Synthesis, characterization and biological studies of azo ligand type NO and Its ($Ni^{(II)}$, $Cu^{(II)}$ and $Zn^{(II)}$) Complexes

Nasry Jassim Hussien
College of Education for Pure Sciences, University of Diyala

Abstract:

The three complexes of Ni(II), Cu (II) and Zn(II)with azo ligand type NO [4-(2,4 – dihydroxyl -6-methyl - phenyl) diazenyl-benzoic acid] [H_3L] derived from P- amino benzoic acid and orcenol were prepared .The complexes were Synthesized in direct reaction of the corresponding metal chloride with the ligand. The ligand and complexes have been characterized by spectroscopic methods (IR /UV- Vis /HNMR/ A.A) ,chloride content, melting point and conductivity measurement. The data of these measurements suggest an octahedral geometry around Ni(II), Cu (II) ions and tetrahedral geometry around Zn(II) ion. The ligand and complexes exhibited biological activity against the two types of bacteria Bacillus (G^+) and the Beudomonase (G^-) strains.

Introduction /

Azo compounds are compounds bearing the functional group R-N=N-R', in which R, R' can be either aryl or alkyl. Attention have been paid during the last decade for the chemistry of the metal complexes of ligands containing nitrogen and oxygen as donor atoms [1], this could be due to the stability of such ligand complexes [2]. Moreover the metal-azo or metal-azomethine complexes' classes have shown more promising optical storage characteristics [3, 4], recently it was reported the chemical structure and the biological activity of some azo compound[5,6]**.** In this paper we present the synthesis and study of some transition metal complexes with [4-(2,4-dihydroxy-6methyl-phenyl)diazenyl-benzoic acid] (H_3L) .

Experimental:

All chemicals supplied from Fluka and Merck companies and used without any further purification. Infrared spectra were performed using a Shimadzu (FT–IR)–8400S spectrophotometer in the range (4000 – 400 cm^{-1}). Spectra were recoded as potassium bromide discs at Ibn-sina Company. The electronic spectra of the compounds were obtained using a (UV–Vis) spectrophotometer type Shimadzu 160, in the range (200–900 nm) using quartz cell of (1.0) cm length with concentration (10^{-3}) mole L^{-1} of samples in DMF at 25°C, and electrical conductivity measurements of the complexes were recorded at (25ºC) for (10^{-3}–10^{-5}) M solutions of the samples in DMF using a PW 9526 digital conductivity meter. The chloride content determined using potentiometric titration method on 686–Titro Processor–665 Dosim A–Metrohm/Swiss. ^{1}HNMR were acquired with Brucker,model: ultrasheid 300 MHZ,origin : switzeland at AL-Bayt University, melting point obtained using an electrothermal apparatus Stuart melting point. Finally metals were determined with a Shimadzu (A.A.) 680G atomic absorption spectrophotometer.

Preparation of Ligand [H_3L]:

To diluted (0.76g, 5.53 mmole) p- Amino benzoic acid in (3 ml HCL + 3 ml distilled water) kept in ice bath, was add drop wise (0.8g, 11.61 mmole) of sodium nitrate solution

with continuous stirring whiles the mixture at (0C) (solution I). Orcenol (0.62g, 5 mmole) in 10% KOH aqueous was cooled in ice bath and mixed with (solution I) with continuous stirring in the ice bath, left for 30 minutes during which an orange precipitate was formed as shown in scheme (1), filtered and washed, yield (74%) and m.p(220 C^o).

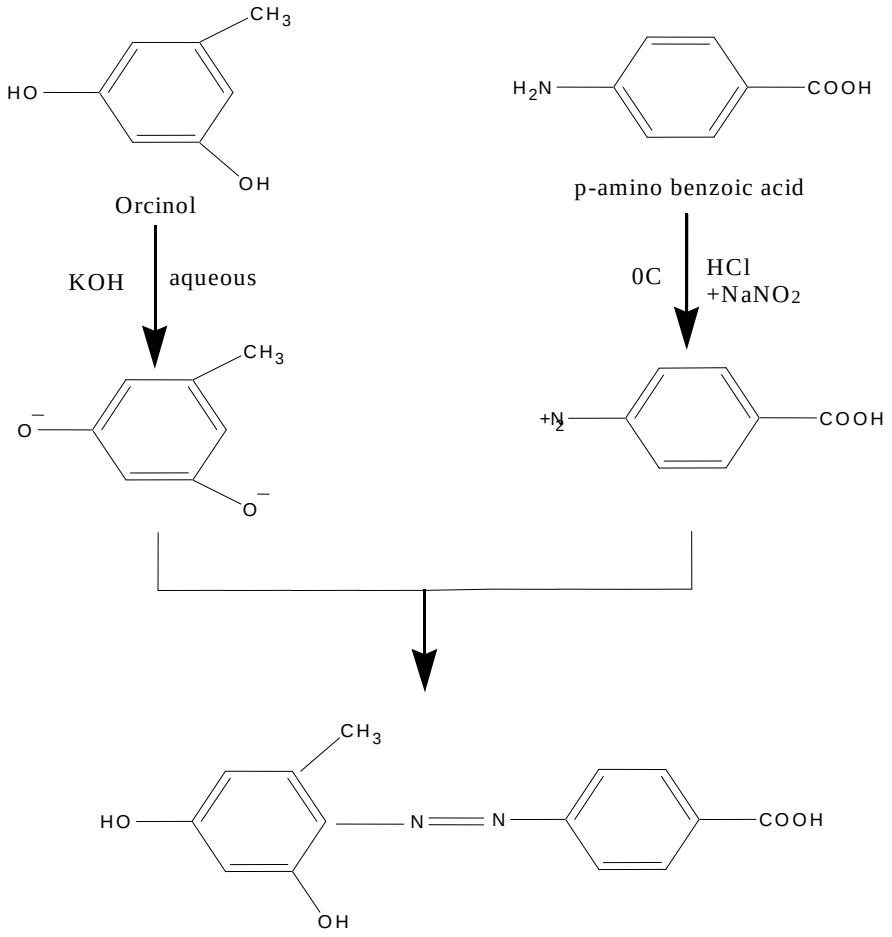
Preparation of complexes:

Preparation of $[Ni(H_2L)_2(OH_2)_2]$(1) :

To a solution of ligand (0.1g, 0.367 mmole) in (20 ml) Ethanol (0.05 ml) of triethyl amine was add solution of (0.043g, 0.183 mmole) $NiCl_2.6H_2O$ in Ethanol (10 ml) . The mixture was refluxed for 3 hours with stirring during which the color of the solution turned to dark brown. After completion of the reaction, it was cooled to afford a solid product. The solid residue was washed with ethanol and dried with diethyl ether.

Preparation of$[Cu(H_2L)_2(OH_2)_2]$(2) and $[Zn\ (H_2L)_2]$(3): The complexes $[Cu\ (H_2L)_2(OH_2)_2]$(2) and $[Zn\ (H_2L)_2]$(3) were obtained in a similar method to that mentioned in the preparation of $[Ni(H_2L)_2(OH_2)_2]$(1).Some physical properties for the ligand $[H_3L]$ and its complexes are summarized in table(1).

Results & Discussion:



Scheme (1): Preparation of the ligand $[H_3L]$

I.R spectral data for the ligand(H_3L)

The spectrum of the ligand showed bands at (3250)cm^{-1},(3500)$cm^{-1}$and(3387)cm^{-1}wich could be attributed to υ(OH)-$_4$- υ (OH)-$_6$- and Carboxylic hydroxyl groups respectively, also the spectrum showed bands at (1683) cm^{-1} and (1602) cm^{-1} wich could be attributed to υ(C=0) carboxylic and υ (C=C). The band at (1423) due to ν(N=N) azo compound[7], finally the band at (1161)cm^{-1}could be attributed to υ (C-O)phenolic. The spectrum of the ligand is shown in Fig(3) .

The (U.V-Vis) data for the ligand (H_3L):

The spectrum displays two peaks at(266) nm and (406) nm were assigned to ($\pi\rightarrow\pi^*$)and ($n\rightarrow\pi^*$) transitions respectively[8] fig(7),table(4).

^{1}H-NMR spectrum of (H_3L):

The ^{1}H NMR spectrum of the ligand [H_3L] is shown in Fig (11). The spectrum of aromatic (C-OH) reveals two chemical shifts at (4.5 and 5) ppm.While the multi signals at the rang (6.5-8.2) ppm aer due to aromatic protons the appearance of these protons as a doublet are due to multual coupling. The methylene group showed chemical shift at (2.1) ppm [9]. Finally carboxylic (OH) showed chemical shift at (14.5)ppm due to effect of azo group. The results are summerised in Table (3).

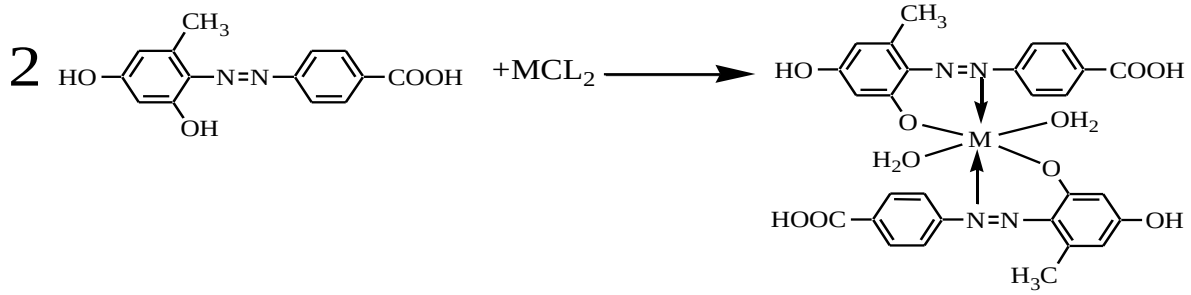
(I.R) Spectral data of the (H_3L) complexes [$Ni(H_2L)_2(OH_2)_2$],(1) [$Cu(H_2L)_2(OH_2)_2$](2)and [$Zn(H_2L)_2$](3).

The assignment of the characteristic bands are summarized in table(2).The band at (1423) cm^{-1} in the free ligand spectrum which assigned to υ (N=N) azo group shifted to lower frequencies and appeared at (1395) cm^{-1}, (1400) cm^{-1} and (1397) cm^{-1} for the complexes (1, 2 and 3) respectively [12,13], these bands were assigned to (N=N) stretches of reduced bond order, this can be attributed to delocalization of metal-electron density into the ligand π-system(HOMO-LOMO). The phenolic (C–O) stretching vibration appeared at (1161) cm^{-1} in the free ligand was shifted to higher frequency and appeared at (1195) cm^{-1}, (1197) cm^{-1}, and (1197) cm^{-1} in the complexes (1,2 and 3) respectively, indicated a weak linkage between oxygen of phenolic group and the metal ions [11]. The additional band observed around (3325) and (3311) cm^{-1} in [$Ni(H_2L)_2(OH_2)_2$] and [$Cu(H_2L)_2(OH_2)_2$] complex is assigned to coordination of aquo (H_2O) molecules to the metal [14]. The spectra showed the appearance of bands at (534) cm^{-1}, (555) cm^{-1} and (501) cm^{-1} refer to υ(M–N) for complexes (1,2 and 3) respectively ,these bands confirms the coordination of nitrogen atom to the metal center, while the bands at (462) cm^{-1}, (501) cm^{-1} and (418) cm^{-1} assigned to υ(M–O) for complexes (1,2and3) respectively these bands confirms the coordination of oxygen atom to the metal center [14,15].The I.R spectra of the complexes(1),(2) and(3) are shown in figs (4,5 and 6).

(U.V-Vis) Spectral data for ligand (H_3L) complexes [$Ni(H_2L)_2(OH_2)_2$] (1)**, [$Cu(H_2L)_2(OH_2)_2$]** (2) **and [$Zn(H_2L)_2$]** (3)**.** The (U.V-Vis) spectra for the complexes are shown in Figs (8), (9) and (10), the results were summarized in Table (4). Complex (1) showed two intense absorption peaks at (266.3 nm) and (397.6 nm) were assigned to ligand field and (C.T) transitions respectively, while a weak broad peak at (686.2 nm) was assigned to (d-d) electronic transition type ($^3A_2g\rightarrow{}^1Eg$) suggesting octahedral geometry around Ni ion [16].Complex (2) showed an intense peak at (268.9 nm) which assigned to ligand field and a peak at (409.3 nm) may assign to (C.T) transition. The peak at (686.2) was assigned to (d-d) electronic transition type ($^2B_{2g}\rightarrow{}^2A_{1g}$) suggesting octahedral geometry around Cu ion [8]. Complex (3) showed an intense peak at (266.3 nm), which assigned to ligand field, while a high intense peak at (409.0 nm) was assigned to (C.T) transition, The d^{10} configuration of Zn^{II} ion along with the data obtained confirms a tetrahedral structure around Zn ion .

The molar conductance: The molar conductance of the complexes in (DMSO) was in the range (9.32–19.02 µS), Table (4), indicated that complexes are all non-electrolyte having molar ratio of metal: ligand as 1:2 [18].

Biological activity: The biological activity of the ligand (H_3L), $[Ni(H_2L)_2(OH_2)]$, $Cu(H_2L)_2(OH_2)]$ and $[Zn(H_2L)_2]$complexes was studied by using inhibition method for two types of pathogenic bacteria. One type of bacteria was gram positive which is Bacillus cereus Fig(12). The second one was gram negative which is Pseudomonase(G-) Fig(13) . The biological effect of the chemical complexes, was studied for the two types of bacteria as shown in table (5).The rate of inhibition diameter was varied according to the variation in the complex type and bacteria type [19]. All compounds exhibited biological activity against Pseudomonas (G^-) and Bacillus(G^+) strains and the ligand was more active from its complexes.

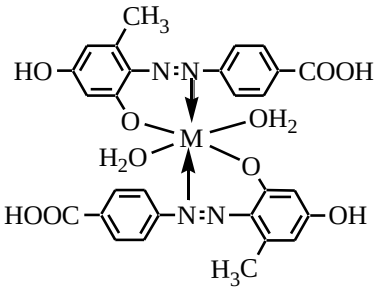


Scheme (2) : Preparation of the complexes

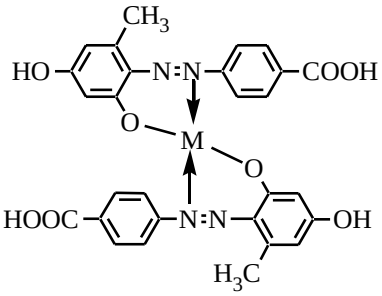
References:

1. Tang J.C., Lui W.S., Chan M.Y., Chin A.S.C.: Chemistry .Lett. , (2001); 12:757-760.
2.Lui C. M .,Xion R. G., You X. Z., Lui Y, J., Chenung Polyhydron and K. K. .(1996) , 15 : 4565-4571 .
3.Bartkowiak W., Challenges and Advances in Computational Chemistry and Physics 1, 299 (2006)
4. Wei B., Feng Y., Wu Y., Gan F., Proc. SPIE .(2005),5966, 235.
5.Samir A.H., Hasan H.A., Aziz M.R., J.Edu.col.Mustansrya .(2010);1,392-406 .
6. Vogel A.I.: " Practical Organig Chemistry ",3rd ed .Long Man Group Lted,London.(1974).
7. Robert M. Silver Schtein , Bassler and Morril :ted by Dr. Hadi Khazem Awad , Dr. Fahad Ali Hussain and Sabri – Azawi , 5th (1981)
8. Lever A. B. P. : "Inorganic electronic spectroscopy " , New york .(1968); 6: 121.
9. Kemp.W , 1987 *" Organic Spectroscopy"* 2nd .Ed., ,144.
10.Pavel kopel, Martin Biler, Zdenek.Travnicek,and Milan Nadvorink ,(1998), *"Iron(111)Salen and Saloph Schiff bases bridged by dicaboxylic acids"* chemical ,37.
11. Nakamoto.K, *"Infrared Spectra of Inorganic and Coordination Compounds "* 4th.Ed.,J.Wiely and Sons , New York ,(1996).
12. Hadzi D. and Premru . L; (1967),Spectrochim . Acta ., 23A:35 .
13. Agarwal R. K., Prased S. and Gahlot N. Turk. J. Chem. (2004), 28, 415
14.Al-Jeboori, M.J .,Al –Dujailli, A.H.,Al-Janabi, A.E.,Transition Metal Chemistry, 34(2009) 109- 113.
15 El-.Table A. S. and T. I Kasher T.I.: Polish J. Chem. (1998); 72: 519.
16. William Kemp "Organic spectroscopy " 2endedition , (1987) ;144 .
17. Green Wood .N.N and Earnshow.A , (1998) . *"Chemistry of the Elements "* , Ed. J. Wiley and Sons Inc. New York ,.

18. Geary , W. J. The use of conductivity measurements in organic solvents for the characterization of coordination compounds . Coord. Chem. Rev. 1971 , 7 , 81-115.
19. Hopper D.C.: Quinolones.In. Mandell G.L., Bennett J.E, R.Dolin(ed.) Mandell,Douglas and Bennett, S: "principles and practice infections disease" 5th ed. Churchill Livingstone,Philadelphia,(2002), 404-423.



$\mathbf{M^{II}}$ = Ni , Cu



$\mathbf{M^{II}}$ = Zn

Figures (1,2) The suggested structure of the complexes

Table (1) some physical properties for the ligand [H_3L] and its complexes.

Compounds	Formula	M .wt	Color	m.p(° C	Yield%	chloride content Prac(Theo.)	Metal content Prac(Theo.)
[H_3L]	$C_{14}H_{12}N_2O_4$	272	Dark orange	220	74	Nil	------
$[Ni(H_2L)_2(OH_2)]$	$C_{28}H_{26}N_4O_{10}Ni$	636.69	brown	280	63	Nil	8.5 (9.217)
$[Cu(H_2L)_2(OH_2)]$	$C_{28}H_{26}N_4O_{10}Cu$	641.55	Dark brown	260	77	Nil	9.1 (9.9)
$[Zn(H_2L)_2]$	$C_{28}H_{22}N_4O_8Zn$	600.39	Orange	290	69	Nil	10.2 (10.891)

Compound	υ(N=N)	$(O-H)_4$ $(O-H)_6$ υ(O–H) carboxylic	υ(C=O) carboxylic	υ(C=C) Aromatic	υ(C–H) Aromatic	υ(C–O)	υ(M–N)	υ(M– O)
H_3L	1423	3250 **3**500 3387	1683	1602	3049	1161	----	----
$[Ni(H_2L)_2(OH_2)]$	1395	3300 - 3404	1665	1606	3010	1195	534	462
$[Cu(H_2L)_2(OH_2)]$	1400	3288 - 3400	1657	1604	3051	1197	555	501
$[Zn(H_2L)_2$	1397	3350 - 3446	1675	1610	3080	1197	501	418

Table (3) H^1 NMR data for the ligand in DMSO–d_6 and chemical shift in ppm(δ)

Compound	Funct .group	δ (p.p.m)
H_3L	OH Carboxilic acide	14.5
	Aromatic C-OH	4.5 and 5
	CH3	2.1
	aromatic proton	6.2-8.2
	DMSO	2.5

Compound	λ nm	Wave number Cm^{-1}	Assignment	Molar conductivity µS	coordination
H_3L	266 406	37593 24630	π→π* n→π*	------	------
$[Ni(H_2L)_2(OH_2)]$	266.3 397.6 686.2	47551 25150 14573	Ligand field C.T ($^3A_2g \rightarrow {}^1Eg$)	19.02	Octahedral
$[Cu(H_2L)_2(OH_2)]$	268.9 409.3 686	73188 24431 14577	Ligand field C.T ($^2B_2g \rightarrow {}^2A_1g$)	16.6	Octahedral
$[Zn(H_2L)_2]$	266.3 406	37551 24630	Ligand field C.T	9.32	Tetrahedral

Table (4) : Electronic spectral data and conductance measurement for the ligand and its complexes

Table **(5): The biological activity of the synthesised compounds(mm)**

Compound	Bacillus (G+)	Pseudomonase (G-)
Control DMSO	5	5
$[H_3L]$	25	35
$[Ni(H_2L)_2(OH_2)]$	15	20
$[Cu(H_2L)_2(OH_2)]$	15	25
$[Zn(H_2L)_2]$	15	20

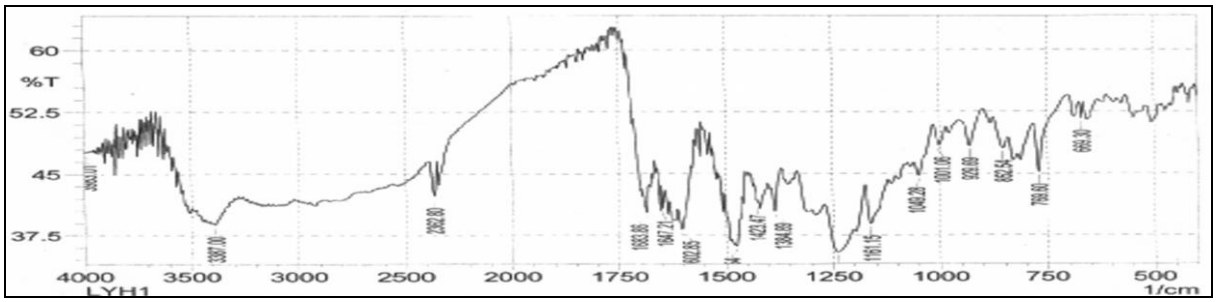


Fig (3) Infrared spectrum of the ligand (H_3L)

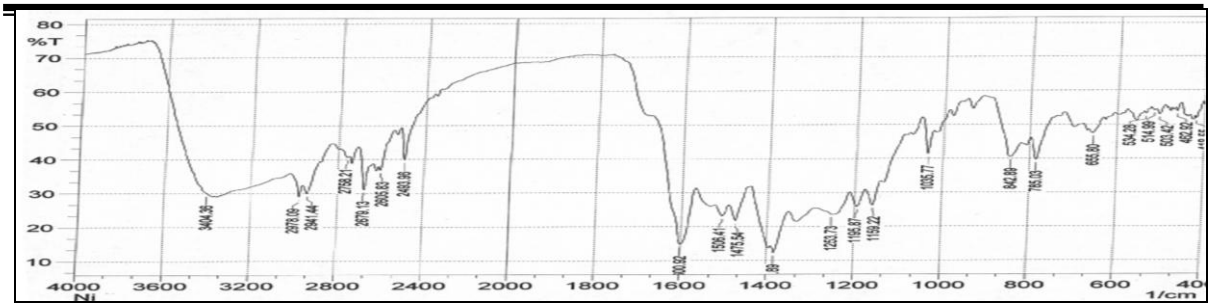


Fig (4) Infrared spectrum of the complex [Ni $((H_2L)_2 (OH_2)_2]$

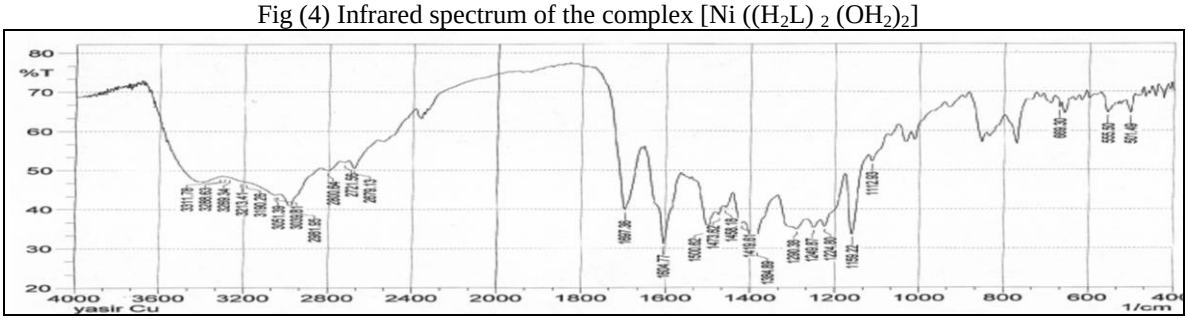


Fig (5) Infrared spectrum of the complex [Cu $(H_2L)_2 (OH_2)_2]$

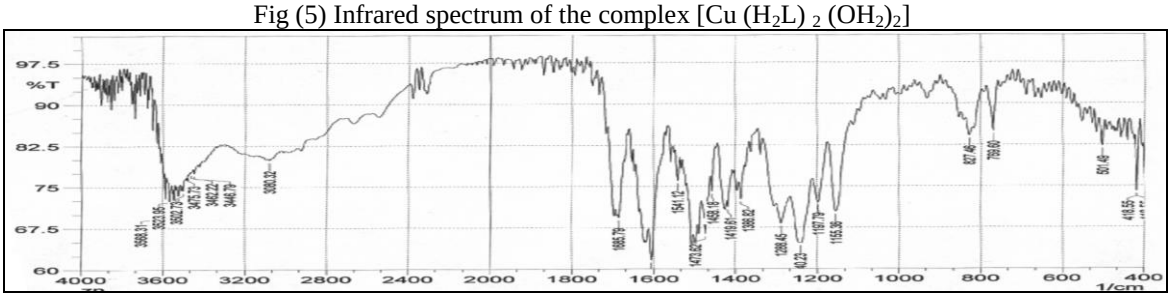


Fig (6) Infrared spectrum of the complex [Zn $(H_2L)_2]$

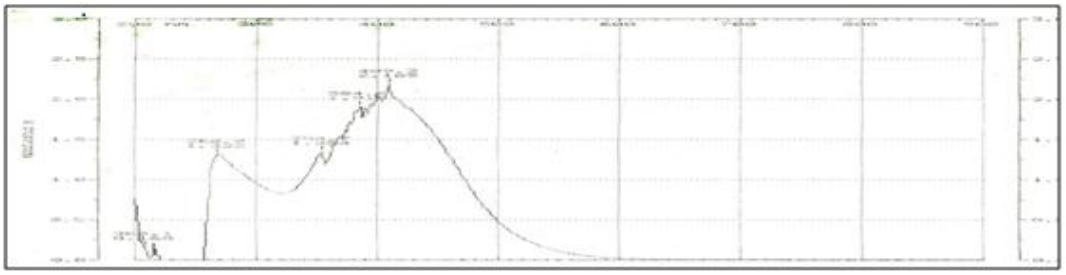


Fig (7) Electronic spectrum of the ligand (H_3L)

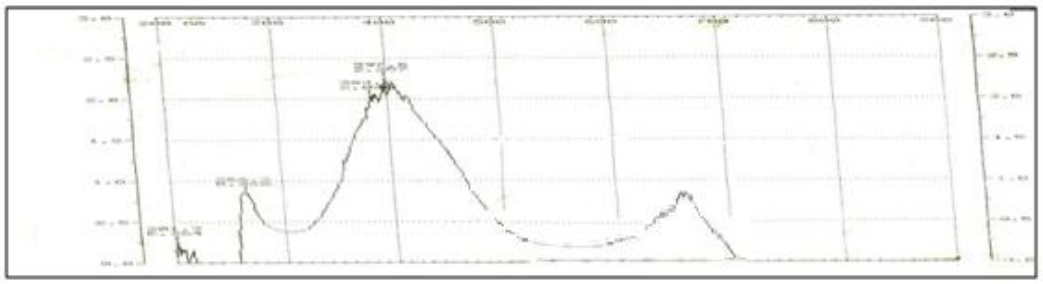


Fig (8) Electronic spectrum of the complex [Ni $(H_2L)_2$ $(OH_2)_2$]

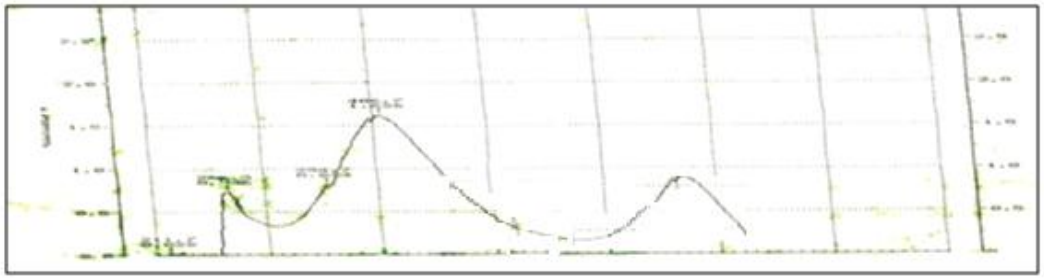


Fig (9) Electronic spectrum of the complex [Cu$(H_2L)_2$ $(OH_2)_2$]

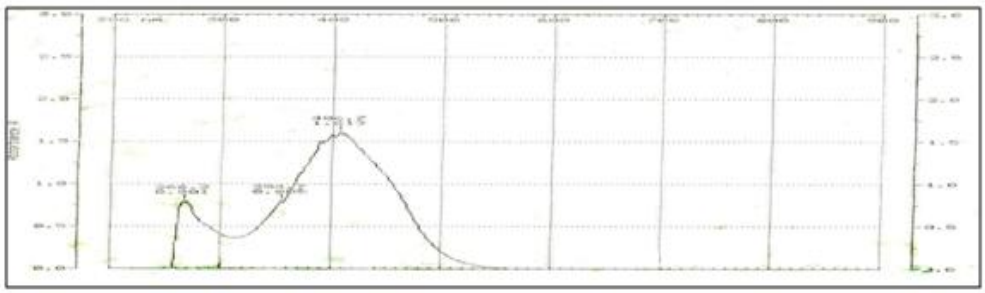


Fig (10) Electronic spectrum of the complex [Zn $(H_2L)_2$]

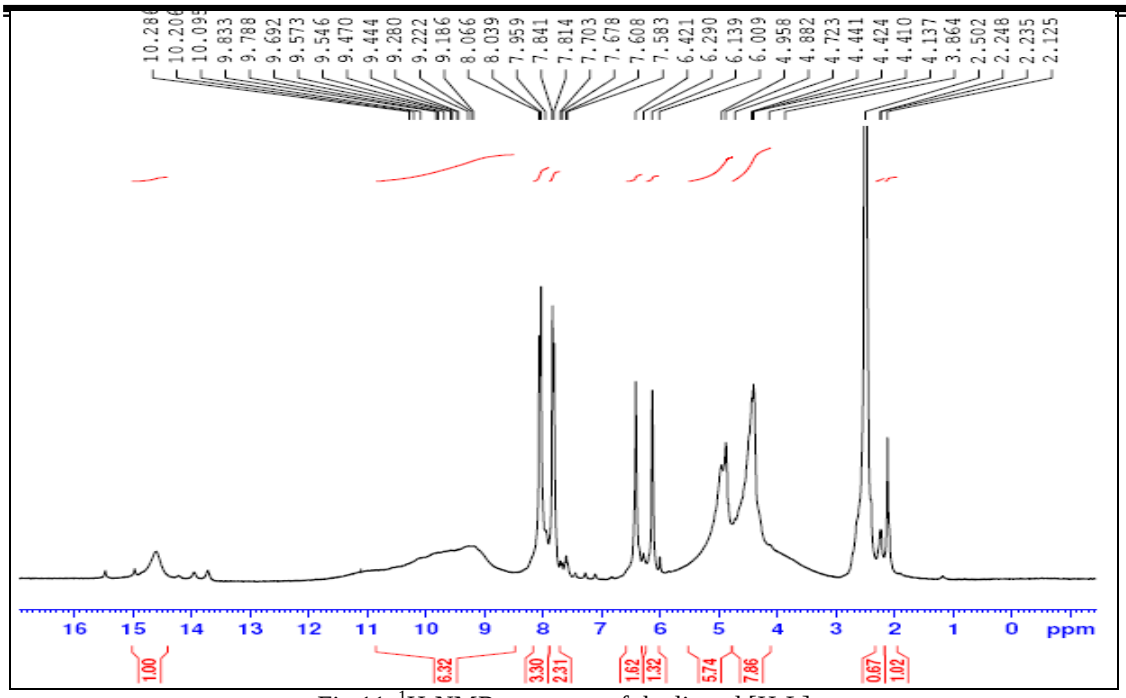


Fig 11: ^{1}H-NMR spectrum of the ligand [H_3L]

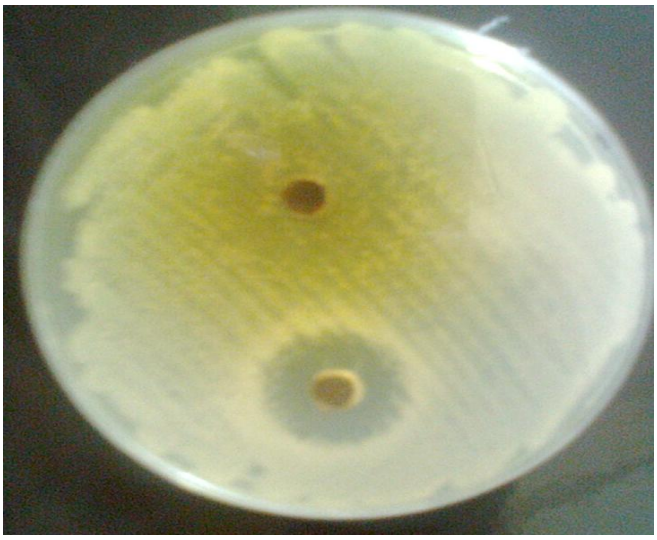


Fig 12: Effect of the ligand towards the Bacillus

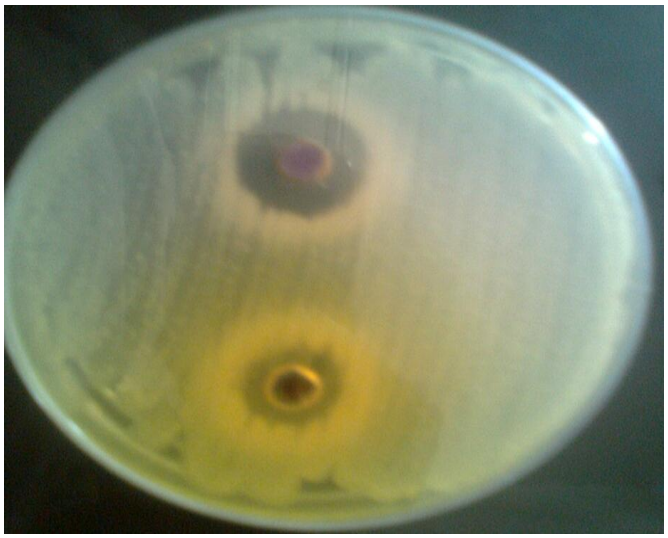


Fig 13: Effect of the complex [$Cu(H_2L)_2(OH_2)$] towards the Pseudomonase

تحضير, تشخيص طيفي ودراسة الفعالية البايلوجية لليكاند أزو نوع مع الأيونات($Ni^{(II)}$, $Cu^{(II)}$ and $Zn^{(II)}$)

نصري جاسم حسين
جامعة ديالى
كلية التربية للعلوم الصرفة- قسم الكيمياء

الخلاصة

تضمن البحث تحضير الليكاند الجديد
[4-(2,4-dihydroxy-6methyl-phenyl)diazenyl-benzoic acid] (H_3L) .
المشتق من p-amino benzoic acid مع Orcenol
ثم مفاعلة الليكاند مع بعض العناصر الفلزية باستخدام الميثانول وسطا للتفاعل وبنسبة (2:1)وبوجود Et_3N كقاعدة حيث تكونت معقدات جديدة ذات الصيغ العامة:

$$[M(H_2L)_2]\ [H_2O]_n$$

حيث:

$$M = Ni^{(II)}, Cu^{(II)}, n=2 \text{ and } M=Zn^{(II)}, n=0$$

شخصت جميع المركبات بالطرق الطيفية التالية (الأشعة تحت الحمراء والأشعة فوق البنفسجية – المرئية ومطيافية الامتصاص الذري للعناصر ومطيافية الرنين النووي المغناطيسي) ومحتوى الكلور ودرجات الانصهار , مع قياس التوصيلية المولارية الكهربائية.، من النتائج أعلاه كان الشكل الفراغي المقترح لمعقدات النيكل,النحاس ثماني السطوح بينما يتخذ الزنك شكل رباعي السطوح المشوه . تم دراسة الفعالية البايولوجية لليكاند و المعقدات المحضرة على نوعين من البكتريا المختلفة وهي الموجبة لصبغة كرام (*Bacilluus Cereus*) والسالبة لصبغة كرام (*Psudomonus Sp.*) وقد لوحظ ان لهذه المركبات فعالية بايولوجية اتجاه نوعين من البكتريا ولكن بنسب مختلفة حيث تبين ان هنالك اختلاف في أقطار التثبيط للمركبات الكيميائية حسب نوع المعقد ونوع البكتريا وقد سجل الليكاند أعلى قطر تثبيط بالنسبة لباقي المعقدات.