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

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Abstract: *Schiff base ligand $[(N^1E,N^2E)-N^1,N^2-bis(4-methoxybenzylidene)benzene-1,2-diamine](L)$ 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$(C.H.N,^1H\&^{13}C-N.M.R,,$ UV-VisandFT-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-Phenanthronline 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 is tetrahedral that the metal ions was coordinated with (L) by and two N atoms of azomethine groups inmixed ligand complexes, in addition of coordination with 1,10-Phenanthronline by nitrogen atoms. The mixed complexes displayed antibacterial effectiveness to (Escherichia coli),(Bacillussubtilis),(Pseudomonas aeruginosa)and (staphylococcus aureus).*
Key words*: antibacterial*
Introduction

I. Introduction

Metal complexes of Schiff bases obtained from {aromaticcarbonyl compounds} have been great searched in linkage with metalloproteinparadigms and asymmetric catalysis,by virtue of the versatility of their electronic and steric characteristics,which can be fine-tuned by selectingtheringsubstituent'sandsuitableamine precursors.[1] While puttingawayan easier synthetic access, they showed to be of significanceN_2O_2 ligands and their transition-metal complexes, as catalysts,has considerableconcern, being pertinent fortheirenforcements, speciallyon the expansion of agrochemicaland pharmaceutical industries.[2,3] Also, due to thepotential catalytic interest of these metal–chelates, a very quickevolution in their chemical study has been developed.[4-7]Several investigations have been done on the molecularstructure of transition-metal Schiff base complexes asligand in the chemistry.[7-9]Abundant metal complexes have strong antimicrobial activitiesand medicinalfield such as silver bandages for bismuth drugs, treatment of burns,zinc antiseptic creams, anti-HIV drugs , and also resistant bacteriaand viral diseasesdrugs.[10-11]The most spectacular advances in medicinal chemistryhave been made whenheterocyclic compoundsplayed an important role in regulating biological activities.[12-14]The present paper describes the synthesis and study of antibacterial activity of themixed ligand complexesof some metal ions $[Hg^{(II)}, Mn^{(II)}, Ni^{(II)}, Cu^{(II)}$ and $Co^{(II)}]$ were synthesized by the reaction of Schiff base $[(N^1E,N^2E)-N^1,N^2-bis(4-methoxy benzylidene) benzene-1,2-diamine]$ and 1,10-Phenanthronline with the divalent metal ions .

II. Experimental

The following compounds were available commercially and used without further purification: benzene-1,2-diamine(99%, SigmaChem. Co),4-Methoxy benzaldehyde(98%, SigmaChem. 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$MnCl_2.4H_2O$(98%, B.D.H Co.),Cobalt (II)chloride hexahydrate$CoCl_2.6H_2O$(99%,Merck Co.),Copper(II) chloridedehydrate $CuCl_2.2H_2O$(98%, B.D.H Co.),Mercury (II) chloride $HgCl_2$ (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 spectrophoto-meter} as KBr disc.Electronic spectra were registeredutilizing{U.V-Vis. spectrophotometer kind CECIL, England},at room temperaturein ethanol in ambit (200-1000) nm. Magnetic $^1H\&^{13}C$-NMR spectra of the compounds were

registeredutilizing{Bruker specrospin ultra shield magnets 300 MHz instrument} utilizing DMSO-d_6 as asolvent. 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°, andelemental microanalysis C.H.N were listed inTable(1).
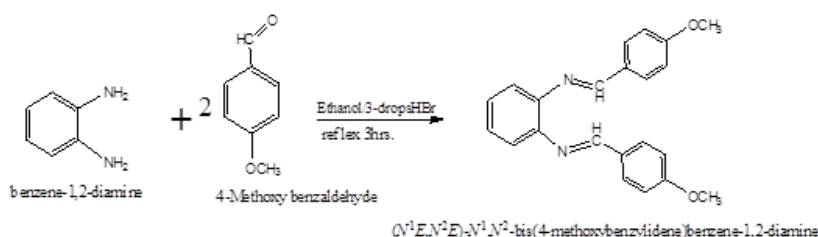
Synthesis of the mixed-ligand [L] and 1,10-phenanthroline complexes with some metal ions

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 frommixtureof solvents[3ml acetone,3ml ethanol,2ml distilled water] (Scheme 2).
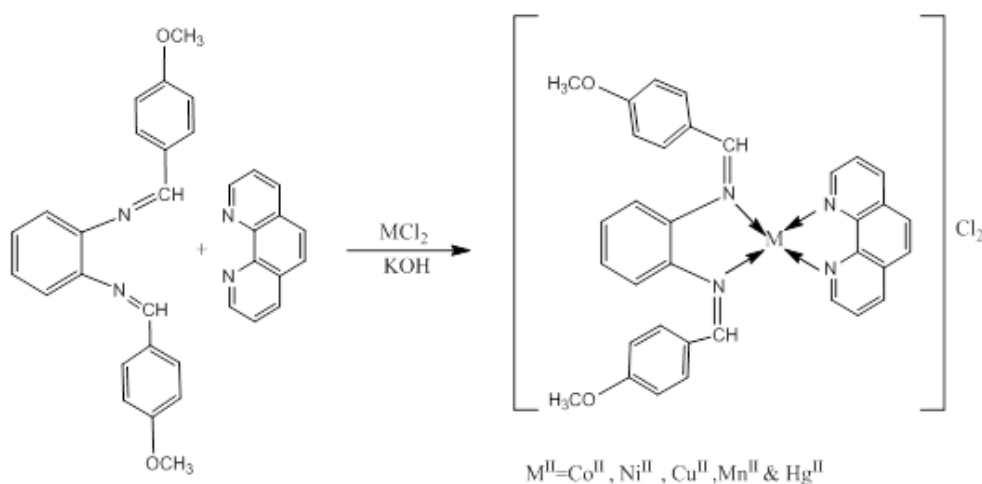
NMR spectrum

^{1}H- NMR spectrum of (L) in DMSO–$d_6$illustrated in Fig.(4), is multiples corresponding to aromatic six protons at (6.86-7.67) *ppm*[14].Thealiphaticprotons (O-CH_3)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*

^{13}C–NMR of (L) Fig (5), showedthecarbon 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 toυ(C–H) aromatic stretching at (3059) cm^{-1}, υ(C–H)aliphaticstretching at (2937) cm^{-1},υ(C=C) aromatic at(1570) cm^{-1}.[9]Absorptionband corresponding at (3446) cm^{-1} due to υ (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 itscomplexes show the absorption bands in the range (1601-1606) cm^{-1} due to azomethineυ(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 benzaldehydeat (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 aquaδ(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[Hg(L)$_2$]Cl$_2$complex in fig(2).

Molar Conductivity

The molar conductance values of the complexes in ethanol lie in the range (71to 87)ohm^{-1}.cm^{2}mol^{-1} which is It 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)displayedtwo absorption peaks, the first peak at (265)nm (37735)cm^{-1} may be assigned to π–π* electronic transition.The second peak at (332) nm, (30120) cm^{-1} was attributed to n–π* 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 Co$^{(II)}$ complexFig.(4)displayed peak at (628)nm (15923)cm^{-1}wasattributed to (d-d) electronic transition type^{4}A$_{2(F)}$→^{4}T$_{1(P)}$,was suggesting high spin tetrahedral geometry around Co$^{(II)}$ central ion.[16]

The U.V-Vis spectrum of the 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}T$_{1(F)}$ →^{3}T$_{1(P)}$ and^{3}T$_1$→^{3}A$_2$ respectively, that is a goodsuggestment with high spin tetrahedral geometry[17].

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

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

The U.V-Vis spectrumof the Hg$^{(II)}$complex displayed peak at (324)nm (308640) cm^{-1} refer to charge electronic transition only.[20]The U.V-Vis spectrum of the Hg$^{(II)}$complex showed no d-d transitions in the visible region, indicating for Hg$^{(II)}$, this is meanelectronic transitions happened tetrahedral geometry has been assigned to the 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 Co$^{(II)}$, Ni$^{(II)}$,Cu$^{(II)}$andMn$^{(II)}$complexes is (5.71),(2.85),(1.81),(5.54)*B.M.*which aresuggested tetrahedral environmentwiththese metal ions shown in Table (3).[22]

Antibacterial Activities

BidentateSchiff base ligand derived by the condensation of 4-Methoxy benzaldehyde with4- Methyl benzene-1,2-diamine and itsMn$^{(II)}$,Ni$^{(II)}$,Co$^{(II)}$, Hg$^{(II)}$and Cu$^{(II)}$ complexes showed biological activities against the type of bacterial(*Escherichiacoli*) except[Ni(L)(PHN)]Cl$_2$in Fig(7).The compounds showed inhibition diameter against the type of bacterial (*Staphylococcus aureu*) except ligand [L] in Fig(8), the consequences suggest that mixed complexes showed more activity than the ligand under comparableempiricalsurroundings, table (6) this may be due to that the coordinationextremely 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 [Cu(L)(PHN)]Cl$_2$complexFig (9).All compounds ligand and its complexes have good biological activity against the type of bacterial (*Pseudomonas*)Fig (10), Table (6)Diameterof zone of inhibition.

III. Conclusion

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

References

[1]. M. S. Singh and P. K.Singh (2000); New Class of Organosilicon(IV) Compounds Based Upon Tetradentate (N_2O_2) Chelating Ligand, *Main GroupMetal Chemistry*, 23, 183-188.

[2]. M Aly, A H Osman, B Abd El-mottaleb and B AGouag,*J.Chil.Chem.Soc.*, 2009,54(4)349-353.

[3]. FM Morad, MMEl.ajailyand S B GeoRef. *, J. Sci. &Appl.*, 2007, 1(1)72-78.

[4]. J Zhang,YTang,JQXie, JZhang,W Zeng and CWuhu,*J.Serb.Chem.Soc.*, 2005, 70(10) 1137–1146.

[5]. MANeelakantan, T Jeyakumar and K Muthukumaran,*SpectrochimicaActa Part A*,2008, 71- 628.

[6]. Z LYou and HLZhu, *Zeitschrift fur Anorganische und AllgemeineChemie*,2004, 630, 15, 2754-2760.

[7]. MGolcu,HTumer,RDemirelli and AWheatley,*J.Inorg.Chem.InorganicaChimicaActa*, 2005, 358, 6, 1785-1797.

[8]. RGarg, N Fahmi and RV Singh, *J.Indian Chem. Soc*., 2009,86-670.

[9]. RVafazadehand, M Kashfi, Bull. *Korean Chem.Soc.*,2007,86: 697.28(7): 1227.

[10]. H. Hassib, and A.A. Razik,*Solid State Communication,2008, 147- 345.*

[11]. SSarkar, V Aydogdu, F Dagdelen, BBBhaumik and K Dey, Material *Chem. Phy.*,2004, 88: 357.

[12]. F Kolodziej,*Prog. Inorg. Chem.*, 1994, 25, 6,493-597.

[13]. H Dawood and N Jasim,*J.Scien.Kerbala University*,2009, 7,2 ,226-272.

[14]. S.Chandra and A. Kumar,*J. Saudi Chem. Soc.*, 2007, 11(2) 299.

[15]. H.Nora and A Al-Sha, Molecules,2007, 3, 9, 12-1080.

[16]. N Nishant,SParveen, S Dhyani and Asma, *J. Coord. Chem.*, 2009, 62(7)1091.

[17]. K Maldhure and AS Aswar, *J. Indian Chem. Soc.*,2009,10,7, 86- 697.

[18]. FHamurcu,ABGunduzalp, SCete and BErk, *Trans. M.Chem.,*2008,9, 16,33-141.

[19]. SAhmedandABenGuzzi,*J. Sci. Appl.*, 2008, 2(1)83:90.

[20]. AOsowle, *E-Journal of Chemistry*,2008, 5(1) 130-135.

[21]. RGarg, NFahmi and RV Singh, *J. Indian Chem. Soc.,*2009,16,6, 86: 670.

[22]. IHBukhari, M Arif, JAkbar and AH Khan, Preparation, Characterization and Biological Evaluation of Schiff Base Transition Metal Complexes with Cephradine, Pak. J. Biol. Sci., 2005,8(4): 614.

[23]. D Bansod, RG Mahale and AS Aswar, *Russian J. Inorg. Chem.*, 2007, 52(6): 882.

[24]. CA Bolos, GS Nikolov, L E kateriniadou, A Kortsaris and DA Kyriakidis, 1998, *Metal-Based Drugs*, 5(6): 323.

Table 1. Some physical properties of prepared lignad(L) and it's complexes

Compounds	Empirical Formula	Yield %	Weight(g)	M.P C°	Colour	Metal salt	Weigh g 1mmol	%(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	$CoCl_2.2H_2O$	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	$CuCl_2.2H_2O$	0.170	(61.96)61.42	(4.28) 4.02	(8.50) 8.34	(9.64) 9.26
[Ni(L)(PHN)]Cl_2	$C_{34}H_{28}Cl_2N_4NiO_2$	88	654.21	204	greenth brown	$NiCl_2.2H_2O$	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	$MnCl_2.H_2O$	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 υ) cm^{-1}for the ligand (L), precursors and its mixed complexes

Compound	υ(C-H)$_{aromatic}$	υ(C-H)$_{aliphatic}$	υ(HC=N)$_{imine}$	υ(C-O)	M–N	M–O
L	3059	2937	1608	1240	-	-
PHN	-	-	1620	-	-	-
[Co(L)(PHN)]Cl$_2$	3068	2937	16041597	1242	547	476
[Mn(L)(PHN)]Cl$_2$	3056	2924	16061592	1243	547	474
[Ni(L)(PHN)]Cl$_2$	3076	2926	16021594	1241	549	460
[Cu(L)(PHN)]Cl$_2$	3026	2924	16011590	1243	582	482
[Hg(L)(PHN)]Cl$_2$	3040	2927	16031598	1242	545	464

Table 3. Electronic spin resonance parameters of the complexes

Compound	μ$_{eff}$	Λ$_m$ohm.cm^{2}mole^{-1}	λnm	υ'wave number cm^{-1}	Assignments	Proposed structure
L	-	-	265	37735	π→π*	-
			332	30120	n→π*	
[Co(L)(PHN)]Cl$_2$	4.71	81	278	35970	L.F	tetrahedral
			341	29325	C.T	
			628	15923	$^4A_{2(F)}$→$^4T_{1(P)}$	
[Ni(L)(PHN)]Cl$_2$	2.85	77	253	39525	L.F	tetrahedral
			362	27624	C.T	
			743	13458	$^3A_{2(F)}$→$^3T_{2 (P)}$	
			792	12626	$^3T_{1(F)}$→$^3A_{2(F)}$	
[Cu(L)(PHN)]Cl$_2$	1.81	75	268	30864	L.F	tetrahedral
			344	30864	C.T	
			578	17301	^2E→$^2B_2$	
[Mn(L)(PHN)]Cl$_2$	5.54	84	277	36101	L.F	tetrahedral
			348	28735	C.T	
			775	12903	$^6A_{1(F)}$→$^4E_{(D)}$	
[Hg(L)(PHN)]Cl$_2$	-	88	350	28571	C.T	tetrahedral
			420	23809	C.T	

Table 4.

Compound.	L	[Co(L)(PHN)]Cl$_2$	[Mn(L)(PHN)]Cl$_2$	[Ni(L)(PHN)]Cl$_2$	[Cu(L)(PHN)]Cl$_2$	[Hg(L)(PHN)]Cl$_2$
Escherichia. Coli	10	15	10	-	17	12
Staphylococcus aureus	-	12	14	14	18	15
Bacillus	12	11	10	15	-	19
Pseudmonas	14	15	13	13	16	10
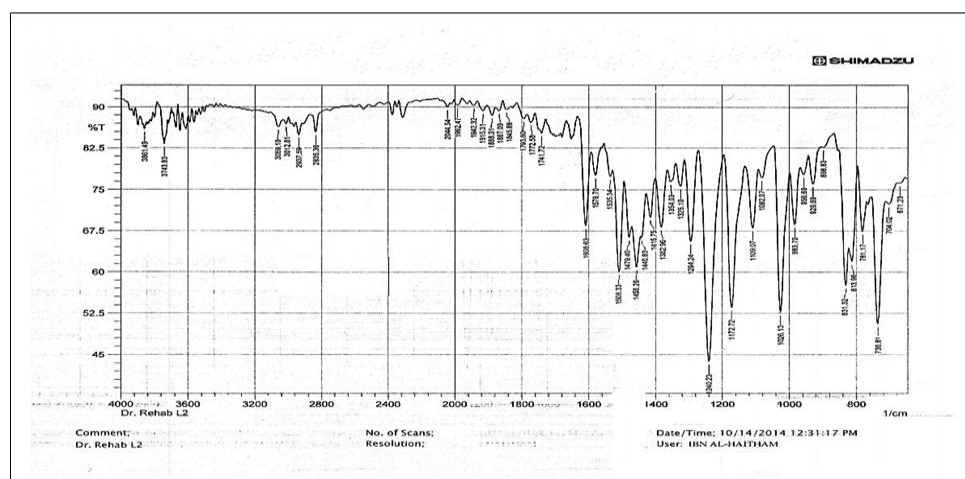
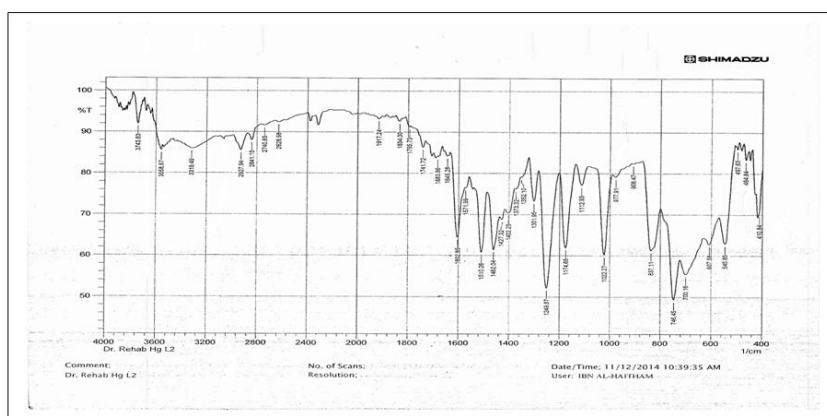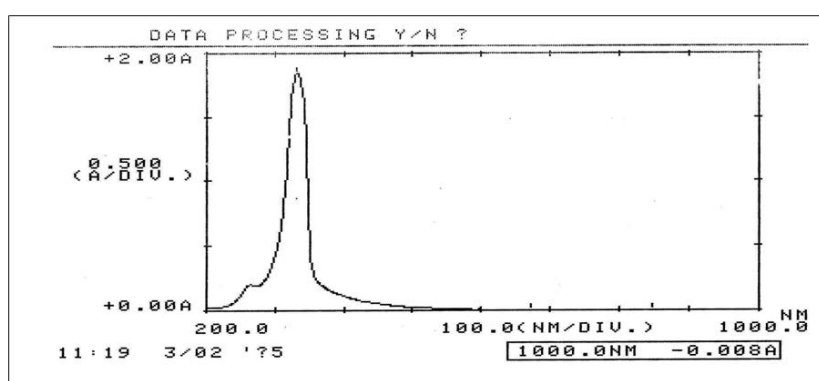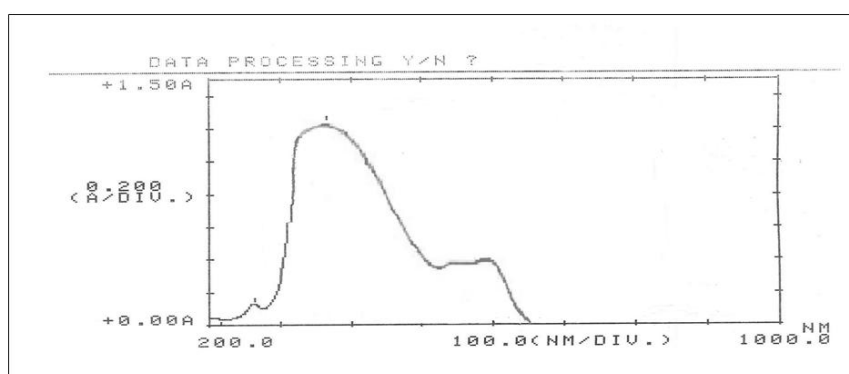**Fig(1):**The IR spectrum of (L)

Fig (2): The IR spectrum of [Hg(L)(PHN)]Cl$_2$

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

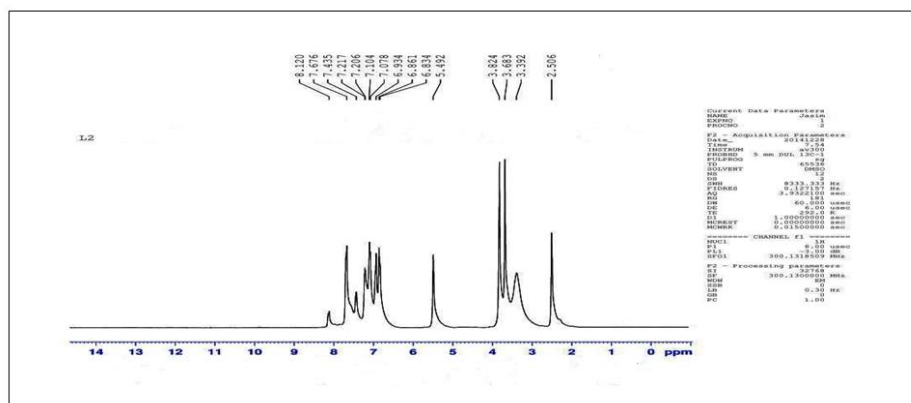**Fig(4):** Electronic spectrum of the ligand[Co(L)(PHN)]Cl$_2$

Fig.(5):*^{1}H-NMR*spectrum*of Ligand*(L)

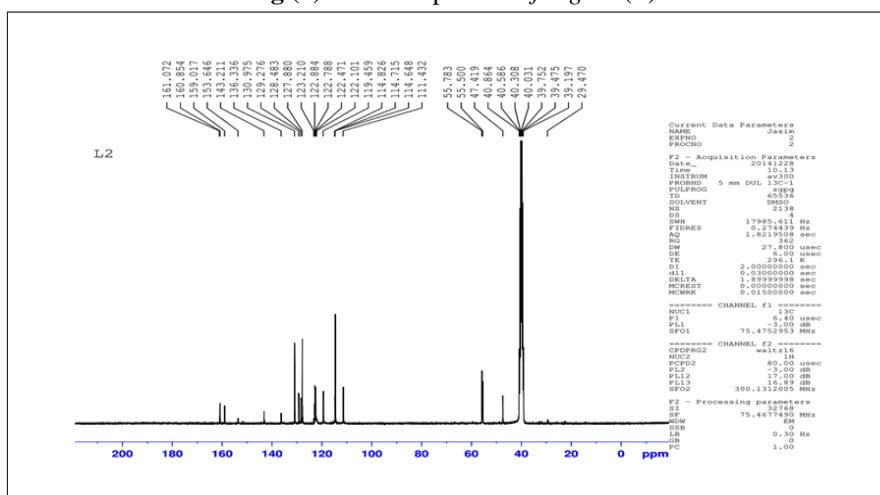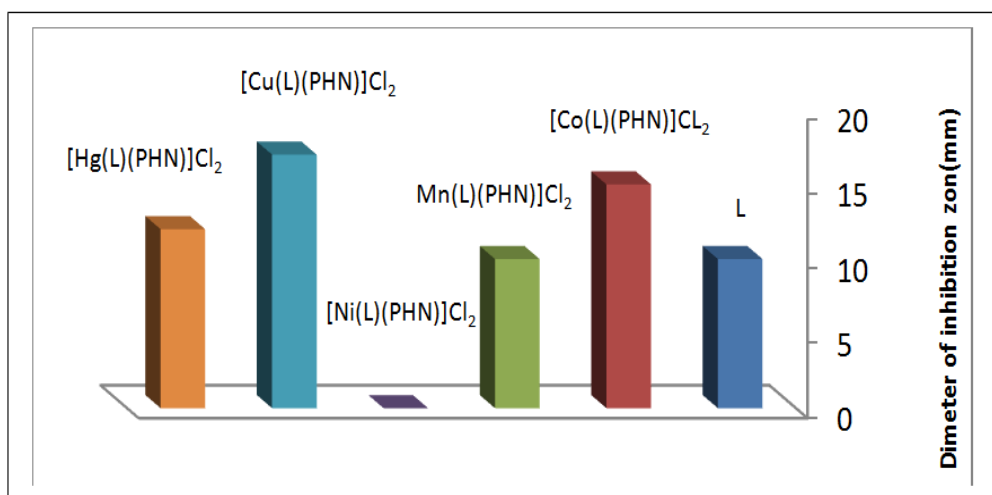**Fig.(6)**^{13}C- NMRspectrum *of Ligand*(L)
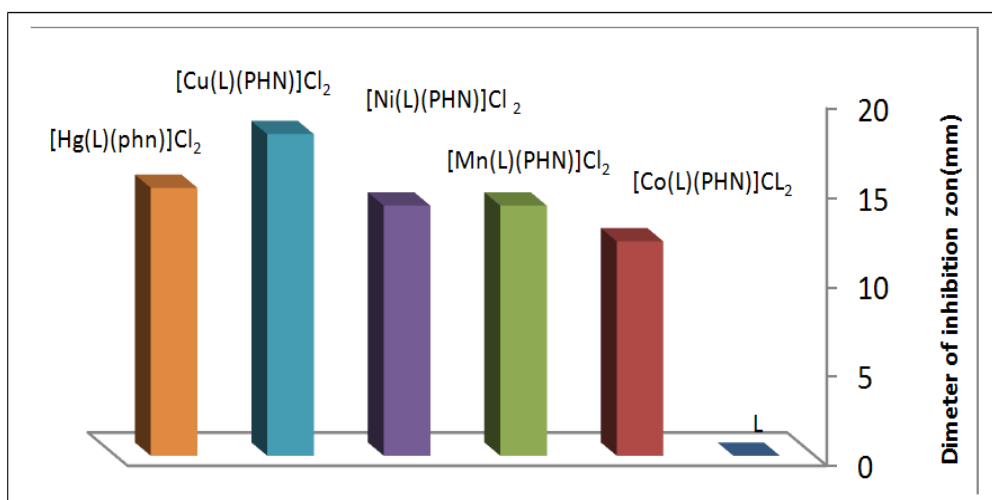

Fig.(7) Effect of *Escherichia.Coli*

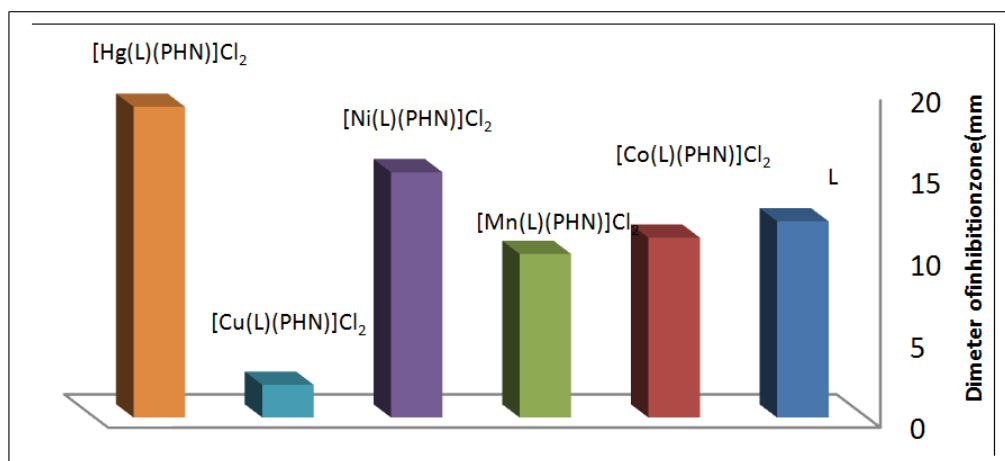**Fig. (8)** Effect of *Staphylococcusaureus*
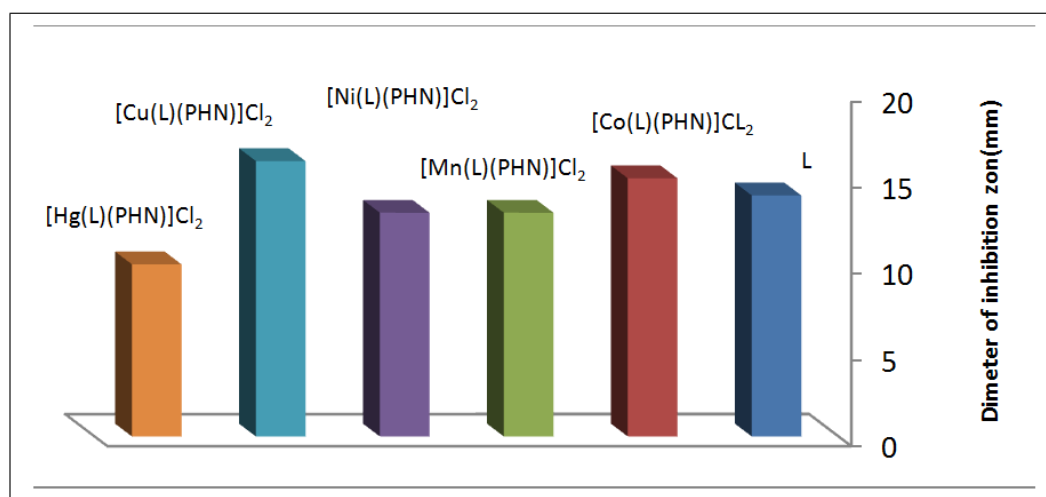
Fig.(9) Effect of *Bacillusgram*

Fig.(10) Effect of *pseudmonas gram*

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