Synthesis and Characterization Mixed Ligands of Phenylalanine and Tributylphosphine Complexes with Selected Metal Ions.

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Abstract

Complexes of Co(II),Ni(II),Cu(II) and Zn(II) with mixed ligands of phenylalanine (L) and tributylphosphine (TBPh) were prepared in aqueous ethanol with (١:٢:٢) (M:L:TBPh). The prepared complexes were characterized using flame atomic absorption,(C.H.N)Analysis, FT.IR and UV-Vis spectroscopic methods as well as magnetic susceptibility and conductivity measurements. In addition biological activity of the phenylalanine and complexes against two selected type of bacteria were also examined. Some of the complexes exhibit good bacterial activities. From the obtained data the octahedral structure was suggested for all prepared complexes.
Keywords: - Mixed ligand complexes, phenylalanine, spectroscopy studies.

Introduction

Metal ion mediated reactions involving nucleic acid constituents and amino acid side chains have been the subject of several investigations[1-4].These reactions provide an opportunity to identify the nature of such interactions in vivo as they serve as models for many metalloenzme reactions[5].The transition metal ions have apical property of forming coordination compounds. The complexes formed by amino acid ligands provide, the metal ions active form biological processes[6].Interactions of amino acids with metal or metal oxide surfaces are often studies as models for biomaterials formed by the adsorption of large biological molecules[7-9].Since ternary complexes of the amino acids are often more relevant models for various biological systems than the binary ones, numerous studies have been performed during the past two years[10-13].The present paper reports the synthesis and characterization of new Co(II),Ni(II),Cu(II) and Zn(II) complexes with mixed ligands of phenylalanine and tributylphosphine.

Experimental

Instrumentation

UV-Vis spectra were recorded on a (Shimadzu UV-١٦٠ A) Ultra Violet-Visble Spectrophotometer. I.R-spectra were taken on a (Shimadzu, FTIR-٨٤٠٠

S) Fourier Transform Infrared. Spectrophotometer (٤٠٠٠-٤٠٠) cm^{-1} with samples prepared as KBr discs.Atomic Absorption was obtained by using a (Shimadzu A.A-١٦٠A) Atomic Absorption / Flame Emission Spectrophotometer. Microelemental analysis (C.H.N) was performed in AL-al-Bayt University, Jordan by using (Euro Vector EA ٣٠٠٠ A Elemental Analyser). Conductivities were measured for ١٠$^{-٣}$M of complexes in DMF at ٢٥$^{°}$C by using (Philips PW- Digital Conductimeter). Magnetic susceptibilities were performed by using (Brucker Magnet B.M.٦) instrument at ٢٥$^{°}$C. In addition, melting points were obtained by using (Melting Point Apparatus).

Materials

The following chemicals were used as received from suppliers; cobaltous chloride hexahydrate ٩٨,٨٪, nickel chloride hexahydrate ٩٩,٩٪, copper chloride dihydrate ٩٨٪, zinc chloride ٩٨,٨٪ (Merck), phenylalanine and tributylphosphine (B.D.H).

Study of Biological Activity

Tow selected type of bacteria were used includes, Escherichia Coli (E.Coli) as Gram Negative Bacteria and Staphylococcus Aurous (Staph.Aurous) as Gram Positive Bacteria in Nutrient Agar medium, using (DMSO) as a solvent and a control, the concentration of the compounds in this exposure was (١٠$^{-٣}$ M) by using disc sensitivity test. This method involves the exposure of the zone inhibition toward the diffusion of micro-organism on agar plate. The plates were incubated for ٢٤hr.at ٣٧^{O}C.

Preparation of Metal Complexes (general procedure)

An aqueous solution of the metal salts containing ٠,٣٦٠g, ٠,٣٦٠g, ٠,٢٥٨g and ٠,٢٠٦g (١mmole) of CoCl$_٢$.٦H$_٢$O, NiCl$_٢$.٦H$_٢$O, CuCl$_٢$.٢H$_٢$O and ZnCl$_٢$ respectively was added gradually with stirring to ethanolic KOH solution (٠,٥g,٢mmol) of phenylalanine(L). (٠,٥ml,٢mmole) of tributylphosphine (TBPh) was added to the mixture in each case by using stichiometric amount (١:٢:٢) Metal:L:TBPh molar ratio. The mixture was refluxed with constant stirring for an hour. The mixture was cooled at room temperature dark precipitate was formed, filtered and recrystillized from ethanol.

Results and Discussion

The solid complexes were prepared by reaction of alcoholic solution of the ligand with the aqueous solution of the metal ions and tributylphosphine in a (M:L:TBPh) of (١:٢:٢). The (C.H.N) analysis with metal contents of these complexes were in good agreements with the calculated values (Table-١) includes the physical properties and elemental analysis. The molar conductance of the complexes as (١٠$^{-٣}$ M) in DMF indicating their non- electrolytic nature[١٤], the data were recorded in (Table- ٢).

The effective magnetic moments (Table-٢) of the complexes lie in the range (١,٨٣-٤,٦٧) B.M. This value refers to a paramagnetic (high spin) which has been reported for most octahedral geometry. In case of Zn(II) complex because of filled-d orbital, therefore the magnetic moment (μ=٠) is diamagnetic[١٥].

The UV-Vis spectra data for the free ligands and all metal complexes are listed in (Table-٢). The UV-Vis spectrum of the ligand (L) (Fig-١) spectrum of the shows two peaks at ٢٥٠ nm and ٣٤٠ nm assigned to (π − π*) and (n − π*) electronic transitions[١٦,١٧]. The electronic spectrum of Co(II) complex (Fig-٢) showed peak at ٢٧٢ nm due to charge transfer. Other three peaks at ٦١٣ nm, ٦٧٨ nm and ٨٠٢ nm were found to be caused by (d-d) electronic transition type $^{٤}T_{١g(F)} \rightarrow {}^{٤}T_{١g(P)}$, $^{٤}T_{١g(F)} \rightarrow {}^{٤}A_{٢g(F)}$ and $^{٤}T_{١g(F)} \rightarrow {}^{٤}T_{٢g(F)}$ respectively[١٨]. The spectrum of Ni(II) complex (Fig-٣) appeared absorption peak at ٢٦٨ nm was related to charge transfer, then other three peaks at ٤٢١ nm, ٦١١ nm and ٧٩٥ nm were assigned to electronic transition type $^{٣}A_{٢g(F)} \rightarrow {}^{٣}T_{١g(P)}$, $^{٣}A_{٢g(F)} \rightarrow {}^{٣}T_{١g(F)}$ and $^{٣}A_{٢g(F)} \rightarrow {}^{٣}T_{٢g(F)}$ respectively[١٩]. The spectrum of Cu(II) complex gave absorption peak at ٢٨٣ nm due to charge transfer. The peak at ٥٤٧ nm was caused by electronic transition[٢٠] $^{٢}E_{g} \rightarrow {}^{٢}T_{٢g}$. The spectrum of Zn(II) complex showed absorption peak at ٢٧٣ nm due to charge transfer. The absence of absorption peaks in the visible region indicated no (d-d) electronic transition happened; this is a good result for octahedral complex [٢١].

In order to study the binding mode of the ligand (phenylalanine) with the metal ions, a comparison was made for the FT.IR spectra of the free ligand and those of the prepared complexes and the data was tabulated in (Table-٣). The IR spectrum of the ligand (L) (Fig-٤) exhibited bands at ٣٢٨٦ cm⁻¹ and ٣١١٠ cm⁻¹ were assigned to ν(NH₂) stretching frequency[٢٢,٢٣], on complexation a shifting with change in shape were observed from these bands, while increasing in intensity were noticed. The significant may be a result of coordination with metal ion (Fig-٥). The bands at ١٦٩٣ cm⁻¹ and ١٦٠٠ cm⁻¹ in the ligand spectrum ascribed to νas(COO) and νs(COO), suffered a great change to lower frequency were also observed on complexation (Fig-٦) with metal ion[٢٤,٢٥]. The new bands observed at (٥٧٦-٤٣٠) cm⁻¹ are tentatively assigned to ν(M-N),ν(M-O) and ν(M-P) (Metal-Ligands) stretching bands[٢٦-٢٨].

According to the results obtained and spectral analysis an octahedral structure has been suggested to these complexes.

$M = Co^{+2}, Ni^{+2}, Cu^{+2}, Zn^{+2}$
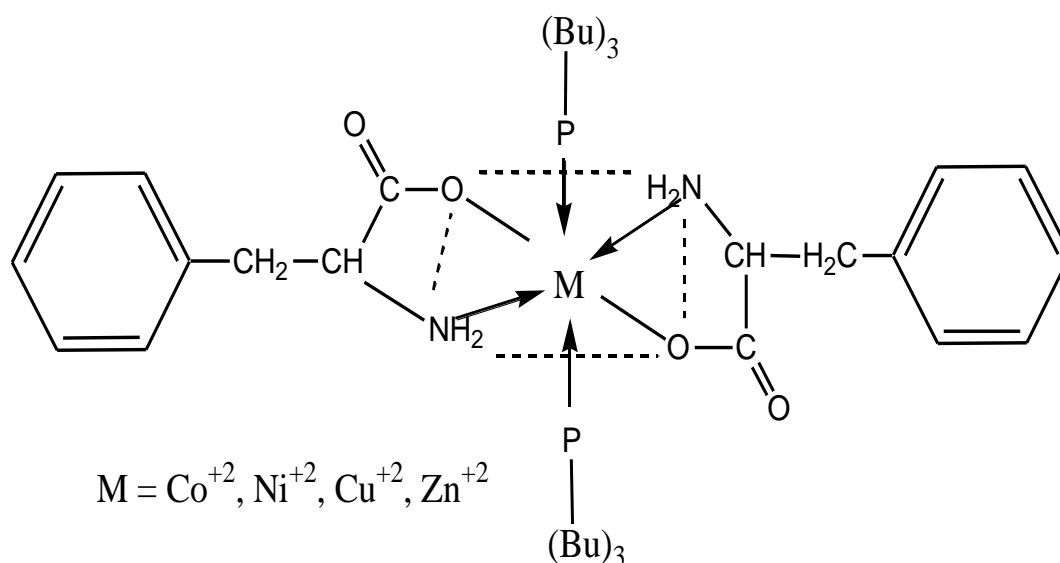
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Table(١):- Physical Properties and Elemental Analysis of the Ligand and It's Complexes.

Compounds	Color	M.P°C	Yield %	Analysis Calc (Found)			
				M%	C%	H%	N%
Ligand(L)	White	٢٦٧	-	-	-	-	-
[Co(L)٢(TBPh)٢]	Pale rose	٢٩٤	٧٧	٧,٤٥ (٧,١١)	٦٣,٧١ (٦٣,٢٣)	٩,٣٥ (٨,٩٣)	٣,٥٣ (٢,٨٨)
[Ni(L)٢(TBPh)٢]	Pale green	٣١٠	٨٥	٧,٣٤ (٦,٨٨)	٦٣,٧٩ (٦٢,٩٤)	٩,٣٦ (٩,٠٥)	٣,٥٤ (٢,٩١)
[Cu(L)٢(TBPh)٢]	Pale blue	٢٩٨	٨٣	٨,٠٤ (٧,٥٧)	٦٣,٣١ (٦٢,٨٦)	٩,٢٩ (٨,٩٨)	٣,٥١ (٢,٨٤)
[Zn(L)٢(TBPh)٢]	White	٢٨٥	٧١	٨,١٥ (٧,٦٦)	٦٣,٢٣ (٦٣,٠٢)	٩,٢٨ (٨,٧٨)	٣,٥١ (٢,٦٩)

Table(٢):- UV-Vis, Magnetic Suscepibility and Conductance Measurements Data.

Compounds	λ_{max} (nm)	ABS	Wave number (cm^{-1})	ϵ_{max} (L.mol^{-1}.cm^{-1})	Λ_m (S.cm^2.mol^{-1}) in DMF(10^{-3}M)	μ_{eff} (B.M)
Ligand(L)	٢٥٠	١,٩٣١	٤٠٠٠٠	١٩٣١	-	-
	٢٩١	١,٤٧٤	٣٤٣٦٤	١٤٧٤		
[Co(L)٢(TBPh)٢]	٢٧٢	١,٧٩٨	٣٦٧٦٤	١٧٩٨	٥٥,٣٧	٤.٦٧
	٦١٣	٠,١٧٧	١٦٣١٣	١٧٧		
	٦٧٨	٠,٢٥٣	١٤٧٤٩	٢٥٣		
	٨٠٢	٠,٠٠٥	١٢٤٦٨	٥		
[Ni(L)٢(TBPh)٢]	٢٦٨	١,٣٩٠	٣٧٣١٣	١٣٩٠	٢٦,٦٨	٣,٠٨
	٤٢١	٠,٣٧٨	٢٣٧٥٢	٣٧٨		
	٦١١	٠,١٠٢	١٦٣٦٦	١٠٢		
	٧٩٥	٠,٠٦١	٢٥٧٨	٦١		
[Cu(L)٢(TBPh)٢]	٢٨٣	١,٤٧٢	٣٥٣٣٥	١٤٧٢	٣٠,٤٨	١,٨٣
	٤٧٥	٠,٥٣٨	٢١٠٥٢	٥٣٨		
[Zn(L)٢(TBPh)٢]	٢٧٣	١,٩٢٥	٣٦٦٣٠	١٩٢٥	١٩,٥٣	Dia

Table(٣):- The Main Frequencies of the Ligands and It's Complexes(cm^{-1}).

Compounds	$\upsilon(NH_2)$	$\upsilon_{as}(COO)$	$\upsilon_s(COO)$	$\upsilon(M-N)$	$\upsilon(M-O)$	$\upsilon(M-P)$
Ligand(L)	٣٢٨٦ sh. ٣١١٠ sho.	١٦٩٣ s.	١٦٠٠ s.	-	-	-
[Co(L)٢(TBPh)٢]	٣٣٧٣ s. ٣١٤٧ s.	١٦٢٠ s.	١٥٨٥ sho.	٥٥٧ w.	٤٨٦ w.	٤٣٠ w.
[Ni(L)٢(TBPh)٢]	٣٣٥٦ sh. ٣٢٩٨ sho.	١٦٣٥ s.	١٥٩٠ sho.	٥٧٦ w.	٥٤٧ w.	٤٨٠ w.
[Cu(L)٢(TBPh)٢]	٣٣٢٨ sh. ٣٢٢٣ sh.	١٦٨١ sh.	١٥٨٣ s.	٥٢٤ w.	٤٧٨ w.	٤٤٧ w.
[Zn(L)٢(TBPh)٢]	٣٣٣٤ sh. ٣٢٥٥ sh.	١٦٢٢ s.	١٥٦٠ sho.	٥٦٩ w.	٥٥٧ w.	٤٧٠ w.

sh =sharp, sho=shoulder, s = strong, w =weak, as = asymmetric, s = symmetric

Table(٤):- Diameters (mm) of Deactivation of Bacteria for the Phenylalanine and It's Complexes.

Compounds	Staphylococcus Aurous	Escherichia Coli
Ligand(L)	++	+
[Co(L)٢(TBPh)٢]	+	-
[Ni(L)٢(TBPh)٢]	+++	++
[Cu(L)٢(TBPh)٢]	+	+++
[Zn(L)٢(TBPh)٢]	-	+

(-) = No inhibition.

(+) =Inhibition diameter (٦-٨) mm.

(++) =Inhibition diameter (٨-١٠) mm.

(+++) =Inhibition diameter (١٠-٢٠) mm.
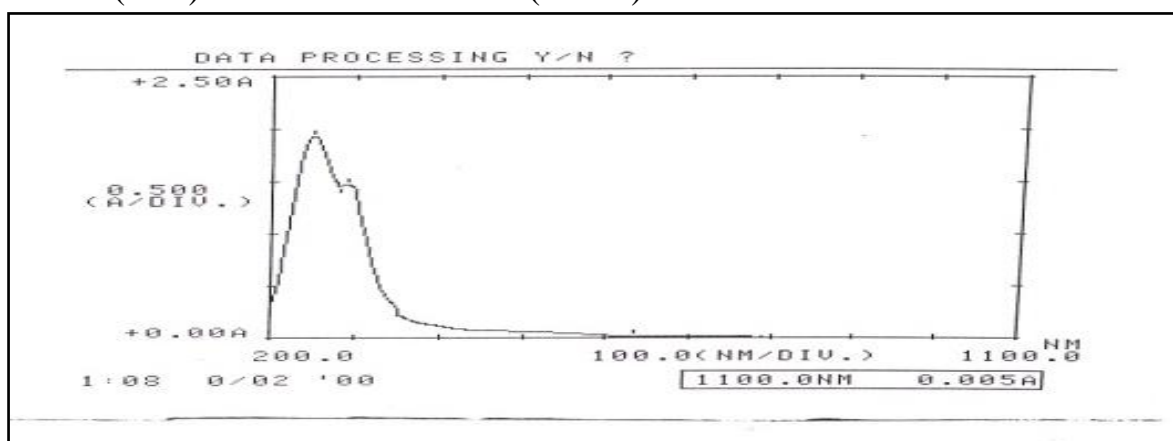
Fig.(١):- UV-Vis Spectrum of the Ligand.
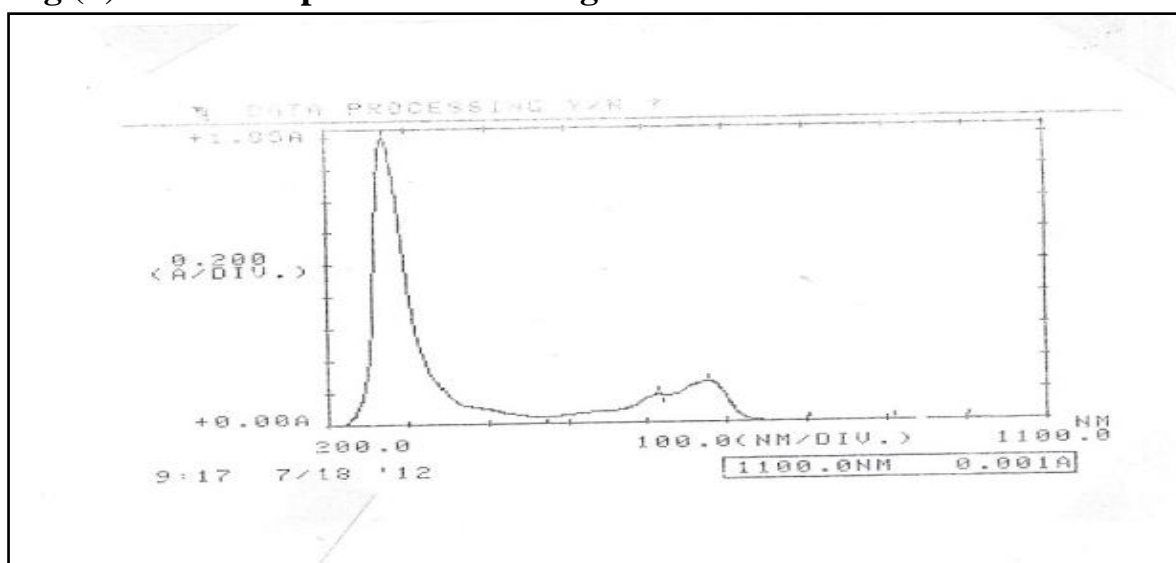
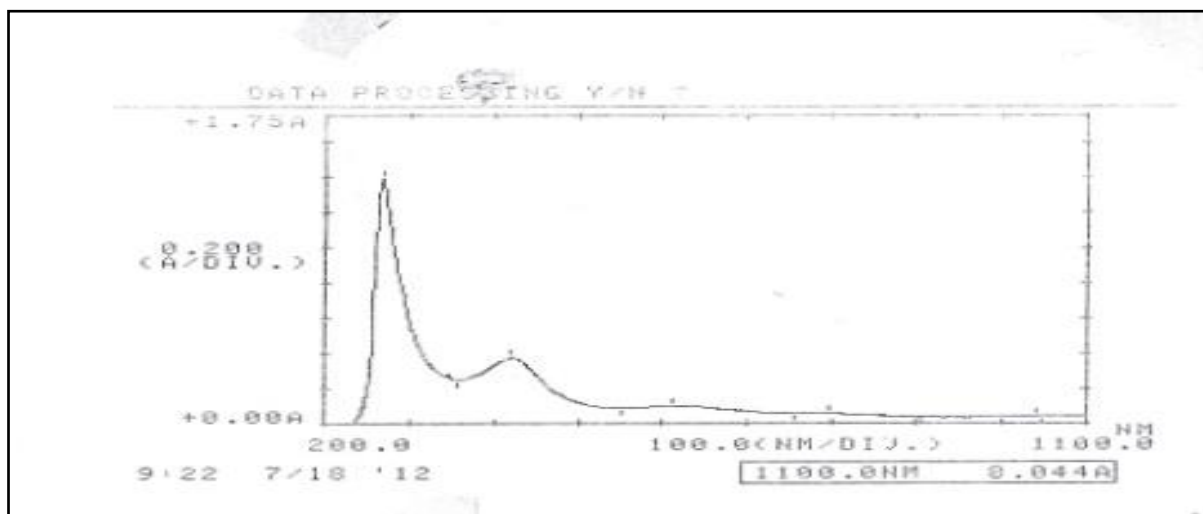**Fig.(٢):- UV-Vis Spectrum of the [Co(L)٢(TBPh)٢] Complex.**

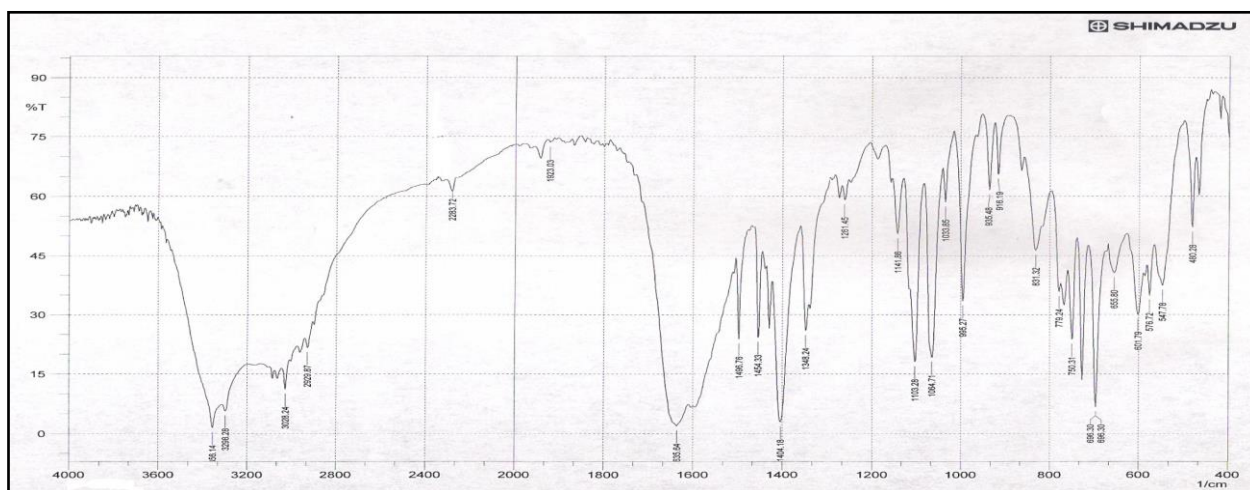**Fig.(٣):- UV-Vis Spectrum of the [Ni(L)٢(TBPh)٢] Complex.**

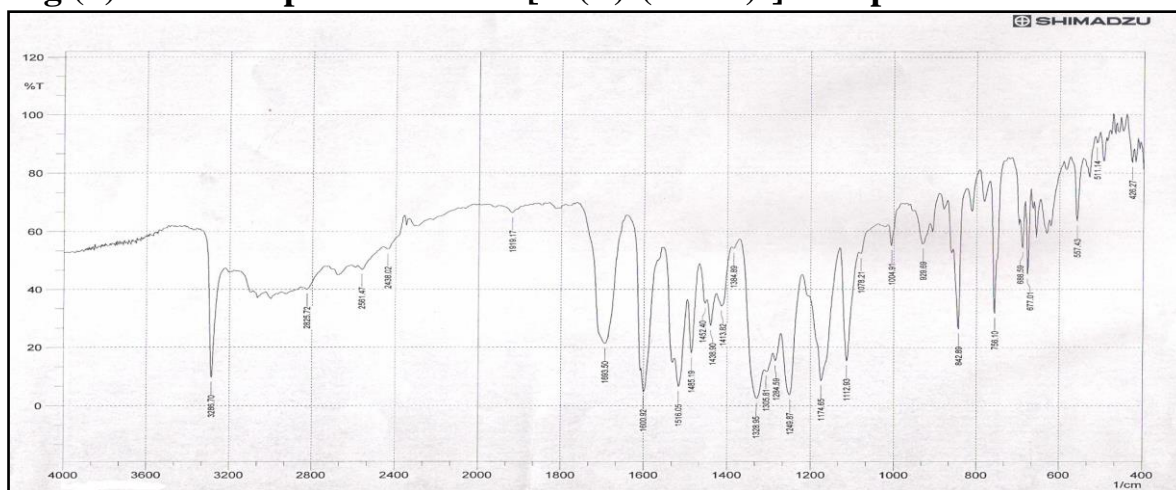**Fig.(٤):- FT-IR Spectrum of the [Ni(L)٢(TBPh)٢] Complex.**

Fig.(٥):- FT-IR Spectrum of the [Zn(L)٢(TBPh)٢] Complex.

تحضير وتشخيص معقدات مختلطة الليكاند للفنيل النين وثلاثي بيوتيل الفوسفين مع ايونات بعض العناصر الفلزية المنتخبة.

عامر جبار جراد

قسم الكيمياء – كلية التربية(ابن الهيثم)– جامعة بغداد

الخلاصة

تم الحصول على معقدات جديدة وذلك من خلال مفاعلة ابونات Co(II),Ni(II),Cu(II) and Zn(II) مع الليكاندات المختلطة للفنيل النين وثلاثي بيوتيل الفوسفين وبنسبة مولية (١:٢:٢) فلز :ليكاند: ثلاثي بيوتيل الفوسفين. شخصت المعفدات المحضرة بوساطة التحليل الدقيق للعناصر(C.H.N)؛ تقنية الإمتصاص الذري اللهبي واطياف الأشعة تحت الحمراء وفوق البنفسجية – المرئية، فضلا عن قياسات الحساسية المغناطيسية والتوصيلية الكهربائية. لقد تمت الإفادة من الليكاندات والمعقدات قيد الدراسة حول إمكانية دراسة الفاعلية البايولوجية ووجد أن لهذه المعقدات قابلية متباينة على قتل الأنواع المنتخبة من البكتريا.ومن النتائج المحصول عليها تم اقتراح الشكل ثماني السطوح للمعقدات المحضرة.