

Preparation, Characterization and Microbiological Activity Studies of Some Mixed Ligand Complexes of 1, 10- Phenanthroline and Schiff base with Some Metal Ions

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Abstract: Schiff base ligand [(N¹E,N²E)-N¹,N²-bis(4-methoxybenzylidene)benzene-1,2-diamine](L) was synthesis through a condensation reaction of benzene-1,2-diamine and 4-Methoxy benzaldehyde in acidic conditions. The synthesis ligand has described with different (C.H.N, ¹H & ¹³C-N.M.R., UV-Vis and FT-IR) techniques. Mixed complexes of some metal ions [Hg^(II), Mn^(II), Ni^(II), Cu^(II) and Co^(II)] were prepared by the reaction of Schiff base (L) and 1,10-Phenanthroline with the divalent metal ions in basic medium. The synthesis mixed complexes were characterized with different (atomic absorption, UV-Vis, FT-IR, micro elemental analysis, molar conductance and magnetic susceptibility) techniques. Based on the results of these diagnoses which showed configuration tetrahedral that the metal ions was coordinated with (L) by and two N atoms of azomethine groups in mixed ligand complexes, in addition of coordination with 1,10-Phenanthroline by nitrogen atoms. The mixed complexes displayed antibacterial effectiveness to (*Escherichia coli*), (*Bacillus subtilis*), (*Pseudomonas aeruginosa*) and (*staphylococcus aureus*).

Key words: antibacterial

Introduction

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I. Introduction

Metal complexes of Schiff bases obtained from {aromatic carbonyl compounds} have been great searched in linkage with metalloprotein paradigms and asymmetric catalysis, by virtue of the versatility of their electronic and steric characteristics, which can be fine-tuned by selecting the ring substituents and suitable amine precursors. [1] While putting away an easier synthetic access, they showed to be of significance N₂O₂ ligands and their transition-metal complexes, as catalysts, has considerable concern, being pertinent for their reinforcements, specially on the expansion of agrochemical and pharmaceutical industries. [2,3] Also, due to the potential catalytic interest of these metal-chelates, a very quick evolution in their chemical study has been developed. [4-7] Several investigations have been done on the molecular structure of transition-metal Schiff base complexes as a ligand in the chemistry. [7-9] Abundant metal complexes have strong antimicrobial activities and medicinal field such as silver bandages for bismuth drugs, treatment of burns, zinc antiseptic creams, anti-HIV drugs, and also resistant bacteria and viral diseases drugs. [10-11] The most spectacular advances in medicinal chemistry have been made when heterocyclic compounds played an important role in regulating biological activities. [12-14] The present paper describes the synthesis and study of antibacterial activity of the mixed ligand complexes of some metal ions [Hg^(II), Mn^(II), Ni^(II), Cu^(II) and Co^(II)] were synthesized by the reaction of Schiff base [(N¹E,N²E)-N¹,N²-bis(4-methoxy benzylidene) benzene-1,2-diamine] and 1,10-Phenanthroline with the divalent metal ions.

II. Experimental

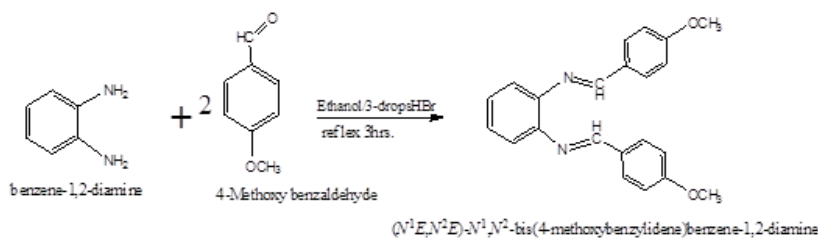
The following compounds were available commercially and used without further purification: benzene-1,2-diamine (99%, Sigma Chem. Co.), 4-Methoxy benzaldehyde (98%, Sigma Chem. Co.), Hydro bromic acid HBr (48% Sigma Chem. Co.), 1,10-phenanthroline (99%, Merck Co.), Nickel (II) chloride hexahydrate (98%, B.D.H Co.), Manganese (II) chloride tetra-hydrate MnCl₂.4H₂O (98%, B.D.H Co.), Cobalt (II) chloride hexahydrate CoCl₂.6H₂O (99%, Merck Co.), Copper (II) chloride dehydrate CuCl₂.2H₂O (98%, B.D.H Co.), Mercury (II) chloride HgCl₂ (98%, B.D.H Co.). The solvents: DMF (99%, Fluka Co.), Ethanol absolute (99.8%, GCC Co.) and DMSO (98%, Fluka Co.).

Methods: A FT-IR spectrum was registered on {SHIMADZU FTIR-8400 spectrophotometer} as KBr disc. Electronic spectra were registered utilizing {U.V-Vis. spectrophotometer kind CECIL, England}, at room temperature in ethanol in ambient (200-1000) nm. Magnetic ¹H & ¹³C-NMR spectra of the compounds were

registeredutilizing{Bruker specrospin ultra shield magnets 300 MHz instrument} utilizing DMSO-d₆ as solvent. susceptibility measurements were registeredutilizingBruker BM6 at 298°K.(C, H, and N %) Microelemental analysis of the compounds was registeredutilizinga{ CHN Analyzer on Perkin Elmer 2400 series II}.

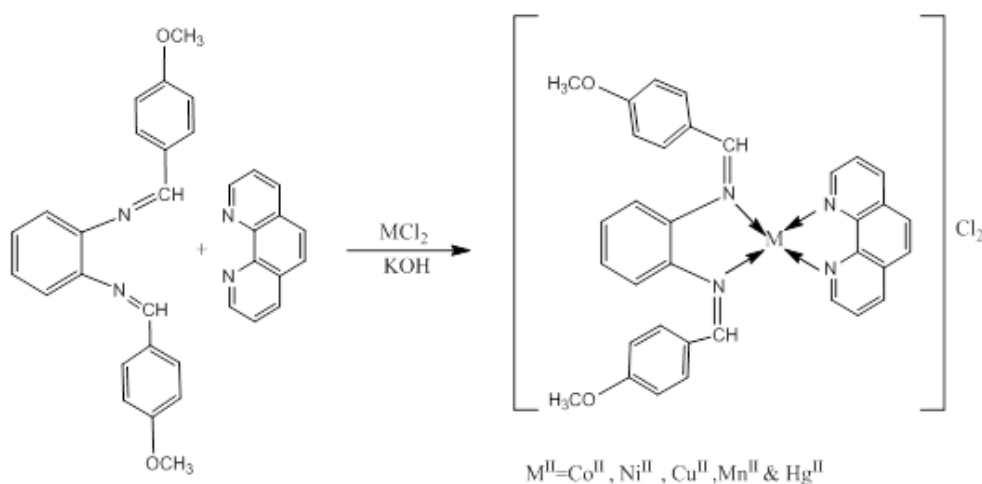
Synthesis of [2,2'-(ethane -1,2- diylbis (azan-1-yl-ylidene)diacetic acid)

To a solution of benzene-1,2-diamine (0.108g. 1mmole) in (5ml) of ethanol , a solution of 4-methoxybenzaldehyde (0.243ml. 2 mmole) in (5ml) of ethanol, was added. The solution was refluxed at 150°C for 4 hrs. upon cooling a dark brown precipitate formed, was filtered off and recrystallized from a hot mixture of methanol:distilled water:acetone [5:2:5] ml.A precipitate, yield 90%, m.p. (120-122)C°, and elemental microanalysis C.H.N were listed inTable(1).



Synthesis of the mixed-ligand [L] and 1,10-phenanthroline complexes with some metal ions

To a solution of metal salt (0.001mmol)in ethanol 10ml ,was added a solution of Schiff base ligand (0.89 g, 0.001mmole) in (12) ml ethanol . Finally a solution of 1,10-phenanthroline (0.18 g, 0.001 mmole) in (7) ml ethanol was also added, the resulting mixture was heated under reflux for (1) h. Then the mixture was filtered and the product was washed with an excess amount of ethanol and recrystallized from mixture of solvents[3ml acetone,3ml ethanol,2ml distilled water] (Scheme 2).



NMR spectrum

¹H- NMR spectrum of (L) in DMSO-d₆ illustrated in Fig.(4), is multiples corresponding to aromatic six protons at (6.86-7.67) ppm[14].The aliphatic protons (O-CH₃) at (3.39) ppm. The advantage signal at (8.12) ppm is designation to HC=N. [7]. The DMSO signal appeared at (2.50) ppm

¹³C-NMR of (L) Fig (5), showed the carbon peak for HC=N at (143.50) ppm, the carbon peaks for aromatic are appeared at (114.64-129.27) ppm and carbon peaks for aliphatic are detected at (47.41-55.78) ppm. The peak at (40.31) ppm. assigned to DMSO [8].

The IR spectra for the ligand and its complexes

The Schiff base was synthesized from the reaction of 4- Methyl Benzene-1, 2-diamine with 4-methoxy benzaldehyde, The IR spectrum of [L] Fig. (1) showed new strong band at (1608) cm⁻¹ is due HC=N imine, that indicate the ligand. Bands corresponding to ν(C-H)_{aromatic} stretching at (3059) cm⁻¹, ν(C-H)_{aliphatic} stretching at (2937) cm⁻¹, ν(C=C)_{aromatic} at (1570) cm⁻¹. [9] Absorption band corresponding at (3446) cm⁻¹ due to ν (O-H) [10]. The IR data are presented in the Table(2) Comparison of the IR spectrum of the Schiff base ligand with that

of spectra its complexes show the absorption bands in the range (1601-1606) cm^{-1} due to azomethine (C=N) groups respectively [11]. The (C=N) vibrations decreased on complexation showing involvement of nitrogen of azomethine group in coordination. The absence of stretching and bending vibrations of free carbonyl group in 4-methoxy benzaldehyde at (1685) cm^{-1} indicates the absence of this group in these complexes [12]. The absorption bands in the range (941-987) cm^{-1} for the complexes assigned to coordinated aqua δ (O-H) ligand. Finally the complexes exhibited bands at the ranges (460-482) and (545-582) cm^{-1} which could be assigned to the ν (M-O) and ν (M-N) stretching vibration modes respectively [13] such as $[\text{Hg}(\text{L})_2]\text{Cl}_2$ complex in fig(2).

Molar Conductivity

The molar conductance values of the complexes in ethanol lie in the range (71 to 87) $\text{ohm}^{-1}.\text{cm}^2.\text{mol}^{-1}$ which is obvious from these data that these chelates are ionic in nature and they are of the type 1:2 electrolytes. [14]

The Electronic Absorption Spectral and Magnetic Studies

The U.V-Vis spectrum of ligand (L) Fig.(3) displayed two absorption peaks, the first peak at (265) nm (37735) cm^{-1} may be assigned to $\pi-\pi^*$ electronic transition. The second peak at (332) nm, (30120) cm^{-1} was attributed to $n-\pi^*$ electronic transition [15]. The U.V-Vis spectral data of the ligand (L) were given in Table (5).

The U.V-Vis spectrum of the $\text{Co}^{(II)}$ complex Fig.(4) displayed peak at (628) nm (15923) cm^{-1} was attributed to (d-d) electronic transition type ${}^4\text{A}_{2(\text{F})} \rightarrow {}^4\text{T}_{1(\text{P})}$, was suggesting high spin tetrahedral geometry around $\text{Co}^{(II)}$ central ion. [16]

The U.V-Vis spectrum of the $\text{Ni}^{(II)}$ complex displayed peak at (445) nm (22471) cm^{-1} and the peak at (792) nm (12626) cm^{-1} , were attributed to (d-d) electronic transition type ${}^3\text{T}_{1(\text{F})} \rightarrow {}^3\text{T}_{1(\text{P})}$ and ${}^3\text{T}_{1} \rightarrow {}^3\text{A}_2$ respectively, that is a good suggestion with high spin tetrahedral geometry [17].

The U.V-Vis spectrum of the $\text{Cu}^{(II)}$ complex exhibited peak at (578) nm (17301) cm^{-1} was referred to (d-d) electronic transition type ${}^2\text{E} \rightarrow {}^2\text{B}_2$. The U.V-Vis spectrum of the $\text{Cu}^{(II)}$ complex was suggesting high spin tetrahedral geometry around $\text{Cu}^{(II)}$ central ion. [18]

The U.V-Vis spectrum of the $\text{Mn}^{(II)}$ complex displayed peak at (755) nm (12903) cm^{-1} was assigned to (d-d) electronic transition type ${}^6\text{A}_1 \rightarrow {}^4\text{T}_{1(\text{G})}$ was as suggested a high spin tetrahedral geometry around $\text{Mn}^{(II)}$ central ion. [19]

The U.V-Vis spectrum of the $\text{Hg}^{(II)}$ complex displayed peak at (324) nm (308640) cm^{-1} referred to charge electronic transition only. [20] The U.V-Vis spectrum of the $\text{Hg}^{(II)}$ complex showed no d-d transitions in the visible region, indicating for $\text{Hg}^{(II)}$, this is mean electronic transitions happened tetrahedral geometry has been assigned to the $\text{Hg}^{(II)}$ complex. According to the elemental analysis and FT-IR spectra, the frameworks of these mixed complexes can be proposed tetrahedral. [21]

The magnetic susceptibility measurement for $\text{Co}^{(II)}$, $\text{Ni}^{(II)}$, $\text{Cu}^{(II)}$ and $\text{Mn}^{(II)}$ complexes is (5.71), (2.85), (1.81), (5.54) B.M. which are suggested tetrahedral environment with these metal ions shown in Table (3). [22]

Antibacterial Activities

Bidentate Schiff base ligand derived by the condensation of 4-Methoxy benzaldehyde with 4-Methyl benzene-1,2-diamine and its $\text{Mn}^{(II)}$, $\text{Ni}^{(II)}$, $\text{Co}^{(II)}$, $\text{Hg}^{(II)}$ and $\text{Cu}^{(II)}$ complexes showed biological activities against the type of bacterial (*Escherichia coli*) except $[\text{Ni}(\text{L})(\text{PHN})]\text{Cl}_2$ in Fig(7). The compounds showed inhibition diameter against the type of bacterial (*Staphylococcus aureus*) except ligand [L] in Fig(8), the consequences suggest that mixed complexes showed more activity than the ligand under comparable empirical surroundings, table (6) this may be due to that the coordination extremely decreases the polarity of the metal ion at most because of partial involvement of its positive charge with the grantersets and potential electron delocalization over the whole chelate 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 [23,24]. Also the compounds against the type of bacterial (*Bacillus*) except $[\text{Cu}(\text{L})(\text{PHN})]\text{Cl}_2$ complex Fig (9). All compounds ligand and its complexes have good biological activity against the type of bacterial (*Pseudomonas*) Fig (10), Table (6) Diameter of zone of inhibition.

III. Conclusion

The Schiff ligand (L) and mixed complexes were prepared $[\text{Mn}(\text{L})(\text{PHN})]\text{Cl}_2$, $[\text{Co}(\text{L})(\text{PHN})]\text{Cl}_2$, $[\text{Ni}(\text{L})(\text{PHN})]\text{Cl}_2$, $[\text{Cu}(\text{L})(\text{PHN})]\text{Cl}_2$ and $[\text{Hg}(\text{L})(\text{PHN})]\text{Cl}_2$. The metal (II) ions are coordinated by two imine (H-C=N) atoms. The tetrahedral geometry is proposed for all complexes

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Table 1. Some physical properties of prepared ligand(L) and its complexes

Compounds	Empirical Formula	Yield %	Weight (g)	M.P C°	Colour	Metal salt	Weight (g)	% (Calc.) Found			
								C	H	N	Metal
L	$C_{22}H_{20}N_2O_2$	92	344.15	173	Dark brown	-	-	(76.72) 77.50	(5.85) 5.40	(8.13) 8.42	-
[Co(L)(PHN)]Cl ₂	$C_{34}H_{28}Cl_2CoN_4O_2$	90	654.45	250	bullish brown	CoCl ₂ .2H ₂ O	0.238	(62.40) 62.24	(4.31) 4.04	(8.56) 8.31	(9.00) 8.76
[Cu(L)(PHN)]Cl ₂	$C_{34}H_{28}Cl_2CuN_4O_2$	85	659.06	210	brown	CuCl ₂ .2H ₂ O	0.170	(61.96) 61.42	(4.28) 4.02	(8.50) 8.34	(9.64) 9.26
[Ni(L)(PHN)]Cl ₂	$C_{34}H_{28}Cl_2NiN_4O_2$	88	654.21	204	greenish brown	NiCl ₂ .2H ₂ O	0.238	(62.42) 61.86	(4.31) 4.20	(8.56) 8.16	(8.97) 8.64
[Mn(L)(PHN)]Cl ₂	$C_{34}H_{28}Cl_2MnN_4O_2$	78	650.46	257	Redish brown	MnCl ₂ .H ₂ O	0.198	(62.11) 62.86	(4.34) 4.23	(8.61) 8.32	(8.45) 8.48
[Hg(L)(PHN)]Cl ₂	$C_{34}H_{28}Cl_2HgN_4O_2$	86	796.11	223	light brown	HgCl ₂	0.271	(51.30) 50.94	(3.55) 3.07	(7.04) 6.21	(25.20) 24.82

Table 2. Infrared spectral data (wave number ν) cm^{-1} for the ligand (L), precursors and its mixed complexes

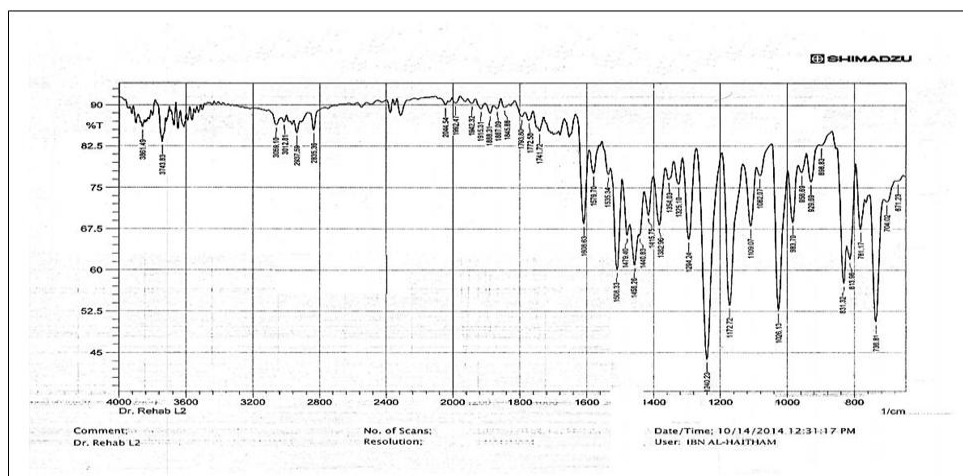
Compound	$\nu(C-H)_{aromatic}$	$\nu(C-H)_{aliphatic}$	$\nu(HC=N)_i$ imine	$\nu(C-O)$	M-N	M-O
L	3059	2937	1608	1240	-	-
PHN	-	-	1620	-	-	-
[Co(L)(PHN)]Cl ₂	3068	2937	1604/1597	1242	547	476
[Mn(L)(PHN)]Cl ₂	3056	2924	1606/1592	1243	547	474
[Ni(L)(PHN)]Cl ₂	3076	2926	1602/1594	1241	549	460
[Cu(L)(PHN)]Cl ₂	3026	2924	1601/1590	1243	582	482
[Hg(L)(PHN)]Cl ₂	3040	2927	1603/1598	1242	545	464

Table 3. Electronic spin resonance parameters of the complexes

Compound	μ_{eff}	Λ_m ohm.cm ³ mole ⁻¹	λ nm	ν wave number cm ⁻¹	Assignments	Proposed structure
L	-	-	265	37735	$\pi \rightarrow \pi^*$	-
			332	30120	$n \rightarrow \pi^*$	
[Co(L)(PHN)]Cl ₂	4.71	81	278	35970	L.F	tetrahedral
			341	29325	C.T	
			628	15923	$^4A_{2(F)} \rightarrow ^4T_{1(P)}$	
[Ni(L)(PHN)]Cl ₂	2.85	77	253	39525	L.F	tetrahedral
			362	27624	C.T	
			743	13458	$^3A_{2(F)} \rightarrow ^3T_{2(P)}$	
			792	12626	$^3T_{1(F)} \rightarrow ^3A_{2(F)}$	
[Cu(L)(PHN)]Cl ₂	1.81	75	268	30864	L.F	tetrahedral
			344	30864	C.T	
			578	17301	$^2E \rightarrow ^2B_2$	
[Mn(L)(PHN)]Cl ₂	5.54	84	277	36101	L.F	tetrahedral
			348	28735	C.T	
			775	12903	$^6A_{1(F)} \rightarrow ^4E_{(D)}$	
[Hg(L)(PHN)]Cl ₂	-	88	350	28571	C.T	tetrahedral
			420	23809	C.T	

Table 4.

Compound.	L	[Co(L)(PHN)]Cl	[Mn(L)(PHN)]Cl	[Ni(L)(PHN)]Cl ₂	[Cu(L)(PHN)]Cl ₂	[Hg(L)(PHN)]Cl ₂
<i>Escherichia. Coli</i>	10	15	10	-	17	12
<i>Staphylococcus aureus</i>	-	12	14	14	18	15
<i>Bacillus</i>	12	11	10	15	-	19
<i>Pseudomonas</i>	14	15	13	13	16	10



Fig(1):The IR spectrum of (L)

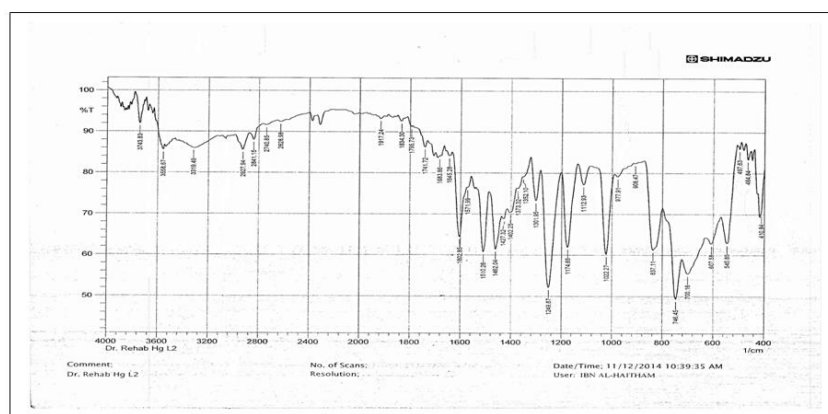
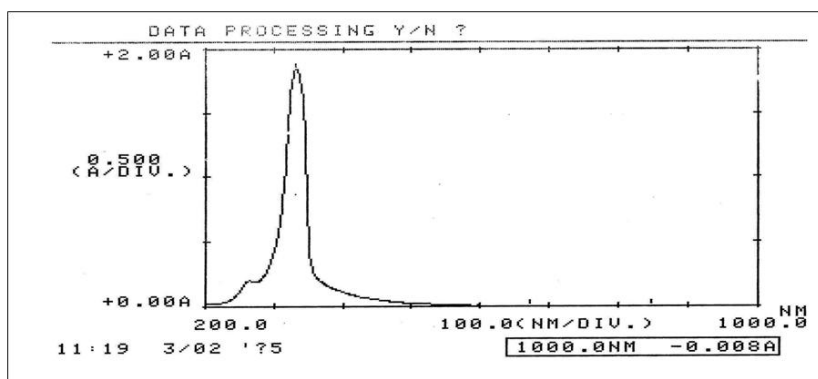
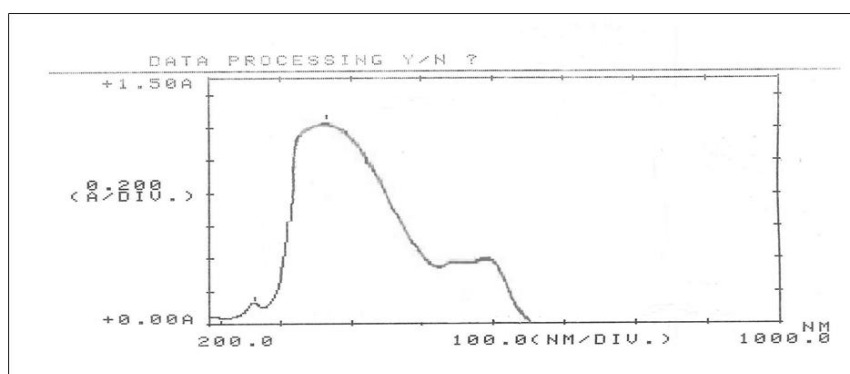


Fig (2):The IR spectrum of [Hg(L)(PHN)]Cl₂



Fig(3): Electronic spectrum of the ligand(L)



Fig(4): Electronic spectrum of the ligand [Co(L)(PHN)]Cl₂

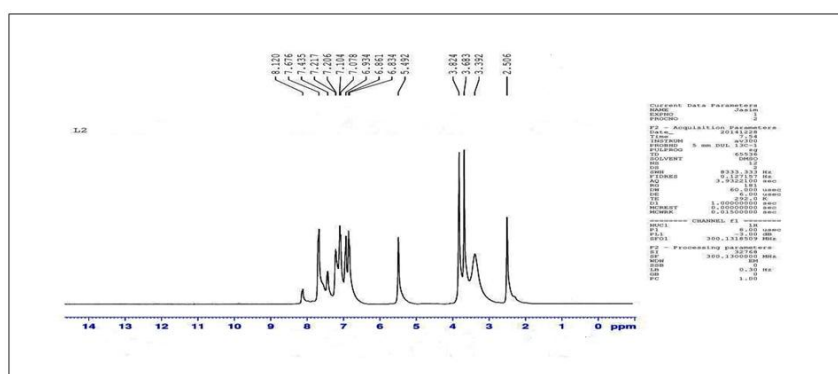


Fig.(5): ¹H-NMR spectrum of Ligand(L)

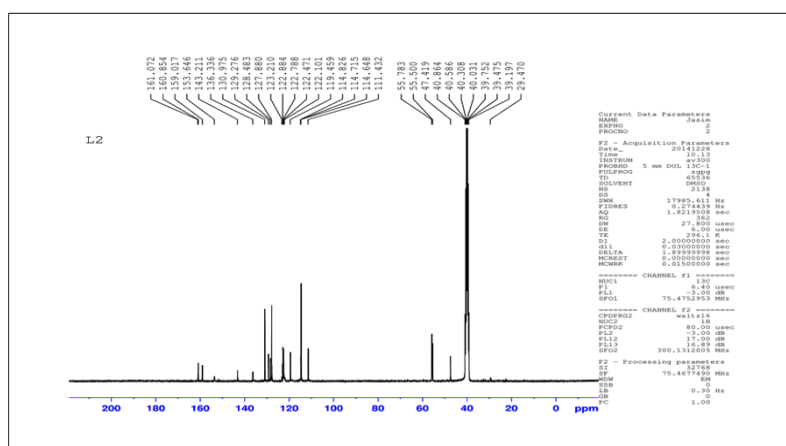


Fig.(6) ¹³C- NMR spectrum of Ligand(L)

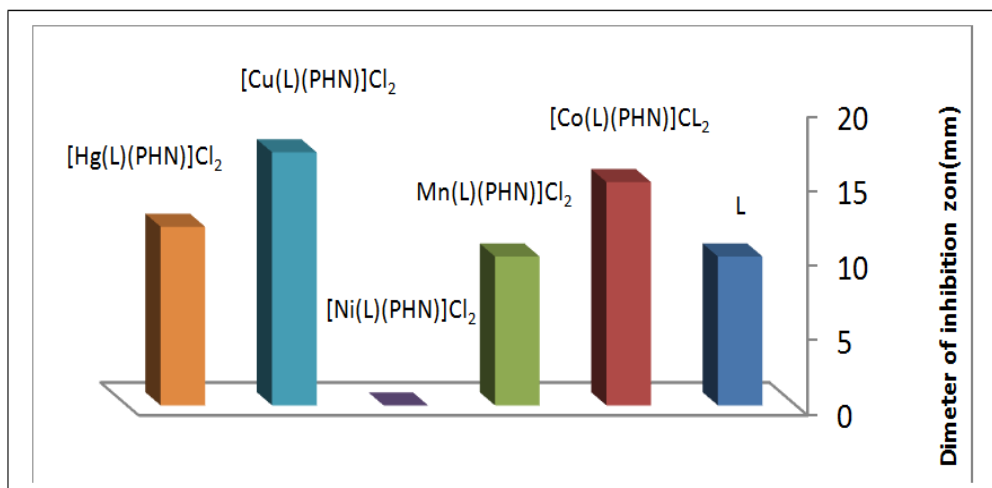


Fig.(7) Effect of *Escherichia.Coli*

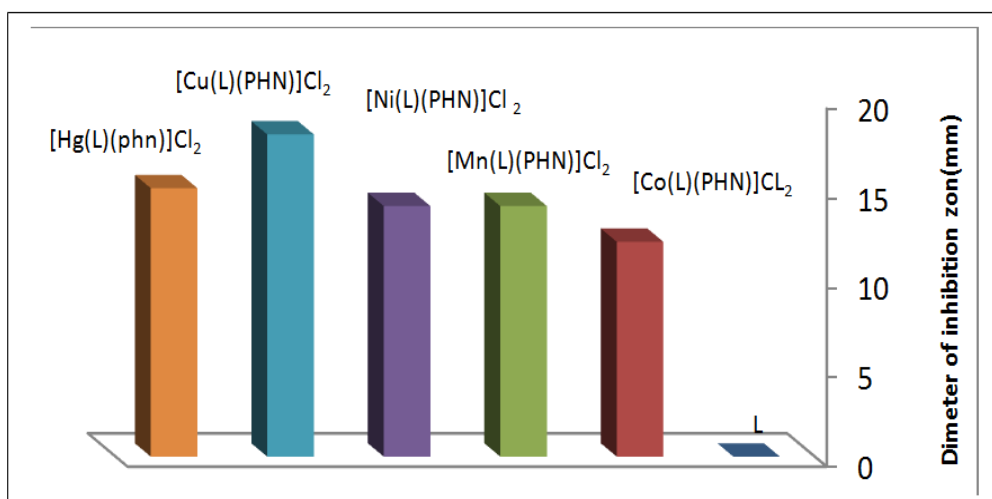


Fig. (8) Effect of *Staphylococcus aureus*

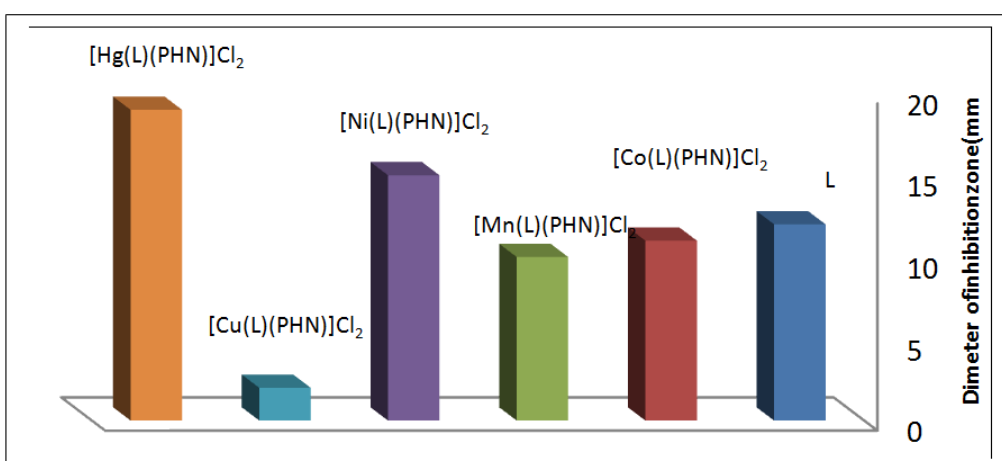


Fig.(9) Effect of *Bacillus gram*

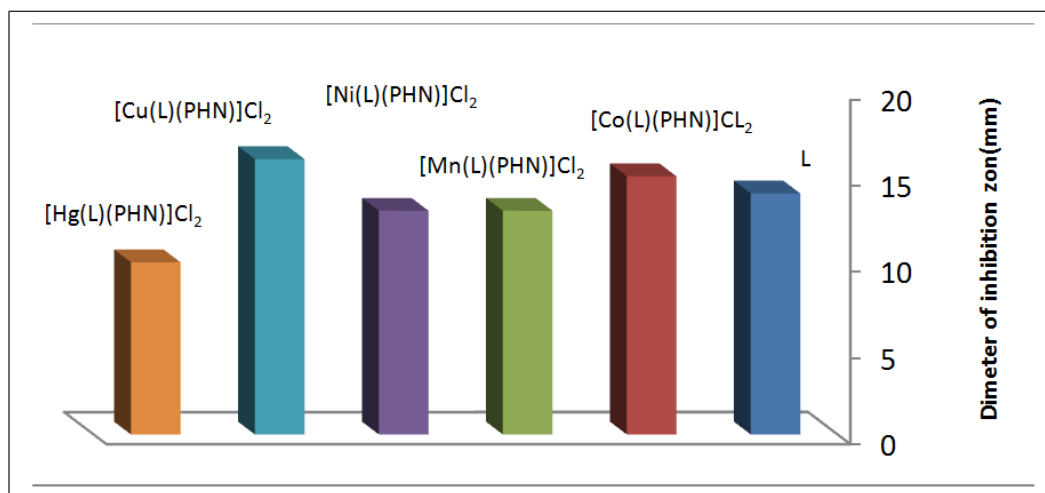


Fig.(10)Effect of *pseudomonas gram*

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