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Synthesis, Spectroscopic and Biological Studies of some metal ions complexes with 1-Phenyl-3-pyridin-2-ylmethyl-thiourea

تحضير ، دراسة طيفية وبايولوجية لبعض المعقدات الفلزية مع 1- فنيل-3- بردين -2- يل مثيل- ثايويوريا

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ABSTRACT

The ligand 1-Phenyl-3-pyridin-2-ylmethyl-thiourea (L) has been prepared from reaction of 2-(aminomethyl) pyridin with phenyl thiocyanate (1:1). The ligand(L) has been characterized by elemental analysis (C.H,N) ,'H,^{13}C-NMR, IR and electronic spectra. The complexes of bivalent (Co,Ni,Cu,Cd and Hg) ions have been synthesized and characterized by IR, electronic spectra, molar conductivity, atomic absorption and molar ratio.The analytical studies for the complexes showed octahedral 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* .

Key words : synthesis , Spectroscopic, complexes , biological activity

الخلاصة :-

حضر الليكاند (L) 1-فنيل-3- بردين -2- يل مثيل-ثايويوريا من تفاعل 2 - أمينو مثيل بردين مع فنيل ايزوثايوسيانيت وبنسبة 1:1 وشخص الليكاند بواسطة التحليل الدقيق للعناصر (C,H,N), الأشعة تحت الحمراء ، الأشعة فوق البنفسجية – المرئية وطيف الرنين النووي المغناطيسي كما حضرت وشخصت معقدات أملاح بعض ايونات العناصر الثنائية التكافؤ (Co,Ni,Cu,Cd and Hg). استخدمت تقنية الأشعة تحت الحمراء ، الأشعه فوق البنفسجية-المرئية , التوصيلية الكهربائية و الامتصاصية الذرية وأستنتج من التحاليل ان المعقدات لها شكل ثماني السطوح .

كما تمت دراسة الفعالية البايولوجية لليكاند ومعقداته وقد اظهرت النتائج امتلاكها فعالية متفاوته اتجاه انواع البكتريا *E.coli* , *Staphylococcus aureus* .

INTRODUCTION

Transition metal complexes containing N,S/or N,O donors have been played an important role in the development of new coordination chemistry. The synthesis of ligands containg oxadiazol, triazol with some of their complexes were performed [1-3], The oxygen, nitrogen and sulphur donor atoms of Urea, thiourea derivatives provide of binding possibilities aswell. Both ligands and their metal complexes display a wide range of biological activities [4,5]. As a part of our continuing efforts to synthesise and characterise metal chelates using polydentale ligand, we describe here the synthesis and spectral investigation of new ligand; 1- phenyl -3- pyridine -2- ylmethylthiorea and some metal complexes

Experimental

a- Chemicals;

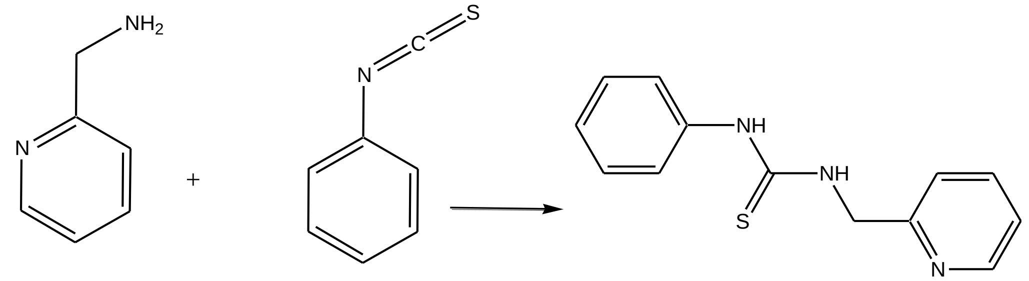
All chemicals were purchased from B. D. H and were used without further purification.2-(aminomethyl)pyridin ($C_6H_8N_2$), phenylisothiocyanate (C_7H_5NS),Cobalt chloride hexahydrate ($CoCl_2.6H_2O$), Nickel chloride hexahydrate ($NiCl_2.6H_2O$) Copper chloride dehydrate ($CuCl_2$.2H2O),Cadimum chloride 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% (CCl4) were purchased from fluka.

b- Instruments;

- Elemetal analysis for the new (L) (C, H, N) was determined by calibration type : Linear Regression Euro EA 3000 A Elemental Analysis were made in the AL-Albayt University Amman –Jordan .
- Melting points were determind by Gallen-Kamp apparatus.
- 'H,^{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°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.

Snythesies of 1- Phenyl -3- pyridin -2- ylmethyl - thiourea (L)

2-(aminomethyl)pyridin (1mmol,0.108g) in ethanol (10 mL) was added to a solution of phenylisothiocyanate (1mmol,0.14g) in (15mL) ethanol.The mixture was stirred for 1h..The product was recrystallised from ethanol and dried (melting point,102°C),yield 88%.The reaction is illustrated as follows;



2 - amino methyl pyridine phenylisothiocyanate 1-Phenyl-3-pyridin-2-ylmethyl-thiourea

Synthesis of metal ions complexes.

An ethanolic solution of the following metal salts $CoCl_2.6H_2O$(0.237g, 1mmol), $NiCl_2.6H_2O$ (0.237g, 1mmol), $CuCl_2$. $2H_2O$ (0.17, 1mmol g), $CdCl_2.H_2O$ (0.201 g, 1mmol) and $HgCl_2$ (0.271g, 1mmol) were added to a solution of the ligand (L) (0.24 g, 1mmol) in ethanol. The mixture was stirred for 30 min. The product was filtered and washed with distilled water and drid under vacuum. Physical properties for the ligand and its complexes are given in Table(1).

Results and Discussion

The ligand (L) checked and confirmed by elemental analysis (C,H,N) , 'H,^{13}C-NMR, IR. The ^{1}H-NMR is represented in table (2) Fig. (1) shows multiplets corresponding to aromatic five protons at 7.12-8.53 ppm. The signal at 9.88 ppm is due to 2- pyridine. The protons of methylene amine CH_2-NH shown singlets at (2.50 NH and 5.06 CH2) ppm. The aromatic C-NH is shown at 4.62 ppm.

The ^{13}C-NMR shows the C=S peak at 181.19 ppm, the pyridine carbon peaks at (158.6-120.6) ppm. The aromatic carbons peaks at (139.4-124.5) ppm. The methyline amine showed peak at 49.39ppm Fig. (2). These data are compitable with chem ^{1}H-NMR ,^{13}C-NMR are shown in table (2-3). IR spectrum of the (L) table (4) and fig.(3) showing appearance of υNH (3381) cm-^{1} and appeared bands at (1595, 1577)cm-^{1} are due to phenylamine and pyridine The stretching vibration at 694 cm-^{1} is due to C=S and band at 1100 cm-^{1} is due υ(C-N) + υ (c=s) [6].

IR Spectra of complexes

The comparative IR spectral study of the ligand(L) and its complexes Fig (4) (Cu- complex as example), reveals the interesting coordination of the ligand during complex formation. The important IR bands with their possible assignment are depicted in Table (4) .

In general upon metal ion interaction, the presence broad is observed at 3257 cm^{-1} , multiple bands at (1606,1541) cm^{-1} are indicating coordination of the nitrogen of the NH. The υ(C=N) stretching of pyridine around 1521cm^{-1} in the free ligand is shifted to higher frequency and observed around 1545 cm^{-1} indicating coordination of nitrogen of the C=N pyridine moiety to the metal atoms. At Lower frequency the complexes exhibited new bands around 437-550 which is assigned to the υ (M-N) vibration mode . All the complexes didn't show shift of the C=S group indicating that not involvement of thio carbonyl sulphur atom in coordination with these metal ions.[7-9].

Electronic absorption spectral studies

The electronic spectral data of free ligand and its complexes are summarized in table (5). The peak at 264 nm (37879) cm^{-1} in the electronic spectrum of free ligand (L) Fig (5) was assigned to n-- π* transition. The peaks at 656 nm (152439) cm^{-1} (Cd complex) and 684 nm (14619) cm^{-1} (Hg complex), which were assigned to a charge transfer [10-11]. The copper complex exhebited broad band around 692nm (14450) cm^{-1} which was assigned to $^2Eg \longrightarrow {}^2T_2g$ typical for an octachedral configuration [12] . The spectrum of the Ni complex showed d-d bands at 698 nm (14327) cm^{-1} and 552 nm (18115) cm-^{1} are assigned to ^3T_1g (F) $\longleftarrow$ ^3A_2g (F) and ^3T_1g (p)$\longleftarrow{}^3A_2g$ (F) transition consistent with its octahedral configuration fig(6) , The electronic spectrum of the Co complex resolved bands around 674 nm (14836) and 550 nm (18182) cm^{-1} which assigned to $^4A_2g\longleftarrow{}^4T_1g$ and ^4A_2g $\longleftarrow$ ^4T_1g, For a high- spin octahedral geometry [12] .

Molar ratio

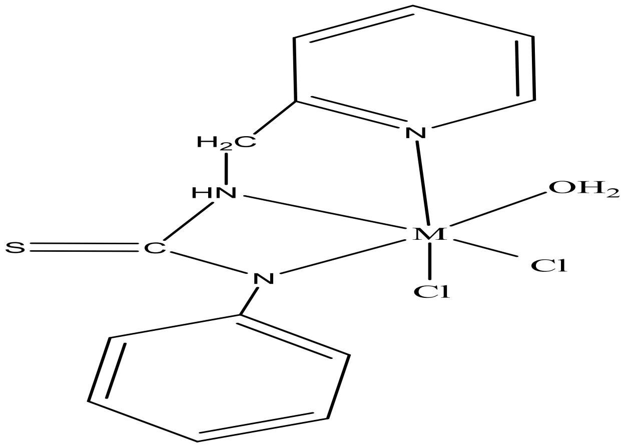
Complex formation by molar ratio of ligand to metal ion was studied in solution. A series of solutions containing constant concentration of metal ion (1×10^{-3} M) were treated with the same volumes of various concentrations of ligands. The result of L:M were obtained by plotting absorbance of solution at λ_{max} (750) nm of the complexes against [L] /[M] which showed a 1:1 M:L for all complexes fig. (7) as observed for the solid state (Atomic absorption) data [13] .

Study of biological activity

The biological activity of the prepared new ligand and its complexes (Co^{II},Ni^{II}, Cu^{II}, Cd^{II} ,Hg^{II}) were studied against selected types of micro organisums which include gram positive bacteria like staphylococcus aureues and gram negative bacteria like E.coli in agar diffusion method , which is used (DMF) as asolvent . Agar diffusion method involves the exposure of the zone of inhibition toward the diffusion of micro organisms on agar plate . The plates were in cubated for (24) hrs. at (37co) The zone of inhibition of bacterial grouth around the disc was observed Fig.(8-9).

Conclusion

A series of (Co^{2+},Ni^{2+},Cu^{2+}, $Cd^{2+}$and Hg^{2+}) complexes with 1-Phenyl-3-pyridin-2-ylmethyl-thiourea (L) have been prepared and characterzed. The thridentate ligand (N,N) is binding metal ions .



M^{2+} = Co , Ni , Cu , Cd , Hg

Table (1): color , melting point , yield , metal analysis and conductivity for the ligand(L) and its complexes

NO	compound	Color	m. p. c^o or (dec)	Yield %	Metal analysis found (calculated)				Conductivity S.cm^2
					C %	H %	N %	M %	
1	(L) $C_{13}H_{13}N_3S$	Green	102	88	72.29 (72.361)	6.531 (6.532)	21.230 (21.105)	—	——
2	L-$CoCl_2.H_2O$	Dark green	202	63	—	—	—	15.17 (14.95)	16.5
3	L-$NiCl_2.H_2O$	Brown	139	74	–	—	—	15.12 (14.87)	11.8
4	L-$CuCl_2.H_2O$	green blue	164	81	—	—	—	16.17 (16.01)	9.5
5	L-$CdCl_2.H_2O$	Green	150	88	—	—	——	22.67 (23.04)	10.7
6	L-$HgCl_2.H_2O$	Green	143	87	—	—	——	37.85 (37.22)	11.69

Table (2): ^{1}H- NMR chemical shifts for (L) in DMSO-d^{6} (practically and theoretically are comptable)

compound	Aromatic(5p)	2- pyridine (CH)	CH_2	Ar-NH	CH_2-NH
(Pract) L	7.12-8.53	9.88	5.06	4.62	2.50
Theoretically	6.46-7.01	8.64	5.04	5.04	2.00

Table (3):^{13}C-NMR chemical shift for logand (L) in DMSO- d6 (practically and theoretically are comptable)

Compound	C=S	2- pyridine (CH)	Aromatic	CH_2-NH_2
L	181.19	158.6-120.6	139.4-124.5	49.36
Theoretically	179.6	149.20-149.4	139.4-125.3	55.80

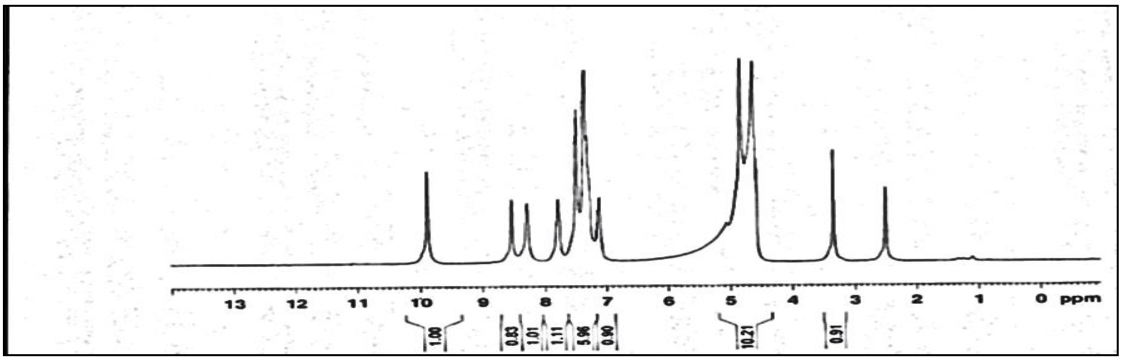
Table (4): Characteristic Vibrational freguencies (cm^{-1}) Located in the FT-IR of the Ligand (L) its complexe

Compounds	υ (N-H)	υ (C-H) aliph	Arom	(C-N) pyridine	υ(C=S)	M-N	OH2
L	3338 1595(be)	2987	3093	1521	694	---	---
$L.CoCl_2.H_2O$	3257(br) 1597(be)	2987	3093	1558	692	416	802
$L.NiCl_2.H_2O$	3282 1597(be)	2987	3093	1543	692	418	835
$[L.CuCl_2.H_2O].2H_2O$	3282(br) 1629(be)	2987	3057	1575	690	418	819
$L.CdCl_2.H_2O$	3203(br) 1600(be)	2968	3035	1570	694	418	837
$L.HgCl_2.H_2O$	3203 1600(be)	2968	3035	——	——	——	——

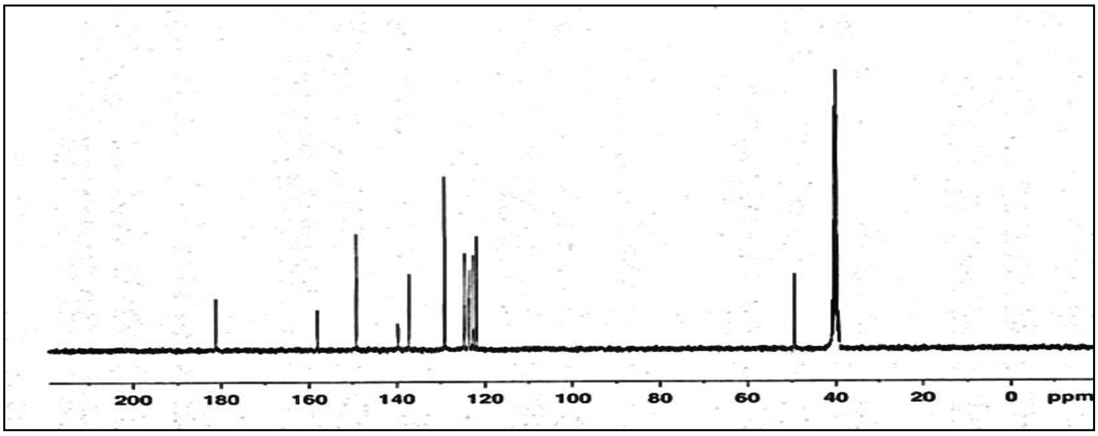
be = bending , br = broad

Table (5): Electronic spectral data of Ligand (L) and its metal Complexes

Compounds	Λnm	ύ wave number	A ssignments bands	Proposed structure
L	264	37879	n-π*	______
$L.CoCl_2.H_2O$	674 550	14836 18182	${}^4A_2g \leftarrow {}^4T_1g$ ${}^4A_2g \leftarrow {}^4T_1g$	Octahedral
$L.NiCl_2.H_2O$	698 552	14327 18115	${}^3T_1g\ (F) \leftarrow {}^3A_2g$ ${}^3T_1g\ (p) \leftarrow {}^3A_2g(F)$	Octahedral
$[L.CuCl_2.H_2O].2H_2O$	692	14450	${}^2Eg \rightarrow {}^2T_2g$	Octahedral
$L.HgCl_2.H_2O$	684	14619	C-T	Octahedral
$L.CdCl_2.H_2O$	656	182439	C-T	Octahedral



`Fig-1:${}^1H$ NMR spectrum of the ligand (L)



`Fig- 2 :${}^{13}C$ NMR spectrum of the ligand (L)

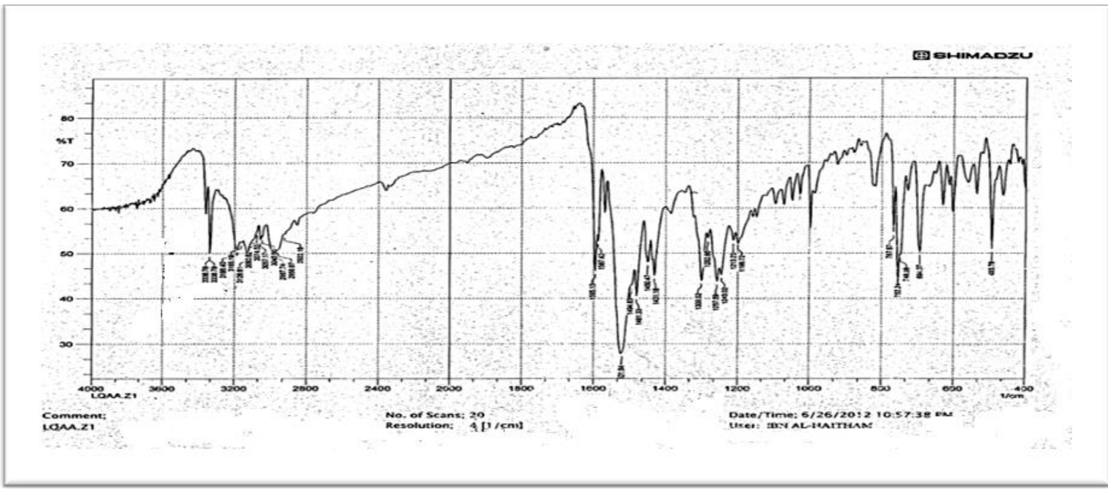


Fig- 3: Infrared spectrum of the ligand(L)

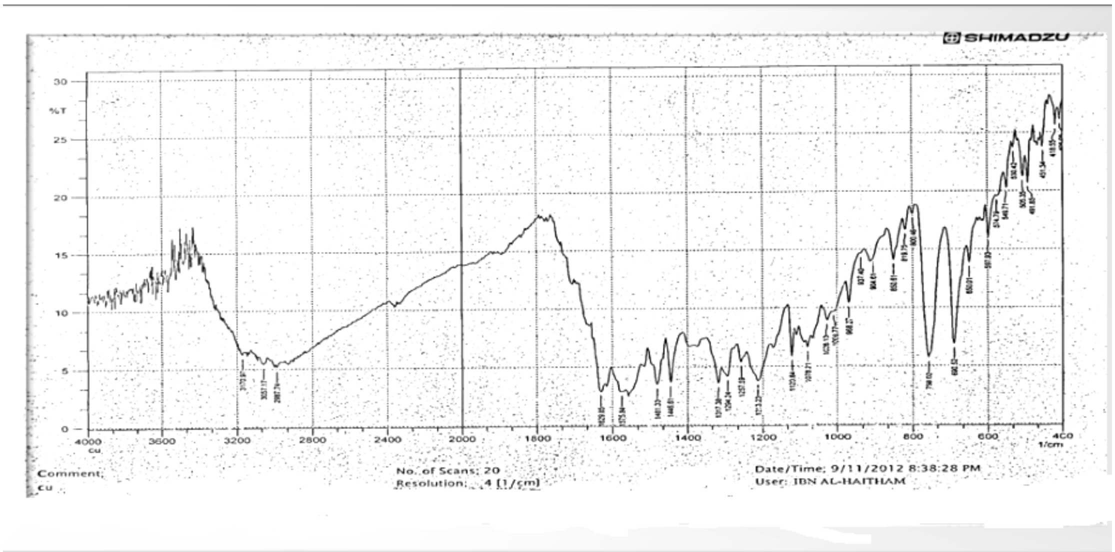


Fig- 4: Infrared spectrum of the [L.CuCl$_2$.H$_2$O].2H$_2$O

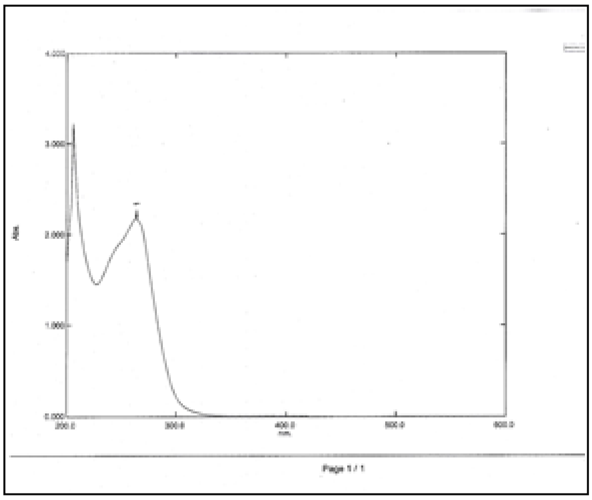


Fig-5:uv-visible spectrum of the (L)

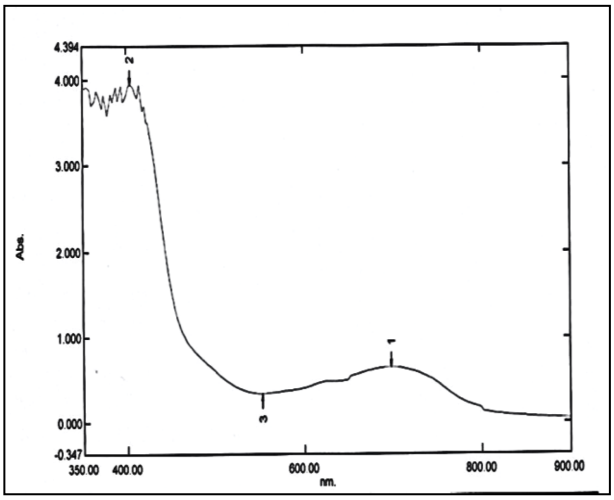
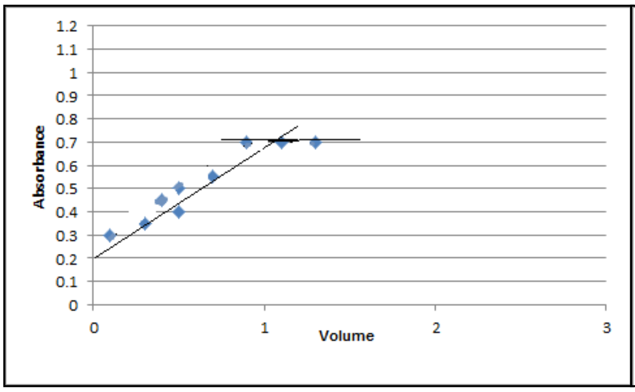
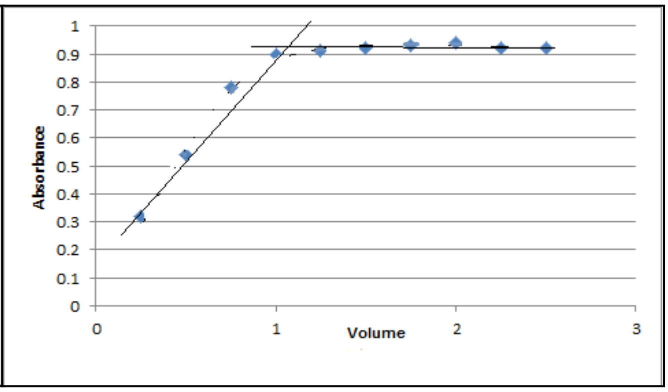


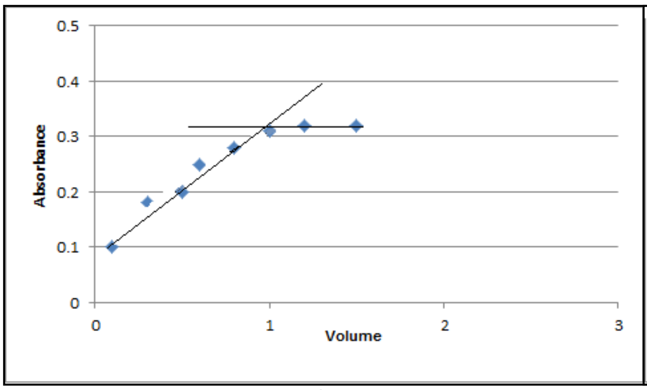
Fig-6:uv-visible spectrum of the L.$NiCl_2.H_2O$

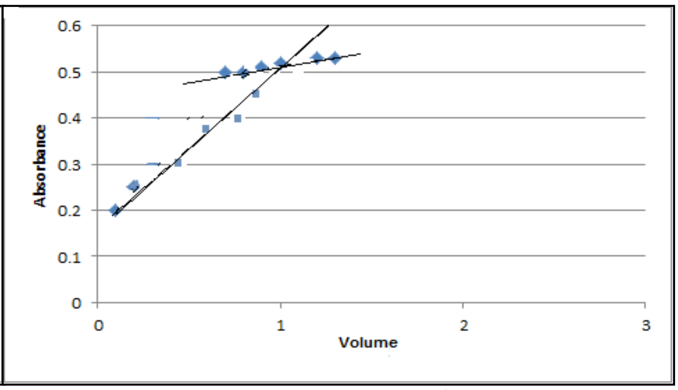




(L/ Co^{+2})

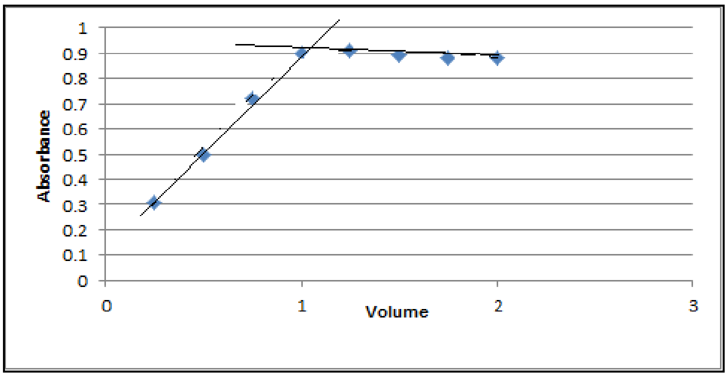
(L/Ni^{+2})





(L/Cu^{+2})

(L/Cd^{+2})



(L/Hg^{+2})

Fig.(7): molar ratio curve for the prepared complexes

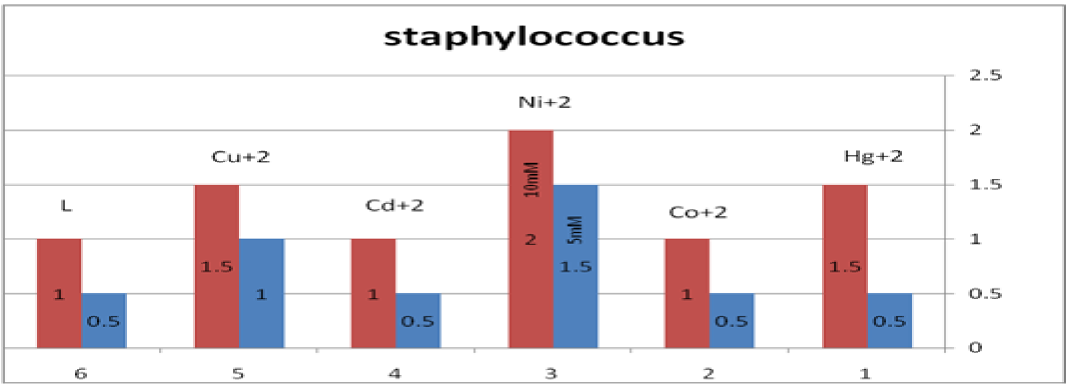


Fig. (8) : biological activity of gram positive bacteria in (5 and 10) mmol

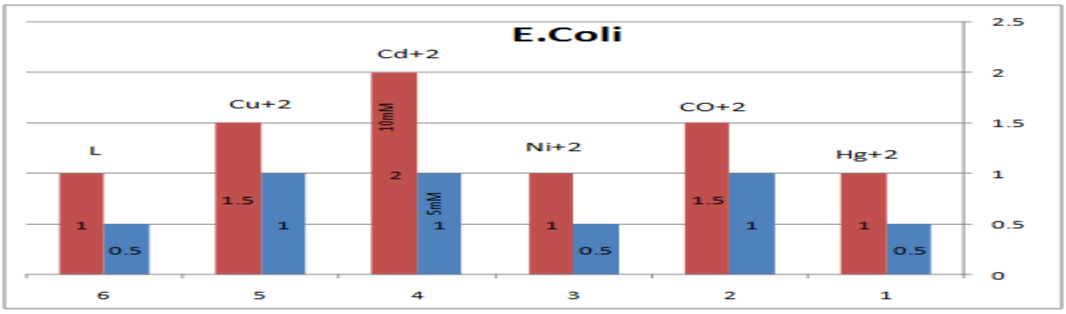


Fig. (9): biological activity of gram negative bacteria in (5 and 10) mmol

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