Synthesis and Characterization Mixed Ligands of Phenylalanine and Tributylphosphine Complexes with Zn(II),Cd(II) and Hg(II) Ions.

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Abstract

Complexes of Zn(II),Cd(II) and Hg(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 conductivity measurements. From the obtained data the octahedral structure was suggested for all prepared complexes.

Introduction

Metal ion mediated reactions involving nucleic acid constituents and amino acid side chains have been the subject of several investigations[١-٤].These reactions provide an opportunity to identify the nature of such interactions in vivo as they serve as models for many metalloenzme reactions[٥].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[٦].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[٧-٩].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[١٠-١٣].The present paper reports the synthesis and characterization of new Zn(II), Cd(II) and Hg(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) $cm^{-١}$ 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).. In addition, melting points were obtained by using (Melting Point Apparatus).

Materials

The following chemicals were used as received from suppliers; zinc chloride ٩٨,٨٪, cadmium chloride monohydrate ٩٩,٩٪ and mercury chloride ٩٨٪ (Merck), phenylalanine and tributylphosphine (B.D.H).

Preparation of Metal Complexes (general procedure)

An aqueous solution of the metal salts containing ٠,٢٠٦g٠, ٠,٣٠٥g and ٠,٤١١g (١mmole) of $ZnCl_٢$, $CdCl_٢.H_٢O$ and $HgCl_٢$ respectively was added gradually with stirring to ethanolic KOH solution (٠,٥g,٢mmol) of phenyl alanine(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

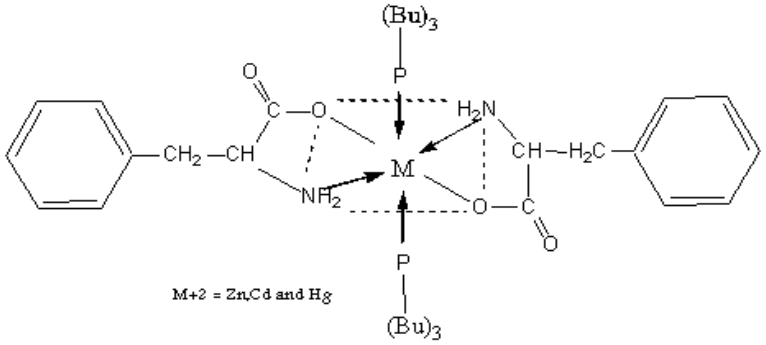
The solid complexes were prepared by reaction of alcoholic solution of the ligand with the aqueous solution of the metal ions and tributylphosphine in a (M:L:TBPh) of (١:٢:٢). The (C.H.N) analysis with metal contents of these complexes were in good agreements with the calculated values (Table-١) includes 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 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 ($\pi - \pi^*$) and ($n - \pi^*$) electronic transitions[١٦,١٧]. The spectra of Zn(II),Cd(II) and Hg(II) complexes showed absorption peaks at ٢٧٣ nm,٢٦٨ nm and ٢٦٦ nm respectively 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 complexes[١٨].

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-٣) exhibited bands at ٣٢٨٦ $cm^{-١}$ and ٣١١٠ $cm^{-١}$ were assigned to $\nu(NH_٢)$ stretching frequency[١٩,٢٠], 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-٤). The bands at ١٦٩٣ cm^{-1} and ١٦٠٠ cm^{-1} in the ligand spectrum ascribed to ν_{as}(COO) and ν_{s}(COO), suffered a great change to lower frequency were also observed on complexation with metal ion[٢١,٢٢]. The new bands observed at (٦١٠-٤٦٨) cm^{-1} are tentatively assigned to ν(M-N),ν(M-O) and ν(M-P) (Metal-Ligands) stretching bands[٢٣-٢٥].

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



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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	-	-	-	-	-
[Zn(L)٢(TBPh)٢]	White	٢٧٣	٧١	٨,١٥ (٧,٦٦)	٦٣,٢٣ (٦٣,٠٢)	٩,٢٨ (٨,٧٨)	٣,٥١ (٢,٦٩)
[Cd(L)٢(TBPh)٢]	White	٢٨٢	٦٦	١٣,٢٧ (١٢,٣٦)	٧٩,٧١ (٧٨,٨٤)	٨,٧٦ (٧,٨٨)	٣,٣١ (٢,٧٣)
[Hg(L)٢(TBPh)٢]	White	٢٧٧	٦٢	٢١,٥٤ (٢٠,٦٣)	٥٤,٠١ (٥٣,٨٧)	٧,٩٣ ٧,٠٣	٣,٠٠ (٢,٥٩)

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

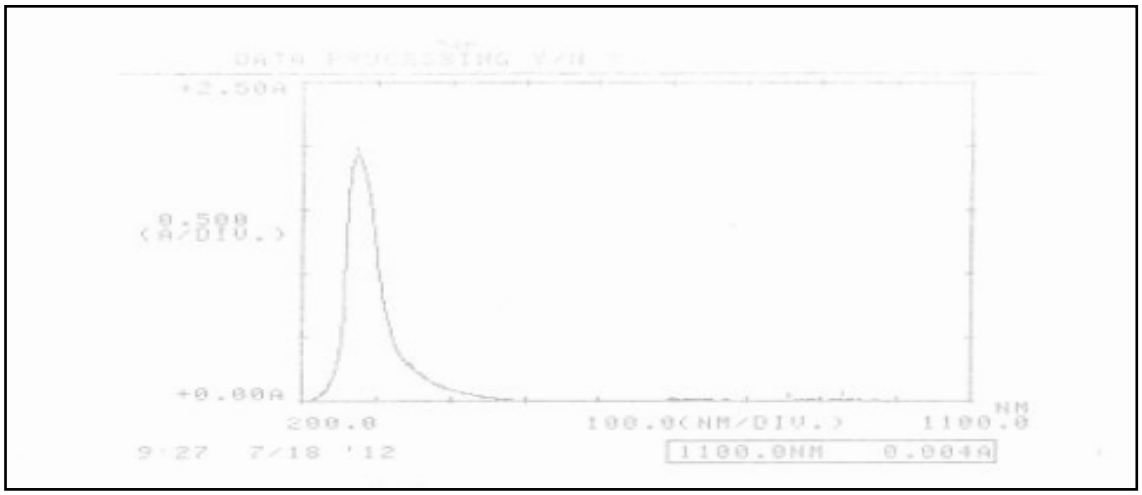
Compounds	**λ_{max} (nm)**	**ABS**	**Wave number (cm^{-1})**	**ϵ_{max} ($L.mol^{-1}.cm^{-1}$)**	**Λ_m ($S.cm^2.mol^{-1}$) in DMF($10^{-3}M$)**
Ligand(L)	٢٥٠ ٢٩١	١,٩٣١ ١,٤٧٤	٤٠٠٠٠ ٣٤٣٦٤	١٩٣١ ١٤٧٤	-
[Zn(L)٢(TBPh)٢]	٢٧٣	١,٩٢٥	٣٦٦٣٠	١٩٢٥	١٩,٥٣
[Cd(L)٢(TBPh)٢]	٢٦٨	١,٢٦٩		١٢٦٩	٩,٢٢
[Hg(L)٢(TBPh)٢]	٢٦٦	١,٠٦٨		١٠٦٨	١٥,٣٨

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

Compounds	**υ(NH٢)**	**υ_{as}(COO)**	**υ_{s}(COO**	**υ(M-N)**	**υ(M-O)**	**υ(M-P)**
Ligand(L)	٣٢٨٦ sh. ٣١١٠ sho.	١٦٩٣ s.	١٦٠٠ s.	-	-	-
[Zn(L)٢(TBPh)٢]	٣٣٣٤ sh. ٣٢٥٥ sh.	١٦٢٢ s.	١٥٦٠ sho.	٥٦٩ w.	٥٥٧ w.	٤٧٠ w.
[Zn(L)٢(TBPh)٢]	٣٣٤٤ sh. ٣٢٦١ sh.	١٥٩١s.	١٥٦٠ sho.	٥٧٩ w.	٥٤٥ w.	٤٦٨ w.
[Zn(L)٢(TBPh)٢]	٣٣٢٩ sh. ٣٢٧٠ sh.	١٦٢٤ s.	١٥٥٨ s.	٦١٠ w.	٥٢٤ w.	٤٦٨ w.

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

Fig.(١):- UV-Vis Spectrum of the Ligand.



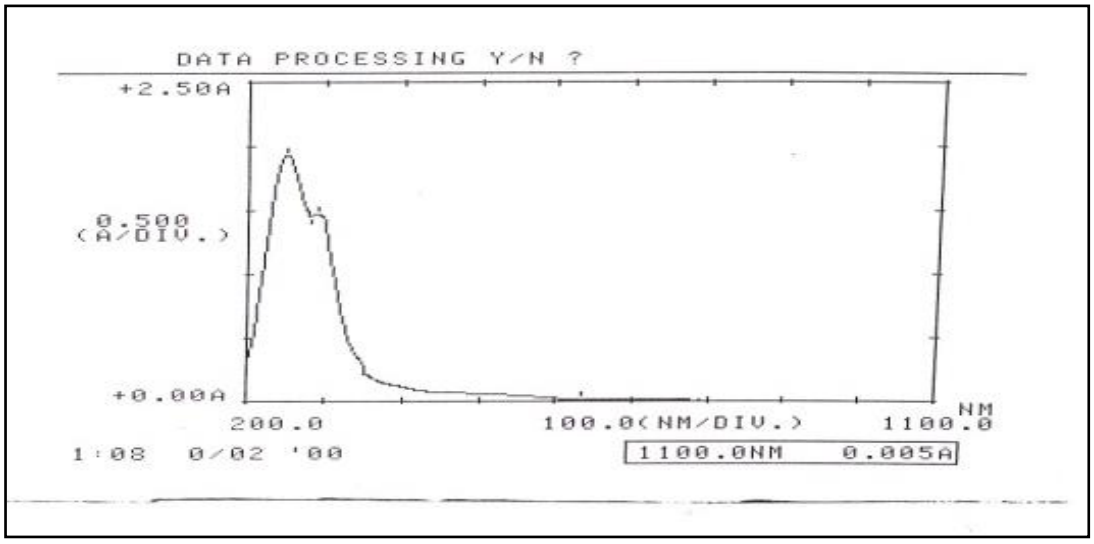


Fig.(٢):- UV-Vis Spectrum of the $[Zn(L)_2T(BPh)_2]$ Complex.

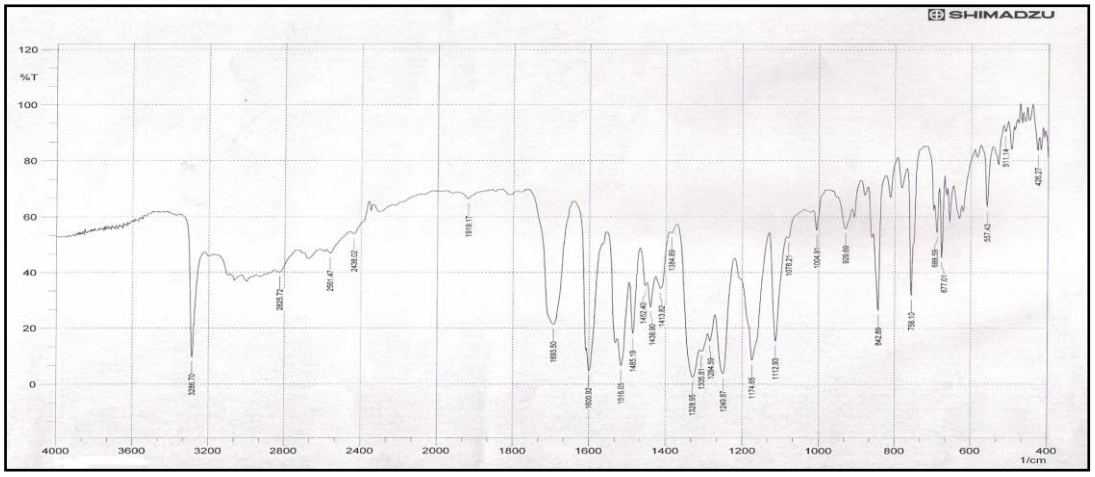
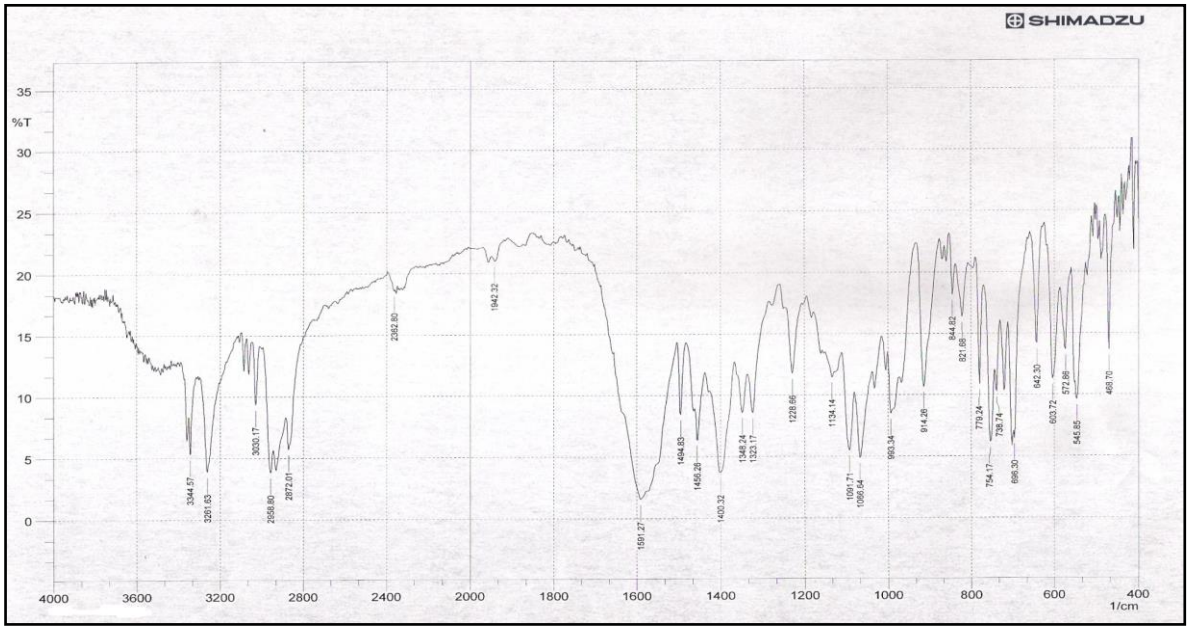


Fig.(٣):- FT-IR Spectrum of the Ligand.



Fig(٤):- FT-IR Spectrum of the $[Cd(L)_2T(BPh)_2]$ Complex.

تحضير وتشخيص معقدات مختلطة الليكاند للفنيل النين وثلاثي بيوتيل الفوسفين مع ايونات الزنك والكادميوم والزئبق الثنائية الشحنة.

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الخلاصة

تم الحصول على معقدات جديدة وذلك من خلال مفاعلة ابونات الزنك والكادميوم والزئبق الثنائية الشحنة مع الليكاندات المختلطة للفنيل النين وثلاثي بيوتيل الفوسفين وبنسبة مولية (١:٢:٢) فلز:ليكاند: ثلاثي بيوتيل الفوسفين. شخصت المعقدات المحضرة بوساطة التحليل الدقيق للعناصر(C.H.N)؛ تقنية الإمتصاص الذري اللهبي واطياف الأشعة تحت الحمراء وفوق البنفسجية - المرئية، فضلا عن قياسات التوصيلية الكهربائية. ومن النتائج المحصول عليها تم اقتراح الشكل ثماني السطوح للمعقدات المحضرة.