

Synthesis, Spectroscopic and Biological Studies of some metal ions complexes with 2-hydroxy-N-pyridin-2-yl methyl-acetamide

Lekaa K. Abdul Karim, Enas H. Ali and *Falih H. Musa

Department of Chemistry, College of Education-Ibn AL-Haitham,
University of Baghdad, Baghdad – Iraq.

*E-mail / dr.Falihhassan@yahoo.com

Key words : synthesis , aminomethyl pyridin , complexes , biological activity

ABSTRACT

The ligand 2-Hydroxy-N-pyridin-2-ylmethyl-acetamide(L) has been prepared from reaction of 2-(aminomethyl)pyridin with chloroacetic acid (1:1).It has been characterized by elemental analysis (C,H,N) ,¹H, ¹³C-NMR, IR and electronic spectra. The complexes of divalent (Co,Ni,Cu,Zn,Cd and Hg) ions and trivalent(Cr) ion have been synthesized and characterized by IR, electronic spectra, molar conductivity, atomic absorption and molar ratio (Ni²⁺) complex. The analytical studies for the complexes show; octahedral for (Cr³⁺),square planar for (Cu²⁺) and (Co,Ni Zn, Cd and Hg) tetrahedral geometries. The study of biological activity of the ligand (L) and its complexes (Co,Ni,Cu,Cd,Hg) in two deferent concentration (1and5) mg/ml showed various activity toward *staphylococcus aureus* and *E.coli* .

الخلاصة

حضر الليكاند (L) , 2- هيدروكسو -N- بردين -2- يل مثيل استمايد من تفاعل 2-(امينو مثيل) بردين مع كلورو استك اسد (1:1) . تم تشخيص الليكاند (L) بواسطة تحليل العناصر (C,H,N) , ¹H, ¹³C-NMR , مطيافية تحت الحمراء و فوق البنفسجية – المرئية. حضرت وشخصت معقدات بعض أيونات العناصر ثنائية التكافؤ (Hg²⁺, Cd²⁺, Zn²⁺, Ni²⁺, Co²⁺) والكروم الثلاثي(Cr³⁺) مستخدمين تقنيات اشعة تحت الحمراء والاشعة فوق البنفسجية – المرئية و التوصيلية الكهربائية و الامتصاصية الذرية و النسبة المولية لمعقد النيكل كنموذج . واستنتج من التحاليل ان معقد الكروم له شكل ثماني السطوح ومعقد النحاس له شكل مربع مستوي ومعقدات (Hg²⁺, Cd²⁺, Zn²⁺, Ni²⁺, Co²⁺) لها شكل هرم رباعي السطوح. تم دراسة الفعالية البيولوجية لليكاند ومعقداته (Co²⁺, Ni²⁺, Cu²⁺, Cd²⁺, Hg²⁺) في تركيزين مختلفين (1 و 5) ملغم/مل, وقد اظهرت النتائج امتلاكها فعالية متفاوتة اتجاه انواع البكتريا *Staphylococcus aureus* و *E.coli* .

INTRODUCTION

The disubstituted 2-pyridin compounds are used in biology ,pharmacy,industry and laboratory⁽¹⁻²⁾.Their transition complexes have received considerable attention largely.Aminomethylpyridin-phosphine ruthenium(III) has been prepared and showing highly active transfer hydrogenation catalysts⁽³⁾.The infrared spectra of twenty-six complexes of 2-(amino methyl)pyridin with first transition metal (II) ions series were descused⁽⁴⁾.Mangense (II) complexes

of set of 2-(amino methyl)pyridine derived ligand bearing a methoxyalkyl have been prepared⁽⁵⁾.N-(2-pyridyl) acetamide complexes of Pd(II),Co(II),Ni(II) and Cu(II) have been reported⁽⁶⁾.The present work aims to study the synthesis and antibacterial activity of new ligand derived from condensation of 2-(aminomethyl)pyridin with chloroacetic acid yielding 2-hydroxy-N-pyridin-2-ylmethyl-acetamide and its corresponding metal ion complexes ⁽⁶⁾.

Experimental

a- Chemicals;

All solvents were obtained commercially and were used without further purification.2-(aminomethyl)pyridin ($C_6H_8N_2$),Chloroaceticacide ($ClCH_2COOH$), Chromium trichloride hexahydrate ($CrCl_3.6H_2O$), cobalt chloride hexahydrate ($CoCl_2.6H_2O$), Nickel chloride hexahydrate ($NiCl_2.6H_2O$) Copper chloride dehydrate ($CuCl_2.2H_2O$),Cadmium chloride dehydrate ($CdCl_2.2H_2O$) , Mercury chloride ($HgCl_2$), Ethanol 99% (CH_3CH_2OH) , Dimethyformamide 99.5%(DMF) , Dimethylsulphoxide 99.5% (DMSO) , carbon tetrachloride 99.5% (CCl_4) were purchased from fluka.

b- Instruments;

- Elemental analysis for the new (L) (C, H, N) was determined by calibration type : Linear Regression Euro EA Elemental Analysis were made in AL-Mustansiriyah University.
- Melting points were determined by Gallen-Kamp apparatus.
- 1H - ^{13}C -NMR spectra were recorded in DMSO using Burker 300 MHz spectro meter at the AL-Albayt University Amman –Jordan .
- IR spectra were recorded as KBr disc in the rang $(4000-400)cm^{-1}$ using Shimadzu-FT-IR.
- UV-Visible spectra were recorded by Shimadzu-UV-Vis. 160 AUltra violet spectro photometer at $25^\circ C$, using 1cm quartz cell and examined at the range of (200-900) nm in DMF at $10^{-3}M$.
- Atomic Absorption (A.A) technique using a Shimadzu- AA680G atomic absorption spectrophotometer.
- Molar conductivity of the complexes were measured on pw 9526 digital conductivity in DMF at $10^{-3}M$.

Syntheses of 2-Hydroxy-N-pyridin-2-ylmethyl-acetamide (L)

2-(aminomethyl)pyridin (1mm,0.108g) in ethanol (10 mL) was added to a solution of chloroacetic acide (1mm,0.095g) in (15mL) diethylether.The mixture was stirred for 3h..The product was recrystallised from ethanol and dried (melting point, $75^\circ C$),yield 88%.

complexes. The amido ν (C=O) stretch were observed at (1647-1614) cm^{-1} . These stretch are shifted by (3-36) cm^{-1} compared to free ligand and indicate the involvement of (O-amid) in the bonding⁽¹¹⁾. Table 2, Fig-(4).

The UV –visible spectra of the ligand (L) in DMSO solution exhibited strong absorption bands at (220nm, 4545 cm^{-1}) and (279.5nm, 3578 cm^{-1}), (326.5nm, 30627 cm^{-1}). Which are due to the $\pi - \pi^*$ and $n - \pi^*$ transition⁽¹²⁾. Fig(5)

The electronic spectrum of Cr(III) complexes showed doublet peak at (677 and 612) nm center at 645nm (15408 cm^{-1}) due to ${}^4A_{2g} \rightarrow {}^4T_{2g}$ transition and peak 462.5 nm (21645) cm^{-1} due to ${}^4A_{2g} \rightarrow {}^4T_{1g}$. It is suggested that Cr(III) coordination geometry is octahedral on the basis of these two transitions⁽¹³⁾ Fig-(5).

The electronic spectrum of Cu(II) complex showed band center at 726 nm (13622 cm^{-1}) attributed to ${}^2B_{1g} \rightarrow {}^2A_{1g}$ transition and a broad band around (400-300)nm center at 380 nm (26315 cm^{-1}) due to ${}^2B_{1g} \rightarrow {}^2E_g$ transition of square planar environment⁽¹⁴⁾. The electronic spectrum of Co(II) complex showed two doublet band at 612.5 nm (16341 cm^{-1}) and 675nm (14844 cm^{-1}) center at 643.5nm (15592 cm^{-1}) due to ${}^4A_2 \rightarrow {}^4T_{1(p)} (v_3)$ transition of tetrahedral environment⁽¹⁵⁾.

Ni complex showed 430 nm (23256 cm^{-1}) due to ${}^3T_1 \rightarrow {}^3T_{1P}$ tetrahedral environment⁽¹⁶⁾.

The electronic spectra of Zn, Cd and Hg complexes showed absorption (316, 379 and 311.5)nm due to charge transfer. On basis of (1:1) stoichiometry and atomic absorption and known preference, tetrahedral geometry for $[MX_2L]M = \text{Zn}^{2+}, \text{Cd}^{2+}$ and Hg^{2+} the ligand and its complexes are given in Table-(3)⁽¹⁶⁾.

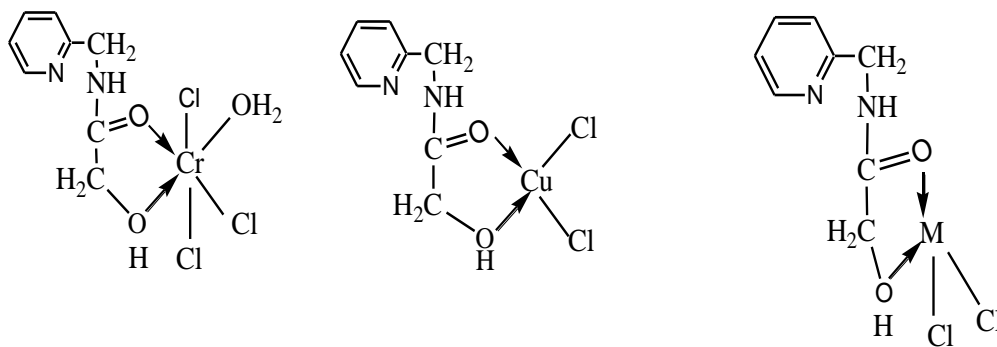
The molar conductance of all complexes in DMF was found to be low which suggested coordination of anion to the metal⁽¹³⁾. The (Ni²⁺) complex was studied in solution using ethanol as a solvent, in order to determine (M:L) ratio in the prepared complexes, following molar ratio method⁽¹⁷⁾. A series of solutions were prepared having a constant concentration (C) 10^{-3}M of the hydrated metal salts and the ligand (L). The (M:L) ratio was determined from the relationship between the absorption of the observed light and the mole ratio (M:L) found to be (1:1). Fig-(6). The result of complexes formation in solution are shown in Table(4).

Study of biological activity

The biological activity of the prepared new ligand and its complexes ($\text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Cd}^{2+}, \text{Hg}^{2+}$) were studied against selected types of micro organisms which include gram positive bacteria like staphylococcus aureus and gram negative bacteria like E.coli in agar diffusion method, which is used (DMF) as a solvent. Agar diffusion method involves the exposure of the zone of inhibition toward the diffusion of micro organisms on agar plate. The plates were incubated for (24) hrs. at (37°C) The zone of inhibition of bacterial growth around the disc was observed Fig-(7-8).

Conclusion

A series of ($\text{Cr}^{3+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+}, \text{Cd}^{2+}$ and Hg^{2+}) complexes with 2-Hydroxy-N-pyridin-2-ylmethyl-acetamide (L) have been prepared and characterized. The bidentate ligand (O,O) is binding metal ions; $\text{Cr}^{3+}, \text{Cu}^{2+}$ forming octahedral and square planar geometries. The ($\text{Co}^{2+}, \text{Ni}^{2+}, \text{Zn}^{2+}, \text{Cd}^{2+}, \text{Hg}^{2+}$) metal ions complexes forming tetrahedral structure as follows;



$M^{2+} = \text{Co, Ni, Zn, Cd, Hg}$

Table (1) Analytical and physical data of the ligands and their complexes

No.	Compound	Color	m.p C°	Metal analysis Found (calculated)					solubility
				Mwt	C%	H%	N%	M%	
1	(L) $C_8H_{10}N_2O_2$	Yellowish	75	166	57.83 (57.83)	6.11 (6.02)	16.59 (16.86)	-	CCl_4 DMF,DMSO
2	L- $CrCl_3 \cdot H_2O$	Green	160	342.49	-	-	-	15.32 (15.18)	=
3	L- $CoCl_2$	Green	140	295.9	-	-	-	19.54 (19.90)	=
4	L- $NiCl_2$	Green-bule	156	295.69	-	-	-	19.54 (19.84)	=
5	L- $CuCl_2 \cdot 2H_2O$	bule	152	336.54	-	-	-	18.67 18.88	=
6	L- $ZnCl_2$	yellow	127	302.39	-	-	-	20.24 (21.62)	=
7	L- $CdCl_2$	yellow	160	349.41	-	-	-	32.21 (32.17)	=
8	L- $HgCl_2$	Light yellow	132	437.59	-	-	-	46.80 (45.83)	=

Table(2) :- The characteristic stretching vibrational frequencies (cm^{-1}) located in the FT-IR of the ligand(L) and its complexes

No.	Compound	ν (O-H)	ν (NH) δ (N-H)	ν (C=O)	ν (M-OH)	ν (M-O) (OH ₂ aq.) OH ₂ -hydr.
1	(L)C ₈ H ₁₀ N ₂ O ₂	3468 3414	3228 1600 1610	1650	-	-
2	L-CrCl ₃ .H ₂ O	3344 3361	3147 1571	1614	933	453 832
3	L-CoCl ₂	3429 3396	3294 1570	1620	960	462
4	L-NiCl ₂	3425 3300	3240 1591	1629	931	514
5	L-CuCl ₂ .2H ₂ O	3452 3414	3290 1589	1635	933	532 3500
6	LZnCl ₂	3483	3240 1593	1640	937	518
7	LCdCl ₂	3496	3277 1598	1645	925	518
8	LHgCl ₂	3587	3118.3 1577	1647	937	457

Table-3: Electronic spectra and conductance in DMF of ligand (L) and its complexes.

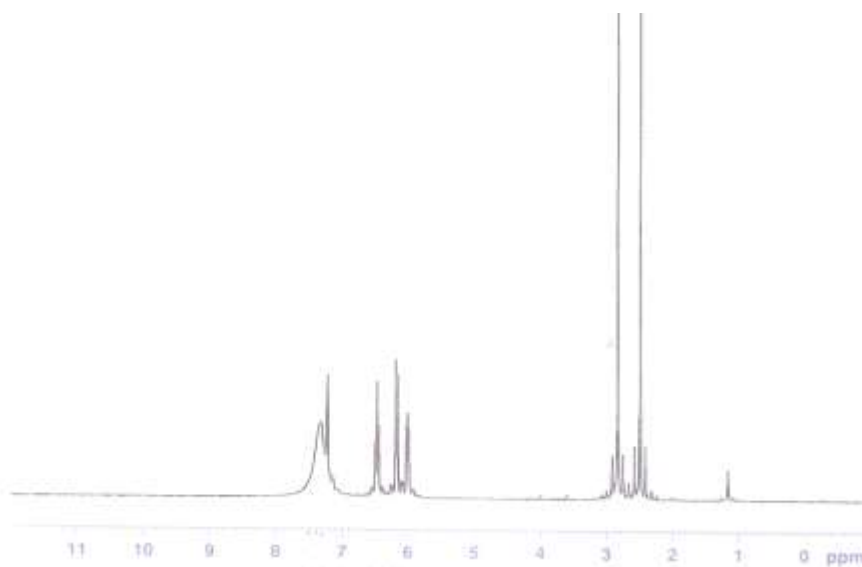
No.	Compound	(λ_{nm}) cm^{-1}	Assignment bands	Λ S. cm^{-1} DMF ($10^{-3}M$)
1	(L) $C_8H_{10}N_2O_2$	(220)4545 (279.5)35778 (326.5)30627	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	-
2	L-CrCl ₃ .H ₂ O	(645)15408 (462)21645	$^4A_{2g}$ $^4T_{2g}$ $^4A_{2g}$ $^4T_{1g}$	17.07
3	L-CoCl ₂	(643.5)15592	4A_2 $^4T_{1(P)}$	17.68
4	L-NiCl ₂	(430)23256	$^3T_1 \begin{matrix} \longrightarrow \\ \longrightarrow \end{matrix} ^3T_{1(P)}$	25.00
5	L-CuCl ₂ .2H ₂ O	(726)13622 (380)26315	2B_1 $^2A_{1g}$ $^2B_{1g} \longrightarrow ^4E_g$	20.30
6	LZnCl ₂	(316)31645	Charge-transfer \longrightarrow	14.41
7	LCdCl ₂	(379)26385	Charge-transfer \longrightarrow	5.35
8	LHgCl ₂	(311.5)32102	Charge-transfer \longrightarrow	15.31

Table- 4 : continuous variation slop for Ni⁺²ion $\lambda(352mm)$

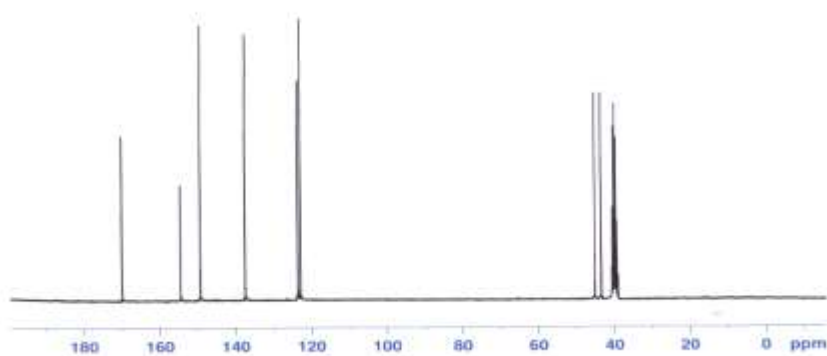
L-NiCl ₂		
V _M	V _L	Abs
1 ml	0.25	0.38
1	0.5	0.87
1	0.75	1.22
1	1	1.6
1	1.25	1.55
1	1.5	1.62
1	1.75	1.62
1	2	1.63

References

- [1] Z. Lakovidou, A.Papageorgiou, M.A. Demertzis, E.Mioqlou, D Mourelatos, A.Kotsis, P.N. Yadav and D. Kovala-Demertiz,"Platinum(II) and Palladium(II) complexes with 2-acetylpyridine thiosemicarbazone:cytogenetic and antiineoplastic effects "Anti-Cancer Drugs 12, 1,2001,65-70.
- [2] R.K. Gouch, T.W. Kensler, L.W. Oberew, R.J. Sorenson, Biochemical and Inorganic copper chemistry 1,1986,139.
- [3] W.B.Eberhardtweck,K..Siega,M.Toniutti and R.Pierluigi,"2-(aminomethyl)pyridine-phosphine Ruthenium (II)"24,7,2005,1660-1669.
- [4] L.N.Margaret,C.P. Gordon and A.T.David "The infrared spectra of 2-aminomethylpyridine complexes of metal(II) ions", J.molecular structure,63,1980,73-80.
- [5] Z.W.Jian,B.Elisabeth,M.M.Allison and L.S.Anthony"Manganese (II) complexes of a set of 2-(aminomethyl)pyridine-derived ligands bearing a methoxalkyl" Inorg . Chem., 357, 2004,2694-2702.
- [6] N.Nonyama,S.Tomita and K.Yamasaki"N-(2-pyridyle)acetamide complexes of metal ions", Inorg . Chem.Acta,12,1975,33-37.
- [7] R.A. Manhel , "synthesis of pheyl alanine Schiff Base ligand and its complexes with some metal (II) ions and Evalulation of their Anti bacterial Activity" , J.Al – Mustansiriya .sci. 21,3, 2010,65 – 78.
- [8] L.J. Bellamy , "The infrared spectra of complex molecules" , Hasted press , Division of John Willey and sons , Inc.,ed. 3rd , 1975, New York .
- [9] J.W.Cooper ," spectroscopic Techniques for organic chemistry", John Willey and sons , ed. 2nd,1980, New York .
- [10] K.S. Nakamato, "Infrared spectro of inorganic and coordination compounds", 4th ed., 81, 1986, wiley Inter, New York.
- [11] A.P.Singh,K.N.Kaushik,A.Vrmak and R.Gupta,"Synthesis,Stucture and anticancer activity of Copper(II) complexes of N-benzyl-2-(diethylamino)-N-phenylethyl acetamide",Indian ,J.chem,50A,2011,474-483.
- [12] W. N .Kadeoka , " Crystal and Molecular structure of Dichloro bis (2 – pyridyl) disulphide cobalt(II)" , Inorg Chem. 15 (12),1976,812 – 820 .
- [13] J. C.Foresman and C .A Frisch ,:Exploring chem , With Electronic structure methods , Gaussian – Inc ed. 2nd., Pittsuburgh ,1996,101.
- [14] G.Budige,M.R.Puchkayula,S.K.Kongara,H.V.Anren and R.Vadde,"Synthesis ,Characterization and Biological Evalution of Mononuclear Co(II) ,Ni(II) ,Cu(II),Pd(II) complexes with new N₂O₂ schiff Base ligands chem. Pharm.Bull59,2,166-171.
- [15] S.N.Dubey and K.Beena, "Triazoles as complexing agents :Synthesis and characterization of Co(II) ,Ni(II) , Co(I)Cu(II),Zn(II) and Cd(II) complexes with 4-amino-mercapto-3n-propyl-3-triazole and 5-Mercapto-3-n-propyl-4-salicylidineamino-s-trizol",Indin J.chem,24A,1985,950-953.
- [16] T.N.Ahmad, O. I. Issa and k.Leqaa,"Synthesis and Characterization of New ions",J. Kerbala University,6,42008,278-285.
- [17] D.A.Skoog,,"Fundamental of Analytical chemistry",Wily Inter,New York,1988,2441.



(Fig 1):¹H NMR spectrum of the ligand (L)



(Fig 2):¹³C NMR spectrum of the ligand (L)

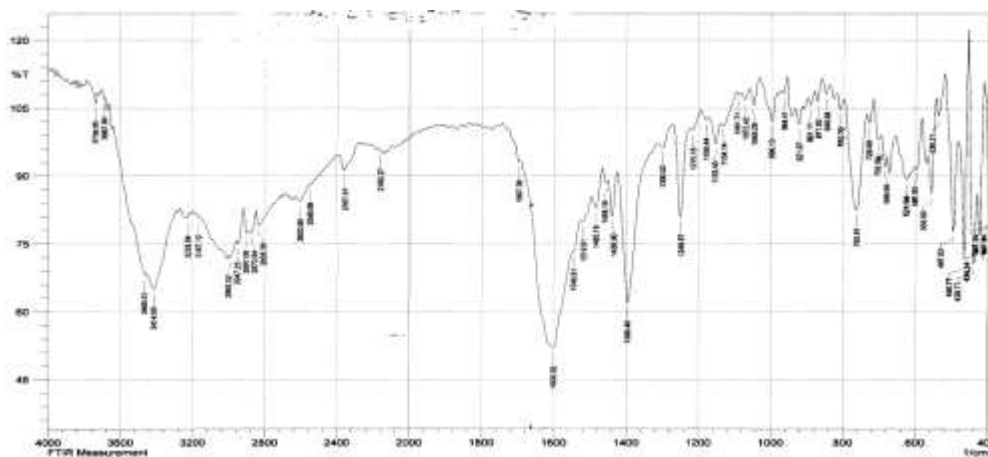


Fig- 3: Infrared spectrum of the ligand(L)

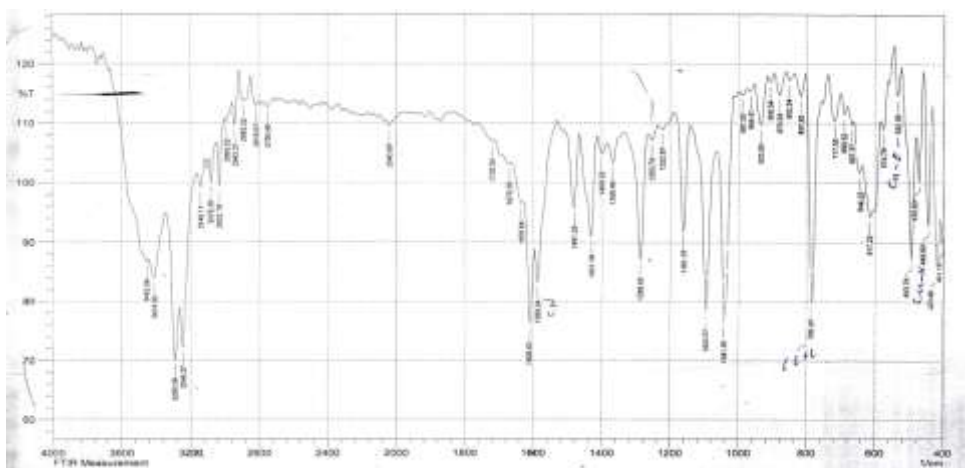


Fig- 4: Infrared spectrum of the $LCuCl_2 \cdot 2H_2O$

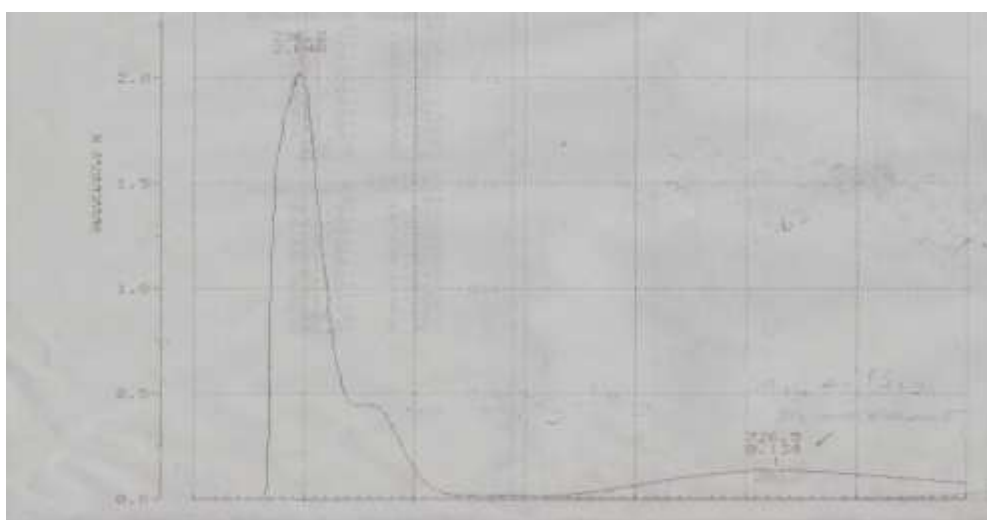


Fig-5:uv-visible spectrum of the $LCuCl_2 \cdot 2H_2O$

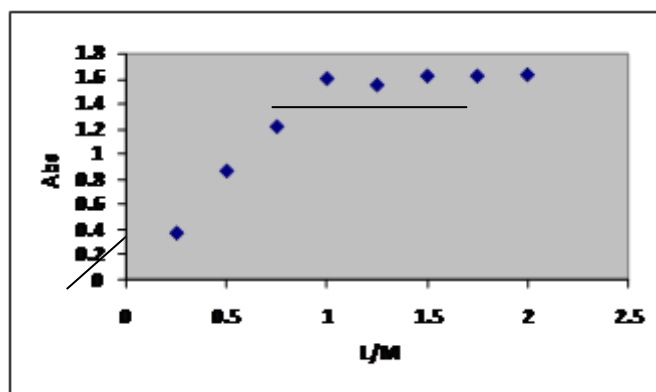


Fig-6: The molar-ratio curve the complex $L-NiCl_2 \cdot H_2O$

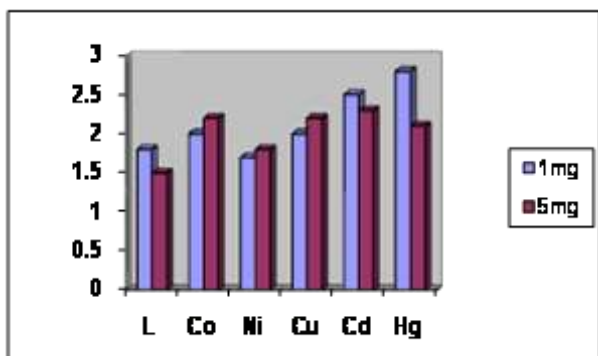


Fig- 7:Effect of ligand and its complexes on *taphylococcosaureus*.

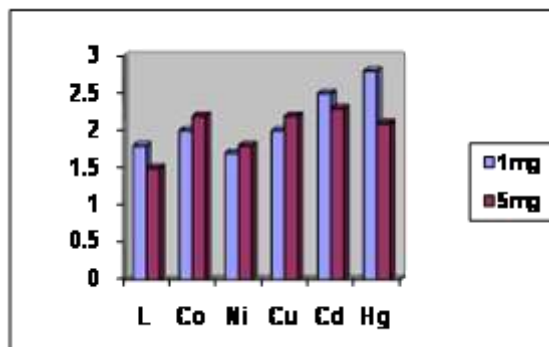


Fig-8: Effect of ligand and its complexes on *E.coli*.