^{-1}) shown at vanadel complex which due to (V=O)bound [80].

Metal-nitrogen and metal-oxygen bands where established by the presence of the stretching vibration of υ(M-O) and υ(M-N) in the range (520-423cm^{-1}) and (486-432cm^{-1}), respectively.

Table (3-23) Shows the IR absorption values by cm^{-1} unit of the ligand(NTP) with its complexes

compound	υ(COO) Asym cm^{-1}	υ(COO) Sym cm^{-1}	Δ υ	υ(NH) υ(OH) cm^{-1}	υ(C=S) cm^{-1}	υ(C=O) cm^{-1}	υ(MN) cm^{-1}	υ(MO) cm^{-1}	υ(VO) cm^{-1}
NTP	1728(s)	1346(s)	----	3417(m) 3178(m)	1257(m)	1676(s)	---	---	------
$[VO(NTP)_2]$	1608(s)	1411(s)	197	3425(b)	1276(m)	1666(s)	443(m)	466(m)	975
$[Mn(NTP)_2]$	1624(S)	1411(S)	213	3433(b)	1280(m)	1662(m)	466(w)	423(m)	------
$[Co(NTP)_2]$	1604(m)	1411(m)	193	3462(b)	1276(m)	1666(m)	470(m)	487(m)	------
$[Ni(NTP)_2]$	1608(m)	1419(s)	189	3425(b)	1275(m)	1627(m)	443(m)	475(m)	------
$[Cu(NTP)_2]$	1604(m)	1418(m)	186	3458(b)	1261(m)	1676(m)	447(m)	482(m)	------
$[Zn(NTP)_2]$	1604(m)	1408(m)	196	3452 (b)	1280(m)	1662(m)	432(m)	489(m)	-------
$[Cd(NTP)_2]$	1620(m)	1400(m)	220	3425(b)	1265(m)	1631(m)	455(b)	482(m)	------
$[Hg(NTP)_2]$	1604(m)	1415(m)	189	3460(b)	1276(m)	1678(m)	486(m)	520(m)	------

s= strong m = medium w = weak

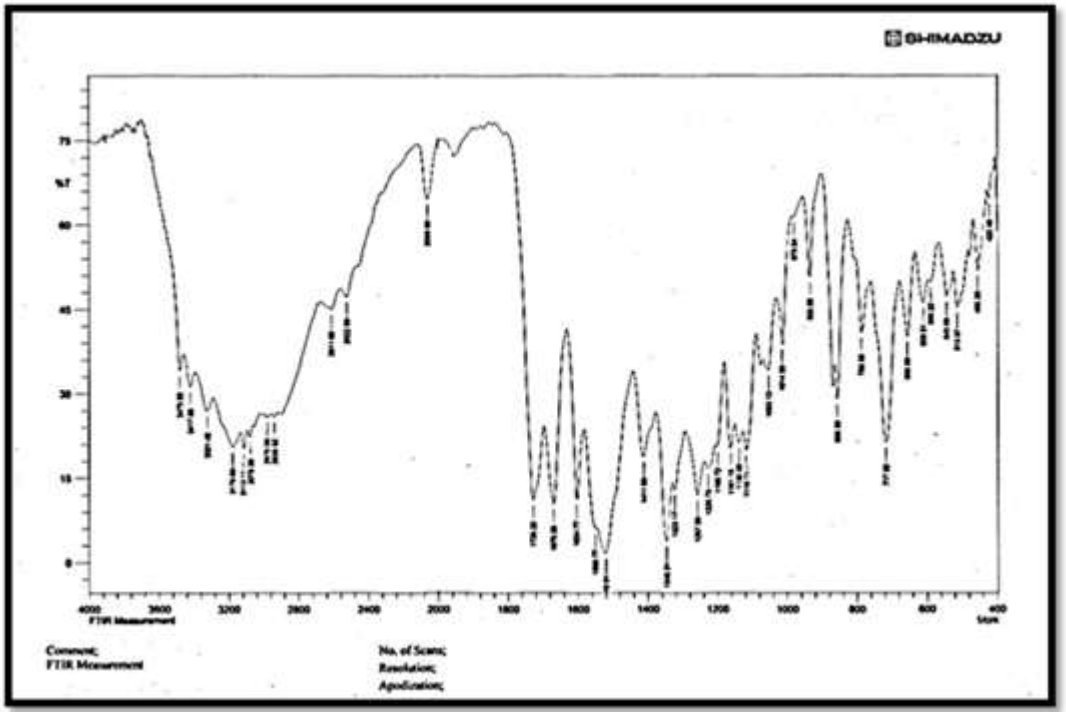


Fig.(3-7)FT-IR spectrum of ligand (NTP)

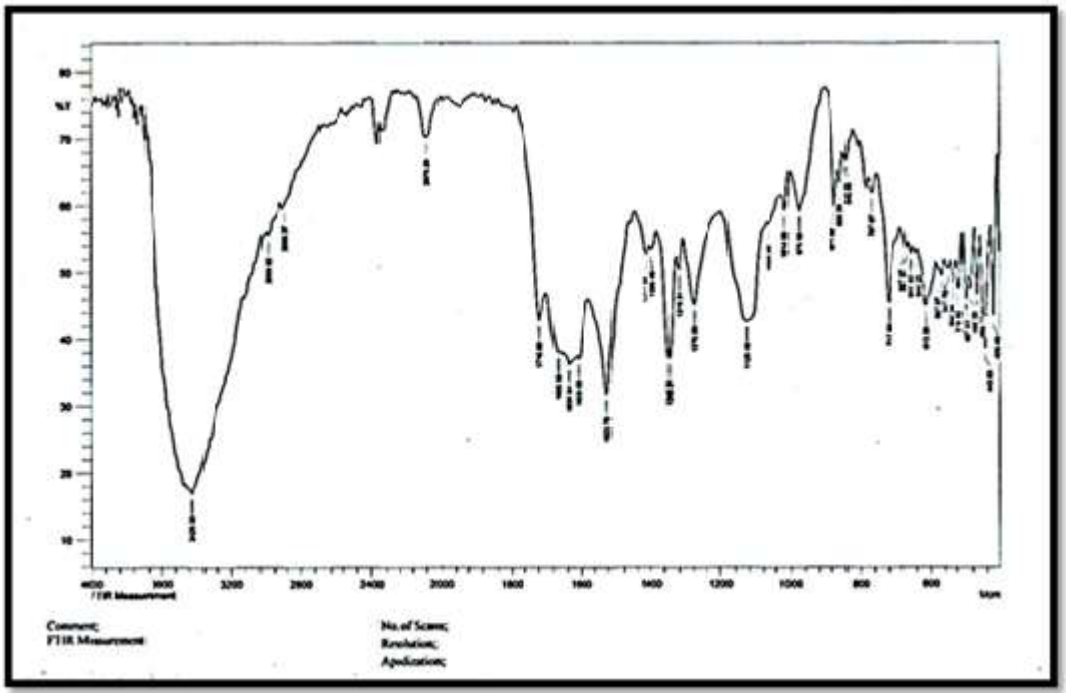


Fig.(3-28)FT-IR spectrum of complex [VO(NTP)$_2$]

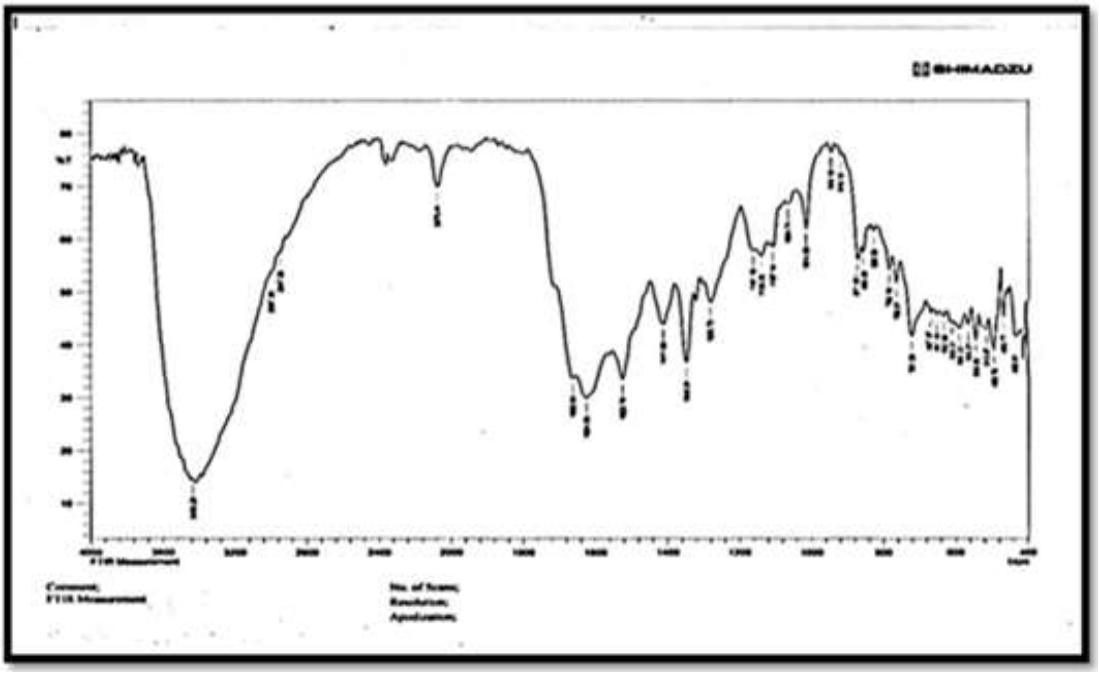


Fig.(3-29)FT-IR spectrum of complex [Mn(NTP)$_2$]

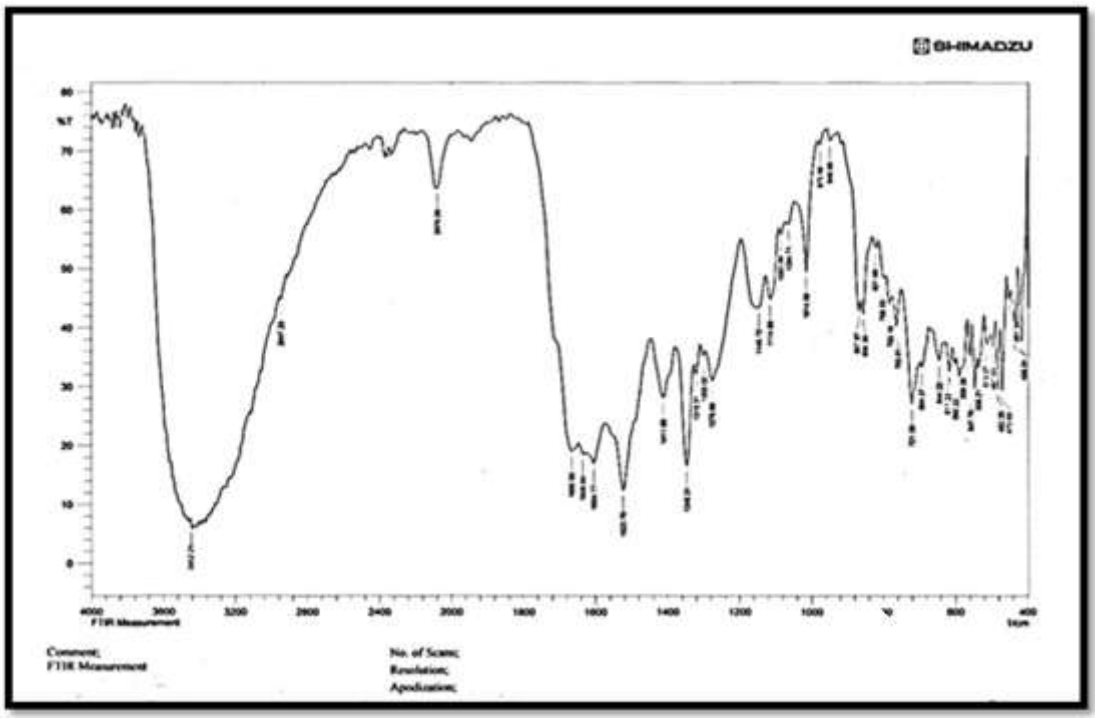


Fig.(3-30)FT-IR spectrum of complex [Co(NTP)$_2$]

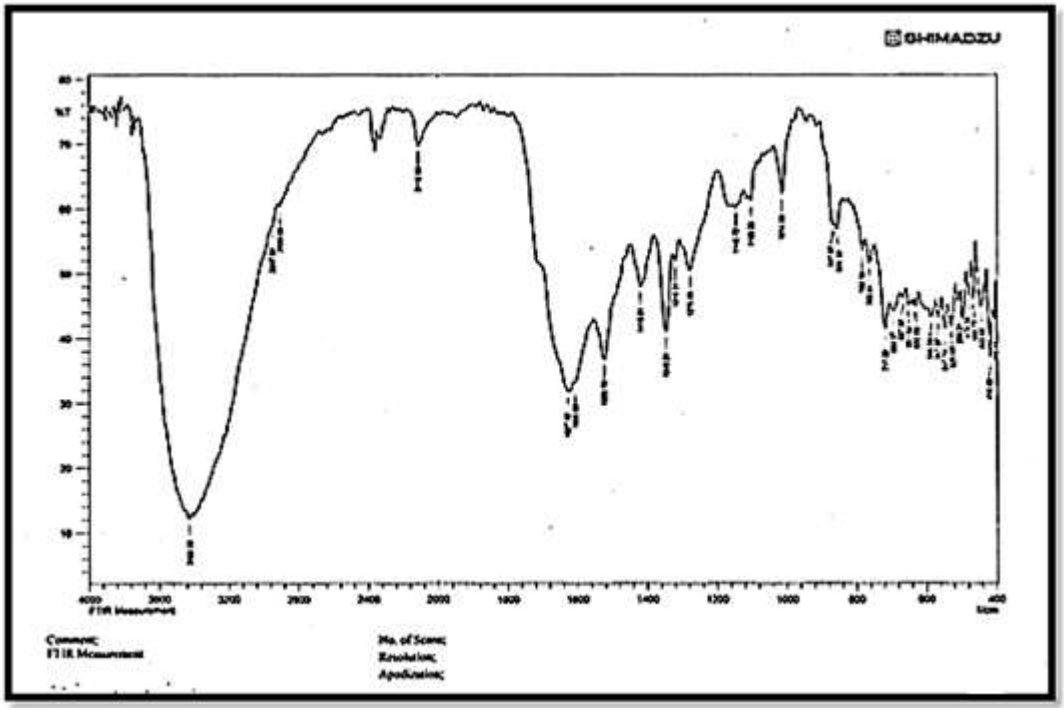


Fig.(3-31)FT-IR spectrum of complex [Ni(NTP)$_2$]

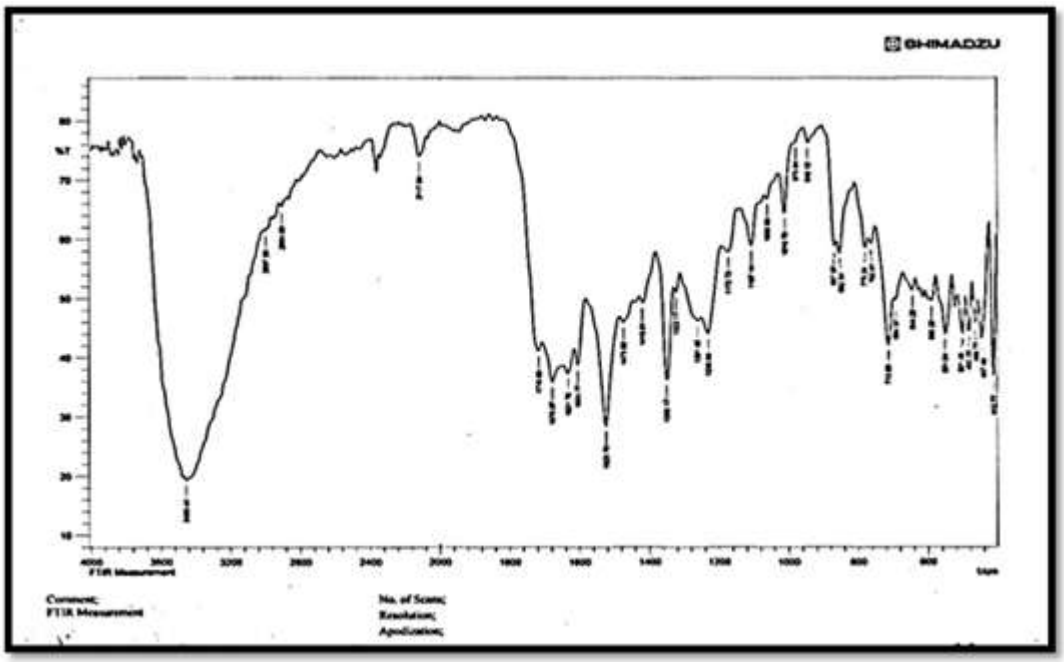


Fig.(3-32)FT-IR spectrum of complex [Cu(NTP)$_2$]

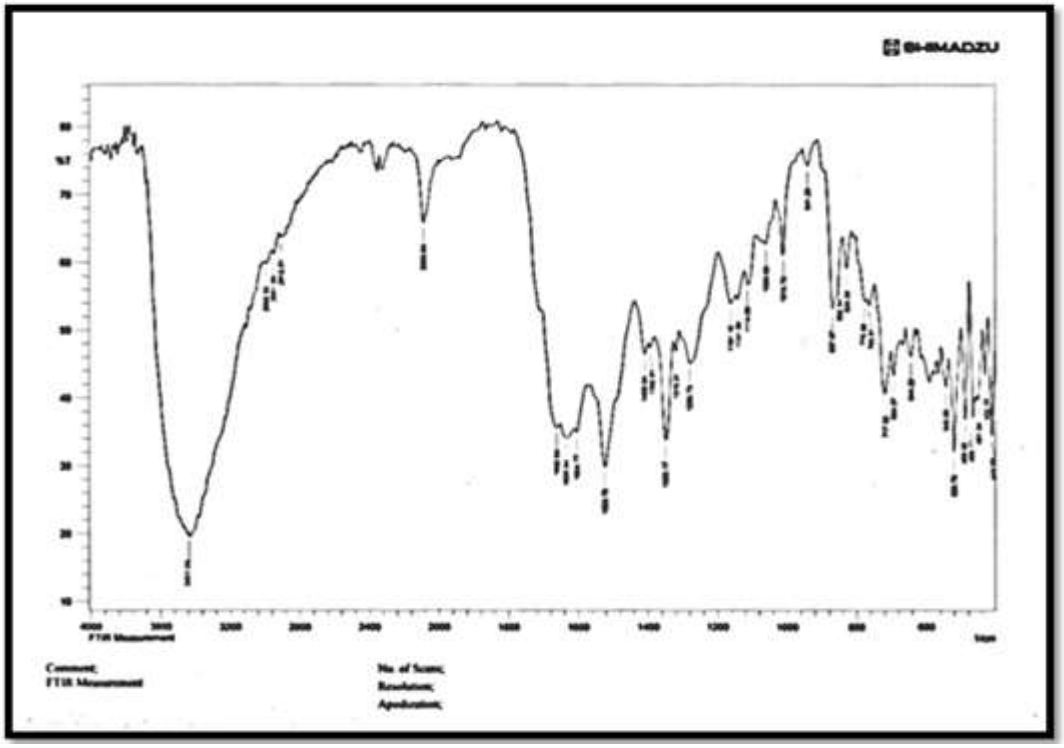


Fig.(3-33)FT-IR spectrum of complex [Zn(NTP)$_2$]

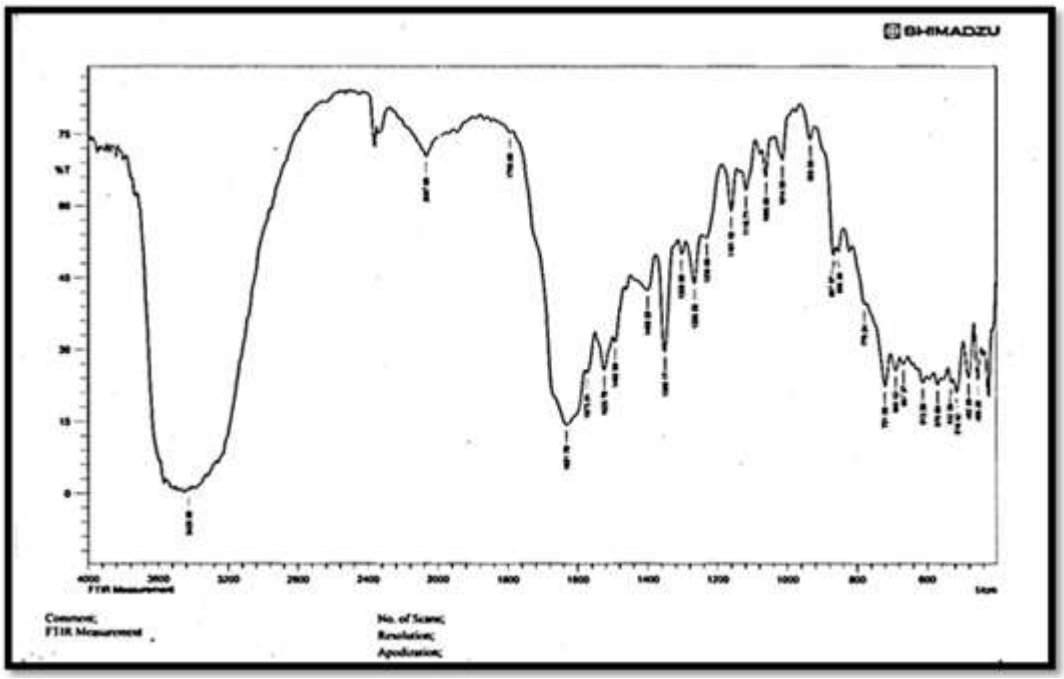


Fig.(3-34)FT-IR spectrum of complex [Cd(NTP)$_2$]

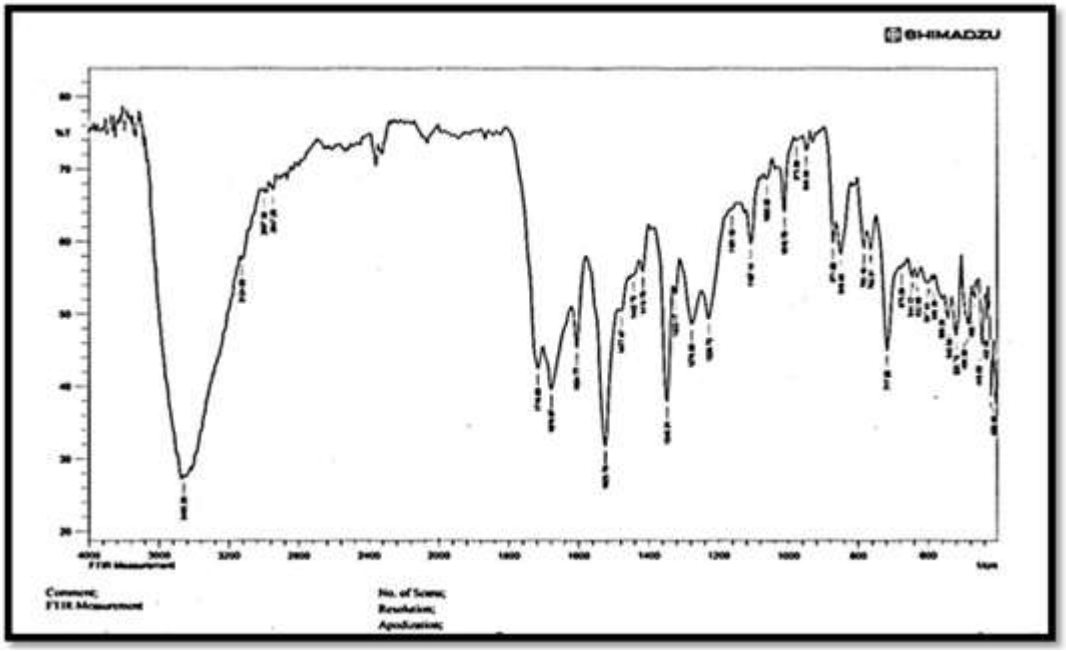


Fig.(3-35)FT-IR spectrum of complex [Hg(NTP)$_2$]

3.3.4.6 UV-Vis Spectra of (NTP)and their metal complexes.

The ligand(NTP)

The spectrum of ligand(NTP) fig(3-11) show bands at (36363cm^{-1}) and (26455cm^{-1}) which attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ respectively [81].

[VO(NTP)$_2$] complex

The deep green complex shows two bands fig(3-36),the first at (36764cm^{-1}) due to ligand-field, the second was at(13157cm^{-1}) which belongs to mix charge transfer and $^2B_2 \longrightarrow {}^2E$ transition[82].

[Mn(NTP)$_2$] complex

The yellow complex of Mn^{+2} shows three bands fig(3-37) the first at (36496cm^{-1}), which belongs to ligand-field and another band at (28735cm^{-1}) which is due to charge transfer, the last band at(13227cm-1) caused by the electronic transition $^6A_1 \rightarrow {}^4T_{2(G)}$ [82].

[Co((NTP)$_2$] complex

The blak-green complex of Co^{+2} shows four bands fig.(3-38)at (36101cm^{-1}), (27027cm^{-1}),(14285cm^{-1})and(10928cm^{-1}) which attributed to ligand-field, $^4A_{2(f)} \xrightarrow{v_3} {}^4T_{1(p)}$ mixed with(C.T), $^4A_{2(F)} \xrightarrow{v_2} {}^4T_{1(F)}$ and $^4A_2 \rightarrow {}^4T_{2(F)}$ transition respectively, and the inter electronic repulsion parameter B$^-$ was intended to be (568.5)cm^{-1}) from the relation($\beta = B^- / B_O$), β was found to be equal to (0.586). These parameters are accepted to Co^{+2} tetrahedral complex [83,84].

[Ni(NTP)$_2$] complex

The electronic spectrum of green-yellow complex of Ni^{+2}, Fig(3-39) has shown four bands at (36630cm^{-1}), (28409cm$^-$1), (13227cm^{-1}) and (10752 cm^{-1}) revealed the following electronic transition; ligand-field, $^3T_{1(F)} \rightarrow {}^3T_{1(P)}$ with C.T, $^3T_{1(F)} \rightarrow {}^3A_{2(F)}$ and $^3T_{1(F)} \rightarrow {}^3T_{2(F)}$ respectively. The B$^-$ value equal to(625cm^{-1}) ,while β was equal to 0.60, These are the characteristics for tetrahedral complexes of Ni^{+2} [85,86].

[Cu(NTP)$_2$] complex

The spectrum of green-yellow complex of Cu^{+2},Fig(3-40) shows two bands at (36900 cm^{-1}) and (12106cm^{-1}) which due to the ligand-field and $^2B_1g \longrightarrow {}^2A_1g$ [87] .

[Zn(NTP)$_2$]complex

The orang complex of Zn^{+2} ,Fig(3-41)shows two bands at(36231cm^{-1}) and (28901cm^{-1}) are due to electronic transition the ligand-field and charge transfer respectively[87].

[Cd(NTP)$_2$] complex

The spectrum of deep-yellow complex of Cd^{+2} showed one absorptions band, fig(3-42) at(36231cm^{-1}) due to ligand field[87].

$[Hg(NTP)_2]$

The yellow complex showed one absorptions band, Fig (3-43) at (36900 cm^{-1}) due to ligand field. The table (3-24) show all these data[87].

Table (3-24): Electronic spectral data of the ligand(NTP) and its metal complexes in $DMSO_{d6}$ solvent

Compounds	λ(nm)	$\upsilon^{-}(cm^{-1})$	A	ε_{max} $molar^{-1}$ cm^{-1}	Type of Transitions
NTP	275 378	36363 26455	2.082 0.500	2082 500	$\pi \longrightarrow \pi^*$ $n \longrightarrow \pi^*$
$[VO(NTP)_2]$	272 760	36764 13157	1.015 0.022	1015 22	L.F $^2B_2 \longrightarrow {}^2E$
$[Mn(NTP)_2]$	274 348 756	36496 28735 13227	1.993 0.686 0.014	1993 686 14	L.F C.T $^6A_1 \longrightarrow {}^4T_{2\,(G)}$
$[Co\ (NTP)_2]$	277 370 700 915	36101 27027 14285 10928	2.302 0.780 0.018 0.015	2302 780 18 15	L.F C.T * $^4A_{2\,(F)} \longrightarrow {}^4T_{1\,(P)}$ $^4A_{2\,(F)} \longrightarrow {}^4T_{1(F)}$ $^4A_{2\,(F)} \longrightarrow {}^4T_{2\,(F)}$
$[Ni(NTP)_2]$	273 352 756 930	36630 28409 13227 10752	2.199 0.765 0.020 0.015	2199 765 20 15	L.F C.T $_{MIX}$ $^3T_1 \longrightarrow {}^3T_{1\,(P)}$ $^3T_1 \longrightarrow {}^3A_{2\,(F)}$ $^3T_1 \longrightarrow {}^3T_{2\,(F)}$
$[Cu(NTP)_2]$	271 826	36900 12106	1.538 0.017	1538 17	L.F $^2B_1g \longrightarrow {}^2A_1g$
$[Zn\ (NTP)_2]$	276 346	36231 28901	2.272 0.097	2272 97	L.F C.T
$[Cd(NTP)_2]$	276	36231	2.227	2227	L.F
$[Hg(NTP)_2]$	271	36900	1.734	1734	L.F

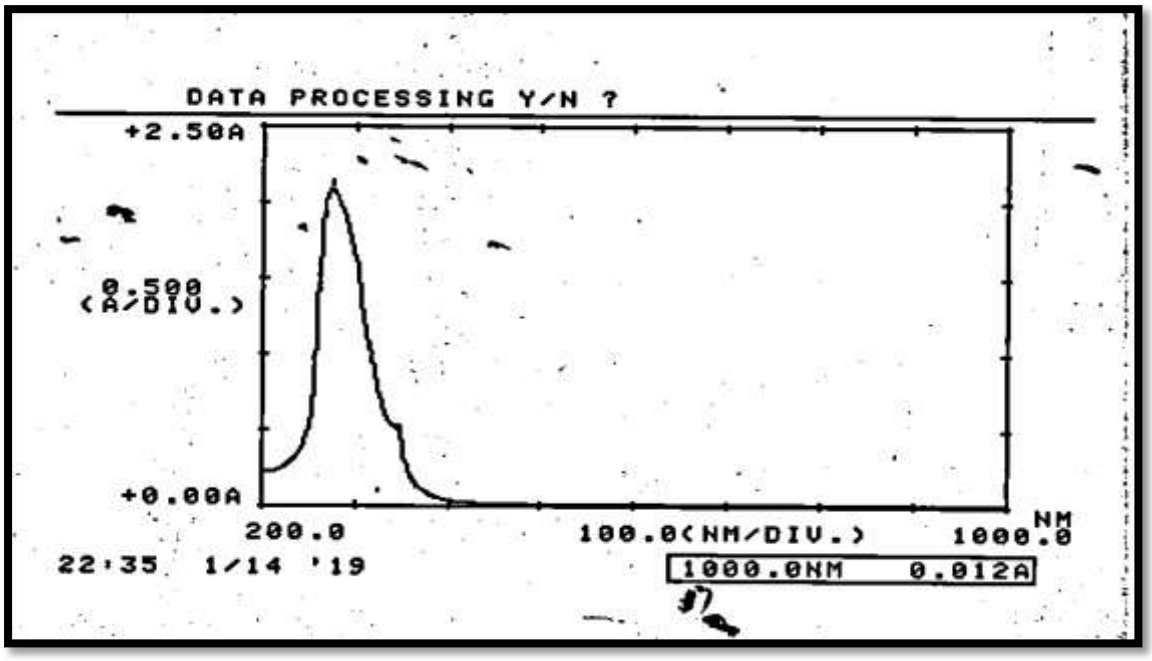


Fig.(3-11)UV-Visible spectrum of ligand(NTP)

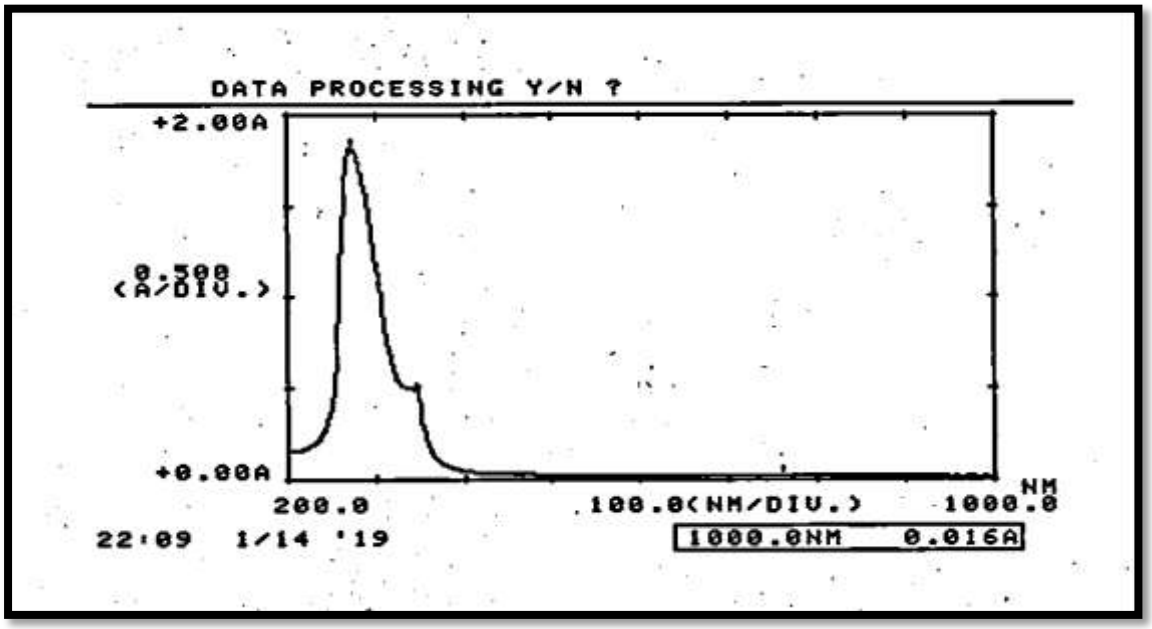


Fig.(3-36)UV-Visible spectrum of[$VO(NTP)_2$]

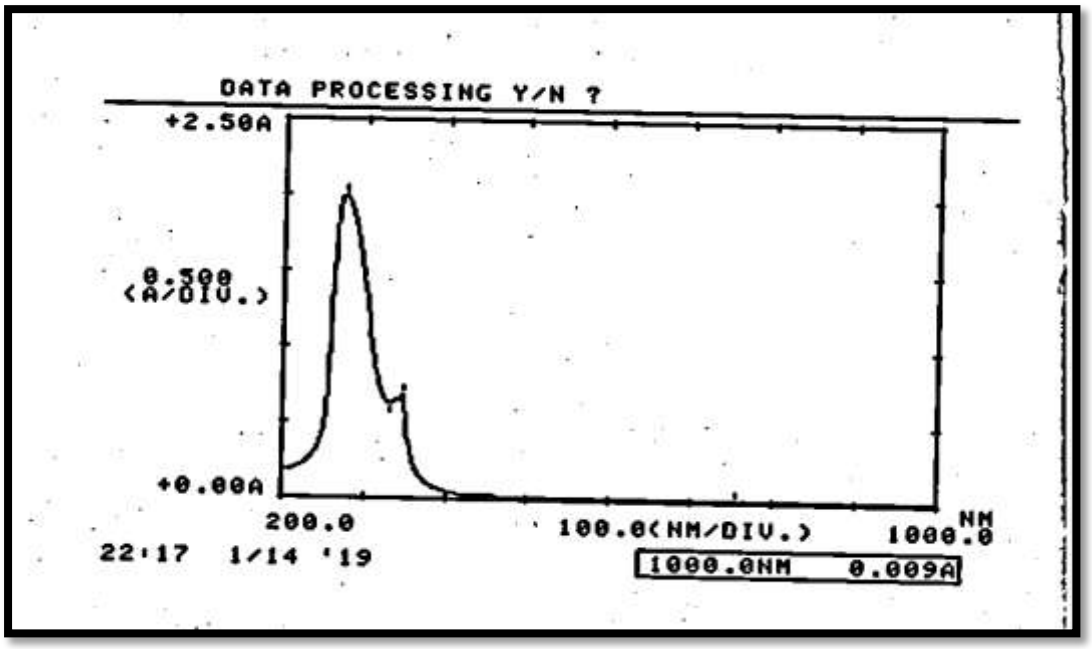


Fig.(3-37)UV-Visible spectrum of[$Mn(NTP)_2$]

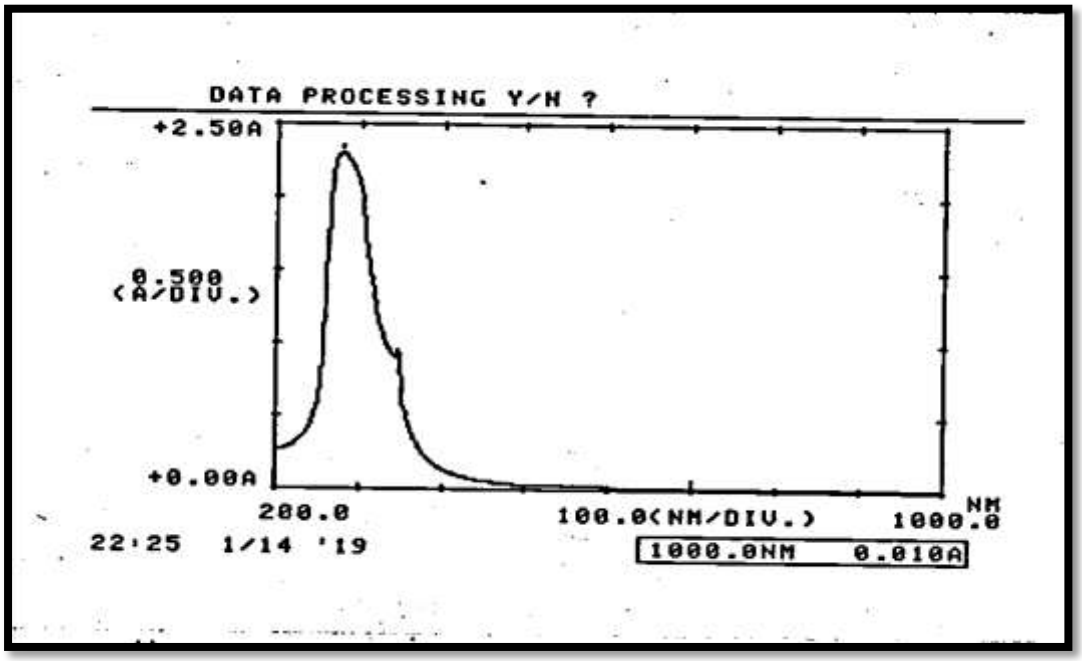


Fig.(3-38)UV-Visible spectrum of[$Co(NTP)_2$]

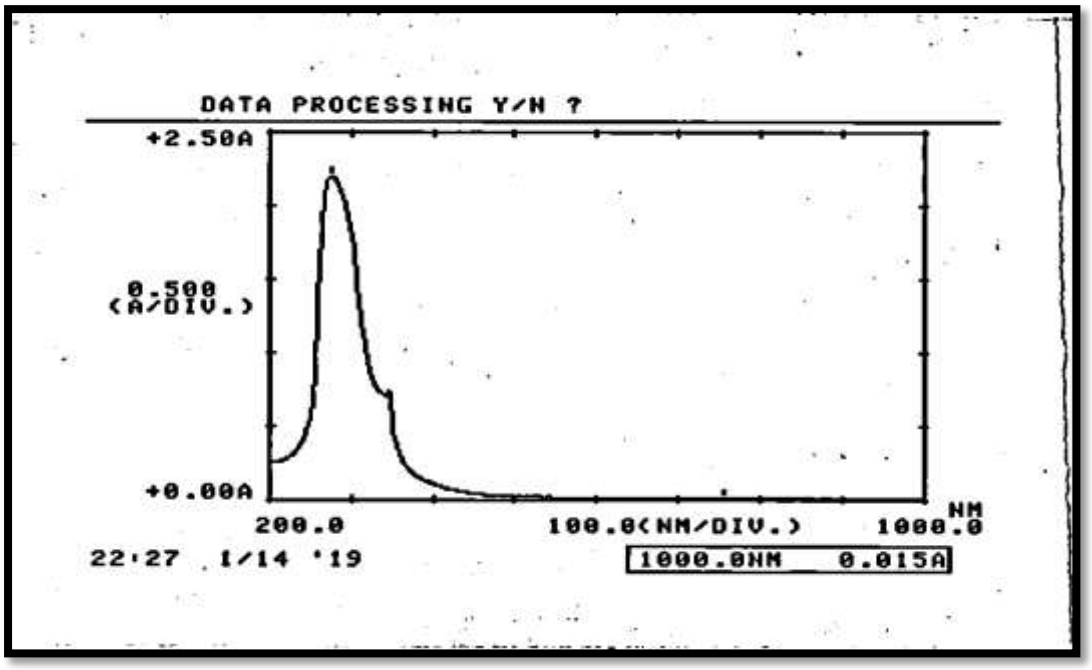


Fig.(3-39)UV-Visible spectrum of[$Ni(NTP)_2$]

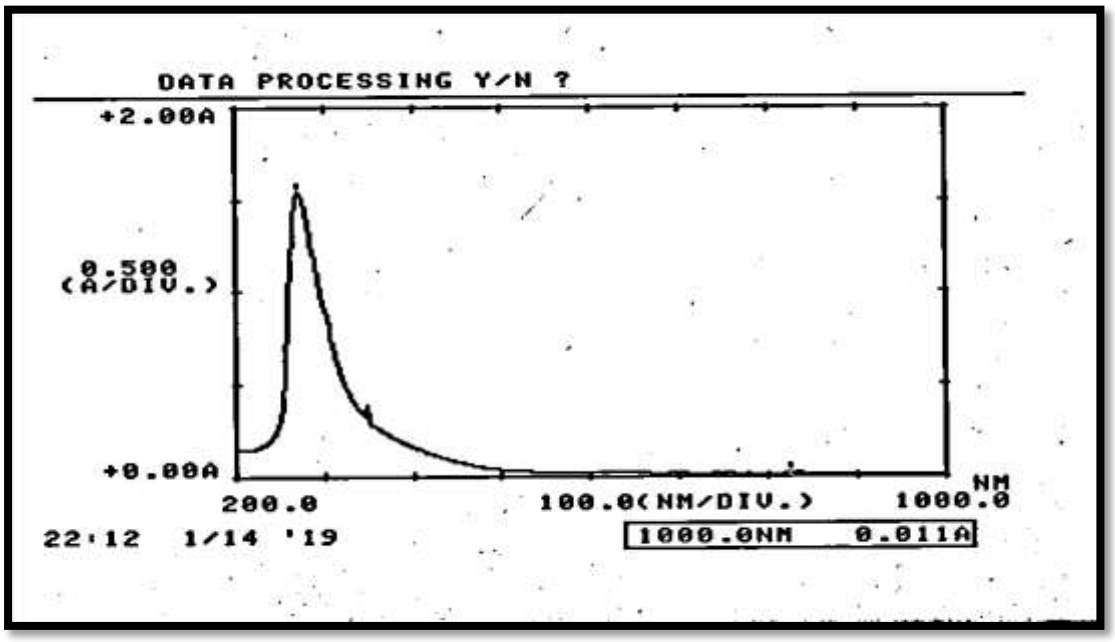


Fig.(3-40)UV-Visible spectrum of[$Cu(NTP)_2$]

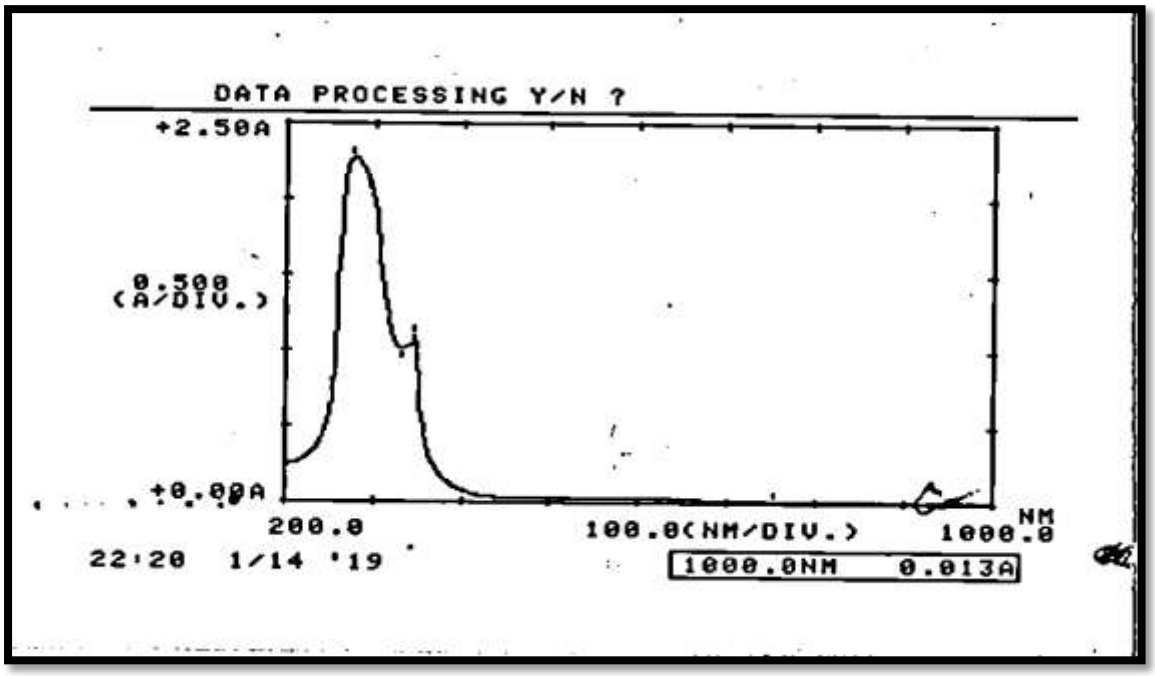


Fig.(3-41)UV-Visible spectrum of[$Zn(NTP)_2$]

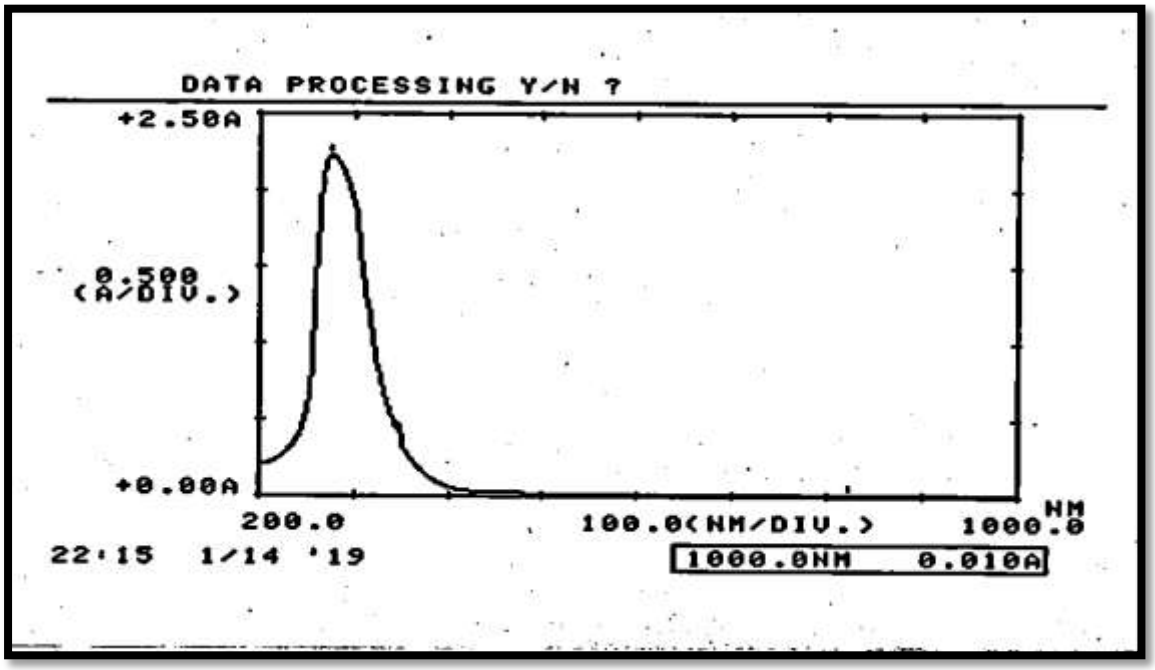


Fig.(3-42)UV-Visible spectrum of[$Cd(NTP)_2$]

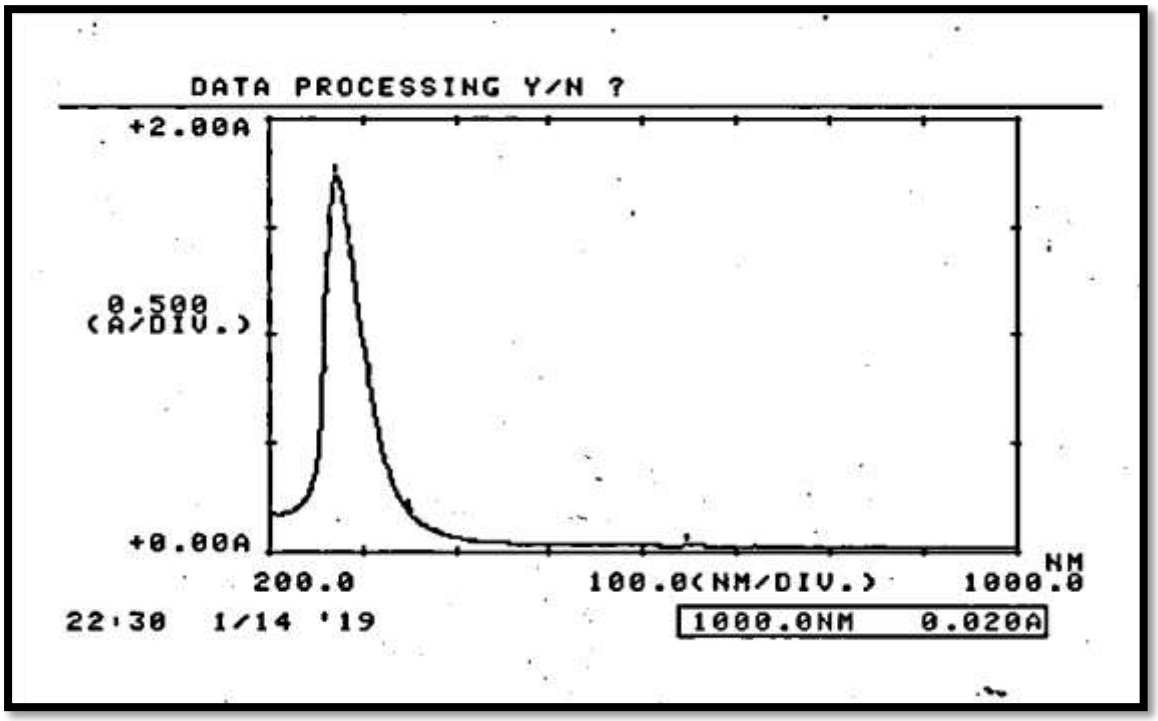


Fig.(3-43)UV-Visible spectrum of[$Hg(NTP)_2$]

(3.5) Nomenclature of the Prepared Complexes

The names of all complexes was according the roles of the International Union of Pure and Applied Chemistry (IUPAC). Table (3-25) shows the names of the metal complexes with the ligand(ATP) and Table (3-26) shows the names for metal complexes with the ligand (NTP).

Table(3-25) (IUPAC) Names of the complexes with the ligand(ATP)

complex	nomenclature
$[VO(ATP)_2]$	Bis(2-(3-acetylthioureido)-3-hydroxypropanato)Vanadyl(II)
$[Mn(ATP)_2]$	Bis(2-(3-acetylthioureido)-3-hydroxypropanato)Manganese(II)
$[Co(ATP)_2]$	Bis(2-(3-acetylthioureido)-3-hydroxypropanato)Cobalte(II)
$[Ni(ATP)_2]$	Bis(2-(3-acetylthioureido)-3-hydroxypropanato)Nickal(II)
$[Cu(ATP)_2]$	Bis(2-(3-acetylthioureido)-3-hydroxypropanato)Copper(II)
$[Zn(ATP)_2]$	Bis(2-(3-acetylthioureido)-3-hydroxypropanato)Zinc(II)
$[Cd(ATP)_2]$	Bis(2-(3-acetylthioureido)-3-hydroxypropanato)Cadmium(II)
$[Hg(ATP)_2]$	Bis(2-(3-acetylthioureido)-3-hydroxypropanato)Mercury(II)

Table(3-26)(IUPAC) Names of the complexes with the ligand (NTP)

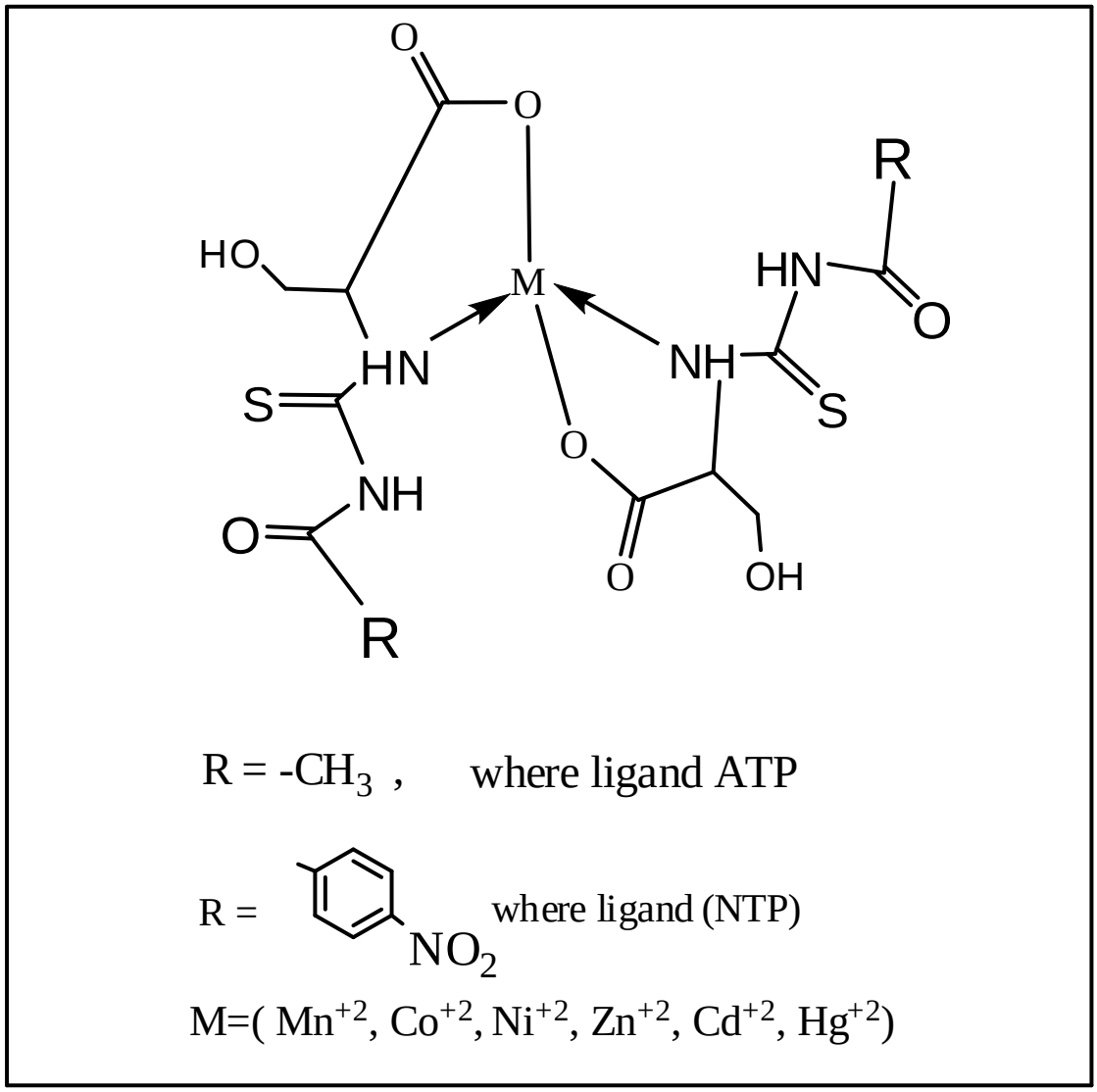
complex	nomenclature
$[VO(NTP)_2]$	Bis(3-hydroxy-2-(3-(4-nitrobenzoyl)thiouriedo)propanato)Vanadyl(II)
$[Mn(NTP)_2]$	Bis(3-hydroxy-2-(3-(4-nitrobenzoyl)thiouriedo)propanato)Manganese(II)
$[Co(NTP)_2]$	Bis(3-hydroxy-2-(3-(4-nitrobenzoyl)thiouriedo)propanato)Cobalte(II)
$[Ni(NTP)_2]$	Bis(3-hydroxy-2-(3-(4-nitrobenzoyl)thiouriedo)propanato)Nickal(II)
$[Cu(NTP)_2]$	Bis(3-hydroxy-2-(3-(4-nitrobenzoyl)thiouriedo)propanato)Copper(II)
$[Zn(NTP)_2]$	Bis(3-hydroxy-2-(3-(4-nitrobenzoyl)thiouriedo)propanato)Zinc(II)
$[Cd(NTP)_2]$	Bis(3-hydroxy-2-(3-(4-nitrobenzoyl)thiouriedo)propanato)Cadmium(II)
$[Hg(NTP)_2]$	Bis(3-hydroxy-2-(3-(4-nitrobenzoyl)thiouriedo)propanato)Mercury(II)

3.6 The suggested geometrical structures.

From all the data which obtained by ultra violet, elemental analysis, Infrared spectra, magnetic susceptibility and molar conductance, the structure have been suggested as below :

A-Tetrahedral geometry;

The complexes which contain metal ions (M^{2+} = Mn, Co, Ni, Zn, Cd and Hg) with ligand (ATP**)** and ligand (NTP), as shown in Fig(3-44).



Fig(3-44)Suggested geometrical structures of complexes with ligands (ATP) and(NTP)

B-squre pyramidal

The complexes that contain Vanadyl ion with both ligands (ATP) and (NTP) are have the squre pyramidal geometry, as showen in the Fig(3-45)

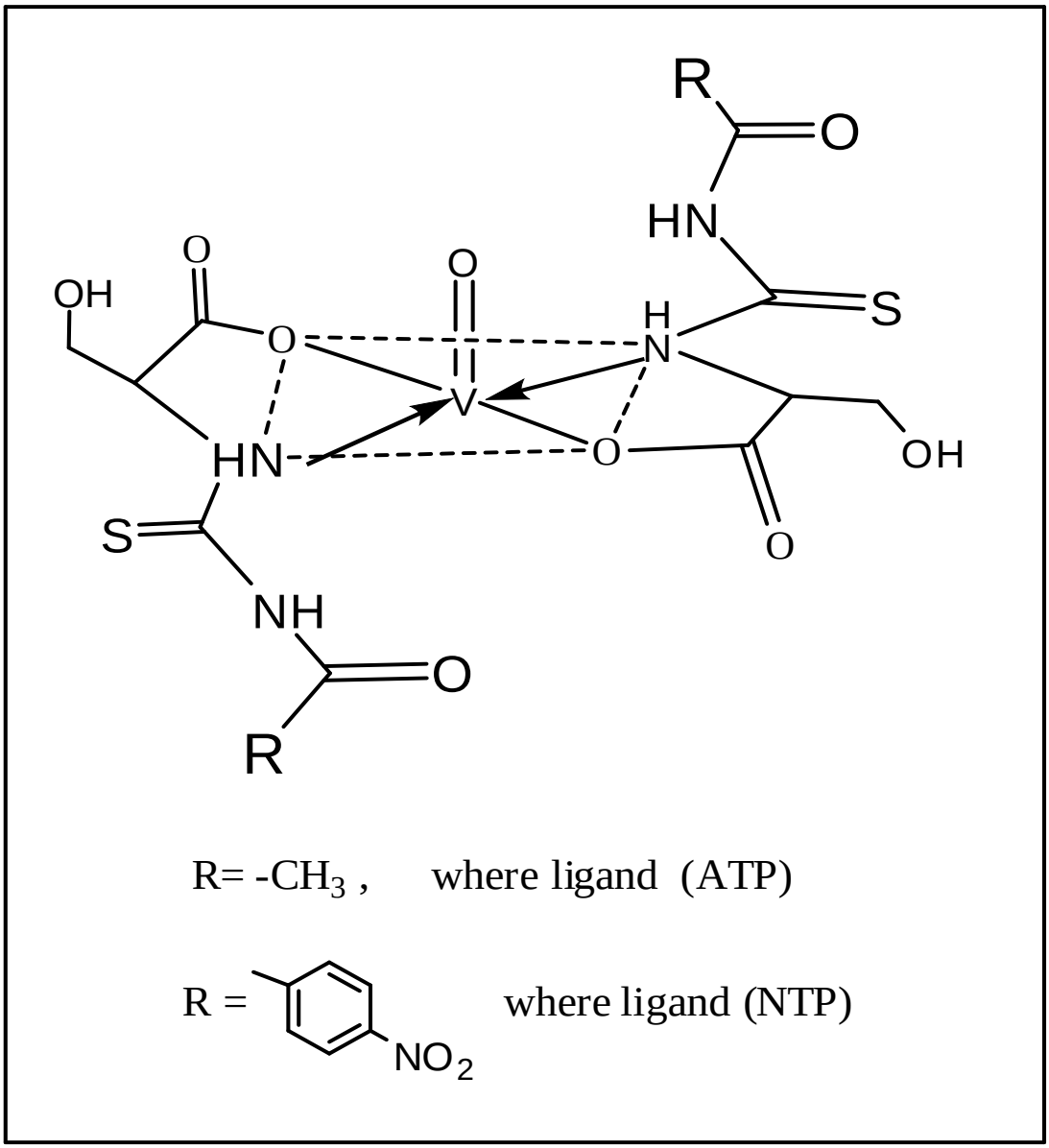


Fig.(3-45)Suggested geometrical structures of VO^{+2} ion complexes

C-square planar geometry

This geometry found at copper ion (Cu^{+2})complexes with both ligands (ATP) and (NTP) as showen in Fig(3-46).

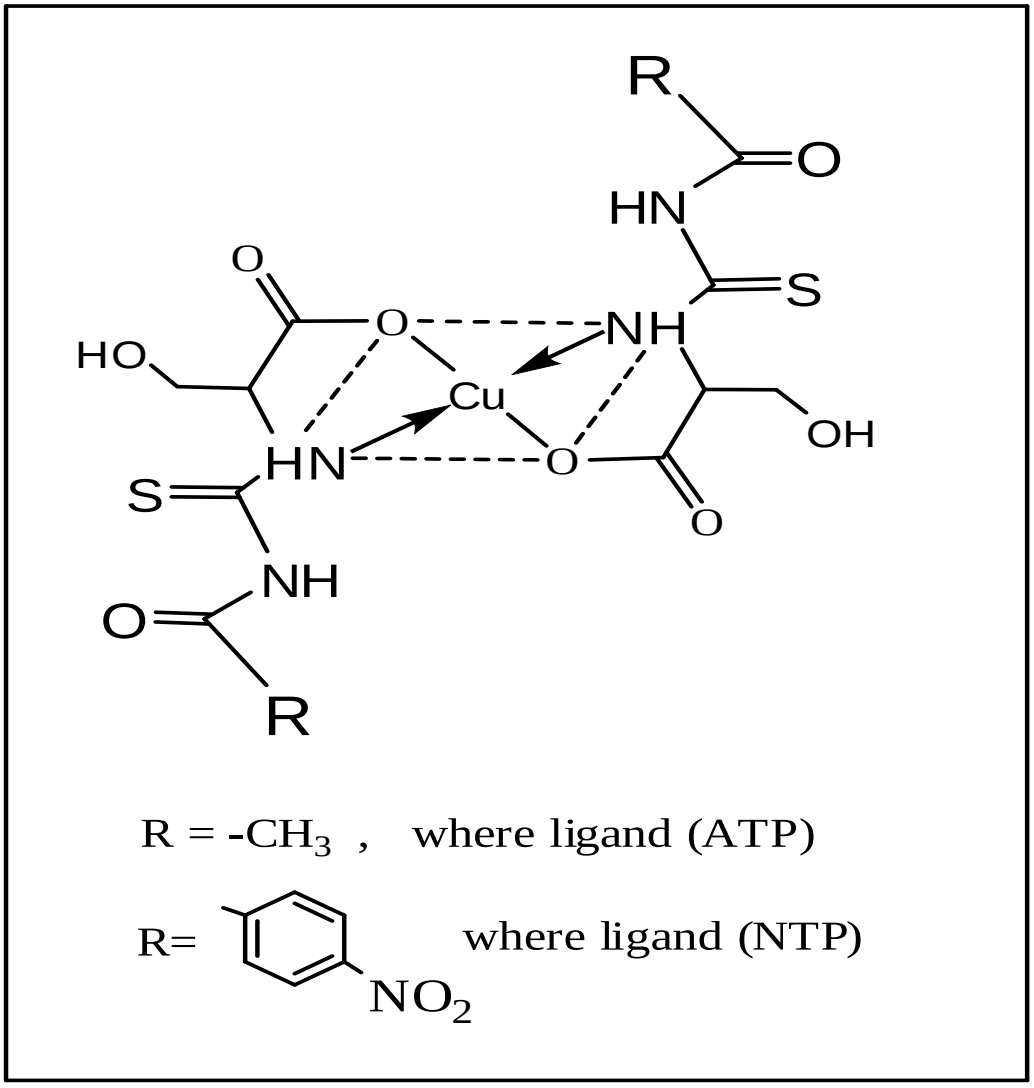


Fig.(3-46) Suggested geometrical structures of copper complexes

Chapter Four

Biological activity

4-1 The biological activity study for the two ligands and their complexes

The activity of the ligands and their complexes was tested against two groups of bacteria and one group of fungi by using the inhibition zone method.

(4.1.1) The biological activity of compounds with bacteria

The group of bacteria which tested were one (G^+) (***Staphylococcus aurous***), and the other were (G^+) bacteria (***Escherichia Coli***), Table (4-1) describe the activity of all prepared ligands and their complexes with (***Staphylococcus aurous***) and (***Escherichia Coli***).

A-Staphylococcus aurous:

This bacteria is a gram-positive group, it found in the soil, water and air, it may be causes the food poisoning in the intestines [88,89] .

From the results in the Table (4-1) we found;

1- Both the ligands (ATP) and (NTP) did not show any inhibition on these groups bacteria.
2- All the other prepared complexes showed different inhibition of the group of bacteria.
3- $[Cu(ATP)_2]$ showed a greater inhibition with the group of bacteria.
4- The complex $[Co(ATP)_2]$and $[Ni(ATP)_2]$ only did not showed any inhibition .

B - *Escherichia Coli*:

This bacteria is a (***G*** -) group , it found in the lower intestine and it often harmless ,but some groups can caused food poisoning [90] .

From the results in the Table (4-1) we found;

1- Both the ligands (ATP)and (NTP) did not showed any inhibition with this group of bacteria.
2- The complex $[Cd(NTP)_2]$ showed the greater inhibition with this group of bacteria.
3- Some of the complexes showed inhibition and some of them did not showed inhibition. Fig.(4-1 to 4-4) showed these activity.

Table (4-1) The inhibition zones in millimeter of the ligands and their complexes bacteria after 24 hr. at 37 ^{0}C

Compound	*Zone of inhibition in millimeter*	
	Escherichia Coli	*Staphylococcus aurous*
ATP	**-**	**-**
[VO(ATP$_2$)	**-**	**15**
[Mn(ATP)$_2$]	**-**	**16**
[Co(ATP)$_2$]	**-**	**-**
[Ni(ATP)$_2$]	**-**	**-**
[Cu(ATP)$_2$]	**10**	**22**
[Zn(ATP)$_2$]	**-**	**13**
[Cd(ATP)$_2$]	**17**	**19**
[Hg(ATP)$_2$]	**13**	**12**
NTP	**-**	**-**
[VO(NTP)$_2$]	**13**	**15**
Mn(NTP)$_2$]	**13**	**15**
[Co(NTP)$_2$]	**13**	**14**
[Ni(NTP)$_2$]	**-**	**14**
[Cu(NTP)$_2$]	**-**	**19**
[Zn(NTP)$_2$]	**13**	**15**
[Cd(NTP)$_2$]	**21**	**17**
[Hg(NTP)$_2$]	**14**	**15**

Fig.(4-1) Biological activity of the ligand(ATP)and their complexes with the (*staphylococcus aurous*) bacteria

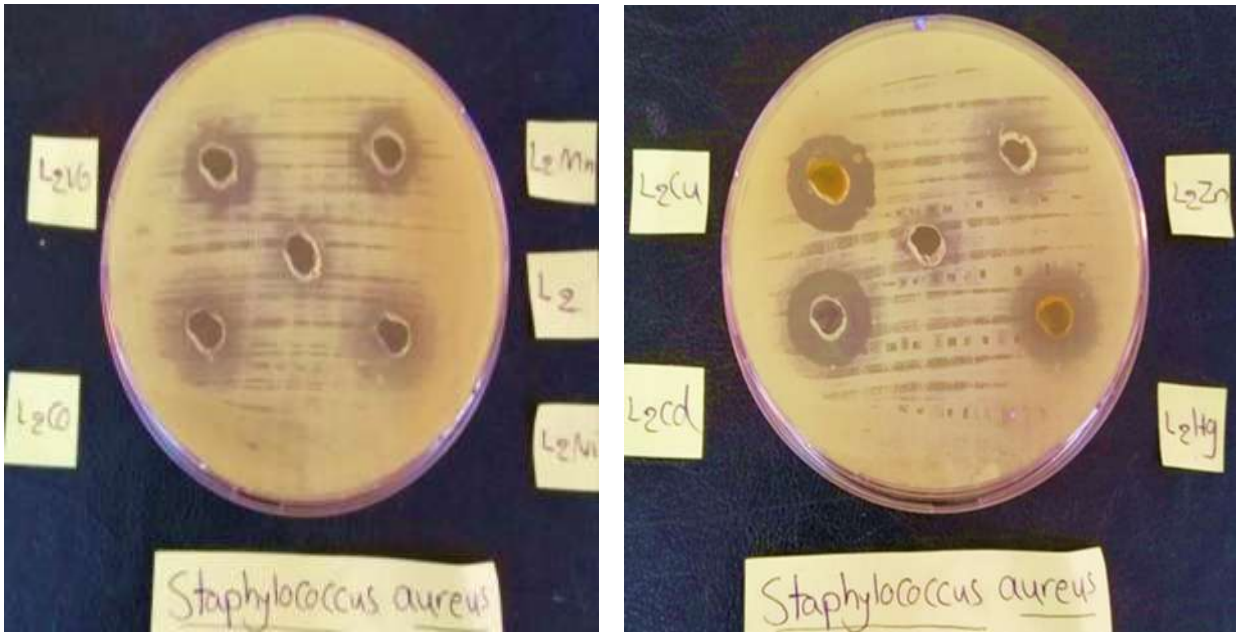


Fig.(4-2) Biological activity of the ligand(NTP)and their complexes with the (*staphylococcus aurous*) bacteria

Fig.(4-3) Biological activity of the ligand(ATP)and their complexes with the (*Escherichia coli*) bacteria

Fig.(4-4) Biological activity of the ligand(NTP)and their complexes with the (*Escherichia coli*) bacteria

4.1.2 The biological activity of the prepared compounds with fungi

The fungi which tested were (***Candida albicans*),** it found in gastrointestinal and genitourinary tract [91]**.** It tested by using the inhibition zone method, Table (4-2) shown the data of the biological activity of the two ligands and their complexes.

Table (4-2) The inhibition zones in millimeter of the ligands and their complexes with fungi after 24 hr. at 37 ^{0}C

compound	*Inhibition zones in millimeter*
	Candida albicans
ATP	**-**
[VO(ATP)$_2$]	**-**
[Mn(ATP)$_2$]	**12**
[Co(ATP)$_2$]	**-**
[Ni(ATP)$_2$]	**-**
[Cu(ATP)$_2$]	**16**
[Zn(ATP)$_2$]	**-**
[Cd(ATP)$_2$]	**14**
[Hg(ATP)$_2$]	**-**
NTP	**-**
[VO(NTP)$_2$]	**-**
[Mn(NTP)$_2$]	**-**
[Co(NTP)$_2$]	**11**
[Mn(NTP)$_2$]	**-**
[Ni(NTP)$_2$]	**17**
[Cu(NTP)$_2$]	**12**
[Zn(NTP)$_2$]	**-**
[Cd(NTP)$_2$]	**21**
[Hg(NTP)$_2$]	**15**

From these data we found;

1- Both two ligands did not showed any inhibition with this group of fungi.
2- The complex [Cd(NTP)$_2$] showed the greater inhibition with this fungi.
3- Some of the prepared complexes showed inhibition and the other did not show any activity. Figures (4-5) and (4-6) show this activity.

Fig.(4-5) Biological activity of the ligand(ATP)and their complexes with the *(Candida albicans*)

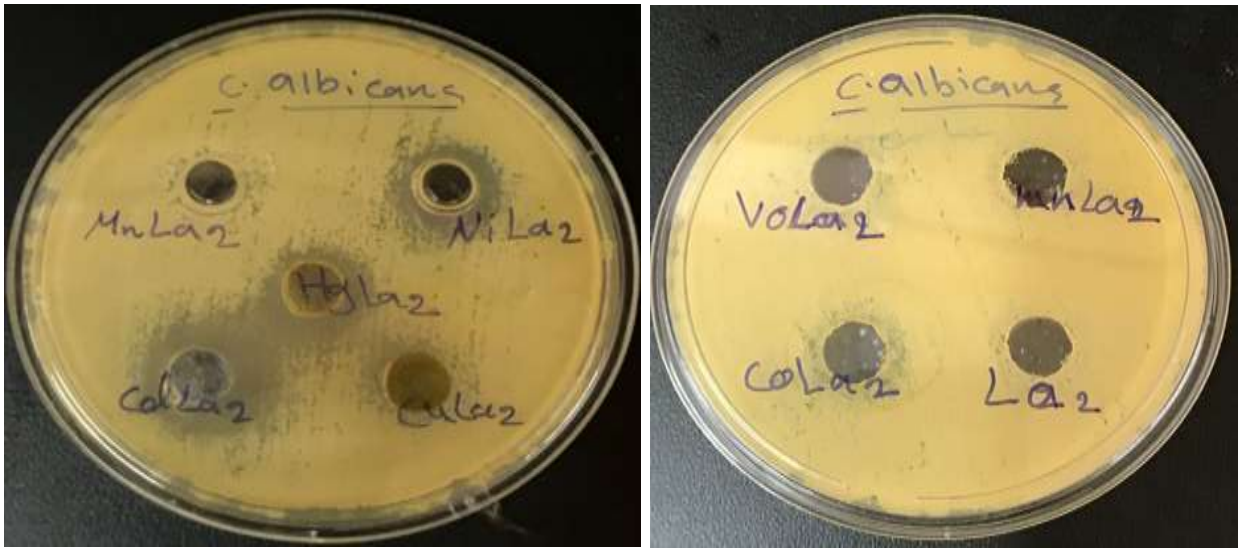


Fig.(4-6) Biological activity of the ligand(NTP)and their complexes with the *(Candida albicans*)

(4-2) Conclusion.

From all the characterization data of the two new ligands (ATP) and (NTP) which prepared by the reaction of acetyl chloride for (ATP) and 4-nitro benzoyl chloride for (NTP), with ammonium thiocyanate and serine. They identified by FT-IR, ^{1}H,^{13}C-NMR, UV-Vis, Melting point, micro elemental analysis (C.H.N.S), and their prepared complexes identified by FT-IR ,UV-Vis, magnetic susceptibility, atomic absorption , molar conductivity, micro elemental analysis (C.H.N.S) and melting point, we found:

1- The new two ligands (ATP)and (NTP) were behavior as bi dentate legands and it coordination from oxygen ion of carboxylate group and nitrogen atom of amine group to form a five member ring around all the metal ions.
2- All the complexes were have a general formula $[M(L)_2]$.
3- The geometrical structure of the complexes were tetrahedral with the metallic ions(M=Mn^{+2},Co^{+2},Ni^{+2},Zn^{+2},Cd^{+2} and Hg^{+2}).
4- The geometrical structure of the complexes were square planer with copper ion.
5- The geometrical structure of the complexes were Square pyramid with the Vanadyl ion.
6- The two prepared ligands did not show any ability to inhibition of growth toward *Staphylococcus aurous* and *Escherichia Coli* bacteria and *candida albicans* fungi.
7- Many of the prepared complexes showed different effective against the two groups of bacteria and some of them only showed effective against the fungi.

4-3 The future Studies;

1- Studying of the stability constant of the two ligands and their complexes and calculate the thermodynamic factors ΔH and ΔS.
2- Studying of the industrial application of these compounds.
3- Use deferent types of bacteria and fungi to testing the biological activity for these compounds.
4- Make a medicine study (as anticancer) of these compounds.
5- Prepare new complexes with these ligands by using other metal ions like the second and third series.
6- Prepare complexes contain a new different ligands derivatives from serine and other amino acid.

Reference

Reference

1. "The Structures of Life". National Institute of General Medical Science. Retrieved 20 May 2008.
2. Elzanowski A, Ostell J. (7 April 2008)."The Genetic Codes". National Center for Biotechnology Information (NCBI). Retrieved 10 March 2010.
3. Wagner I, Musso H, Angew. Chem. Int. Ed. Engl.(1983);22 (22): P816–828 .
4. Jaeken J., Detheux M., Van M., 3-phospho glyserate dehydrogenase defisency:an inborn error of serine biosynthesis.,Archives of disease in childhood 1996,74,p542-545.
5. He G., Bo Wang, William A. Nack, and Gong Ch., Syntheses and transformations of α-amino acids via palladium-catalyzed auxiliary-directed sp3 C–H functionalization. Accounts of chemical research, 2016. 49(4): p. 635-645.
6. Orhan E., Arslan (7 August 2014). Neuro anatomical Basis of Clinical Neurology, Second Edition. CRC Press.2014, pp. 309.
7. Michael C. Latham, Human nutrition in the developing world – United Nations Food and Agriculture Organization, ch.8 (1997);v 29, p(1014-3181).
8. Wade L. G., Organic Chemistry, 7th Edition, chapter 24 amino acids, peptides, and proteins,(2010);p1153-1199.
9. Young V.R., "Adult amino acid requirements:the case for amajor revision in current recommendation", J. Nutr. (1994), v8;p(124).
10. Biomol J. Struct Oyn."Giectronic properties of the amino acids chain" Jun. (2001),18(6); p881-892.
11. John Mc. Mary “Organic Chemistry “Books \Cole USA 5thEd, (2000),1094; p1074-1078.
12. Robert B. “Organic chemistry” MC. Graw –Hill, Companies; (1997),p531-535.
13. Meierhenrich, U .J.Amino acids and the asymmetry of life (IstEd) Springer I5BN, (2008), 978(3) p540.
14. Morrison, R. and Boyed R."Organic Chemistry" 3rh Ed , Sone , Limited London (1994).

15. Soltani, A., Ramzani. M,Vahed,E. Javan,M.Heidari, Serine adsorption through different functionalities on the B12N12 and Pt-B12N12 nanocages. Materials Science and Engineering: C, 2018. 92: p. 216-227.
16. Lehninger A., W. H. Freeman, Nelson D.L and Cox M., Principles of Biochemistry (3rd ed.). New York:, 2000. ISBN 1-57259-153-6.
17. Freeman W.H., Stryer L. Biochemistry (3rd ed.). New York:. (1988), p. 580. ISBN 978-0-7167-1843-7.
18. Drauz K, Grayson I, Kleemann A, Krimmer H, Leuchtenberger W, Weckbecker C. "Amino Acids". Ullmann's Encyclopedia of Industrial Chemistry. Weinheim: Wiley-VCH. (2005) doi:10.1002/ 14356007 .a02 _057.pub2.
19. Carter H.E, West H.D. "dl-Serine". Org. Synth. (1940), 20: p81. doi:10.15227/orgsyn.020.0081.
20. Boto A., Hernandes,R.,Montoya,A.,Suares,E., One-pot synthesis of aryl glycines and other unnatural amino acids from serine derivatives. Tetrahedron letters, 2002. 43(46): p. 8269-8272.
21. Boto A., Juan A. Gallardo G. Dacil H., and Rosendo H. Synthesis of Unnatural Amino Acids from Serine Derivatives by β-Fragmentation of Primary Alkoxyl Radicals, Org.chem ,(2007),vo72,No19.
22. Higgins, G., Slassi A., and Isaac M. , Use of D-serine derivatives for the treatment of anxiety disorders, international application published under the patentcooperation treaty(PCT) Patents2013,N 070994.
23. Ana M. Cardoso , Catarina M. Morais, A. Rita Cruz a,c, Sandra G. Silva d, M. Luísa do Vale d,Eduardo F. Marques d, Maria C. Pedroso de Lima ,Amália S. Jurado , New serine-derived gemini surfactants as gene delivery systems,2015,v89,p347-356.
24. Ebrahim M., Homayoon B., Shabnam S.,Vahid A., and Behrouz notash. Palladium(II) Mixed-Ligand Complexes Containing 2,2'-Bipyridine Derivaties and 4-Toluenesulfonyl-l-Serine: Synthesis, Characterizationand Crystal Structure Determination, doi(2015).V37-41,No1072954.
25. Oh, Y.S.,Lee,T.,Shin,S.,Sharstha,J.,Lee,D.,and Beak,D., Synthesis of FTY720 *(Fingolimod)* Derivatives Containing Serine Structure. Bulletin of the Korean Chemical Society, 2018. **39**(2): p. 261-264.

26. Hakimi, M., and Aliabadi,T.S., Coordination Chemistry of Copper α-Amino Acid Complexes,2012, v(2),p431-443.
27. Casari B.M., Mahmoudkhan A.H., Langer V. and Acta Crystallogr. ,Sect.E: Struct .Rep.Online,2004 ,60:1949,.
28. Mirceva A., Thomas J.O., Gustafsson T., Crystallogr A., Sect.C: Cryst. Structure of trans-bis(DLalaninato)cooper(II)mono hydrate Commun. 1989, 45:1141.
29. Patra A.K., Bhowmick T., Roy S. and Ramakumar S.,Cooper(II)complexes of L-argenine as netropsin mimics showing DNA cleavage activity in red light , Inorg.Chem. 2009, v48: p2932,.
30. Yajima T., Takamido R., Shimazaki Y., Odani A., Nakabayashi Y., Yamauchi O. Dalton Trans, Pi-pi stacking assisted buiding of aromatic amino acids by cooper(II)-aromatic diimine complexes.2007, p299.
31. –Evertsson B., Crystallogr A., Sect B,:Struct.Crystallogr.Cryst. Chem. 1969,v25: p30.
32. Venkatasubramanian K., Saha N.N., Curr.Sci.1984, v53: p385.
33. Fawcett T.G., Ushay M., Rose J.P. , Lalancette R.A., Potenza J.A., Schugar H.J. Exchange itractions in bis(L-leucinato)cooper(II). Inorg.Chem.1979, 18: p327.
34. Antolini L., Menabue L., Pellacani G.C., Saladini M., Marcotrigiano G., Morini P., . ActaCrystallogr.,Sect. A:Cryst.Phys.,Diffr.,Theor .Crystallogr.Synthesis and spectroscopic properties of som thermcromic cooper(II)complexes of N(2-aminoethyl)hetrosyclic derivatives.1981, 37: p230.
35. Sugimori T., Masuda H., Ohata N., Koiwai K., Odani A.,Yamauchi O. Amino acids, peptides and proteins. Inorgang Chemistry.1997, 36:p576.
36. Markovic M., Judas N, Sabolovic J. Inorgang Chemistry.2011, 50: p3632.
37. Le X.Y. ,Tong M.L. ,Fu Y.L.,Ji L.N. Huaxue Xuebao(Chin.)(Acta Chim.Sinica).2002, 60: p367.
38. Schveigkardt J.M. , Rizzi A.C. , Piro O.E., Castellano E.E., de Santana R.C. , R.Calvo, Brondino C.D. . Eur.J.Inorg.Chem.2002, p2913,.

39. Le X.Y.,Tong M.L.,Fu Y.L.,Ji L.N. Chin.J.Chem.2003, 21: p44.
40. Martino D.M., Steren C.A., Calvo R., Piro O.E.,Solid State Chem.1991, 90: p211.
41. Zhang S., ZhuY.,Tu C.,Wei H.,Yang Z.,Lin L., Ding J.,Zhang J., Guo Z . J.Inorgang Biochemstry.2004, 98: p2099.
42. D'yakon I.A., Donu S.V., Chapurina L.F., Kairyak N.L . Kristallografiya (Russ.) (Crystallogr.Rep.)1992 .37: p1391.
43. Amirthalingam V., Muralidharan K.V. Pramana.1982,19: p51.
44. Sevgi F., Bagkesici U., Kursunlu A.N., Guler E., Fe (III), Co(II), Ni(II), Cu(II(and Zn(II) complexes of schiff bases based-on glycine and phenylalanine: Synthesis, magnetic/thermal properties and antimicrobial activity, Journal of Molecular Structure , doi: 10.1016/j.molstruc . 2017.10.052.
45. Violet Dhayabaran V., Daniel Prakash T., . Spectral And Theoretical Studies On The Impact Of M(II)Complexes Of Amino Acid-Nucleobase Hybrid Ligand On BSA Binding: An Approach Towards New Metallodrugs,2017,Vo(4),p(9).
46. Mary Juliet B. and Amaladasan M., Synthesis and Characterization of Macrocyclic Complexes of Mn(II) , Co(II) and Cu(II),interational journal of chemtech reserch 2017,Vo(10),No(7).
47. Wang H.,Geo J.,Xu X., Yao P.,Jiang Y., Synthesis, structure and magnetic properties of two nickel (II) complexes of N-(pyridyl-3-sulfonyl)-l-threonine. Transition Metal Chemistry, 2017. 42(4): p. 293-299.
48. Rodrigues T.A., De aruda E.J., Fernandes M.F., De carvalho C.T., Copper II-polar amino acid complexes: toxicity to bacteria and larvae of Aedes aegypti. Anais da Academia Brasileira de Ciências, 2017. 89(3): p. 2273-2280.
49. Abdel-Rahman L.H., Abu-Dif A.M., Ismail N.M., Ismail M., Synthesis, characterization, and biological activity of new mixed ligand transition metal complexes of glutamine, glutaric, and glutamic acid with nitrogen based ligands. Inorganic and Nano-Metal Chemistry, 2017. 47(3): p.467-480.
50. dos Santos E.R., Coria R.S., Pozzi L.V., Graminha A.E., Araujo H.S., Pavan F.R., Antitumor and anti-Mycobacterium tuberculosis

agents based on cationic ruthenium complexes with amino acids. Inorganica Chimica Acta, 2017. 463: p.1-6.
51. Perrone M.L., Salveda E., Pasotti L., Casela L., A dinuclear biomimetic Cu complex derived from l-histidine: synthesis and stereoselective oxidations. Dalton Transactions, 2017. 46(12): p.4018-4029.
52. Zhang N., Fan Y., Huang G., Buac D., Bi C., Ma Y., l-Tryptophan Schiff base cadmium (II) complexes as a new class of proteasome inhibitors and apoptosis inducers in human breast cancer cells. Inorganica Chimica Acta, 2017. 466: p.478-485.
53. Dhakshanamoorthy S., Murali Krishnan M, and Arumugham M., Ternary Copper (II) Complexes Containing Thiosemicarbazide: DNA Binding, Antimicrobial Activities, and DFT Studies. Indian J. Adv. Chem. Sci, 2018. 11: p.53-58.
54. Vusak D., Prugove B., Mili D., Marcove M., and Alogove D.M., Synthesis and crystal structure of solvated complexes of copper (II) with serine and phenanthroline and their solid-state-to-solid-state transformation into one stable solvate. Crystal Growth & Design, 2017. 17(11): p.6049-6061.
55. Sarhan B. M., Neema B. N., Synthesis and Spectroscopic Studies of some Divalent Metall Ion Complexes of 3-(4-hydroxyphenyl)-2-(3-(4-nitrobenzoyl) thioureido) propanoic acid, University of Baghdad,2017,V.14(3).
56. Sarhan B.M., Ibrahem S.S., Kalaf A,Z., synthesis spectral characterization and studies of some divalent metal ion complexes with ligand of [3-(1H-indol-3-yl)-2-(3-(4-methoxy benzoyl) thiouereido)propanoic acid], J.of al-anbar university for pure science , 2018,V.12 ,No.1.
57. Kabbani A.T, Rammadan H., Hammud H.H., Gannoum A.M., Mouneimue Y., Synthesis of some metal complexes of N-[(Benzoyl amino)-thioxomethyl]Amino acid, Journal of the university of chemical technology and metallurgy,2005,40.4,p339-344.
58. Bandekar J.; Genzel L.; Kremer F. and Santo L.;the temeratur-dependence of the far-infrared spectra of L-Alanine; spectrochimica Acta;1983, 3, P357.

59. March J.; Advanced organic chemistry reaction, Mechanisms" Harcourt , Academic press, (2002).
60. London G. M., organic chemistry" 4th Ed oxford university press, Inc; New York (2002).
61. Cary F.; "organic chemistry", 6th Ed; The MCGraw-Hill Compounds ; Inc; New York 2006 ,pp767.
62. Mohammadi K.and Rastegari S. M.;New treatment Schiff bases 2,2-di methyl-1,3 di amino propan and acetylacetone derivatives and their vanadyl complexes, (2012),p337-341.
63. Dyes R.G., Prentice –Hall, Inc., Englewood cliffs, N. J. London; (1996),p299-307.
64. Nicholas D., (1979),6(4),p146.
65. Wanathan G.y., Hussain F.A., Ali M.J., foundamental of organg chemistry, first adition ,unversty of Mostansseria.
66. Fieming,H. and Williams, D.; "spectroscopic methods in organic chemistry " 1st Ed . Mc Graw Hill publishing company lst Ed; London , (2007).
67. Yanga G., and hong W.; (2009), 27(NO:1),p131−136.
68. Alim A., Kudrat M., Science Journal of Chemistry;(2015),39,33-35.
69. Battaglia L. P., Corradi A.B. and Pellacani G.C.,Am J. Chem. Soc ; (1980), 102(8),p2663-2669.
70. Carlin R. and Duynevacldt J., New York ;(1977), p353-357.
71. Mulay I., ((Magnetic Susceptibility)), John Wiley and Sons, New York, Part 1;(1977),4.
72. Geary W.J., Coordination Chemistry Reviews, 1971. 7(1),p81-122.
73. Al-Nahary T. T. Journal of Saudi Chemical Society; (2009),13, p253–257.
74. Silverstein, Bassler R.M.G.C and Movrll T.C;(1981), "Spectroscopic Identification of organic compound", 4th ed,Wiley, NewYork.
75. Socrates, G.; Infrared characteristic group Frequencies" wiley, Newyork, (1981).
76. Nakamoto K;"Infrared spectra of Inorganic and coordination compounds"4th ed. John wiley and sons.NewYork, (1996).

77. Nakamoto K and kleft J;"Infrared spectra of some platinum(II) glycine complexes "J.Inor.Nucl.Chem;(1967), 29, 2561-2567.
78. Al Hashimi S.M., Sarhan B.M and Salman A.W; "Synthesis and characterization of complexes of N-acetyl-Dl Tryptophane with some metal ions Iraq.J.Chem.28,2002, pp 1-11.
79. Jackovitz J.F, Durkin J.A and Lwalter J;"Infrared absorption spectra of meta-amino acid complexes"Spectra Chem.Acta,(1967),23A, p67-80.
80. Dhafir M., Mudhaffar H.A, Dawoods. Al-Ednai and Suma M. Dawood; "Synthesis characterization and Biological activity of some complexes of some new amino acid derivatives N-[(Benzoyl amino)Thioxo methyl]amino acid(HL); Journal of the karean Chemical Sociely;(2010) 54(5)p(506-514).
81. Dyer, R.;Application of absorption spectroscopy of organic compounds" prentice-Hall, Inc; Engl wood cliffs;N. J. London(1965).
82. Heidt L.I, Koster G.F. and Johnson A.M;"Absorption spectrum of manganese(II) di ethylene tri amine complexes"J. Am .Chem .Soc; (1958),80 p 6471.
83. Hanna,W.A. and Moaead M.M;"Synthyesis and characterization and anti microbialo activity of Co(II),Ni(II)and Cu(II) complexes with new asymmetrical Schicff base ligand"Transition metal Chemistry; (2002),7,p140-144.
84. Sarhan B.M., Rumeza R.M and Ali M.A, Ibn Al-Haitham Journal for pureand applicd science; (2015), vol(28) ,NO(1) ,p142-156.
85. Al Hashimi S.M, Sarhan B.M and jarad A.j;"Synthesis and Identification of complexes of N-acetyl glycine with some metal salts", Ibn-Al-Haitham.J.for Pure and App.Sci, (2004), 17(2).
86. Sarhan B.M., and Fyadh B.M., synthesis and spectroscopic studies of some Divalcant metal Ion complexes of [3-(3(2-chloro acetyl thiourido) pyrazine-2-carboxylic acid)], Al-Qadisiyha Journal of pure sciences, 2017,Vol(22),No;2, p10-19.
87. Sarhan B.M.,and Ali M., AL-Qadisyha Journal for sciences; 2014, Vo(19), No;(4),p150-165.

88. Tauber S.C., and Nau R., ((Immunomodulatory Properties of Antibiotics)) ,Current Molecular Pharmacology ;(2008), 1,p68-79.(ch4)
89. Umedum C.U., and Okeke C.J ., Nigerian Journal of Microbiology , (2016),30(2): p3439-3441.
90. Singleton P. Bacteria in Biology, Biotechnology and Medicine (5th ed.). Wiley. (1999). p444–45.
91. Sudbery P., Gow N. and Berman J., The distinct morphogenic states of Candida albicans, TRENDS in Microbiology 2004,Vol.12 No.7,P(317-324).

الخلاصة:-

في هذا البحث تم تحضير وتشخيص مشتقين جديدين للحامض الاميني السيرين مع معقداتهما الفلزية وكما يلي:-

الليكاند الاول (L1) ،(2-(3-اسيتايل ثايويوريدو)-3-هيدروكسي بروبانويك) وتم اعطاءه الرمز(ATP)، حيث تم تحضير هذا المشتق من مفاعلة كلوريد الاسيتايل مع محلول ثايوسيانات الامونيوم في الاسيتون وبعد ذلك تم مفاعلة ناتج المحلول السابق مع محلول السيرين في الاسيتون كمذيب مع التحريك لمدة 6 ساعات .

الليكاند الثاني(L2) (3-هيدروكسي-2-(3-(4-نايتروبنزويل)ثايويوريدو)بروبانويك) وقد تم اعطاءة المختصر(NTP) ، وحضر المشتق الثاني من مفاعلة 4-نايتروبنزويل كلورايد مع محلول ثايوسيانات الامونيوم في الاسيتون ومن ثم مفاعلة ناتج التفاعل السابق مع محلول السيرين في الاسيتون كمذيب مع التحريك لمدة 6 ساعات.

كلا الليكاندين (ATP) و(NTP) تم تشخيصهما بواسطة اطياف الاشعه تحت الحمراء(FT-IR) ، اشعة الرنين النووي المغناطيس (^{13}C-NMR و^{1}H)، التحليل الدقيق للعناصر (C.H.N.S) والاطياف الالكترونية (UV-Vis).ومن تلك النتائج تم استنتاج الصيغ الكيميائية للمركبين وكما يلي:-

$C_6H_{10}N_2O_4S$ = (ATP)

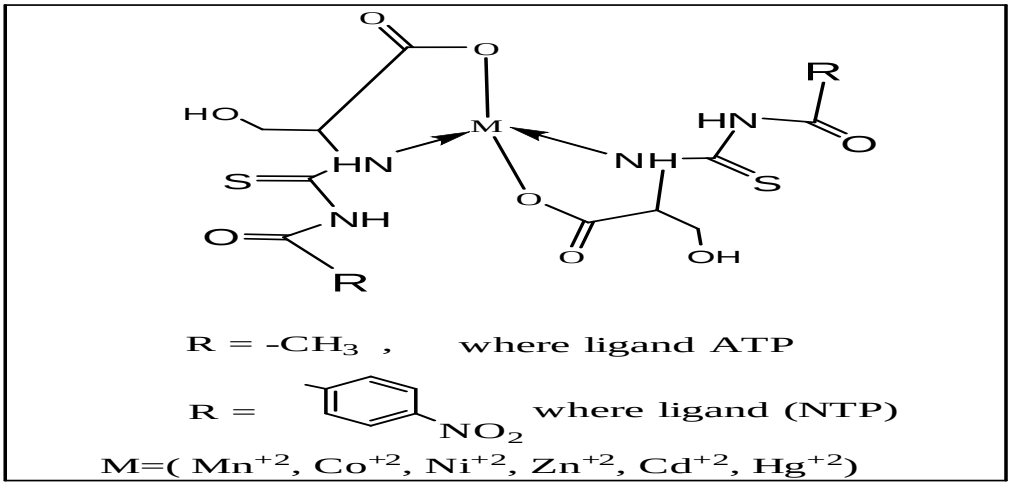
$C_{11}H_{11}N_3O_6S$= (NTP)

كما تم مفاعلة الليكاندين مع عدد من ايونات الاملاح الفلزية مثل (VO^{+2},Mn^{+2},Co^{+2},Ni^{+2}) (Cu^{+2},Zn^{+2},Cd^{+2},Hg^{+2},) لتحضير عدد من المعقدات والتي شخصت بواسطة قياس الذوبانية، درجات الانصهار والتفكك ، اطياف الاشعه تحت الحمراء، الاطياف الالكترونية، التوصيلية المولارية، الحساسية المغناطيسية، والتحليل الدقيق للعناصر(C.H.N.S) لبعض المعقدات.

ومن خلال نتائج تلك القياسات تم استنتاج الشكل رباعي السطوح لكل من معقدات الايونات (Mn^{+2},$Co^{+}2$,Ni^{+2},Zn^{+2},Cd^{+2},Hg^{+2}))

بينما معقدات ايون النحاس (Cu^{+2}) فاخذت شكل المربع المستوي، وشكل الهرم مربع القاعده لمعقدات ايون الفناديل(VO^{+2}).

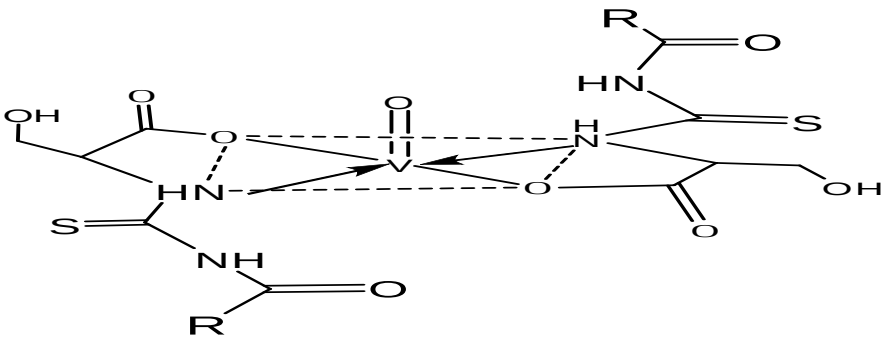
كما تم دراسة الفعالية البايولوجية لكلا الليكاندين مع معقداتهما مع نوعين من البكتريا (***Staphylococcus aurea***) و(***Escherichia coli***) ونوع واحد من الفطريات(***Candida albicance***) وقد اعطت المركبات نتائج مختلفة في تثبيط نموها.



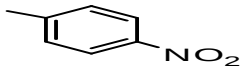
$R = -CH_3$, where ligand ATP

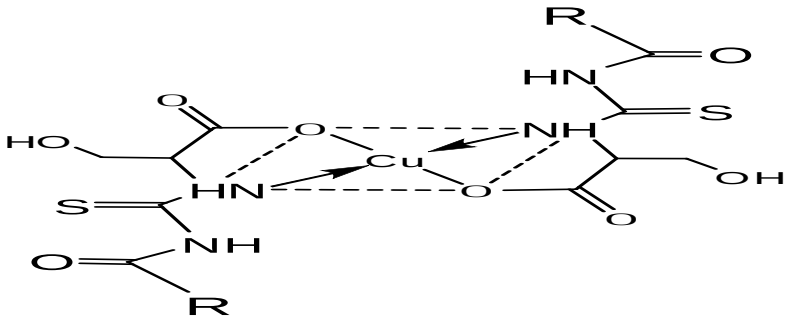
R = where ligand (NTP)

M=(Mn^{+2}, Co^{+2}, Ni^{+2}, Zn^{+2}, Cd^{+2}, Hg^{+2})

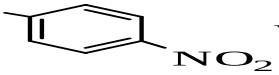


$R= -CH_3$, where ligand (ATP)

R =  where ligand (NTP)



$R = -CH_3$, where ligand (ATP)

R=  where ligand (NTP)

مخطط : التراكيب الكيميائية للمعقدات

جمهورية العراق
وزارة التعليم العالي والبحث العلمي
جامعة بغداد
كلية التربية للعلوم الصرفة (ابن الهيثم)
قسم الكيمياء

تحضير وتشخيص بعض مشتقات الاحماض الامينية الجديدة مع بعض الايونات الفلزية ودراسة فعاليتها الحياتية

رسالة مقدمة الى

مجلس كلية التربية للعلوم الصرفة ابن الهيثم/ جامعة بغداد
وهي جزء من متطلبات نيل درجة الماجستير في الكيمياء اللاعضوية

من قبل

عباس محمد عباس الساعدي

بكلوريوس علوم كيمياء(٢٠٠٣) كلية التربية للعلوم الصرفه-ابن الهيثم

باشراف

أ.د باسمه محسن سرحان

١٤٤١ هـ **٢٠١٩ م**