Coordination Behavior of N_2o Donor Ligand with Some Metalsions

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Abstract

Tridentate Schiff base ligand L^2 and its complexes with nickel(II), cobalt (II), copper (II), manganese (II) and mercury (II) ions have been synthesized by the condensation of 4-Aminoantipyrine, Benzoin, then the ligand (L^1) and 3-amino benzoic acid. The ligand and its complexes were described by ^{1}H-&^{13}C-NMR, UV-visible, FT-IR, (only ligand), molar conductance elemental, analysis and magnetic susceptibility, calculations. It has been set that the ligand acts as (N, N, O) neutral tridentate forming chelates with stoichimetry (metal: ligand) (1:1). all metal complexes is suggested Octahedral configuration. Most of the prepared compounds show antibacterial activity to *(Staphylococcus aureus*),(*Escherichia coli*), (*Bacillussubtilis*) and *(Pseudomonas aer*oginosa*).*

Key words: Schiff base, tridentate, Metal complexesand3-amino benzoic acid.

Introduction

Imins derived from aromatic aldehydes and {substituted aliphatic amines} and {aromatic aldehydes} have a many applications in variety fields, e.g. inorganic, analytical and biological chemistry [1-4]. Schiff bases form an important class of organic compounds in chemistry due to their useful physical and chemical properties and large number of reactions they undergo [5,6]. They are also having many pharmacological activities and industrial enforcements. In enzymatic reactions, Schiff bases play a significantintermediate through of an enzyme with an amino group or carbonyl group of the substrate [7,8]. Biochemists worked earlier [9, 10], reported that metal complexes showed greater activity, when compared to the organic compounds [11]. The new ligands formed by the reaction of ketones, carbazides, aldehydes and thiocarbazides with 4-aminoantipyrine. have been to give the coordinating properties were modified [12-16], A continuation of our work on the synthesis of Schiff bases using benzoin, 4-aminoantipyrine and 3-aminobenzoic acid, we have synthesized the Cobalt (II), Nickel (II), Copper (II), Manganese (II) and Mercury (II) complexes with the Schiff base ligand prepared. We are reporting five complexes of metal (II) with Schiff base ligand, their characterization and antibacterial activity.

Experimental

3-aminobenzoic acid,benzoinand 4-aminoantipyrine were purchased from sigma aldrichCo.(China). Allreagentand solvents were of high purity (sigma)and were used without further purification. The metal salts usedforcomplexation: Copper(II) chloridedihydrate, Cobalt(II) chloride hexahydrate, Nickel(II) chloride hexahydrate, Manganese (II) chloridetetrahydrate and Mercury (II) chloride were obtained from British Drug House (BDH) chemical limited company**.**

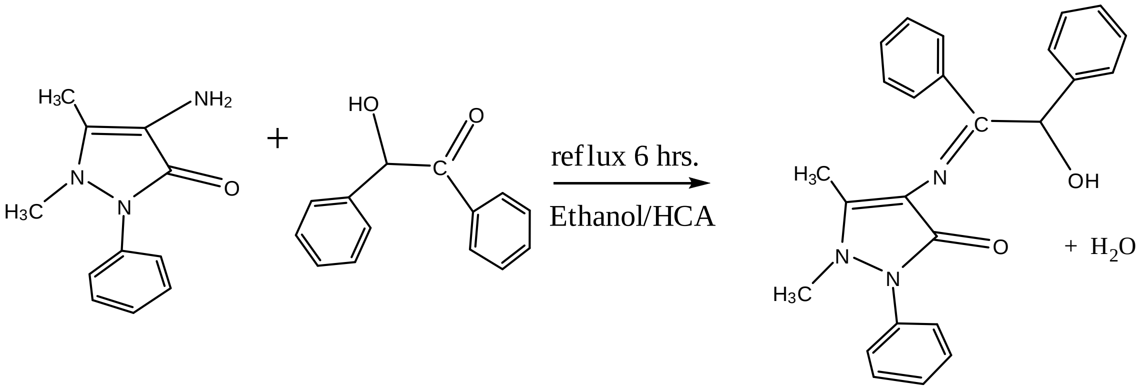
Instrumentation

Melting point was determined on "Gallenkamp Melting point Apparatus". Elementalmicroanalyses C.H.N. were carried out using Euro Vector EA 3000 A Elemental Analysis (Italy).FT-IR measurements were recorded on Shimadzu- spectrophotometer type CECIL, England, in range (200-1000) nm in ethanol .^{1}H and^{13}C-NMR spectra were recorded by using a Bruker 300 MHZ (Switzerland), Chemical shift was recorded in δ(ppm) unit downfield internal reference (TMS),using DMSO-d_6. Conductivity measurements were obtained from WTW conductivity meter by using 10^{-3}M of ethanol. Magnetic susceptibility measurements were obtained at room temperature on using Bruker BM6 instrument. Metal analyses of complexes were determined by Atomic Absorption (A.A.) Technique.

Preparation of Schiff base ligand

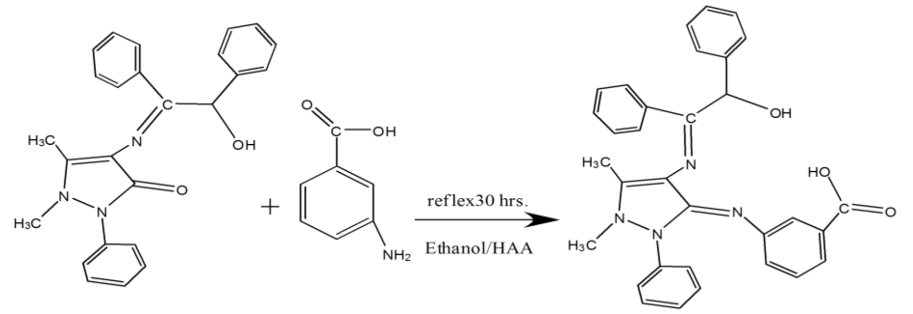
Preparation of 4-(2-hydroxy-1, 2-diphenylethylideneamino)-1, 5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-one (L^1)[20]

4-aminoantipyrine (0.005 mol, 1.01 g) and benzoin (0.005mol, 1.64 g) in ethanol solvent (25 mL) added few drops of glacial acetic acid to solution the mixture was refluxed for (6 hr), then by the filtration and recrystallized for the product precipitate
. m.p (145^{o}C) (Yeild 76 %)(Scheme 1).



Preparation of (L^2)

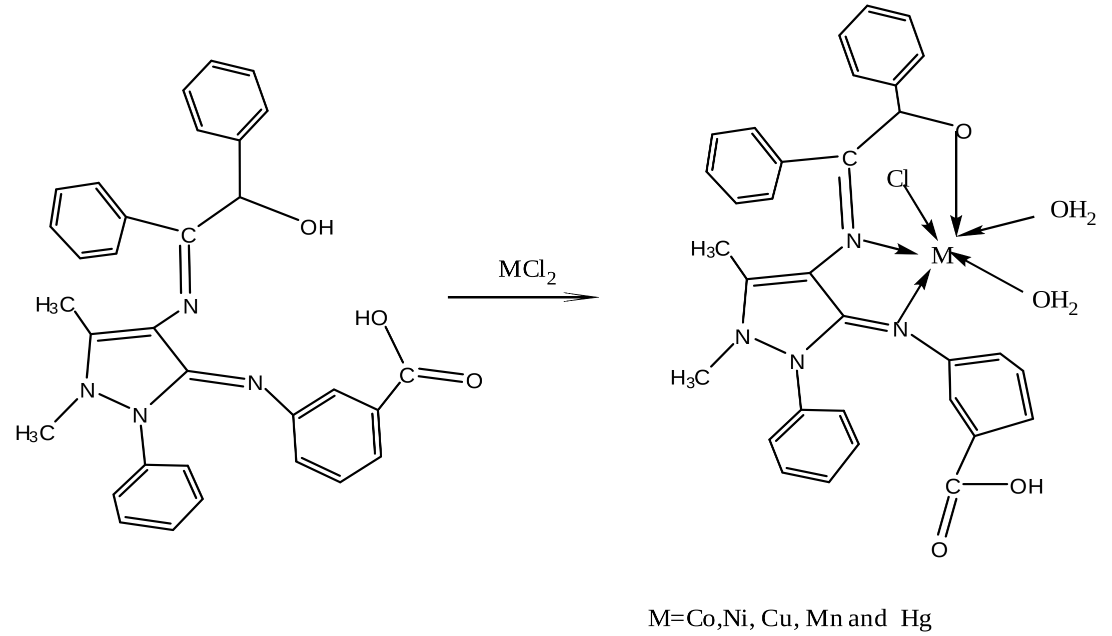
The ligand (L^2) was prepared by condensation of ligand (L^1) (0.005 mole, 1.73 g) which was in 50 mL of ethanol solution and refluxed with (0.005 mole, 0.66 g) of 3-amino benzoic acid adding glacial acetic acid about 3 drops for (30 hr.), a solution was obtained. Then by evaporation , recrystallized and dried over $CaCl_2$ (Scheme 2).



3-((*Z*)-4-((*E*)-((*R*)-2-hydroxy-1,2-diphenylethylidene)amino)-1,5-dimethyl-2-phenyl-1*H*-pyrazol-3(2*H*)-ylideneamino)benzoic acid

Preparation of metal complexes

Metal salt ($CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$, $MnCl_2.4H_2O$ and $HgCl_2$) dissolved and mixed with(0.001mol, 1.05 g)of the ligand (L^2) in(30 mL) the ethanol solution ,then refluxed on a water bath for (1 hr). The result was filtered, washed with ethanol and dried (**Scheme 3**).



M=Co,Ni, Cu, Mn and Hg

Results and Discussion

^{1}H NMR spectrum

The ^{1}H-NMR spectrum of L_2 solution shows the next signals: DMSO at δ_H 2.49,N-C$\underline{H_3}$ at δ_H 3.38,OH-C$\underline{H}$at δ_H 4.68, $C_6\underline{H}_5$ as multiplet at δ_H6.54~8.78Ph-NH- at δ_H 8.78. The peaks observed at δ_H 12.31 and at δ_H 2.07, are attributable to the acidic OH group present in the 3-aminobenzoic acid and alcoholic OH group present in benzoin moiety[5], respectively show in Table(6).

The ^{13}C-NMR spectrum of L_2 solution shows the signals at:(8.64 for =C-$\underline{C}H_3$ group);(33.85 for N-$\underline{C}H_3$ group); (40.59 for DMSO); (75.14 attributed to -$\underline{C}$-OH moiety);(105.08 for=C-N); (123.56~134.17) to 4 benzene rings) and(149.27 for C=C in antipyrine).The peak observed at 165.79is due to the acidic$\underline{C}$OOH group present in the3-aminobenzoicacid[6].The peaksobserved at (161.17 and162.54) were attributable to the twoC=N imine groups.

Infrared spectra of ligand and complexes

The spectrum of free ligand showed band 3518 cm^{-1} which was due to υ (O-H) of benzoin[7].This band is absent in the spectra of complexes indicating the dissociation of the alcohol proton on complexation and involvement of alcohol anionic oxygen in coordination[8].The spectra of ligand showed band at(3388)cm^{-1}due toυ(O-H) of 3-amino benzoic acid [9].All the complexes displayed the bands at range (3426-3409)cm^{-1}and the weak bands at(871-852cm^{-1})were due to ν(OH) and δ(OH) for refer to presence to coordinate aqua (H_2O)[10]. All the complexes displayed this band at range (3388-3368)cm^{-1}and the weak bands at(871-852cm^{-1})were due to ν(OH) and δ(OH) for refer to presence to coordinate aqua (H_2O)[11].The absorptions at (1660)cm^{-1}and (1604)cm^{-1}in ligand showed two{stretching vibration} υ (C=N) of imine nitrogen. These bands shifted to lower wave numbers at range (3429-3382) cm^{-1}in the complexes suggesting theco-ordination of the two azomethine nitrogen to the metal centers.The spectra of the free ligand showed band at (1157) cm^{-1}due to υ(C-O) of benzoin. This band shifted to higher wave numbers at range (1173-1165) cm^{-1}in the complexes suggesting the co-ordination of the oxygen atom of benzoin. The appearance of a new non-ligand band around (547-516) and (466-434) cm-1 cm^{-1} in all complexes due to υ (M-O) and υ (M-N)substantiates it[11]. given in Fig. 2.

Magnetic measurement and electronic spectra

The UV-Vis spectrum of the ligand is characterized mainly by two bands at 385 nm (25839cm^{-1}), and 275 nm (36363cm^{-1}), which may be assigned to {n → π*and π → π* transitions}. These transitions were also found in the spectra of the complexes[13], but they were shifted towards lower frequencies/ (Fig. 3).

i) Co (II) complex shows exhibits absorption at(657 nm (15220cm^{-1}) and (486) nm (20576cm^{-1}). These bands may be assigned to the transitions:{ $^4T_1g_{(F)} \rightarrow {}^4T_1g_{(p)}and^4T_1g_{(F)} \rightarrow {}^4A_2g_{(F)}$(d-d)} transitions respectively. [14].

(ii) The electronic spectrum exhibits two bands at (543) nm (18416cm^{-1}) and (668) nm (15197cm^{-1}) which may assigned to {$^3A_2g \rightarrow {}^3T_1g_{(P)}and^3A_2g \rightarrow {}^3T_1g_{(F)}$}, respectively in octahedral [15].

(iii) Cu (II) spectrum shows band centered at 530 nm (18867cm^{-1}) which may assigned to $^2Eg \rightarrow {}^2T_2g$ transition in octahedral.

(iv) Mn (II) spectrum, show absorption at (553nm)(18083 cm^{-1}) due to{ $^6A_1g_{(S)} \rightarrow {}^4T_2g_{(G)}$ } in octahedral.

(v) Mercury (II) complex is diamagnetic moment for d^{10} ions andthe electronic spectra there complex do not show any d-d band in Fig. 4. [18].

magnetic moment values of the Co(II), Cu (II), Ni(II) ,Mn(II) complexes (4.32,1.78, 5.32 , 3.33 B.M)

Conductivity measurement

The conductivity values showed the complexes in range (19.56-12.18) ohm^{-1}.cm^2. Mole^{-1}[19].These values suggested that the complexes are non-electrolytes .According to these results the structural formula of the complexes shown in (Scheme 3).

Biological Activities

The biological activities of the prepared ligand and its complexes were studied by using inhibition method [21,22] for four types of pathogenic bacteria. Two types of bacteria were gram positive which are *Staphylococcus aureus* and *Bacillus*; the second two were grams negative which are *Escherichia coli* and *Pseudomonas*. The data reveal that all compounds have good biological activity and some complexes have higher activities than the free ligand. This may be due to that the chelation considerably reduces the polarity of the metal ion mainly because of partial sharing of its positive charge with the donor groups and possible electron delocalization over the whole cheated ring such, chelation could also enhance the lipophilic character of the central metal atom, which subsequently favors its permeation through the lipid layer of the cell membrane [26, 32]. Diameter of zone of inhibition Table. 4 and (Fig.7)

Conclusion

The ligand L^2 and its complexes have been prepared. The geometry is proposed for all complexes show {octahedral stereochemistry}.

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Table (1): Physical characterization, analytical data of the ligand and its complexes

Compounds	Molecular Weight	Colour	Yeild%	M.P.	%Elemental Analysis Found % (Calculated)				
					C	H	N	Cl	M
L^2	516.59	Light brown	80	202	59.98 (74.40)	5.66 (5.46)	10.43 (10.85)	-	-
$[Co(L^2)(H_2O)_2Cl]$	646.0	Brown	74	230	59.98 (59.50)	4.79 (4.84)	8.44 (8.67)	5.12 (5.49)	9.89 (9.12)
$[Ni(L^2)(H_2O)_2Cl]$	645.76	Brown	76	221	59.43 (59.52)	4.67 (4.84)	8.09 (8.68)	5.46 (5.49)	9.78 (9.09)
$[Cu(L^2)(H_2O)_2Cl]$	650.61	Deep brown	82	236	58.57 (59.07)	4.58 (4.80)	8.34 (8.61)	5.32 (5.45)	9.45 (9.77)
$[Mn(L^2)(H_2O)_2Cl]$	642.0	Brown	72	227	59.08 (59.87)	4.26 (4.87)	8.33 (8.73)	5.00 (5.52)	7.89 (8.56)
$[Hg(L^2)(H_2O)_2Cl]$	788.17	Off-White	71	223	48.00 (48.80)	3.64 (3.97)	6.89 (7.11)	4.87 (5.50)	25.45 (25.47)

Table (2): IR values (wave number υ′) $cm^{-1}$for the ligand(L^2) and its complexes

Compound	υ(OH)	$\upsilon(CH)_{aroma.}$	$\upsilon(CH)_{alipha}$	$\upsilon(C=O)_{carboxyl}$	υ(C=N)	υ(C=C)	υ(C-O)	υ(OH)	υ(M–N) υ(M–O)
L^2	3518 3388	3059	2918	1708	1660 1604	1546	1157	-	-
$[Co(L^2)(H_2O)_2Cl]$	3417 3373	3062	2923	1706	1639 1585	1585	1171	864	523 443
$[Ni(L^2)(H_2O)_2Cl]$	3429 3368	3096	2835	1705	1620 1590	1590	1165	852	516 466
$[Cu(L^2)(H_2O)_2Cl]$	3409 3388	3088	2967	1707	1624 1587	1587	1168	875	535 457
$[Mn(L^2)(H_2O)_2Cl]$	3405 3378	3103	2988	1704	1630 1582	1582	1170	863	547 434
$[Hg(L^2)(H_2O)_2Cl]$	3412 3382	3075	2974	1707	1623 1584	1584	1173	871	520 448

Table (3): UV.- Visible data of the compounds

Compound	μ_{eff}	Λ_m S.Cm^2 molar^{-1}	λnm	υ–wave number cm^{-1}	Assignments
L^2	-	-	275	36363	π→π*
			385	25839	n→π*
$[Co(L^2)(H_2O)_2Cl]$	3.98	17.8	289	34602	L.F
			486	20576	$^4T_1g_{(F)}\rightarrow{}^4T_1g_{(P)}$
			657	15220	$^4T_1g_{(F)}\rightarrow{}^4A_2g_{(F)}$
$[Ni(L^2)(H_2O)_2Cl]$	3.57	14.5	298	33557	L.F
			543	18416	$^3A_2g(F)\rightarrow{}^3T_1g(P)$
			668	15197	$^3A_2g(F)\rightarrow{}^3T_1g(F)$
$[Cu(L^2)(H_2O)_2Cl]$	1.83	12.6	295	33898	L.F
			530	18867	$^2Eg\rightarrow{}^2T_2g$
$[Mn(L^2)(H_2O)_2Cl]$	5.76	12.7	297	33670	L.F
			376	26595	L.F
			553	18083	$^6A_1g(s)\rightarrow{}^4T_2g(G)$
$[Hg(L^2)(H_2O)_2Cl]$	-	16.9	290	34482	L.F
			407	24570	C.T

Table (4):Diameter of zone of inhibition (mm)of L^2

Comp.	L^2	$[Co(L^2)(H_2O)_2Cl]$	$[Ni(L^2)(H_2O)_2Cl]$	$[Cu(L^2)(H_2O)_2Cl]$	$[Mn(L^2)(H_2O)_2Cl]$	$[Hg(L^2)(H_2O)_2Cl]$
Escherichia. Coli	4	8	7	6	13	12
Staphylococcus aureus	6	6	9	9	6	9
Bacllus	10	11	10	12	11	15
pseudmonas	8	10	14	14	9	7

Table (5)^{1}H-NMR for ligand (L^2) (ppm in DMSO)

$HC\text{-}O\underline{H}$	DMSO	$N\text{-}C\underline{H}_3$	$HO\text{-}C\underline{H}$	$C_6\underline{H}_5$	$COO\underline{H}$
2.07	2.49	3.38	4.68	6.54 ~8.78	12.31

Table (6):^{13}C-NMR forligandS (L^2) (ppm in DMSO)

$C\text{-}\underline{C}H_3$	$N\text{-}\underline{C}H_3$	DMSO	$HO\text{-}\underline{C}H$	=C-N	$\underline{C}_6H_5$	C=C	C=N	$\underline{C}OOH$
8.64	33.85	40.59	75.14	105.08	123.56~134.17	149.27	161.17 162.54	165.79

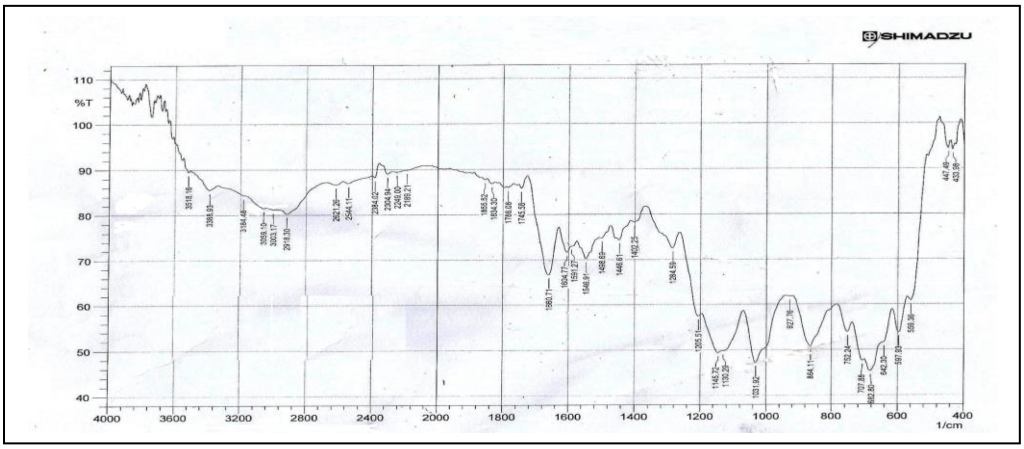


Figure (1):IR spectrum of ligand (L^2)

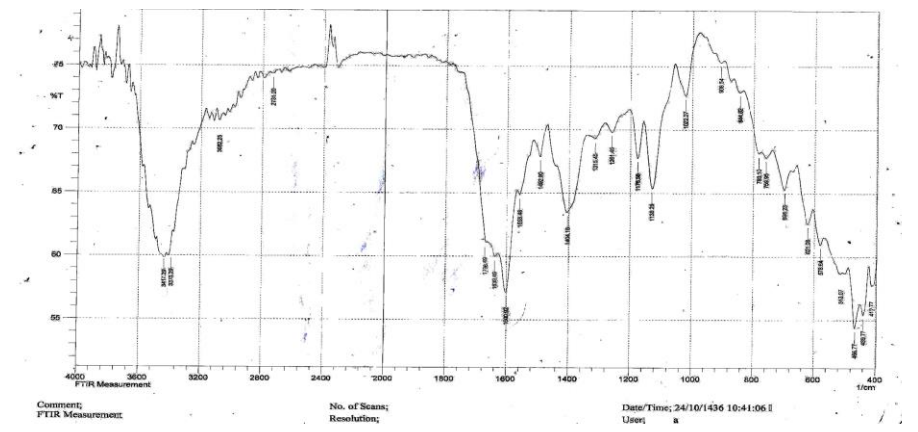


Figure (2):IR spectrum of $[Co(L_2)(H_2O)_2Cl]$ complex

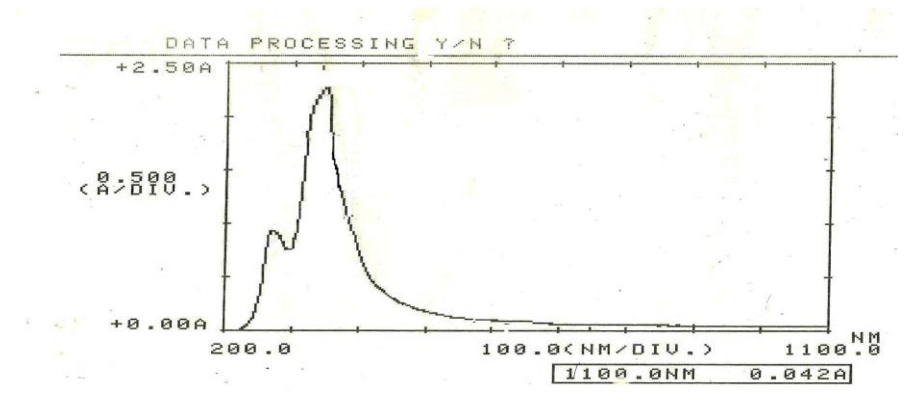


Figure (3): UV-Visible spectrum of the ligand(L^2)

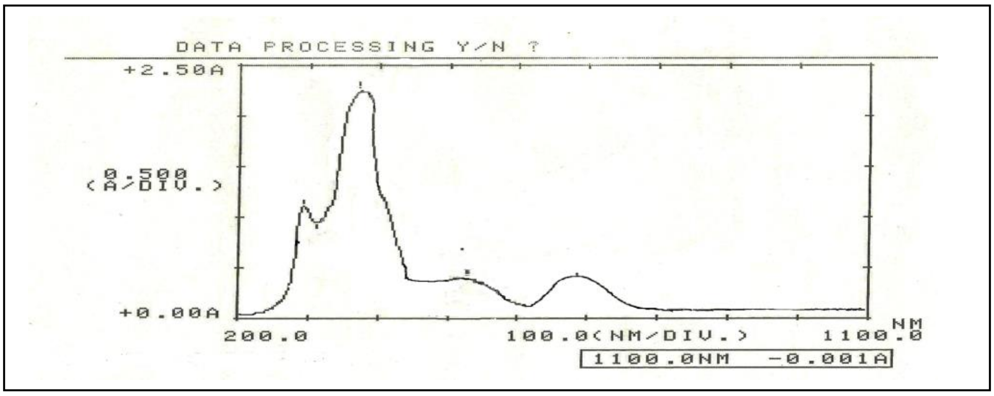


Figure (4):Electronic spectrum of Ni(L^2)(H_2O)$_2$Cl]complex

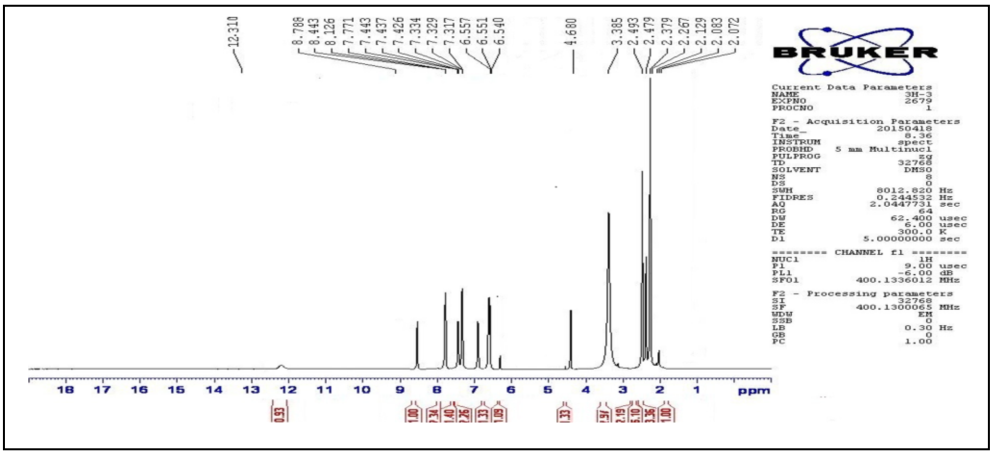


Figure (5): The^{1}H-NMR spectrum of the ligand (L^2)

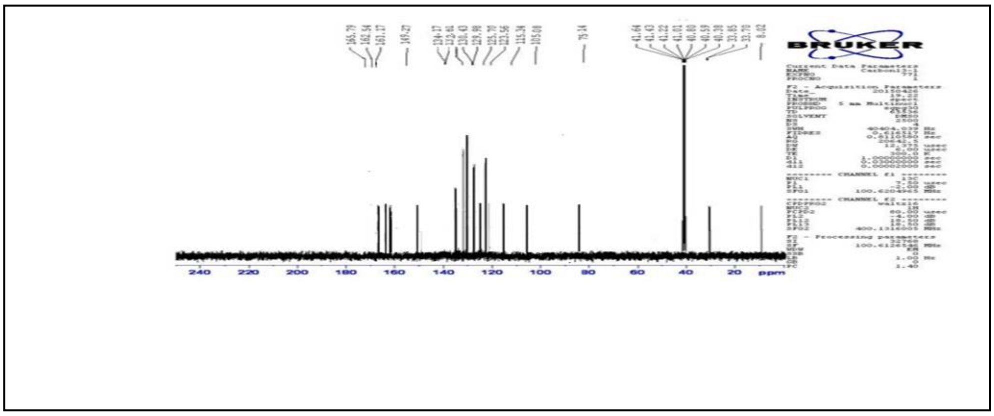
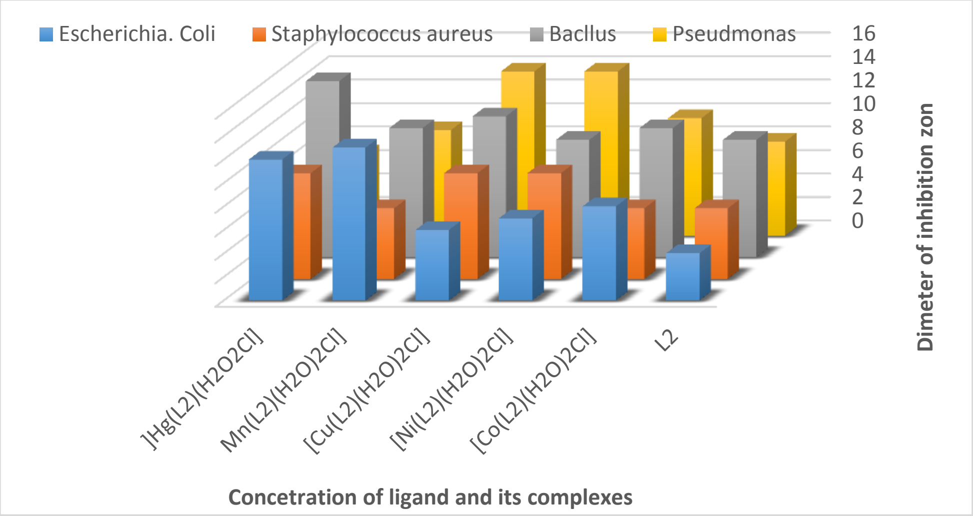


Figure (6): The ^{13}C-NMR of the ligand (L^2)



Figure(7):Difference between the antimicrobial activity of ligand(L_2)& metal complexes

سلوك التناسق لليكاند مانح N_2O مع بعض ايونات الفلزات

علي مضر الخزرجي
جامعة بغداد /كلية التربية للعلوم الصرفة (أبن الهيثم) /قسم الكيمياء

استلم في:16/كانون الأول/2015، قبل في:5/نيسان/2016

الخلاصة

ليكاند قاعدة شف ثلاثي السن(L_2) لمعقدات الكوبلت والنيكل والنحاس والمنغنيز والزئبق الذي حضر من تكاثف 4-Aminoantipyrine مع Benzoin ثم الليكاند (L_1) مع 3-amino benzoic acid وقد شخص الليكاند والمعقدات باستخدام الاشعة المرئية وفوق البنفسجية و الاشعة تحت الحمراء و الرنين النووي المغناطيسي للبروتون والكاربون 13 (فقط لليكاند)وتحليل العناصر وقياسات الحساسية المغناطيسية زحيث وجد ان الليكاند شف بيس يسلك كطبيعة ثلاثي السن (N, N, O) تشكل بتناسقه مع الفلز (1:1)الكيمياء الرياضية . واقترحت البيئة الثمانية السطوح لكل المعقدات . معظم المركبات المحضرةوجد انها تمتلك فعالية تثبيط البكتريا (*Staphylococcus aureus*), (*Escherichia coli*), (*Bacillussubtilis*) and (*Pseudomonas aeroginosa*).

الكلمات المفتاحية: قاعدة شف وثلاثي السن ومعقدات فلزية و3-امينو حامض البنزوك.