

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 (1:2:2) (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 metalloenzyme 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 studied 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-160 A) Ultra Violet-Visible Spectrophotometer. IR-spectra were taken on a (Shimadzu, FTIR-8400

S) Fourier Transform Infrared. Spectrophotometer ($4000-400$) cm^{-1} with samples prepared as KBr discs. Atomic Absorption was obtained by using a (Shimadzu A.A-160A) Atomic Absorption / Flame Emission Spectrophotometer. Microelemental analysis (C.H.N) was performed in AL-al- Bayt University, Jordan by using (Euro Vector EA 3000 A Elemental Analyser). Conductivities were measured for 10^{-3}M of complexes in DMF at 25°C by using (Philips PW-Digital Conductimeter). Magnetic susceptibilities were performed by using (Bruker Magnet B.M.6) instrument at 25°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 98.8%, nickel chloride hexahydrate 99.9%, copper chloride dihydrate 98%, zinc chloride 98.8% (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 (10^{-3}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 24hr. at 37°C .

Preparation of Metal Complexes (general procedure)

An aqueous solution of the metal salts containing 0.360g, 0.360g, 0.258g and 0.206g (1mmole) of $\text{CoCl}_2.6\text{H}_2\text{O}$, $\text{NiCl}_2.6\text{H}_2\text{O}$, $\text{CuCl}_2.2\text{H}_2\text{O}$ and ZnCl_2 respectively was added gradually with stirring to ethanolic KOH solution (0.5g, 2mmol) of phenylalanine(L). (0.5ml, 2mmole) of tributylphosphine (TBPh) was added to the mixture in each case by using stichiometric amount (1:2:2) 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

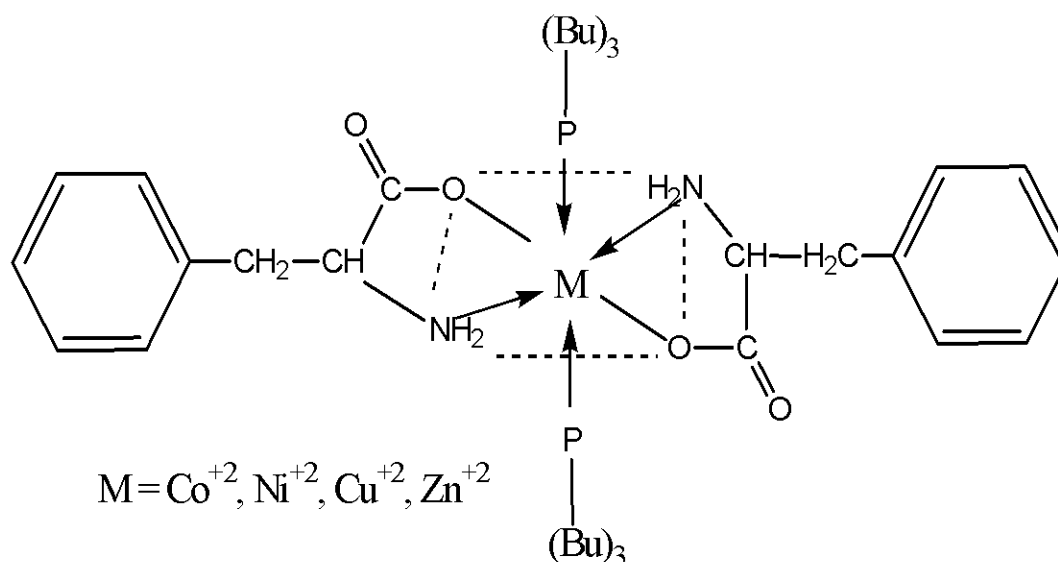
The solid complexes were prepared by reaction of alcoholic solution of the ligand with the aqueous solution of the metal ions and tributylphosphine in a (M:L:TBPh) of (1:2:2). The (C.H.N) analysis with metal contents of these complexes were in good agreements with the calculated values (Table-1) includes the physical properties and elemental analysis. The molar conductance of the complexes as (10^{-3}M) in DMF indicating their non- electrolytic nature⁽¹⁴⁾, the data were recorded in (Table- 2).

The effective magnetic moments (Table-2) of the complexes lie in the range (1.83-4.67) 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 ($\mu=0$) is diamagnetic⁽¹⁵⁾.

The UV-Vis spectra data for the free ligands and all metal complexes are listed in (Table-2). The UV-Vis spectrum of the ligand (L) (Fig-1) spectrum of the shows two peaks at 250 nm and 340 nm assigned to ($\pi - \pi^*$) and ($n - \pi^*$) electronic transitions^(16,17). The electronic spectrum of Co(II) complex (Fig-2) showed peak at 272 nm due to charge transfer. Other three peaks at 613 nm, 678 nm and 802 nm were found to be caused by (d-d) electronic transition type ${}^4T_{1g(F)} \rightarrow {}^4T_{1g(P)}$, ${}^4T_{1g(F)} \rightarrow {}^4A_{2g(F)}$ and ${}^4T_{1g(F)} \rightarrow {}^4T_{2g(F)}$ respectively⁽¹⁸⁾. The spectrum of Ni(II) complex (Fig-3) appeared absorption peak at 268 nm was related to charge transfer, then other three peaks at 421 nm, 611 nm and 795 nm were assigned to electronic transition type ${}^3A_{2g(F)} \rightarrow {}^3T_{1g(P)}$, ${}^3A_{2g(F)} \rightarrow {}^3T_{1g(F)}$ and ${}^3A_{2g(F)} \rightarrow {}^3T_{2g(F)}$ respectively⁽¹⁹⁾. The spectrum of Cu(II) complex gave absorption peak at 283 nm due to charge transfer. The peak at 547 nm was caused by electronic transition⁽²⁰⁾ ${}^2E_g \rightarrow {}^2T_{2g}$. The spectrum of Zn(II) complex showed absorption peak at 273 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⁽²¹⁾.

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-3). The IR spectrum of the ligand (L) (Fig-4) exhibited bands at 3286 cm^{-1} and 3110 cm^{-1} were assigned to $\nu(\text{NH}_2)$ stretching frequency^(22,23), 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-5). The bands at 1693 cm^{-1} and 1600 cm^{-1} in the ligand spectrum ascribed to $\nu_{as}(\text{COO})$ and $\nu_s(\text{COO})$, suffered a great change to lower frequency were also observed on complexation (Fig-6) with metal ion^(24,25). The new bands observed at $(576-430)\text{ cm}^{-1}$ are tentatively assigned to $\nu(\text{M-N})$, $\nu(\text{M-O})$ and $\nu(\text{M-P})$ (Metal-Ligands) stretching bands⁽²⁶⁻²⁸⁾.

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



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Table(1):- 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	267	-	-	-	-	-
[Co(L) ₂ (TBPh) ₂]	Pale rose	294	77	7.45 (7.11)	63.71 (63.23)	9.35 (8.93)	3.53 (2.88)
[Ni(L) ₂ (TBPh) ₂]	Pale green	310	85	7.34 (6.88)	63.79 (62.94)	9.36 (9.05)	3.54 (2.91)
[Cu(L) ₂ (TBPh) ₂]	Pale blue	298	83	8.04 (7.57)	63.31 (62.86)	9.29 (8.98)	3.51 (2.84)
[Zn(L) ₂ (TBPh) ₂]	White	285	71	8.15 (7.66)	63.23 (63.02)	9.28 (8.78)	3.51 (2.69)

Table(2):- 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)	μ_{eff} (B.M)
Ligand(L)	250 291	1.931 1.474	40000 34364	1931 1474	-	-
[Co(L) ₂ (TBPh) ₂]	272 613 678 802	1.798 0.177 0.253 0.005	36764 16313 14749 12468	1798 177 253 5	55.37	4.67
[Ni(L) ₂ (TBPh) ₂]	268 421 611 795	1.390 0.378 0.102 0.061	37313 23752 16366 2578	1390 378 102 61	26.68	3.08
[Cu(L) ₂ (TBPh) ₂]	283 475	1.472 0.538	35335 21052	1472 538	30.48	1.83
[Zn(L) ₂ (TBPh) ₂]	273	1.925	36630	1925	19.53	Dia

Table(3):- The Main Frequencies of the Ligands and It's Complexes(cm⁻¹).

Compounds	$\nu(\text{NH}_2)$	$\nu_{as}(\text{COO})$	$\nu_s(\text{COO})$	$\nu(\text{M-N})$	$\nu(\text{M-O})$	$\nu(\text{M-P})$
Ligand(L)	3286 sh. 3110 sho.	1693 s.	1600 s.	-	-	-
[Co(L) ₂ (TBPh) ₂]	3373 s. 3147 s.	1620 s.	1585 sho.	557 w.	486 w.	430 w.
[Ni(L) ₂ (TBPh) ₂]	3356 sh. 3298 sho.	1635 s.	1590 sho.	576 w.	547 w.	480 w.
[Cu(L) ₂ (TBPh) ₂]	3328 sh. 3223 sh.	1681 sh.	1583 s.	524 w.	478 w.	447 w.
[Zn(L) ₂ (TBPh) ₂]	3334 sh. 3255 sh.	1622 s.	1560 sho.	569 w.	557 w.	470 w.

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

Table(4):- Diameters (mm) of Deactivation of Bacteria for the Phenylalanine and It's Complexes.

Compounds	Staphylococcus Aurous	Escherichia Coli
Ligand(L)	++	+
[Co(L) ₂ (TBPh) ₂]	+	-
[Ni(L) ₂ (TBPh) ₂]	+++	++
[Cu(L) ₂ (TBPh) ₂]	+	+++
[Zn(L) ₂ (TBPh) ₂]	-	+

- (-) = No inhibition.
- (+) =Inhibition diameter (6-8) mm.
- (++) =Inhibition diameter (8-10) mm.
- (+++)=Inhibition diameter (10-20) mm.

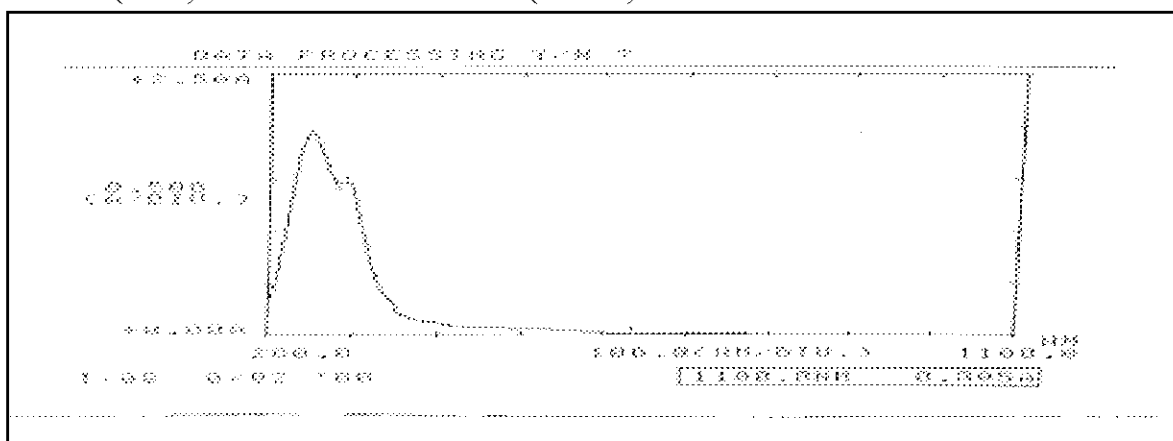


Fig.(1):- UV-Vis Spectrum of the Ligand.

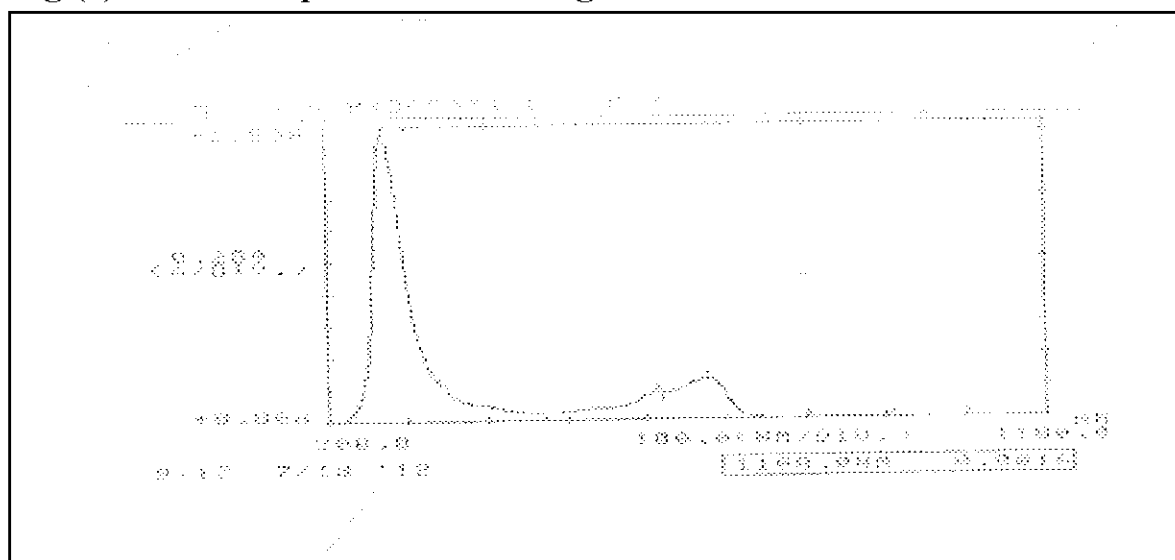


Fig.(2):- UV-Vis Spectrum of the [Co(L)₂(TBPh)₂] Complex.

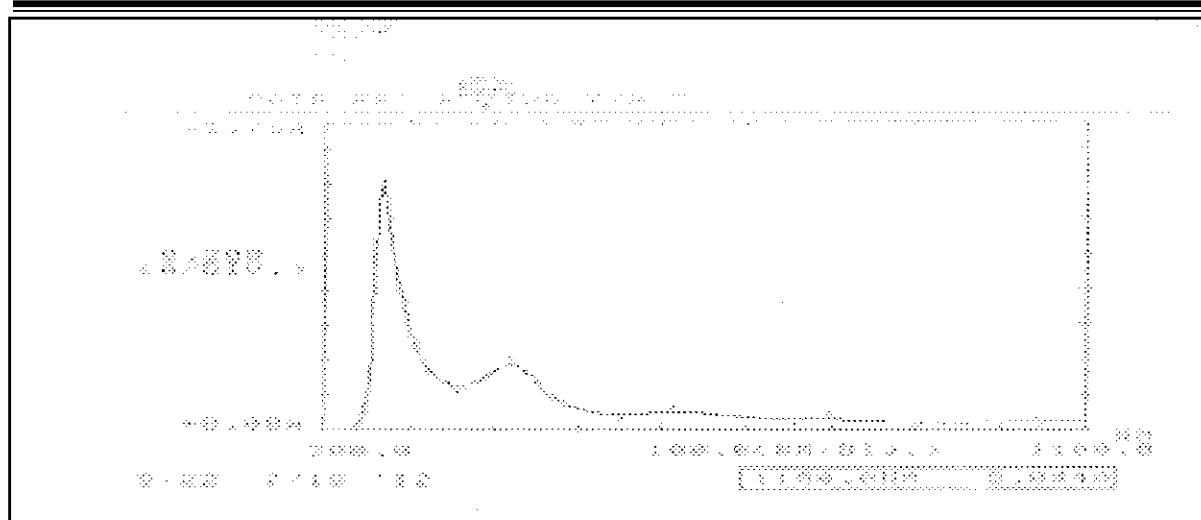


Fig.(3):- UV-Vis Spectrum of the $[\text{Ni}(\text{L})_2(\text{TBPh})_2]$ Complex.

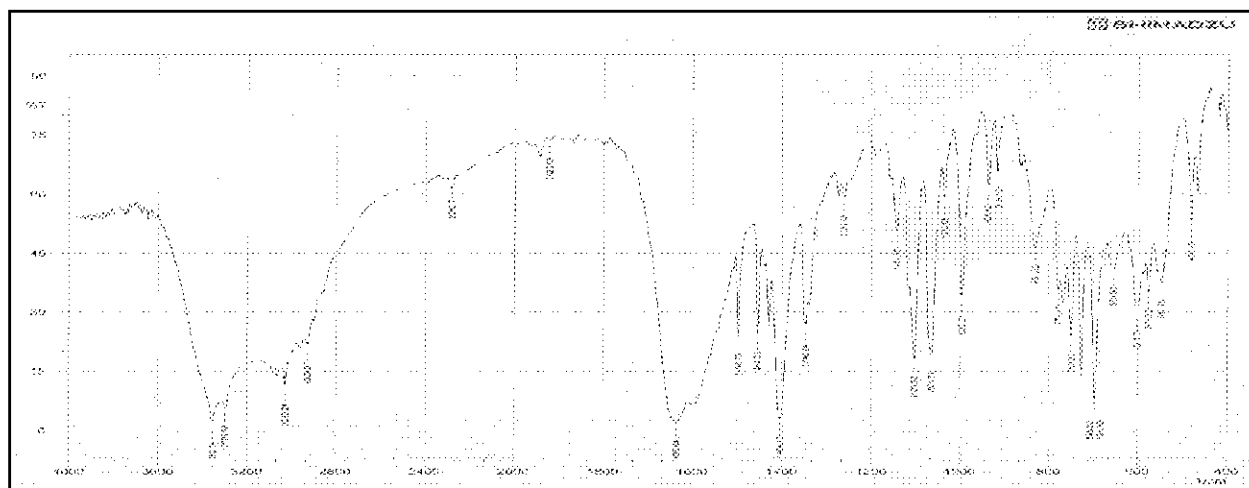


Fig.(4):- FT-IR Spectrum of the $[\text{Ni}(\text{L})_2(\text{TBPh})_2]$ Complex.

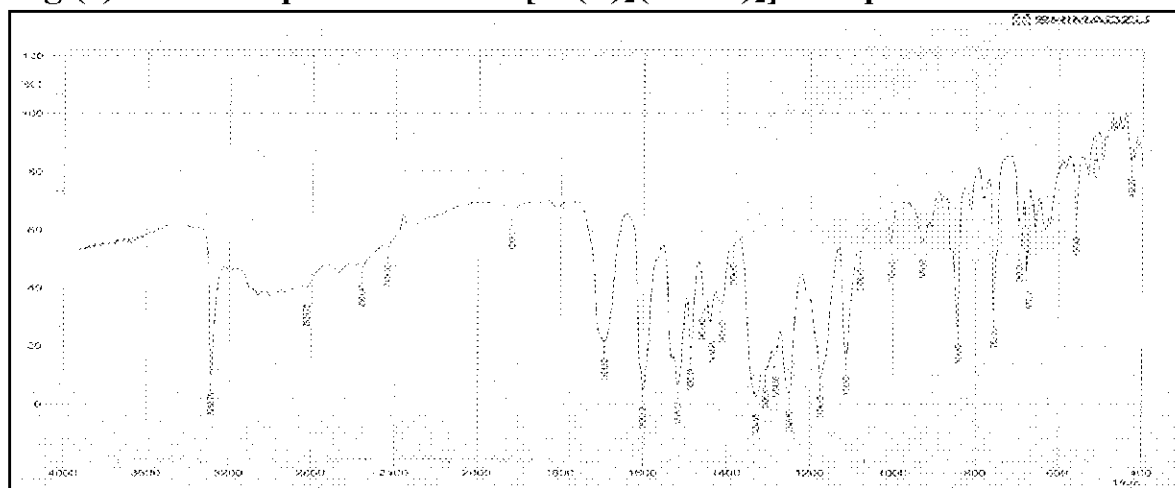


Fig.(5):- FT-IR Spectrum of the $[\text{Zn}(\text{L})_2(\text{TBPh})_2]$ Complex.

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

عامر جبار جراد

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الخلاصة

تم الحصول على معقدات جديدة وذلك من خلال مفاعلة ايونات Co(II) , Ni(II) , Cu(II) and Zn(II) مع الليكاندات المختلطة للفنيل النين وثلاثي بيوتيل الفوسفين وبنسبة مولية (2:2:1) فلز:ليكاند: ثلاثي بيوتيل الفوسفين. شخّصت المعقدات المحضرة بوساطة التحليل الدقيق للعناصر (C.H.N)؛ تقنية الإمتصاص الذري اللهبّي 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.