Preparation, Characterization and Biological Activity Studies for Some Mixed Ligands Complexes of 1, 10- Phenanthroline and Schiff Base Ligand with Metal Ions

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Abstract

The ligand (H_2L) Schiff base was synthesized via a reaction of oxo ethanoic acid and Ethane-1,2-diamine environment and characterized by different techniques such as: (1H-N.M.R, C.H.N, UV-Vis, and FTIR). Mixed ligands complexes of some metal ions [Hg(II), Cu(II),Mn(II), Ni(II), and Co(II)] were prepared by the reaction of 1,10- Phenanthroline and ligand. The preparation mixed ligand complexes were diagnosed with different techniques such as :(micro-elemental analysis, molar conductance, atomic absorption, UV-Vis, FT-IR, and magnetic susceptibility). Based on the products that characterized its geometric arrangement is octahedral that the metal ions was coordinated with (H_2L) by two oxygen atoms of carboxyl groups and two nitrogen atoms of imine groups in mixed ligand complexes, in addition to coordination with 1,10-Phenanthronline by nitrogen atoms. All complexes showed antibacterial activity toward two types Gram-positive and two types (Gram-negative bacteria.

Keywords: mixed ligand complexes, antibacterial activity, Oxoethanoic acid**,** 1,10-Phenanthronline

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تحضير وتشخيص ودراسة الفعالية البيولوجية لبعض معقدات مزيج الليكاندات قاعدة شف و - 1, 10 Phenanthroline مع الايونات الفلزية

رحاب كاظم آلشمري [1] ، فائزة حسن غانـــم[2] و زهير علي شفيـــق [3]

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الخلاصة

تم تحضير ليكاند قاعدة شف (H_2L) عن طريق تفاعل التكثيف من حامض الاوكزوايثانوك وأيثان2,1- ثنائي امينو في محيط حامضي . تم تشخيص الليكاند المحضر بمختلف القياسات (طيف الرنين النووي المغناطيسي ^1H ، التحليل الدقيق للعناصر CHN ، الاشعة الفوق البنفسجية – المرئية UV-Vis و الاشعة تحت الحمراءFTIR) . تم تحضير معقدات مختلطة الليكاند لبعض العناصر الثنائية التكافؤ وفي وسط قاعدي [Hg(II) ، Cu(II)، Mn(II) ، Ni(II) و Co(II)] بتفاعلها مع 10,1 - فينانثرولين وليكاند (H_2L) . شخصت معقدات مختلطة الليكاند والمحضرة بمختلف التقنيات مثل : (التحليل الدقيق للعناصر ،التوصيلية المولارية ،الامتصاص الذري ، الاشعة فوق البنفسجية –المرئية ،تحت الحمراء و الحساسية المغناطيسية) . على اساس النواتج المشخصة ،كان ترتيبها الهندسي ثماني السطوح ، الايونات الفلزية في معقدات مختلطة الليكاند تناسقت مع (H_2L) من خلال ذرتين اوكسجين مجموعة الكاربوكسيل وذرتين نتروجين مجموعة الامين بالاضافة الى تناسقها مع 10,1 - فينانثرولين بذرتين نتروجين . معقدات مختلطة الليكاند أظهرت فعالية ضديدة للبكتريا أتجاه نوعين من البكتريا (الموجبة الغرام) ونوعين من البكتريا (السالبة الغرام) .

الكلمات المفتاحية: معقدات مختلطة الليكاند، حامض الاوكزوايثانوك ، فعالية ضديدة للبكتريا و 10,1 - فينانثرولين

Introduction

A metal complex composes of a central metal atom and ion collected by anions, a set of ligands or neutral molecules that have one or more atom carried one pair(s) of electrons. The metal ion is associated with these donor atoms metal ions by electrostatic and/or covalent bonds. Schiff's bases are compounds formed via a condensation reaction of aldehydes or ketones with any primary amine under specific conditions [1].They are used widely in organic synthesis field as intermediates, polymers stabilizers, dyes and pigments catalysts [2], bioinorganic chemistry[3], inorganic pharmacology [4], and dye lasers [5] and separation of a trace amount of metal ions [6].Imine groups are present in various natural [6], natural-derived [7], and non-natural compounds [8]. Ligands can be divided into monodentate,

bidentate and multidentate types, according to the availability of one, two or more donor atoms bonding with metal [9, 10]. Metal complexes of great importance for many years [11]. Schiff's bases are applied as privileged ligands because of good solubility of the complexes in common solvents and high stability of their chelation compositions [12]. The geometrical construction appears often in the π-system of a Schiff's base and thermo chemically characterizes of Schiff's as well, impacts the electronic composition have attracted much investigator notice in view of their capability to chalet metal ions, appearing as bidentate ligands in metal coordinates including (N,N,O,O) donor atom positions [13, 14]. The Schiff's bases composed of N, N-donor atoms are important chelating ligands for designing supramolecular synthesis, medicinal and catalytically useful metal complexes [16, 17].

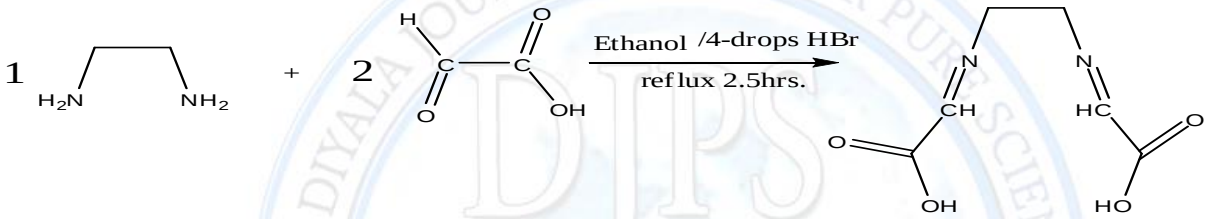
Experimental

Oxoethanoic acid (98%, sigma chemical Co.), Hydrobromic acid (48%, sigma chemical Co.) ,Ethane-1,2-diamine (EDA) (98%, Dow chemical Co.) **,**1,10-phenanthroline (99%, Merck Co.), Cobalt (II) chloride hexahydrate (99%, Merck Co),Manganese (II) chloride tetra -hydrate (98%, B.D.H Co.), Mercury (II) chloride $HgCl_2$ (98%, B.D.H Co.), Copper(II) chloride dehydrate (98%, B.D.H Co.), Nickel (II) chloride hexahydrate (98%, B.D.H Co.), Potassium hydroxide (solid) (98%, Fluka Co.).The solvents: DMSO (98%, Fluka Co.), DMF (99%, Fluka Co.) and Ethanol absolute (99.8%, GCC Co.),

Instrumentation: ^{1}H-NMR spectra of the compounds were measured by utilizing {Bruker SPE CRO spin ultra shield magnets 300 MHz } appliance utilized an internal standard was (TMS) tetra methyl silane and a solvent was DMSO-d_6. An FT-IR spectrum was recorded on SHIMADZU FTIR–8400 spectrophotometer as KBr disc. Electronic spectra were measured by utilizing U.V-Vis. spectrophotometer kind CECIL, England, with quartz cell of path length around (1cm) in range (200-1000) nm in ethanol at room temperature. Magnetic susceptibility measurements were obtained using Bruker BM6 at 298˚K. (C, H, and N %) Micro elemental analysis of the synthesized compounds was executed using a CHN Analyzer on Perkin Elmer 2400 series II.

Synthesis of ligand (H_2L)

By dissolving (0.03g. 0.5mmole) from (ethane1,2-diamine) in (6mL) of ethanol and added to a solution of (0.74g. 1mmole) from oxo ethanoic acid in (6 mL) of ethanol with the existence of (4 drops 48% HBr). The mixture was refluxed for 2.5 hrs at 75^{o}C ,a product formed after cooling , then filtered off and added hot mixture from [2.5mL) acetone, (2.5mL) methanol and (1mL) distilled water] for recrystallization .A pale brown result, yield 91%, melting point 173°C, were listed in Table(1).(Scheme 1).



Scheme 1: Synthetic route of the Schiff base ligand (H_2L)

Synthesis of mixed ligand complex

To a solution of metal salt (0.001mmol) in ethanol 10ml, was appended a solution of 2,2′ -**(**ethane-1,2- diylbis(azan-1-yl-ylidene)diacetic acid)] (H_2L) (0.172g , 0.001mmole) in (15) ml ethanol .The pH of the solution was adjusted 7 using (12%) ethanolic solution of KOH . Lastly, a solution of 1, 10-phenanthroline (0.18 g, 0.001 mmol) in (8) ml ethanol was also appended; the resulting mixture was reflux for (1.5) h. Then the mixture was filtered then washed the product with too much amount of solvent and recrystallized from a mixture of solvents [2.5ml acetone, 2.5ml ethanol, 1ml distilled water]. (Scheme 2).

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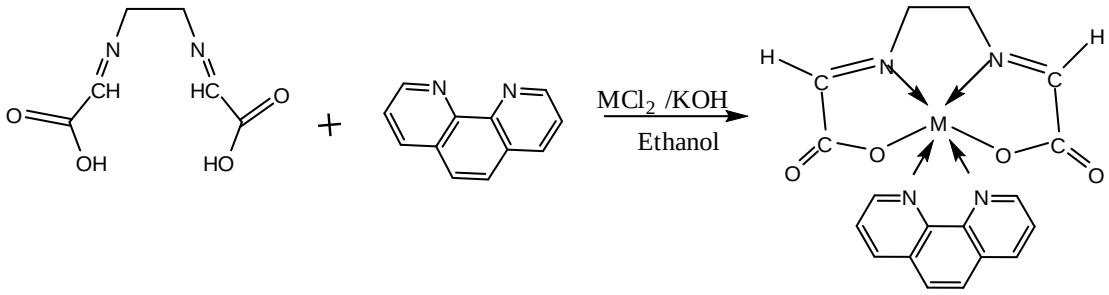

Scheme 2: Synthetic route of the mixed ligand complexes

Result and dissection

The ligand (H_2L) was prepared in one step. The composition of (H_2L) was examined and assured by elemental microanalyses values which are in good congruence with submitted formula $C_6H_8N_2O_4$.

Table (1): Some physical properties of synthesized ligand (H_2L) and mixed ligand-complexes and weight of metal salts

compounds	Empirical Formula	Weight	Yield %	M.P °C	Colour	Metal salt	Weight g 1mmol	% (.Calc)Found			
								C	H	N	Metal
H_2L	$C_6H_8N_2O_4$	172.14	91	173	pale brown	-	-	(41.12) 41.86	(4.65) 3.94	(15.88) 16.27	-
[Co(L)(PHN)]	$C_{18}H_{14}CoN_4O_4$	409.26	89	225	Reddish brown	$CoCl_2.2H_2O$	0.238	(52.83) (52.83	(3.45) 3.45	(13.69) 13.14	(14.40) 14.31
[Cu(L)(PHN)]	$C_{18}H_{14}CuN_4O_4$	413.87	88	218	brown	$CuCl_2.2H_2O$	0.170	(52.24) 51.94	(3.41) 3.27	(13.54) 13.21	(15.35) 15.46
[Ni(L)(PHN)]	$C_{18}H_{14}N_4NiO_4$	409.02	94	204	greenth brown	$NiCl_2.2H_2O$	0.238	(52.86) 52.54	(3.45) 3.45	(13.35) 13.08	(14.35) 14.21
[Mn(L)(PHN)]	$C_{18}H_{14}MnN_4O_4$	405. 27	88	234	brown	$MnCl_2.H_2O$	0.198	(53.35) 53.35	(3.48) 3.06	(13.82) 13.34	(13.56) 13.21
[Hg(L)(PHN)]	$C_{18}H_{14}HgN_4O_4$	550.92	91	200	brown	$HgCl_2$	0.271	(39.24) 39. 40	(2.56) 2.42	(10.17) 9.87	(36.41) 36.22

NMR spectrum for the ligand (H_2L)

The integral intensities of each signal in the ^{1}HNMR spectrum of (H_2L) were established to agree with the values of different kinds of protons existent [11].The ^{1}H NMR spectrum of the Schiff base Fig(1) in DMSO-d_6 appeared the following signals: -C$\underline{H}_2$- as a triplet at δ_H (2.76-3.86) and N= CH as at δ_H (8.32).The peak at δ_H11.62 is attributed to the the-COOH group.

Table (2)^{1}H-NMR Chemical Shifts for (H_2L) in DMSO (ppm)

Aliphatic protons	HC=N	COOH
2.77-3.87.	8.42	11.62

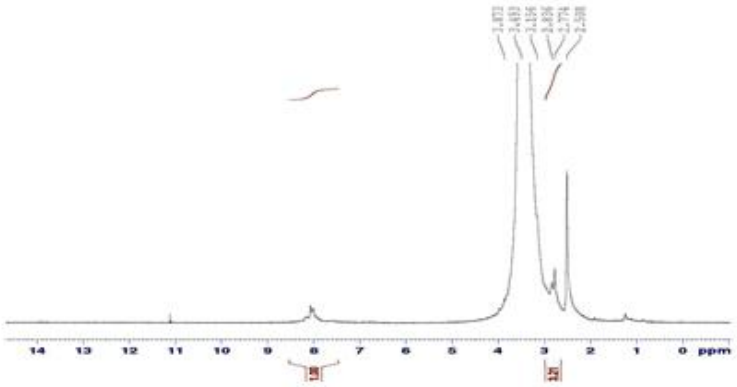

Fig. (1):- ^{1}HNMR spectrum of H_2L

IR spectra

The ligand was diagnosed from the reaction of ethane-1,2- diamino with oxo ethanoic acid , The IR spectrum of the [H_2L] Fig. (3) displayed strong absorption band at (1647) cm^{-1} is indicated HC=N azomethine compared with the starting materials, which suggested the ligand [14].The new two bands at (1436, 1319) cm^{1} are attributed to $\upsilon_{asym.}(COO^{-})$ and υ_{sym} (COO^{-}) respectively. The middle intensity for stretching band at (3446) cm^{-1} due to υ (OH) of carboxylic group, which indicates the ligand (H_2L) has been obtained. The IR spectra supply worthy information concerning of the nature of the efficient group related to the metal ion. The IR values are presented in the Table (3). In complexation the (IR) spectra displayed frequency at the range (1626-1631) cm^{-1} were attributed to υ(C=N) azomethine groups, which moved to a lower frequency in comparison with that of the Schiff base, pointing the sharing of –C=N nitrogen in chelation to the metal ion [15]. Wherefore, the ligand represents as a tetradentate coordinating agent, bonded to the metal ion *via* the nitrogen (–C=N) atoms and the oxygen atoms of carboxylic groups of the Schiff base [16]. In the spectrum of the Schiff base ligand appeared band at (1719) cm^{-1}, in the complexes ,this band disappeared and showed frequencies in the range (1478-1450) cm^{-1} and (1334-1377)cm^{-1} are observed υ_{asym}

(COO^-) and $\upsilon_{sym}(COO^-)$ stretching vibrations of the carboxylate O are observed frequencies in range (1478-1450) cm^{-1} and (1334-1377)cm^{-1}, ($\Delta\upsilon_{asym.}$-$\Delta\upsilon_{sym.}$) = (101-128)cm^{-1}, supporting the idea that the ligand chalet through deprotonated oxygen of carboxylate [17]. The new bands at range (594-570)cm^{-1}were assigned to υ(M-N) mode[18].The other new bands at (482-465) cm^{-1} were assigned to υ(M-O) mode [18]. Subsequently, from IR spectra, it is concluded that the Schiff base occurs off ligand conduct as anion tetradentate and connect to the metal ions through two carboxylate -O and the two imine N Fig. (3).

Table (3): F-IR spectral values (wave number υ′) $cm^{-1}$for (H_2L), and its mixed-ligand complexes

Compound	υ(OH)	$\upsilon(C=O)_{carboxylic}$	$\upsilon(HC=N)_{imine}$	$\upsilon_{assm.}COO^-$	$\upsilon_{symm.}COO^-$	$\Delta\upsilon cm^{-1}$	M–N M–O
H_2L	3446	1719	1647	-	-	-	-
PHN			1620				
[CO(L)(PHN)]		-	1628 1601	1450	1342	108	553 460
[Cu(L)(PHN)]		-	1630 1603	1467	1339	128	541 448
[Ni(L)(PHN)]		-	1626 1600	1471	1334	123	588 459
[Mn(L)(PHN)]		-	1631 1592	1478	1377	101	575 444
[Hg(L)(PHN)]		-	1631 1606	1469	1351	113	539 467

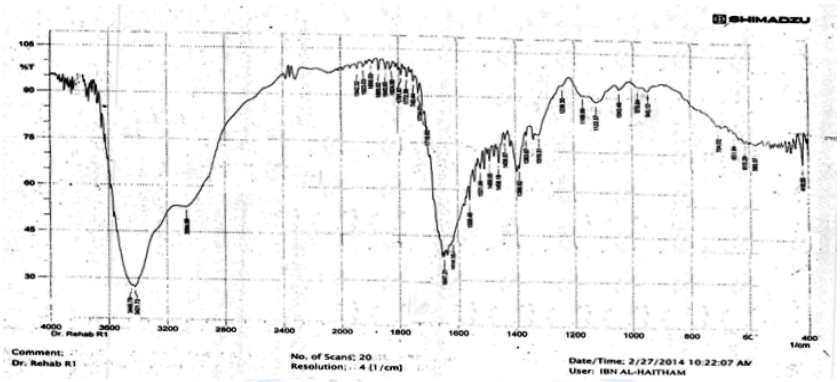

Fig. (2):- IR spectrum of H_2L

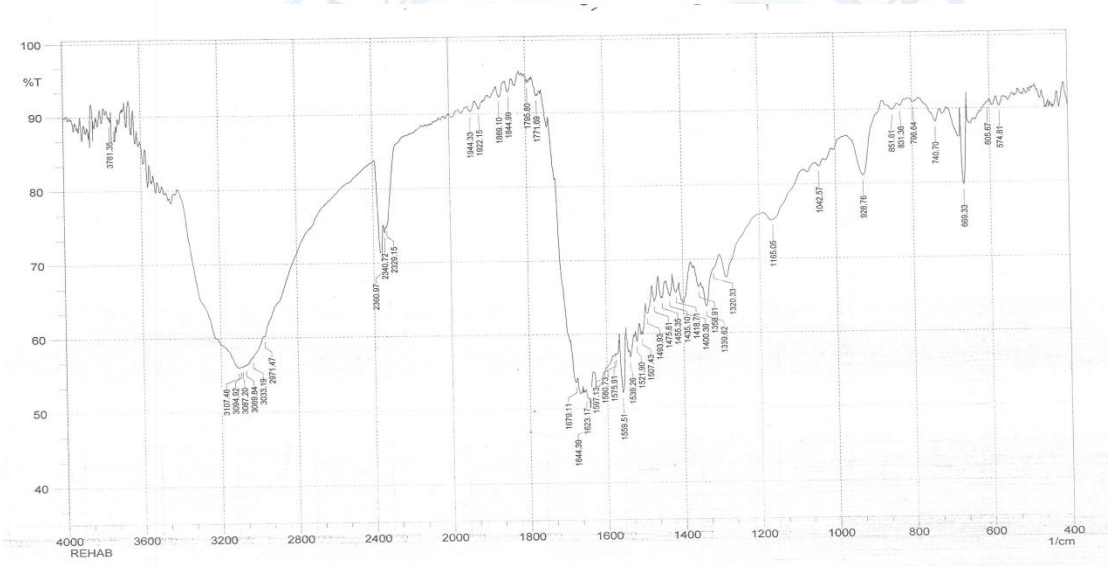

Fig. (3): IR spectrum of complex Cu (II)

The UV-Vis spectra

The UV-Vis spectrum of the ligand (H_2L) displayed two peaks at (222) nm and (356) nm attributed to ($\pi \rightarrow \pi^*$) and ($n \rightarrow \pi^*$) electronic transitions.The electronic of Co (II) complex showed a peak at 245 nm assigned to L.F transition. The second peak at (364) nm due to C.T transition .Also, two peaks at 793nm and 817 nm were got to be occasioned by (d-d) electronic transition type $^4T_{1g(F)} \rightarrow {}^4A_{2g(p)}$ and $^4T_{1g(F)} \rightarrow {}^4T_{2g(F)}$ respectively[20].

The spectrum of Ni(II)complex displayed a peak at (251)nm was assigned to L.F transition. The second peak at (363) nm attributed to C.T transition, then other two peaks at (625) nm and (892) nm were due to electronic transition type $^3A_{2g\,(F)} \rightarrow {}^3T_{1g(P)}$, and$^3A_{2g(F)} \rightarrow {}^3T_{2g(F)}$ respectively[19].

The electronic of Cu(II) complex displayed absorption peak at (249) nm was assigned to L.F transition.The second peak at (372) nm due to C.T transition. Other one peak at (741) nm was caused by electronic transition type $^4E_g \rightarrow {}^4T_{2g}$.

The electronic of Mn(II) complex showed a peak at (241) nm due to was assigned to L.F transition. The second peak at (376) nm due to C.T transition. Other two peaks at (400) nm and (744) nm were assigned to electronic transition type $^6A_{1g\,(F)} \rightarrow {}^4T_{2g\,(G)}$ and $^6A_{1g\,(F)} \rightarrow {}^4T_{1g\,(G)}$ respectively [20].

The spectrum of Hg(II) complex appeared to peak at (253) nm assigned to L.F transition . The second peak at (411) nm due to C.T transition in the visible region suggested no (d-d) electronic transition occurred; this is a good consequence for octahedral complex [21].

The effective magnetic moments (Table 5) of the complexes lie in the range (5.72 -1.81) BM. This value refers to a paramagnetic (high spin) which has been concluded for generality octahedral geometry. In the case of Hg(II) complex because of filled d-d orbital, therefore the magnetic moment (μ=0) is diamagnetic.

The conductance data of the mixed ligand- complexes in DMSO lie in the range (70 to 92) $S.cm^2mol^{-1}$which is expected their non-electrolytic nature as in Table(4)

Table (4): UV-Vis spectral values of the ligand (H_2L) and its mixed ligand complexes

Comp.	μ_{eff}	Λ_m S.Cm^2 molar^{-1} in DMSO	λnm	υ–wave number cm^{-1}	(εmax molar^{-1}	Assignments
H_2L	-	-	222	45045	2295	π→π*
[Co(L)(PHN)]	5.40	83	245	47169	1909	L.F
			364	28571	264	C.T
			793	12610	22	$^4T_1g(F) \rightarrow {}^4A_2g(P)$
			817	12240	21	$^4T_1g(F) \rightarrow {}^4T_2g(F)$
[Cu(L)(PHN)]	1.81	79	249	46511	2031	L.F
			372	28011	392	C.T
			741	13495	32	$^4Eg \rightarrow {}^4T_2g$
[Ni(L)(PHN)]	3.28	70	251	45045	2281	L.F

			363	28089	238	C.T
			625	12610	16	$^3A_2g(F)\rightarrow{}^3T_1g(F)$
			892	12240	4	$^3A_2g(F)\rightarrow{}^3T_2g(F)$
[Mn(L)(PHN)]	5.58	92	241	47619	1821	L.F
			376	28248	124	C.T
			400	25000	106	$^6A_1g(F)\rightarrow{}^4T_2g(G)$
			744	13440	8	$^6A_1g(F)\rightarrow{}^4T_1g(G)$
[Hg(L)(PHN)]	-	72	253	47169	1888	L.F
			411	28572	242	C.T

Antibacterial Activities

The significance of this unparalleled characterizes of the inspected Schiff base and its complexes lie in the truth that, it may be utilized significantly in the processing of infections and some prevalent diseases e.g. Septicaemia , Gastroenteritis, Urinary tract infections and hospital gained infections. The ligand and its complexes have been tested for in vitro growth inhibitory activity against Gram(+)e.g Staphylococcus aureus and Gram(-) e.g *Escherichia Coli*, *Bacillus*, *Pseudomonas* by using well-diffusion process .The minimum inhibitory concentration (MIC) values of the investigated compounds are summarized in Tables (6). From the table, the observed MIC data signal that the complexes have higher antimicrobial efficacy and intermediate efficacy for fungi. The metal complexes Co(II), Cu(II), Ni(II) Mn(II), and Hg(II) have higher antimicrobial activity than the ligand are shown in Figs 5.

Table (6): Diameter of zone of inhibition (mm) for (H_2L)& mixed -ligand complexes

Comp.	*Escherichia. Coli*	*Staphylococcus aureus*	*Bacillus*	*Pseudomonas*
H_2L	4	2	1	3
[Co(L)(PHN)]	6	2	5	7
[Cu(L)(PHN)]	8	4	5	2
[Mn(L)(PHN)]	8	3	4	6
[Ni(L)(PHN)]	6	2	4	2
[Hg(L)(PHN)]	9	3	5	8

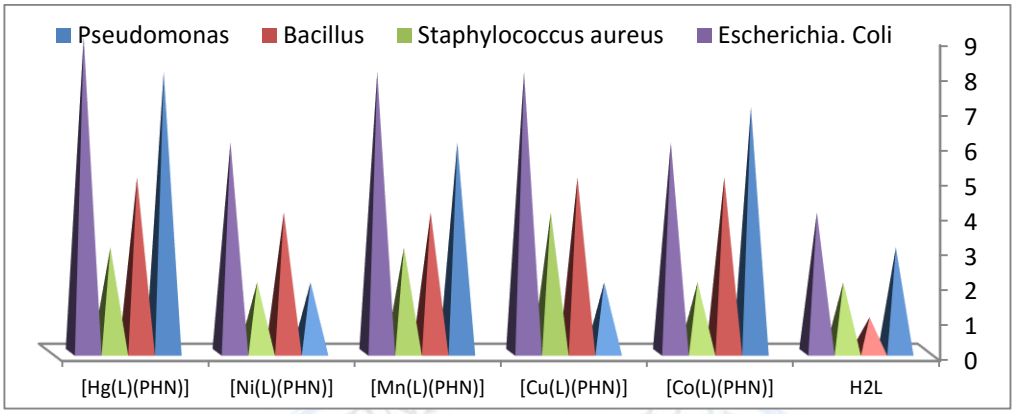

Fig.(4) Difference between the antimicrobial activity of ligand (H_2L)& mixed -ligand complexes

Conclusions

From the molar conductivity, elemental analysis, UV–Vis, ^{1}H& ^{13}C- NMR and F-IR spectra values, it is possible to measure the kind of chelation of the ligand and mixed -ligand complexes. The metal (II) ions are coordinated by two imines (H-C=N) atom and-and two carboxylic–O atom. Spectroscopic, structural and magnetic data show that all complexes are six- coordinate metal complexes owing to the legation of tridentate Schiff base. The synthesized ligand and mixed -ligand complexes showed antibacterial properties. In comparison, the copper (II), cobalt(II), nickel (II), manganese(II) and mercury(II) complexes of these compounds observed activity against bacterial strains.

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